

Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas

Industrial Emissions Directive 2010/75/EU
(Integrated Pollution Prevention and
Control)

JOINT RESEARCH CENTRE
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Sustainable Production and Consumption Unit
European IPPC Bureau

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Picture: Slovnaft Bratislava, member of the MOL Group

WORKING DRAFT IN PROGRESS

This document is one from the series of foreseen documents listed below (at the time of writing, not all documents have been drafted):

Reference Document on Best Available Techniques	Code
Ceramic Manufacturing Industry	CER
Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector	CWW
Emissions from Storage	EFS
Energy Efficiency	ENE
Ferrous Metals Processing Industry	FMP
Food, Drink and Milk Industries	FDM
Industrial Cooling Systems	ICS
Intensive Rearing of Poultry and Pigs	IRPP
Iron and Steel Production	IS
Large Combustion Plants	LCP
Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers Industries	LVIC-AAF
Large Volume Inorganic Chemicals – Solids and Others industry	LVIC-S
Large Volume Organic Chemical Industry	LVOC
Management of Tailings and Waste-rock in Mining Activities	MTWR
Manufacture of Glass	GLS
Manufacture of Organic Fine Chemicals	OFC
Non Ferrous Metals Industries	NFM
Production of Cement, Lime and Magnesium Oxide	CLM
Production of Chlor-Alkali	CAK
Production of Polymers	POL
Production of Pulp, Paper and Board	PP
Production of Speciality Inorganic Chemicals	SIC
<i>Refining of Mineral Oil and Gas</i>	REF
Slaughterhouses and Animals By-products Industries	SA
Smitheries and Foundries Industry	SF
Surface Treatment of Metals and Plastics	STM
Surface Treatment Using Organic Solvents	STS
Tanning of Hides and Skins	TAN
Textiles Industry	TXT
Waste Incineration	WI
Waste Treatments Industries	WT
Wood and Wood Products Preservation with Chemicals	WPC
Wood-based Panels Production	WBP
Reference Document	
Economics and Cross-media Effects	ECM
General Principles of Monitoring	MON

Electronic versions of draft and finalised documents are publicly available and can be downloaded from <http://eippcb.jrc.es>

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PREFACE

1. Status of this document

Unless otherwise stated, references to ‘the Directive’ in this document refer to Directive 2010/75/EU of the European Parliament and the Council on industrial emissions (integrated pollution prevention and control) (Recast).

This document is a working draft of the European IPPC Bureau (of the Commission’s Joint Research Centre). It is not an official publication of the European Union and does not necessarily reflect the position of the European Commission.

The original best available techniques (BAT) reference document (BREF) for the Refining of Mineral Oil and Gas (REF) was adopted by the European Commission in 2003. This document is the result of a review of that BREF. The review commenced in January 2008.

This BAT reference document for the Refining of Mineral Oil and Gas forms part of a series presenting the results of an exchange of information between EU Member States, the industries concerned, non-governmental organisations promoting environmental protection and the Commission, to draw up, review, and where necessary, update BAT reference documents as required by Article 13(1) of the Directive. This document is published by the European Commission pursuant to Article 13(6) of the Directive.

As set out in Article 13(5) of the Directive, the Commission Implementing Decision [yyyy/xx/EU] on the BAT conclusions contained in Chapter 5 was adopted on [date of decision] and published on [date of publication of decision in OJ + reference to OJ in footnote]¹.

2. Participants in the information exchange

As required in Article 13(3) of the Directive, the Commission has established a forum to assist the work, which is composed of representatives from Member States, the industries concerned and non-governmental organisations promoting environmental protection (Commission Decision of 16 May 2011 establishing a forum for the exchange of information pursuant to Article 13 of the Directive 2010/75/EU on industrial emissions (2011/C 146/03), OJ C 146, 17.05.2011, p. 3).

Forum members have nominated technical experts constituting the technical working group (TWG) that was the main source of information for drafting this document. The work of the TWG was led by the European IPPC Bureau (of the Commission’s Joint Research Centre).

3. Structure and contents of this document

Chapters 1 and 2 provide general information on the **Refining of Mineral Oil and Gas** and on the industrial processes and techniques used within this sector.

Chapter 3 provides data and information concerning the environmental performance of installations within the sector in terms of current emissions, consumption and nature of raw materials, water consumption, use of energy and the generation of waste reflecting the situation in installations in operation at the time of writing.

Chapter 4 describes in more detail the techniques to prevent or, where this is not practicable, to reduce the environmental impact of installations in this sector that were considered in determining the BAT. This information includes, where relevant, the environmental performance levels (e.g. emission and consumption levels) which can be achieved by using the techniques,

¹ OJ [series] [number], [dd.mm.yyyy], p. [starting page].

the associated monitoring and the costs and the cross-media issues associated with the techniques.

Chapter 5 presents the BAT conclusions as defined in Article 3(12) of the Directive.

Chapter 6 presents information on 'emerging techniques' as defined in Article 3(14) of the Directive.

Concluding remarks and recommendations for future work are presented in Chapter 7.

4. Information sources and the derivation of BAT

This document is based on information collected from a number of sources, in particular through the TWG that was established specifically for the exchange of information under Article 13 of the Directive. The information has been collated and assessed by the European IPPC Bureau (of the Commission's Joint Research Centre) who led the work on determining BAT, guided by the principles of technical expertise, transparency and neutrality. The work of the TWG and all other contributors is gratefully acknowledged.

The BAT conclusions have been established through an iterative process involving the following steps:

- identification of the key environmental issues for the sector;
- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these environmental performance levels were achieved, such as costs, cross-media effects, and the main driving forces involved in the implementation of the techniques;
- selection of the best available techniques (BAT) their associated emission levels (and other environmental performance levels) and the associated monitoring for this sector according to Article 3(10) of and Annex III to the Directive.

Expert judgement by the European IPPC Bureau and the TWG has played a key role in each of these steps and in the way in which the information is presented here.

Where available, economic data have been given together with the descriptions of the techniques presented in Chapter 4. These data give a rough indication of the magnitude of the costs and benefits. However, the actual costs and benefits of applying a technique may depend strongly on the specific situation of the installation concerned, which cannot be evaluated fully in this document. In the absence of data concerning costs, conclusions on the economic viability of techniques are drawn from observations on existing installations.

5. Review of BAT reference documents (BREFs)

BAT is a dynamic concept and so, the review of BREFs is a continuing process. For example, new measures and techniques may emerge, science and technologies are continuously developing and new or emerging processes are being successfully introduced into the industries. In order to reflect such changes and their consequences for BAT, this document will be periodically reviewed and, if necessary, updated accordingly.

6. Contact information

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SCOPE

This BREF covers the following activities within the scope of Annex I of Directive 2010/75/EU: Energy industries 1.2. Refining of mineral oil and gas.

This document only addresses the refining industry from both sectors (mineral oil refineries and natural gas plants), and more especially the activities and processes set out in the following table.

Activity	Subactivities or processes included in each category of activity
Alkylation	All alkylation processes: HF, H ₂ SO ₄ and solid-acid
Base oil production	Deasphalting, aromatic extraction, wax processing, and lubricant oil hydrofinishing
Bitumen production	All technique from storage to final product additives
Catalytic cracking	All types of catalytic cracking units such as fluid catalytic cracking
Catalytic reforming	Continuous, cyclic and semi-regenerative catalytic reforming
Coking processes	Delayed and fluid coking processes. Coke calcination
Cooling systems	Cooling techniques applied in refineries
Desalting	Desalting of crude oil
Combustion for energy production	Refinery power plants including all types of techniques applied within EU refineries and burning refinery fuels. Energy production techniques using only conventional or commercial fuels are not covered
Etherification	MTBE, ETBE and TAME production
Gas separation processes	Separation of light fractions of the crude oil e.g. refinery fuel gas (RFG), liquefied petroleum gas (LPG)
Hydrogen consuming processes	Hydrocracking, hydrotreating, hydrorefining, hydroconversion, hydroprocessing and hydrogenation processes
Hydrogen production	Partial oxidation, steam reforming, gas heated reforming and hydrogen purification
Integrated refinery management	Environmental activities, utility and overall refinery management
Isomerisation	Isomerisation of hydrocarbons compounds C ₄ , C ₅ and C ₆
Natural gas plants	Natural gas (NG) processing including liquefaction of NG
Polymerisation	Polymerisation, dimerisation and condensation
Primary distillation units	Atmospheric and vacuum distillation units
Product treatments	Sweetening and final product treatments
Storage and handling of refinery materials	Storage, blending, loading and unloading of refinery materials
Visbreaking and other thermal conversions	Thermal treatments such as visbreaking or thermal gas oil
Waste gas treatment	All techniques to reduce or abate emissions to air
Waste water treatments	Techniques to reduce or treat waste water prior to release
Waste management	Techniques to reduce the generation of waste

This document does not address the following activities:

- the exploration and production of crude oil and natural gas;
- the transportation of crude oil and natural gas;
- the marketing and distribution of products.

Scope

As far as biofuels are concerned, the present document covers their handling and processes in conventional refining units within the mineral oil refinery site but it does not cover specific biological or biochemical processes used for their production.

Finally, the TWG has considered that soil remediation techniques are not included within this BREF. The reason given is that these techniques are not techniques to prevent nor to control emissions. They are techniques used to clean up the soil when it has already been contaminated.

The present document is designed to be as comprehensive as possible, taking into consideration the need to avoid duplication with other BREFs. It contains priority information specific to the refinery sector. This means, in particular, that:

- generally applicable information on storage, cooling systems, energy efficiency, monitoring, waste water and waste gas treatments, or economics and cross-media effects pertain to other relevant horizontal BREFs and may have not been developed or even covered in the present document;
- generally applicable and specific information on particular processes or units covered by other vertical BREFs **have not been covered**, or may have been only partially covered in the present document, for example:
 - the steam cracker for the production of lower olefins, the production of aromatics (i.e. BTX), cyclohexane and cumene, or the alkylation of aromatics, that are covered in the Large Volume Organic Chemicals (LVOC) BREF [85, EC 2003];
 - the production of hydrogen by steam methane reforming, that is covered by the Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers (LVIC-AAF) BREF [92, EC 2007]. This BREF has been selected to include the generic information on this subject (IEF Strategy to review the Chemicals BREFs, March 2007 [250, EC 2007]).
 - the energy production techniques (i.e. boilers and furnaces) when burning exclusively commercial fuels, that are already covered in the Large Combustion Plant (LCP) BREF [7, EC 2006].

Other reference documents which are of relevance for the sector covered in this document are the following:

Reference document	Subject
Common Waste Water and Waste Gas Treatment/Management System in the Chemical Sector (CWW)	Waste water management and treatment techniques
Industrial Cooling Systems (ICS)	Cooling processes
Economics and Cross-Media Effects (ECM)	Economics and cross-media effects of techniques
Emissions from Storage (EFS)	Storage, blending, loading and unloading of refinery materials
Energy Efficiency (ENE)	Energy efficiency and integrated refinery management
Large Combustion Plants (LCP)	Use of commercial fuels in refineries
Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers Industries (LVIC-AAF)	Steam reforming and hydrogen purification
Large Volume Organic Chemical Industry (LVOC)	Etherification process (MTBE, ETBE and TAME production)
General Principles of Monitoring (MON)	Emissions to air and water
Waste Incineration (WI)	Waste and waste water management
Waste Treatments Industries (WT)	Waste and waste water management

The scope of this document does not include matters that only concern safety in the workplace or the safety of products, because these matters are not covered by the Directive. They are discussed only where they affect matters within the scope of the Directive.

WORKING DRAFT IN PROGRESS

WORKING DRAFT IN PROGRESS

1 GENERAL INFORMATION

1.1 The purpose of refineries

The purpose of refining is to convert natural raw materials such as crude oil and natural gas into useful saleable products. Crude oil and natural gas are naturally occurring hydrocarbons found in many areas of the world, in varying quantities and compositions. In refineries, these are transformed into different products such as:

- fuels for cars, trucks, aeroplanes, ships and other forms of transport;
- combustion fuels for the generation of heat and power for industry and commercial and domestic use;
- raw materials for the petrochemical and chemical industries;
- speciality products such as lubricating oils, paraffins/waxes and bitumen;
- energy as a by-product in the form of heat (steam) and power (electricity).

In order to manufacture these products, these raw materials are handled and processed in a number of different refining facilities, alone or as a mixture with biofuels. The combination of these processing units which convert crude oil and natural gas into products, including supporting units and facilities, is called a refinery. The market demand for the type of products, the available crude quality and certain requirements set by authorities influence the size, configuration and complexity of a refinery. As these factors vary from location to location, no two refineries are identical.

1.2 Refinery sector in the EU

1.2.1 General

The economic and political worldwide refining industry has undergone considerable changes over time. In recent years, the increased effort in oil and gas exploration and production, as well as cost reductions achieved in these activities, has resulted in the stability of the recognised reserves worldwide.

In 2006, oil and gas provided respectively 42 % and 23 % of the EU-27 final energy consumption. They represent the first and the second most important sources of energy in Europe. About 94 % of the fuels required for transport originated from oil products, while natural gas represented 36 % of energy consumption for services and domestic use, and 20 % of the energy used for power generation.

Despite the progressive increase of biofuels in the transport sector (increasing from less than 0.2 % prior to 2000 to 1.78 % in 2006 for EU-27), the health and viability of the refining industry remains of critical strategic importance to the EU for maintaining a successful and internationally competitive position for industry as a whole, and for providing competitively priced products to consumers [8, EUROSTAT 2008].

1.2.1.1 Oil refining

In 2012, there were 655 refineries worldwide, with a total capacity of around 4 400 million t/yr. The world's largest refining region is Asia (25 %), followed by North America and Europe (around 20 % each). The top refining countries in the world are the US, followed by China, Russia and Japan. [132, O&Gas Journal 2011]

The refining industry has suffered from a structural overcapacity for distillation for most of the time since the oil crisis in 1973/1974. Only in the early 1980s, early 1990s and late 1990s were attractive margins achieved due to high oil prices at these times. Moreover, severe competition, environmental compliance of the refining industry and regulatory uncertainty have added to the decrease in profitability in certain periods. This long-lasting recession has led oil and gas companies to make significant adjustments in upstream and downstream operations, such as cuts in production costs, innovations in technology, and organisational restructuring. Some big investments have been made to cover diesel demand (e.g. Repsol and Cepsa in Spain - Cartagena, Huelva). But the economic crisis starting in 2008 has led to a decrease in demand on energy products.

Even though, some European oil refineries have closed in the last 25 years there has been a progressive increase of crude oil processing capacity since the 1990s, mainly by 'capacity creep' (debottlenecking, improvements in equipment reliability and longer cycles between turnarounds) to cope with a 1 – 2 % increase in product demand per year in Europe. Since 2005, there has been a stabilisation and even a slight decrease of the overall European demand. At the worldwide level, the 'capacity creep' is estimated to be equivalent to six to ten additional global scale refineries going on stream every year.

Economic experts foresee low margins for future decades due to a low possibility of capacity rationalisation. As a general trend, investment has shifted towards exploration and drilling. According to the International Energy Agency, 15 European refineries (in CZ, FR, GE, IT and UK) were shut-down within the 2008-2013 period with an associated capacity decline of about 8 %. [279, IEA 2013]

Within the context of a constant demand for transportation products with lower environmental impact, the European Union is promoting biofuels, bioproducts and biorefinery investment to reduce EU dependency on fossil-fuel feedstocks and foreign raw materials.

1.2.1.2 Natural gas refining

In parallel to the consumption of petroleum products, the gross inland consumption of natural gas in the EU-27 has progressively increased during the last decades, reaching a peak of around 446 Mtoe in 2005. Despite a slight decrease in 2006 and 2007, EU demand is still expected to grow rather significantly, with a CAGR of around +1.8 % until at least 2020, mainly driven by thermoelectric requirements.

On the other hand, EU indigenous gas production has been stable over the last decade, but is now showing a clear decreasing trend starting in 2004. This production is expected to fall, notably in the UK, Netherlands, Germany and Italy. Consequently, EU-27 dependence on gas importation could rise from a current level of 58 % in 2005 to approximately 81 % in 2025.

This context drives a significant number of projects for new infrastructure imports, both for gaseous feedstock (new pipelines or pipeline connections to the existing network from Russia, the Caspian region, North Africa and the Middle East production fields) and for a number of new LNG terminals. According to some authors, 16 regasification plants devoted to imported liquefied natural gas (LNG) reception, storage and final process were in operation in 2008 in the EU, and five more were under construction. Up to 35 new terminals are under consideration [10, Ruggeri 2008], [11, Van Putten 2008], [12, Basolas 2008].

1.2.2 Feedstock

1.2.2.1 Crude oil feedstock

After a period of steady production in Europe during the 1990s, a decreasing trend has been observed since 2002 and a shift towards lighter (North Sea) crudes, especially Northern Europe. The world reserve of crude oil seems to guarantee the availability of raw materials for a reasonably long period (~40 years). Table 1.1 shows a summary of the world reserves and the consumption of crude oil per geographical area during the last decade.

Table 1.1: Crude oil reserves and consumption per geographical region (1999 – 2012)

Proved reserves of oil (thousands million barrels)	1999	2008	2009	2010	2011	2012	2012 share of total
North America	233	216	219	222	221	220	13.2 %
South and Central America	98	199	237	324	327	328	19.7 %
Europe and Eurasia	97	137	138	138	140	141	8.5 %
Middle East	686	754	753	766	798	808	48.4 %
Africa	85	120	123	125	127	130	7.8 %
Asia Pacific	40	42	41	42	41	41	2.5 %
Total world reserves	1239	1468	1511	1617	1654	1668	100 %
Consumption (thousands of barrels daily)							
North America	23 467	23 860	22 959	23 464	23 397	23 040	25.8 %
South and Central America	5 023	5 892	5 921	6 222	6 405	6 533	7.3 %
Europe and Eurasia	19 589	20 017	19 149	19 057	18 974	18 543	20.7 %
Middle East	4 928	7 185	7 526	7 861	7 992	8 354	9.3 %
Africa	2 467	3 218	3 302	3 463	3 359	3 253	3.6 %
Asia Pacific	20 606	25 881	26 205	27 766	28 754	29 781	33.3 %
Total world consumption	76 080	86 053	84 062	87 833	88 881	89 504	100 %
<u>Proved reserves of oil:</u> quantities that geological and engineering information indicates with reasonable certainty can be recovered in the future from known reservoirs under existing economic and operating conditions.							
<u>Consumption:</u> inland demand plus international aviation and marine bunkers and refinery fuel and loss. Consumption of fuel ethanol and biodiesel is also included.							
Source: [277, BP 2013]							

The advent of North Sea crude oils and the continuous increase in the production of these light, low-sulphur crudes is mainly responsible for the lowering of the average sulphur content of the crude oils processed in European refineries. Since 1985, the average sulphur content has fluctuated at around 1.0 to 1.1 %. However, the difference between type of crude processed in each European region should be noted, i.e. an average of 1.17 % S in the crude oils processed in the refineries of North West Europe, an average of 0.91 % S in the Atlantic region, 1.2 % S in the Mediterranean and 0.64 % S in the 'Others'. The availability of the type of crude oil going to refineries is not the same.

Some local factors for these differences are the following:

- location close to oil fields where low-sulphur crudes are produced (freight for crude from the North Sea to the Mediterranean costs up to USD 1/bbl, so low-sulphur crudes from the North Sea are rarely processed in the Mediterranean area);
- refinery equipped with insufficient desulphurisation/upgrading capacity to process (heavy) high-sulphur crudes;
- exclusion from markets where high-sulphur products can be sold (e.g. bitumen, bunker fuel);
- some other form of specialisation in the use of low-sulphur crudes (e.g. base oil production).

Figure 1.1 shows the sulphur balance for EU refineries, trend up to 2006.

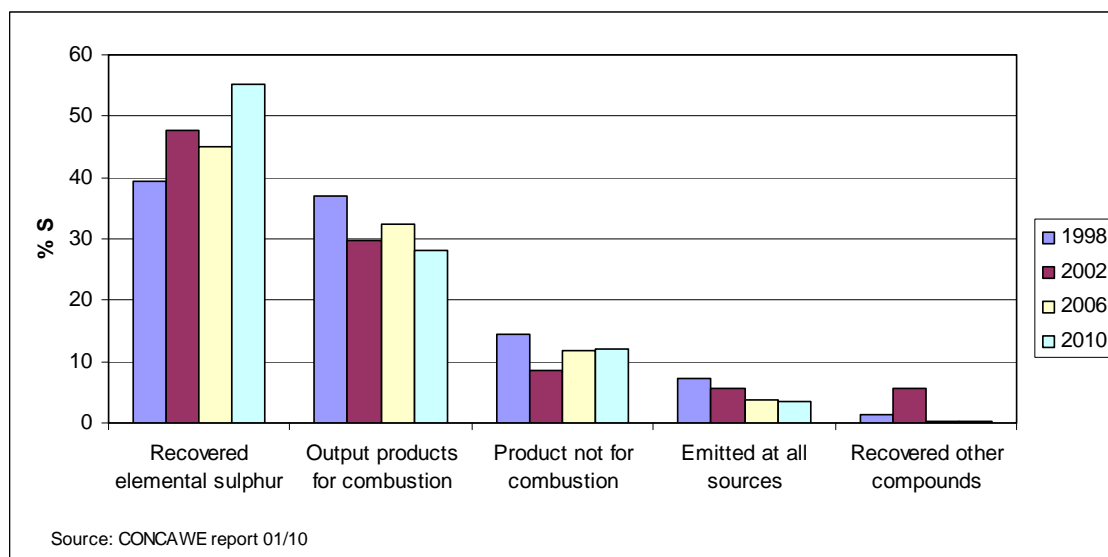


Figure 1.1: Refinery sulphur balance trend up to 2010

1.2.2.2 Biofuels feedstock growth

Specific support policies worldwide aim to replace fossil fuel consumption with biofuels and stimulate biofuel production and expansion in domestic markets. They result in a fast growing production of these products (mainly bioethanol and biodiesel), which are then blended with petroleum products for use as transport fuels.

Figure 1.2 shows the quota (%) on blending versus the target set by the EU Directive on biofuel (2003/30/EC). Obviously, this has led to an increase of the European consumption of these products for transport that are normally commercialised by the large oil companies.

Table 1-2 shows the consumption of biodiesel and ethanol for transport in the EU in the year 2009 in tonnes of oil equivalent (toe).

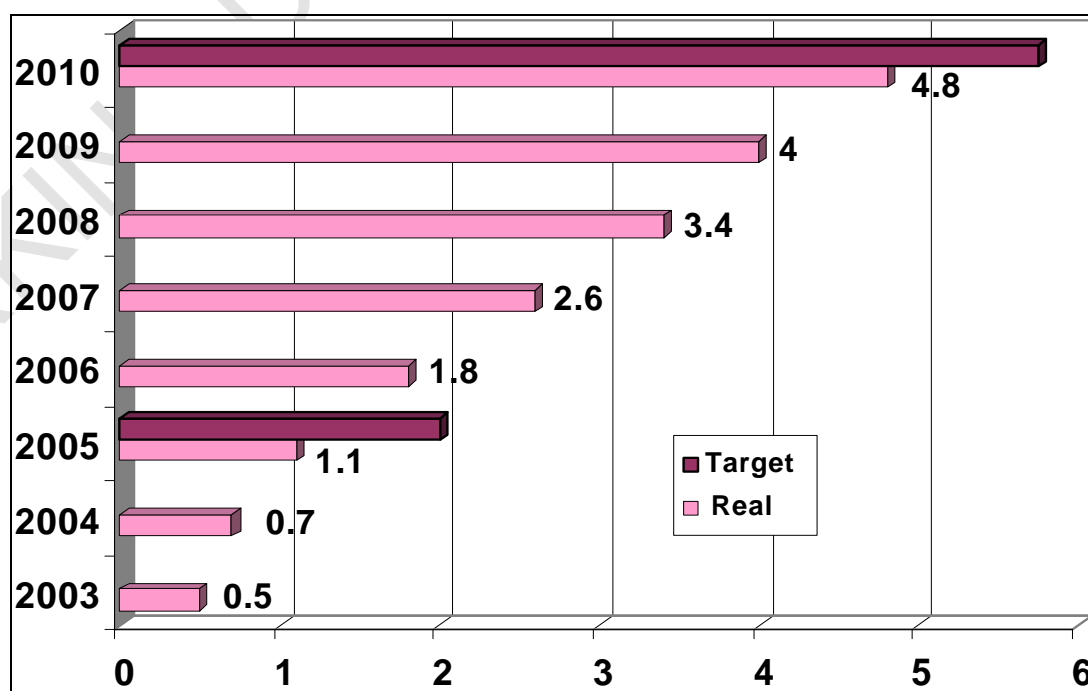


Figure 1.2: Percentage of biofuel blend (Source: Biodiesel EurObserv'er)

Table 1.2: Biofuels consumption for transport by country (2009 - tonnes of oil equivalent)

Country	Bioethanol	Biodiesel	Other	TOTAL
Germany	581 686	2 224 349	88 272	2 894 307
France	455 933	2 055 556		2 511 489
Italy	118 014	1 048 988		1 167 002
Spain	152 193	894 335		1 046 528
UK	159 000	822 872		981 872
Poland	136 043	568 997		705 040
Austria	64 249	424 901	13 369	502 519
Sweden	199 440	159 776	35 015	394 231
Netherlands	138 650	228 886		367 536
Belgium	37 577	221 252		258 829
Portugal	0	231 468		231 468
Romania	53 274	131 328		184 602
Hungary	64 488	119 303		183 791
Czec Rep.	51 097	119 809		170 906
Finland	79 321	66 280		145 601
Ireland	19 733	54 261		73 994
Slovakia	6 820	55 041		61 861
Greece	0	57 442		57 442
Lithuania	14 091	37 770		51 861
Luxembourg	740	39 915	498	41 153
Slovenia	1 859	27 993		29 852
Cyprus	0	15 024		15 024
Bulgaria	0	6 186		6 186
Latvia	1 120	3 570		4 690
Denmark	3 913	243		4 156
Malta	0	583		583
Estonia	NA	NA	NA	
TOTAL EU 27	2 339 241	9 616 128	137 154	12 092 523
<i>Source: EurObserver, 2010</i>				

Bioethanol

Worldwide, the US and Brazil dominate bioethanol production, as seen in Figure 1.3. Worldwide production amounted to 22 Mtoe in 2006, with almost half of it produced in the US from corn crops grown in the Midwest, representing 2 % - 3 % of the countries fuel.

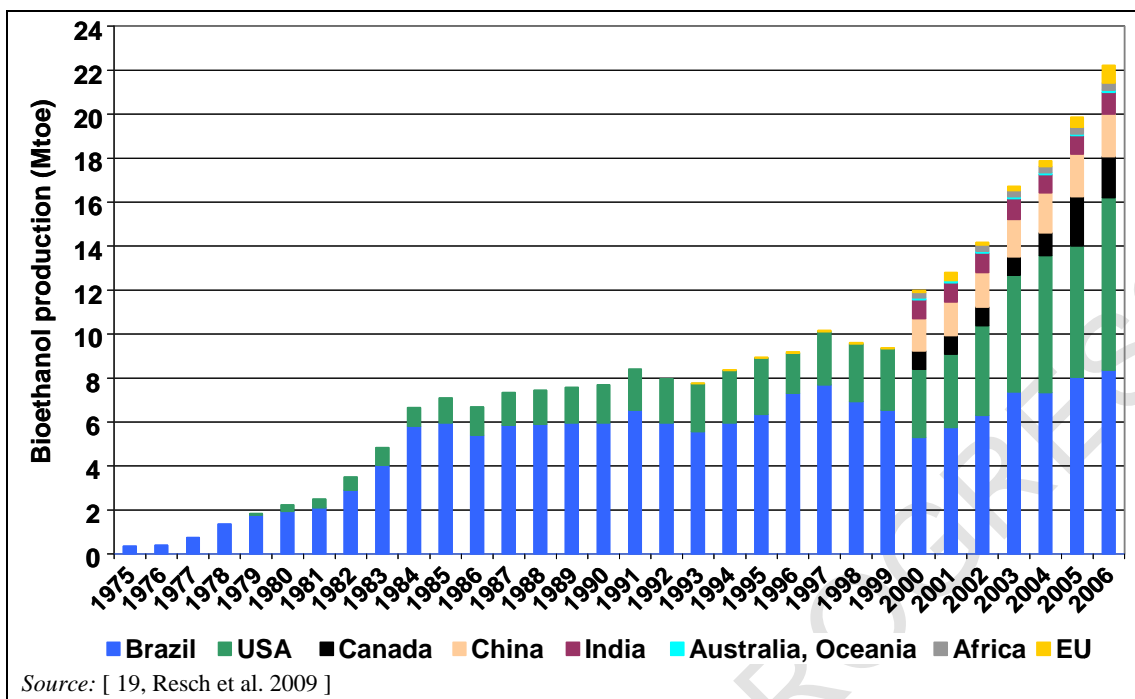


Figure 1.3: World bioethanol fuel production

Biodiesel

Biodiesel remains a small fraction of the fuel used worldwide but, as seen in Figure 1.4, has experienced strong growth rates in the last years, especially in Europe where biodiesel (mainly from rapeseed and sunflower oil) accounts for 75 % of the total EU biofuel production. In 2006, the European Union produced 4.7 Mt (3.2 Mtoe), experiencing a 66 % growth compared to 2005. In 2007, this capacity grew more than double to 11 Mt (7.5 Mtoe) in Europe. Germany is the world's leading biodiesel producer, making 40 % of the world total in recent years, followed by France and Italy.

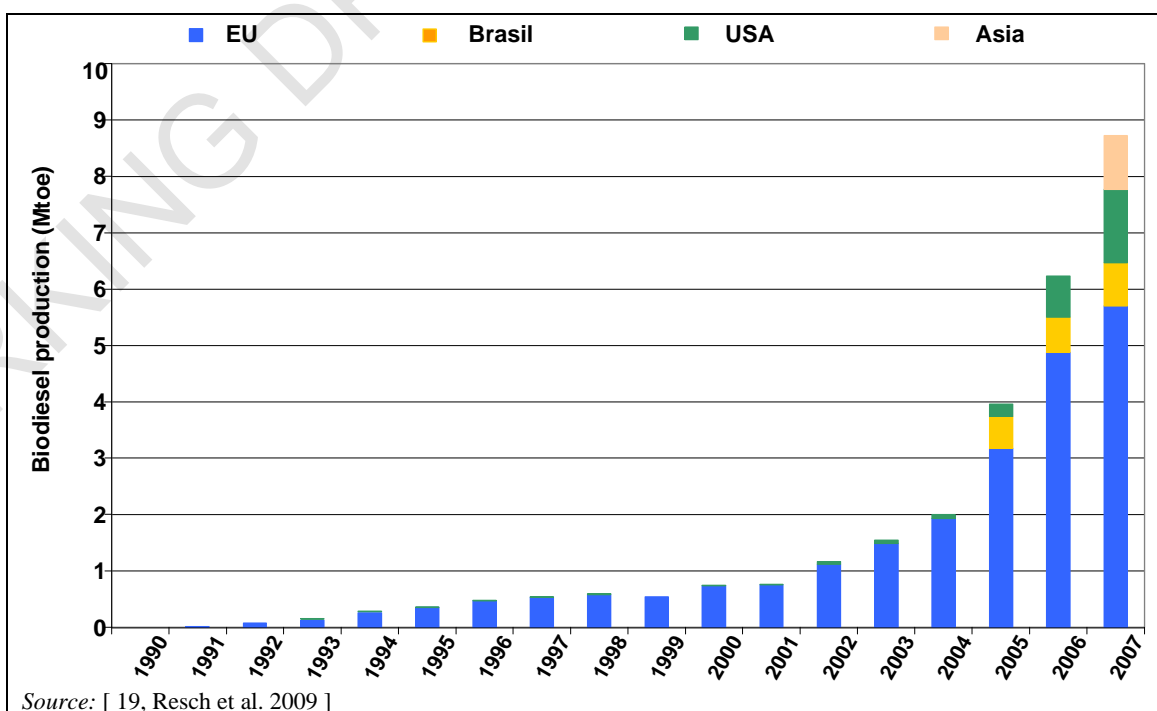


Figure 1.4: World biodiesel fuel production (European Biodiesel Board, EU Barometer, Biofuels Global Potentials 2007)

According to the European Biodiesel Board, Europe is the largest biodiesel market in the world at the time of writing. In 2007, Europe consumed over 7.5 Mm³ (5.15 Mtoe) of biodiesel. In December 2007, biodiesel imports to Europe had reached 0.8 Mt (0.6 Mtoe), which corresponds to a 500 % increase from 2006. Over 50 % of feedstock imports to Europe in 2007 came from Russia and Ukraine, accounting for 0.4 Mt (0.27 Mtoe).

1.2.2.3 Natural gas feedstock

In 2005, proven world gas reserves were equal to 60 years of gas production at current rates. Since 2005, the proven reserves increased faster than gas consumption and estimated reserves could represent the equivalent of another 200 years of consumption.

The highest percentage of gas supplied in the EU-27 comes from indigeneous production, covering 37 % of total net supplies (432 Mtoe) in 2007. The main external sources are Russia (24 %), Norway (19 %), and Algeria (10 %). The decrease in the EU-27 indigeneous production over the period is mainly compensated for by the growing imports from Norway.

Table 1-3 shows the proven reserves of natural gas (see table for definitions) [277, BP 2013].

Table 1.3: Natural gas proven reserves (2012)

	At end 1989	At end 1999	At end 2009	At end 2012	2012 Share of total	Reserves-to-production R/P Ratio (years)
	Trillion cubic metres	Trillion cubic metres	Trillion cubic metres	Trillion cubic metres		
Total North America	9.5	7.3	9.8	10.8	5.9 %	12.1
of which USA	4.7	4.7	7.7	8.8	4.8 %	12.5
Canada	2.7	1.7	1.7	2	1.1 %	12.7
Total S. and Cent. America	4.8	6.8	7.0	7.5	4.1 %	42.8
Total Europe and Eurasia	37	41.6	47.3	58.4	31.7 %	56.4
of which Azerbaijan	n/a	0.9	0.9	0.9	0.5 %	57.1
Denmark	0.1	0.1	0.1	-	-	-
Germany	0.3	0.2	0.1	0.1	0.1 %	6.1
Italy	0.3	0.2	0.1	0.1	0.1 %	7
Kazakhstan	n/a	1.2	1.3	1.3	0.7 %	65.6
The Netherlands	1.6	1.6	1.2	1.0	0.5 %	16.3
Norway	1.7	1.2	2.0	2.1	1.1 %	18.2
Poland	0.2	0.1	0.1	0.1	0.1 %	28.3
Romania	0.1	0.3	0.6	0.1	0.1 %	9.3
Russian Federation	n/a	29.8	31.1	32.9	17.9 %	55.6
Turkmenistan	n/a	2.3	7.3	17.5	9.5 %	(*)
Ukraine	n/a	0.7	0.7	0.6	0.3 %	34.6
United Kingdom	0.6	1.3	0.3	0.2	0.1 %	6
Uzbekistan	n/a	1.1	1.1	1.1	0.6 %	19.7
Other Europe and Eurasia	32.1	0.5	0.4	0.3	0.2 %	29.2
Total Middle East	37.8	54.7	75.9	80.5	43.7 %	(*)
Total Africa	8.5	11.4	14.8	11.5	6.2 %	67.1
Total Asia Pacific	9.5	12.1	15.2	15.5	8.4 %	31.5
Total World	107.1	134	170	184.2	100 %	55.7

Proven reserves: quantities that geological and engineering information indicates with reasonable certainty can be recovered in the future from known reservoirs under existing economic and operating conditions.

Reserves-to-production (R/P) ratio: reserves remaining at the end of any year divided by the production in that year.

The result is the length of time that these remaining reserves would last while having the same production rate.

(*) >100 years

Source: BP Statistical review of world 2013 [277, BP 2013]

1.2.3 Europe refining capacity

1.2.3.1 European oil refining capacity

European refineries are characterised by an excess in primary processing capacity, and by some 'misfits' (incompatibility between production and market demand) and excess in conversion capacity. European downstream sectors have too many refineries producing too much gasoline.

Table 1.6 shows, per type of process, the charge and production capacity of European oil refineries for the European Union (EU-27) and for EU+ Countries, which will correspond hereafter in this document to EU-27 enlarged by associated and official candidate Countries: Croatia, Former Yugoslav Republic of Macedonia (FYROM), Norway, Switzerland and Turkey. The crude oil capacity of the 106 plants operating in the EU-27 at the beginning of 2013 was below 1 billion tonnes per year. This corresponded to 17 % of the entire global capacity, whereas the US capacity accounted for 20 % of the entire global capacity. The average individual capacity of European sites was about 7.9 Mm³/yr, similar to the other parts of the world. As a comparison, at the same time, the refining crude oil capacity of the 125 plants operated in the US was reaching around 1 billion m³/yr, leading to an individual average capacity of 8.2 Mm³/yr. At the global level, 655 plants were under operation at the beginning of 2012, with an average individual capacity of 7.8 Mm³/yr for an overall crude capacity of around 5 billion m³/yr in 2012 [132, O&Gas Journal 2011].

Refining distillation capacity decreased substantially in the early 1980s following the oil price shocks of the 1970s. At the same time, the industry had to invest heavily in conversion capacity to convert fuel oil and adapt to demand for lighter transport fuels. Official figures for nameplate capacity show small further capacity reductions until the end of 1995. Combined with a slow rise in demand since 1986 this has increased apparent distillation capacity utilisation from a low point of 60 % in 1981 to an average above 90 % in 1997, higher in northern Europe and lower in southern Europe.

There are differences in supply and demand balances between different countries, with Germany and Spain in particular having a large supply deficit. The growth of oil products demand in Iberia has been well above the average for the EU, particularly in transport fuels. However, oil demand growth in the 1990s showed the Mediterranean region to be in line with the rest of Europe.

For the future, according to the Commission [72, EC 2010] and based on specific modelling, the investments required to upgrade EU+3 (including Switzerland, Norway and Turkey) refining capacities could reach EUR 17.8 billion (including 3.3 for international maritime organisation (IMO) changes) between 2005 and 2030. These amounts would be mainly dedicated to extra gas oil hydrodesulphurisation units. The CONCAWE projections keeping trade levels constant for the period 2005 – 2030, indicate it would require EUR 29.2 billion of investment.

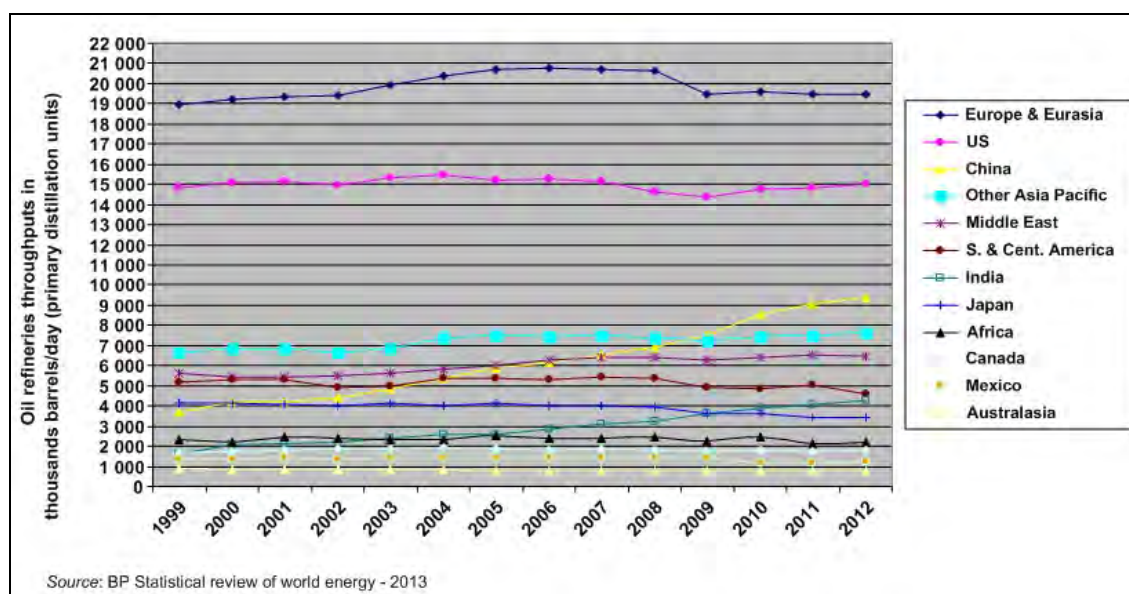


Figure 1.5: Global oil refining throughputs

1.2.3.2 European natural gas refining capacity

There has been a mild decline in the European gas refining output. The following tables give some background information on the worldwide production and consumption of gas within the period 1999 – 2012. Member States from EU27 are shown in italics.

Table 1.4: Worldwide gas production (1999 – 2012)

	Production expressed as billion of cubic metres					2012 share of total
	1999	2009	2010	2011	2012	
Total North America	748	807.4	821.1	866.5	896.4	26.8 %
of which US	533	584.0	603.6	648.5	681.4	20.4 %
Canada	177	164.0	159.9	159.7	156.5	4.6 %
Total S. and Cent. America	92	155.9	166.6	171.5	177.3	5.3 %
Total Europe and Eurasia	913.4	958.8	1031.2	1039.9	1035.4	30.7 %
of which Azerbaijan	5.4	14.8	15.1	14.8	15.6	0.5 %
Denmark	7.8	8.4	8.2	7.1	6.4	0.2 %
Germany	17.8	12.2	10.6	10.0	9.0	0.3 %
Italy	16.0	7.3	7.6	7.7	7.8	0.2 %
Kazakhstan	6.6	17.8	17.6	19.3	19.7	0.6 %
Netherlands	60.2	62.7	70.5	64.2	63.9	1.9 %
Norway	48.5	104.8	107.7	101.7	114.9	3.4 %
Poland	3.4	4.1	4.1	4.3	4.2	0.1 %
Romania	14.0	11.3	10.9	10.9	10.9	0.3 %
Russian Federation	535.7	527.7	588.9	607.0	592.3	17.6 %
Turkmenistan	20.6	36.4	42.4	59.5	64.4	1.9 %
Ukraine	16.4	19.2	18.1	18.6	18.6	0.6 %
United Kingdom	99.1	62.4	59.7	47.6	41.0	1.2 %
Uzbekistan	50.3	60.0	59.6	57.0	56.9	1.7 %
Other Europe and Eurasia	11.4	9.7	10.2	10.2	9.8	0.3 %
Total Middle East	195	407.3	472.7	518.7	548.4	16.3 %
Total Africa	119	200.4	214.3	211.2	216.2	6.4 %
Total Asia Pacific	263	439.6	486.5	483.6	490.2	14.5 %
Total world	2330	2970	3192	3291	3364	100.0 %

Source: BP Statistical review of world energy – 2013 [277, BP 2013]

Table 1.5: Worldwide gas consumption (1999 – 2012)

	Consumption expressed as billion of cubic metres					2012 share of total
	1999	2009	2010	2011	2012	
Total North America	761	816	850	868	907	27.4 %
of which US	634	649	682	691	722	21.8 %
Canada	87	95	95	101	101	3 %
Total S. and Cent. America	90	137	152	156	165	5 %
Total Europe and Eurasia	967	1050	1130	1106	1083	32.6 %
of which Austria	8.5	9.3	10.1	9.5	9.0	0.3 %
Azerbaijan	5.4	7.8	7.4	8.1	8.5	0.5 %
Belarus	14.8	16.1	19.7	18.3	18.6	0.6 %
Belgium	14.8	16.8	18.8	16.6	16.9	0.5 %
Bulgaria	3.0	2.3	2.6	2.9	2.7	0.1 %
Czech Republic	8.6	8.2	9.3	8.4	8.2	0.2 %
Denmark	5.0	4.4	5.0	4.2	3.9	0.1 %
Finland	3.7	3.6	3.9	3.4	3.1	0.1 %
France	37.7	42.6	47.4	40.9	42.5	1.3 %
Germany	80.2	78.0	83.3	74.5	75.2	2.3 %
Greece	1.5	3.4	3.7	4.5	4.2	0.1 %
Hungary	11.0	10.2	10.9	10.4	9.7	0.3 %
Ireland	3.3	4.8	5.2	4.6	4.5	0.1 %
Italy	62.2	71.5	76.1	71.3	68.7	2.1 %
Kazakhstan	6.2	7.8	8.2	9.2	9.5	0.3 %
Lithuania	2.4	2.7	3.1	3.4	3.3	0.1 %
Netherlands	38.5	38.9	43.6	38.1	36.4	1.1 %
Norway	3.6	4.1	4.1	4.3	4.3	0.1 %
Poland	10.3	14.4	15.5	15.7	16.6	0.5 %
Portugal	2.3	4.7	5.1	5.2	4.7	0.1 %
Romania	17.2	13.3	13.6	13.9	13.5	0.4 %
Russian Federation	352.8	389.6	414.1	424.6	416.2	12.5 %
Slovakia	6.4	4.9	5.6	5.2	6.0	0.2 %
Spain	15.0	34.6	34.6	32.2	31.4	0.9 %
Sweden	0.8	1.1	1.6	1.3	1.1	0.05 %
Switzerland	2.7	3.0	3.3	3.0	3.2	0.1 %
Turkey	12.4	35.7	39.0	45.7	46.3	1.4 %
Turkmenistan	11.0	19.9	22.6	25.0	23.3	0.7 %
Ukraine	70.9	47.0	52.1	53.7	49.6	1.5 %
United Kingdom	93.6	91.2	99.2	82.8	78.3	2.4 %
Uzbekistan	47.8	43.5	45.5	49.1	47.9	1.4 %
Other Europe and Eurasia	13.4	14.0	15.1	15.7	16.1	0.5 %
Total Middle East	181	345	377	395	412	12.4 %
Total Africa	52	100	108	114	123	3.7 %
Total Asia Pacific	270	497	560	594	625	18.8 %
Total world	2320	2944	3176	3232	3314	100.0 %
The difference between the world consumption figures and the world production statistics is due to variations in stocks at storage facilities						
Source: BP Statistical review of world energy – 2013 [277, BP 2013]						

Table 1.6: EU+ capacity for mineral oil refining

Charge capacity in Mm ³ /yr									
Country	No. of oil refineries	Crude	Vacuum distillation	Coking	Thermal operations	Catalytic cracking	Catalytic reforming	Catalytic hydrocracking	Catalytic hydrotreating
Austria	1	12.1	3.8		1.0	1.5	1.9		8.1
Belgium	4	42.9	14.5		1.7	7.8	6.1		39.9
Bulgaria	1	6.7	2.9		1.2	1.4	0.2		3.7
Cyprus	0								
Czech Republic	4	10.6	4.6		1.0		1.6	2.0	6.0
Denmark	2	10.1	1.3		3.7		1.3		2.5
Estonia	0								
Finland	2	15.1	8.5		2.0	3.3	2.9	5.2	17.3
France	11	86.9	35.1		6.8	18.1	12.7	4.2	68.4
Germany	13	140.3	63.6	6.1	14.4	20.3	23.5	11.8	116.74
Greece	4	24.5	8.8		2.8	4.4	2.9	2.5	21.0
Hungary	1	9.3	4.5	1.0	0.8	1.4	1.7		7.0
Ireland	1	4.1					0.6		2.6
Italy	15	135.6	47.3	2.6	26.0	18.7	16.7	17.6	72.58
Latvia	0								
Lithuania	1	11.0	5.2		1.7	2.5	2.7		8.9
Luxembourg	0								
Malta	0								
Netherlands	5	68.9	40.8	2.4	5.3	5.9	8.6	11.5	59.0
Poland	5	28.6	15.4			1.9	3.9	8.5	15.1
Portugal	2	17.7	5.1		2.1	2.4	2.9	0.5	11.7
Romania	9	31.2	15.9	4.0	2.2	6.4	3.6	0.1	13.8
Slovakia	1	6.7	3.2			1.0	1.2	2.4	5.1
Slovenia	0	0.8							
Spain	10	73.8	24.0	3.5	8.7	11.1	11.4	7.6	47.9
Sweden	5	25.4	7.9		3.9	1.7	4.1	2.8	15.6
United Kingdom	9	102.5	50.3	3.7	6.2	25.8	19.7	2.1	73.8
EU-27	106	864.8	362.6	23.4	91.5	135.4	130.2	78.9	616.7
% Word Capacity	17 %	17 %	21 %	9 %	41 %	16 %	20 %	25 %	23 %
Croatia	2	14.5	5.1	0.3	1.4	3.0	2.9	0.7	4.0
FYROM	1	2.9					0.6		1.3
Norway	2	18.5		1.4	1.9	2.8	2.0		7.3
Switzerland	2	4.2				1.2	0.7		1.9
Turkey	6	41.4	11.7		1.4	1.7	3.8	3.1	15.4
EU+	119	946.4	379.3	25.1	96.0	144.1	140.3	82.7	646.5
% Word Capacity	19 %	19 %	22 %	9 %	44 %	17 %	21 %	26 %	24 %

Sources: [9, Koottungal 2008], [132, O&Gas Journal 2011], reviewed by TWG, 2013

Production capacity in Mm ³ /yr (except units mentioned specifically)										
Country	Alkylation	Polymerisation dimerisation	Aromatics	Isomerisation	Base oil production	Etherification	Hydrogen (MNm ³ /d)	Coke (t/d)	Sulphur (t/d)	Bitumen
Austria				0.84		0.09			180	0.09
Belgium	1.02					0.22	2.79		971	1.54
Bulgaria	0.15		0.12			0.05	0.29		63	0.09
Czech Rep.			0.04	0.42	0.13	0.13	3.17		144	0.63
Denmark				0.37						0.46
Finland	0.45	0.03			0.31	0.33	4.53		540	0.39
France	1.55	0.17	0.17	2.81	1.72	0.27	3.45		1362	1.47
Germany	1.79	0.48	4.17	5.47	0.83	0.76	21.86	3813	2914	3.52
Greece	0.14	0.10	0.53	1.37	0.20	0.23	0.67		519	0.98
Hungary	0.19		0.70	0.20	0.35	0.07	2.16	600	226	0.37
Ireland				0.44			0.29		4	
Italy	2.34	0.09	0.78	6.51	1.39	0.68	8.65	2046	1776	0.91
Lithuania		0.42		1.10		0.16	0.71		320	
Netherlands	0.9		4.00	0.51	0.67	0.16	10.16		1726	0.62
Poland	0.20		0.60	1.35	1.03	0.15	4.73		560	1.94
Portugal	0.31		1.00				2.42		252	
Romania	0.13		0.45	0.22	0.60	0.08	0.51	2555	143	0.80
Slovakia	0.26		0.54	0.35	0.12	0.09	2.54		270	0.15
Slovenia										
Spain	0.98		1.5	2.09	0.56	0.56	8.50	3565	1762	1.54
Sweden		0.20		1.66			1.52		334	1.59
UK	5.35	0.79	0.85	6.99	1.39	0.23	3.60	2400	792	1.65
EU-27	16	2	15	33	9	4	83	14 979	14 858	19
% World capacity	13 %	20 %	19 %	34 %	20 %	38 %	21 %	7 %	18 %	18 %
Croatia			0.55	0.32	0.03			200	123	
FYROM				0.25						
Norway		0.64		0.22				610	20	
Switzerland		0.22		0.37			0.79			
Turkey				0.82	0.34		6.16	180	315	1.17
EU+	16	3	16	35	10	4	89	15 969	15 316	20
% World capacity	13 %	28 %	20 %	36 %	21 %	38 %	22 %	8 %	18 %	19 %
NB for Table 1.6 (first part): - Vacuum distillation has been included in primary distillation sections in this document. - Thermal operations include visbreaking (within this document) and thermal cracking (within LVOC BREF). - Catalytic hydrocracking, hydrotreating and hydrotreatment are included in hydrogen-consuming processes. NB for Table 1.6 (second part): - Aromatic production is included in the LVOC BREF, although some refineries have it.										

1.2.4 Product market

1.2.4.1 Petroleum products

The European market is characterised by a growing demand for petrochemicals, kerosene and diesel, and a declining demand for gasoline, light heating oil and heavy fuel oil. There is ongoing competition because of the increasing capacity in the Middle East and Asia.

In the particular case of automotive fuels, and despite the progressive technical adaptation of European sites which lead them to produce (on average) more middle distillates than in every other region in the world except Asia (as seen in Table 1.7), EU refineries are still not producing the mix demanded by EU consumers due to their technical design. They cannot satisfy the existing demand for diesel and they continue to produce gasoline in excess. Due to favourable taxation, the share of the diesel fleet has risen from 23 % in 1996 to 53 % in 2006, and is expected to increase to 60 – 65 % over the next decade.

Table 1.7: Product group consumption per region – Evolution from 2002 to 2012

Product Consumption (Thousands of barrels per day)	Light distillates		Middle distillates		Fuel oil		Others	
	2002	2012	2002	2012	2002	2012	2002	2012
North America	10 514	10 594	6 654	6 417	1 187	635	5 442	5 394
(of which US)	(9 167)	(9 221)	(5 735)	(5 281)	(686)	(343)	(4 172)	(3 976)
South and Central America	1 401	1 898	1 706	2 535	752	678	1 146	1 422
Europe	4 125	2 976	6 939	7 389	1 866	1 063	3 040	2 724
Former Soviet Union	1 056	1 352	1 039	1 453	635	418	863	1 169
Middle East	1 175	1 886	1 740	2 753	1 374	1 916	1 163	1 799
Africa	602	873	1 135	1 641	388	431	443	577
Asia Pacific	6 198	9 281	8 182	10 487	3 383	3 633	4 323	6 379
(of which China)	(1 359)	(3 182)	(1 785)	(3 741)	(783)	(820)	(1 335)	(2 477)
(of which Japan)	(1 728)	(1 632)	(1 944)	(1 360)	(632)	(811)	(1 053)	(911)
World	25 071	28 862	27 395	32 675	9 854	8 773	16 421	19 463
Light distillates: aviation, motor gasolines and light distillate feedstock (LDF) Middle distillates: jet and heating kerosines, gas and diesel oils Fuel oil: marine bunkers and crude oil used directly as fuel. Others: refinery gas, liquified petroleum gas (LPG), solvents, petroleum coke, lubricants, bitumen, wax, other refined products and refinery fuel and loss. Source: BP Statistical review of world energy – 2013 [277, BP 2013]								

According to the Commission [72, EC 2010], the evolution of the petroleum product demand mix in the EU between 1990 and 2008 is the following:

- the share of jet fuel and kerosene has increased from 5.5 % to 9.4 %;
- the share of gas oil (including diesel, not heating oil) has increased from 17.7 % to 31 %;
- the share of gasoline has decreased from 22.7 % to 16.1 %;
- the share of heavy fuel oil has decreased from 16.3 % to 6.4 %.

At the time of writing, the EU production-consumption gap is still closed via international trade in refined products. The EU imports diesel (mostly from the Russian Federation) and exports gasoline (mostly to the United States of America, and in a lesser extent, to Africa and the Middle East). As Figure 1.6 shows, this import-export EU market was almost balanced in 2005.

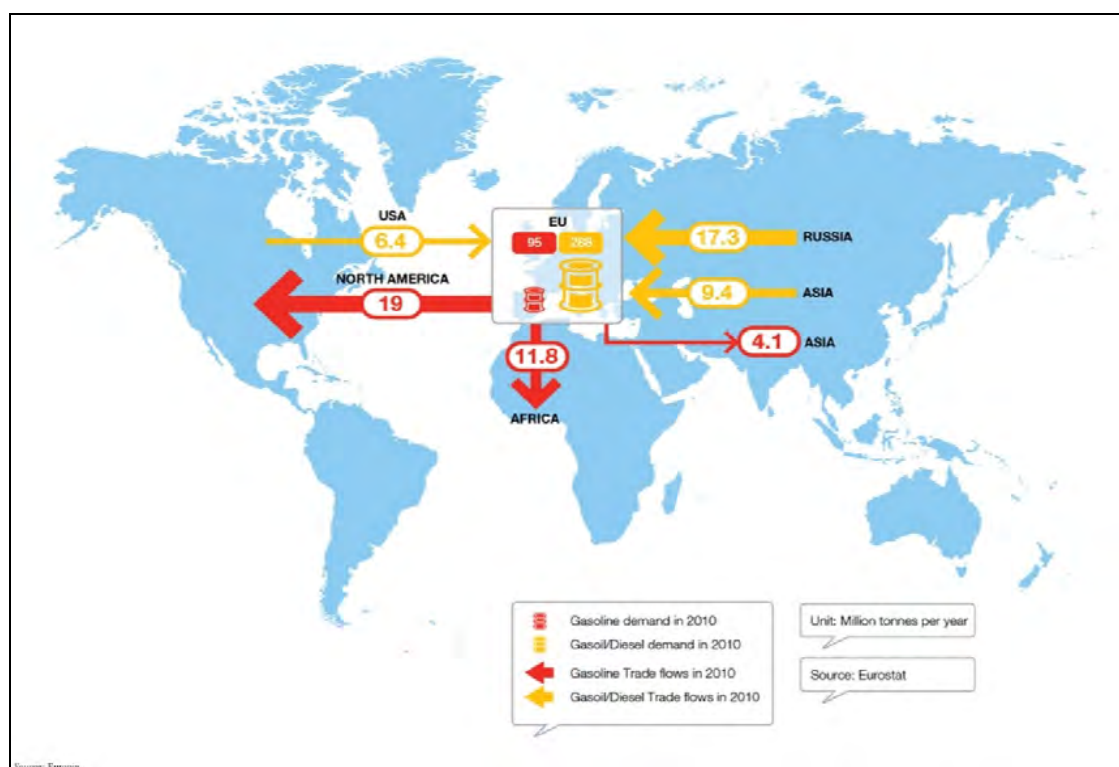


Figure 1.6: Major gasoline and diesel trade to and from the EU

However, the US, and the Middle Eastern and Asian countries have been increasing their refining capacity. Also, North America is expected to become an important diesel exporter. In Table 1.8, the total imports and exports of petroleum products for the year 2009 by region are given.

Table 1.8: Worldwide import/export of products (2009 – 2012)

Import/export of oil products Million of tonnes per year	2009		2012	
	Product imports	Product exports	Product imports	Product exports
US	122.0	89.5	100.5	127.5
Canada	15.3	25.7	10.1	29.7
Mexico	21.0	8.0	27.9	3.7
South and Central America	41.3	54.4	67.7	33.1
Europe	152.0	72.9	142.8	85.9
Former Soviet Union	3.2	105.1	5.5	122.2
Middle East	10.5	91.6	26.8	98.5
North Africa	10.0	25.3	15.0	22.3
West Africa	12.1	5.3	11.4	11.3
East and Southern Africa	5.7	0.3	12.5	0.7
Australasia	17.1	2.0	18.2	7.9
China	49.8	29.4	83.0	25.8
India	10.4	35.4	15.5	64.7
Japan	35.3	16.5	48.2	10.6
Singapore	79.8	72.0	96.7	71.0
Other Asia Pacific	127.6	59.9	120.2	87.0
Total world	714		802	
Note: Bunkers are not included as exports. Intra-area movements (e.g. between countries in Europe) are excluded				
Source: [71, BP 2010], [277, BP 2013]				

As far as the quality of refined products is concerned, the phasing out of lead from gasoline has been completed and new specifications (see Table 1.9) have required a reduction of the sulphur content for all types of automotive fuels, lower aromatics, particularly benzene in gasoline, and reduced polyaromatic hydrocarbons and a higher cetane number in diesel. The trend is that environmental quality requirements will become more stringent for all refinery products. Moreover, EU acidification puts additional pressure on the sulphur content of liquid fuels, and therefore also on the sulphur content of the fuels used in refineries. Meeting these new specifications require additional investment, particularly in desulphurisation capacity, adding more pressure to the restructuring process of the sector.

Table 1.9: Evolution of mineral oil product specifications

Refinery product	Unit	Product specification	2000	2005	2009
		Before 2000			
Gasoline					
Sulphur	ppm	500 max.	150 max.	50 max.	10 max.
Lead	g/l	0.15	0.005 max.	10 max.	10 max.
Aromatics	% v/v	none	42 max.	35 max.	35 max.
Olefins	% v/v	none	18 max.	18 max.	18 max.
Aromatics	% v/v		42 max.	35 max.	35 max.
Benzene	% v/v	5 max.	1.0 max.	1.0 max.	1.0 max.
Evaporation at 100 °C (summer)	%	65/70 max.	46 min.	46 min.	46 min.
Evaporation at 150 °C (winter)	%	none	75 min.	75 min.	75 min.
RVP, summer	kPa	80	60 max.	60 max.	60 max.
Oxygen	%	2.5 max.	2.7 max.	2.7 max.	3.7
Methanol	% v/v		3	3	3
Ethanol	% v/v		5	5	10
Iso-propyl alcohol	% v/v		10	10	12
Ter-butyl alcohol	% v/v		7	7	15
Iso-butyl alcohol	% v/v		10	10	15
Ethers >C ₄	% v/v		15	15	22
Other oxygenates	% v/v		10	10	15
Diesel					
Sulphur	ppm	500 max.	350 max.	50 max.	10 max.
Cetane number		49 min.	51 min.	51 min.	51 min.
Density @ 15°C	kg/m ³	860 max.	845 max.	845 max.	845 max.
Distillation 95 % (v/v)	°C	370 max.	360 max.	360 max.	360 max.
Polycyclic Aromatics	% m/m	none	11 max.	11 max.	8 max.
FAME - EN 14078	% v/v	none	none	none	7 max.
Heating gas oil					
Sulphur	% m/m				2008 0.1 max.
Inland heavy fuel oil					
Sulphur	% m/m			2003 1	
Bunker fuel oil in SO_x emission control zones					
Sulphur	% w/w			IMO - 2003 1.5	

Directive 2012/33/EU of 21 November 2012 amending Directive 1999/32/EC as regards the sulphur content of marine fuels aims at taking into account the more stringent rules for the sulphur content of fuels used by maritime transport agreed under the International Maritime Organisation (IMO) through the revised Annex VI to the MARPOL convention.

It introduces, in particular, stricter sulphur limits for marine fuel:

- in Sulphur Emission Control Areas (SECAs): 1 % as of 1 July 2010 and 0.10 % as of 1 January 2015;
- in sea areas outside SECAs: 3.5 % as of 1 January 2012 and 0.50 % from either 1 January 2020 or 2025 (to be decided in 2018).

1.2.4.2 Natural gas

In 2007, the world's largest exporter of natural gas was by far Russia (around 200 billion m³/yr), followed by Canada and Norway with around 87 billion m³/yr. The first EU-27 exporter, the Netherlands, ranked in the 9th place with 30 billion m³/yr.

Table 1.10 gives the imports of natural gas by region for the year 2009.

Table 1.10: Natural gas imports in 2009

Natural gas imports	Pipeline imports (billion m ³)	LNG imports	Total imports
North America	122.49	17.33	139.82
South and Central America	12.49	3.28	15.77
Europe and Eurasia	443.97	69.02	512.99
Austria	7.98	–	7.98
Belgium	15.01	6.53	21.54
Bulgaria	2.64	–	2.64
Croatia	1.20	–	1.20
Czech Republic	9.40	–	9.40
Estonia	0.71	–	0.71
Finland	4.10	–	4.10
France	35.99	13.07	49.06
Germany	88.82	–	88.82
Greece	2.55	0.74	3.29
Hungary	8.10	–	8.10
Ireland	5.08	–	5.08
Italy	66.41	2.90	69.31
Latvia	1.19	–	1.19
Lithuania	2.77	–	2.77
The Netherlands	17.21	–	17.21
Poland	9.15	–	9.15
Portugal	1.59	2.82	4.41
Romania	2.05	–	2.05
Slovakia	5.40	–	5.40
Slovenia	0.89	–	0.89
Spain	8.99	27.01	36.00
Sweden	1.31	–	1.31
United Kingdom	30.88	10.24	41.12
Rest of Europe and Eurasia	114.55	5.71	120.26
Middle East	30.42	0.89	31.31
Africa	5.25	–	5.25
Asia Pacific	19.16	152.27	171.43
Total	633.77	242.77	876.54

Source: BP Statistical Review Of World Energy 2010

Unconventional gas: The use of horizontal drilling in conjunction with hydraulic fracturing has greatly expanded the ability of producers to profitably produce natural gas from low permeability geologic formations, particularly shale formations. Application of fracturing techniques to stimulate oil and gas production began to grow rapidly in the 1950s, although experimentation dates back to the 19th century.

Shale gas (see definition below) has become a 'game changer' for the natural gas market. The proliferation of activity into new shale plays has increased dry shale gas production in the United States from 11 billion cubic metres in 2000 to 136 in 2010, or 23 % of US dry gas production. Wet shale gas reserves have increased to about 1 700 billion cubic metres by year-end 2009, when they comprised about 21 % of overall US natural gas reserves, now at the highest level since 1971.

Thus, adding the identified shale gas resources to other gas resources increases total world technically recoverable gas resources by over 40 % to 640 000 billion cubic metres.

Shale gas is extracted by fracking technique that involves high pressure injection of water, sand and chemical additives, and thus environmental impacts need to be taken into consideration.

Some useful definitions about these new techniques are provided:

- Shale gas - Natural gas stored in extremely small pore spaces or bonded to organic material within rock composed mostly of consolidated clay and siltstone.
- Tight gas - Natural gas stored in small pore spaces in very low permeability underground formations, such as sandstone, siltstone or limestone.
- Deep gas - Unconventional natural gas that is located deep within geological formations.
- Coalbed methane (CBM) - Natural gas stored in naturally occurring fracture systems or bonded onto coal. A liquid, low-pressure sweet gas, CBM gas is used to fuel hot water heaters, furnaces and ranges.

Mid size companies lead this extraction activity: e.g. Chesapeake, Exco, XTO Energy, Atlas, Encana or Duvenay.

Table 1.11: Estimated technically recoverable shale gas resources in 32 countries

Country	Estimated technically recoverable reserves (billion m ³)
China	36 104
United States	24 409
Argentina	21 917
Mexico	19 284
South Africa	13 734
Australia	11 214
Canada	10 987
Libya	8 212
Algeria	6 541
Brazil	6 400
<i>Poland</i>	5 295
<i>France</i>	5 097
Norway	2 350
Chile	1 812
India	1 784
Paraguay	1 756
Pakistan	1 444
Bolivia	1 359
Ukraine	1 189
<i>Sweden</i>	1 161
<i>Denmark</i>	651
Uruguay	595
<i>United Kingdom</i>	566
Colombia	538
Tunisia	510
<i>Netherlands</i>	481
Turkey	425
Morocco	311
Venezuela	311
<i>Germany</i>	227
Western Sahara	198
<i>Lithuania</i>	113
Total	186 977
NB: Italics: EU-27 member states	
Source: [73, US DOE 2011]	

1.3 European refineries

1.3.1 Oil refineries

At the time of writing (2013), there are close to 120 crude oil refineries spread around the EU+ countries. Of these refineries, about ten are specialist refineries producing mainly lubricating oil basestocks or bitumen.

Figure 1.7 and the associated Table show the distribution of European refineries by country. As can be seen on the map, refineries are mainly placed close to the sea or to a big river, to satisfy their need for large amounts of cooling water, as well as to facilitate the sea transport of raw materials and products. There are some places in Europe with a high concentration of refineries (e.g. Rotterdam in Netherlands; Antwerp in Belgium and Sicily in Italy).

As a result of overcapacity in the European refinery sector, very few new oil refineries have been built in the last 35 years. In fact, only 9 % of the existing refineries have been built in this period and only two % before 2000, 95 % being built before 1981 and 44 % before 1961 (see Table 1.12). Although most refineries will have had upgrades and new units built since they were first commissioned, their overall structure, and in particular items like the pattern of sewer systems, will have remained essentially unchanged.

Table 1.12: Percentage of refineries built during different time periods in EU-27

Time period	Number of refineries built in the time period	Percentage of refineries built during the time period (%)	Cumulative percentage
Before 1900	1	1	1
1900 – 1910	2	2	3
1911 – 1920	1	1	4
1921 – 1930	9	9	13
1931 – 1940	7	7	19
1941 – 1950	8	8	27
1951 – 1960	17	17	44
1961 – 1970	41	40	83
1971 – 1980	12	12	95
1981 – 1990	3	3	98
1991 - 2000	2	2	100
2000 – 2010	0	0	100
Total	103 (*)		

(*) Refinery in Martinique not included within the table. Some refineries have been demolished recently.
Source: CONCAWE

1.3.2 Gas refineries

Seventeen onshore natural gas plants have been identified in Europe. Three have been identified in the Netherlands, six in Norway, including LNG plants, and nine in the United Kingdom.

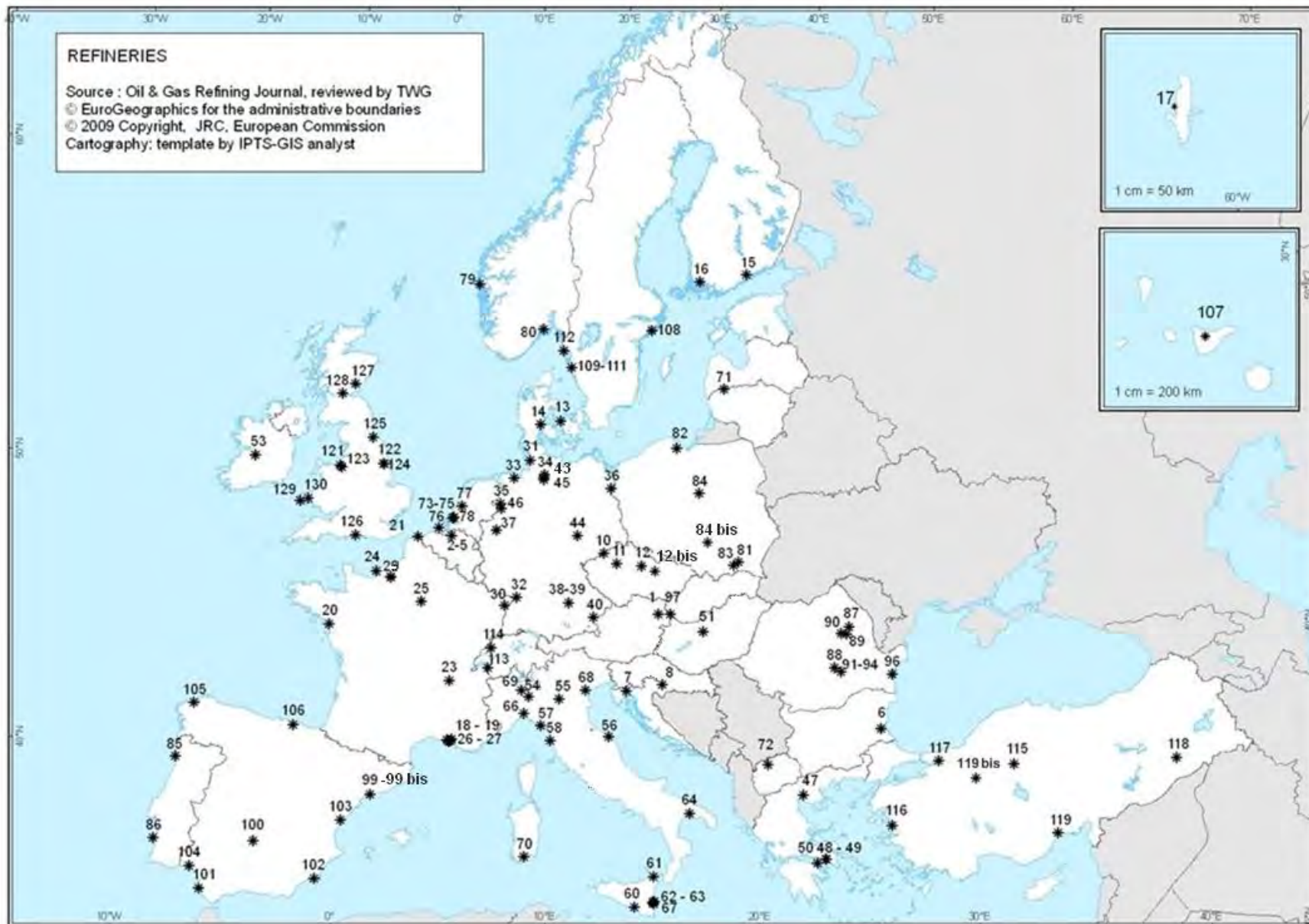


Figure 1.7: Geographical distribution of the European refineries

ID	Country	Refinery location	ID	Country	Refinery location	ID	Country	Refinery location		
1	Austria	Schwechat	51	Hungary	Szazhalombatta	97	Slovakia	Bratislava		
2 – 5	Belgium	Antwerpen	53	Ireland	Whitegate	99-99bis		Tarragona		
6	Bulgaria	Burgas	54		Sannazzaro, Pavia	100		Puertollano, Ciudad Real		
7	Croatia	Rijeka	55		Mantova	101		Cadiz		
8		Sisak	56		Falconara, Marittima	102		Cartagena, Murcia		
9		Zagreb	57		Ravenna	103		Castellon de la Plana		
10	Czech Republic	Litvinov	58		Livorno	104		Huelva		
11		Kralupy	59		Cremona	105		La Coruña		
12		Pardubice	60		Gela, Ragusa	106		Muskiz Vizcaya		
12bis		Kolin	61		Milazzo, Messina	107		Tenerife		
13	Denmark	Kalundborg	62	Italy	Priolo, Sicily	108		Nynashamn		
14		Fredericia	63			Augusta, Siracusa	109 – 111	Sweden	Gothenburg	
15	Finland	Porvoo	64			Taranto	112		Brofjorden - Lysekil	
16		Naantali	65			Rome	113	Switzerland	Collombey	
17	France	Fort-de-France	66			Busalla	114			Cressier
18		Fos-sur-Mer	67			Melilli, Sicily	115	Turkey	Kirikkale	
19		Berre l'Etang *	68			Porto Marghera	116			Aliaga - Izmir
20		Donges	69			S. Martino Di Trecate S.	117			Izmit
21		Dunkerque	70			Sarroch	118			Batman, Siirt
23		Feyzin	71		Lithuania	Mazeikiai	119			Mersin
24		Gonfreville L'orcher	72	FYROM	Skopje	119 bis		Narli, Kahramanmaras		
25		Grandpuits	73 – 75		Rotterdam	120	United Kingdom	Coryton Essex		
26		La Mede	76	The Netherlands	Vlissingen	121			Eastham	
27		Lavera	78			Pernis		122		South Killingholme
29		Port Jérôme	79	Norway	Mongstad	123			Stanlow	
31	Heide	80			Slagen	124			South Killingholme	
32	Karlsruhe	81	Poland	Jaslo	126			Fawley		
33	Wilhelmshaven	82			Gdansk	127			Dundee	
34	Hamburg	83			Gorlice	128			Grangemouth	
35	Lingen	84			Plock	129		Milford Haven		
36	Schwedt	84 bis		Trzebina	130		Pembroke, Dyfed			
37	Gelsenkirchen	85	Portugal	Leca Da Palmeira Porto						
38 - 39	Vohburg/Ingolstadt/Neustadt	86			Sines					
40	Burghausen	87	Romania	Bacau						
43	Harburg	88			Campina					
44	Leuna, Spergau	89			Onesti, Bacau					
45	Rheinland	90			Darmanesti					
46	Salzbergen	91 – 94			Ploiesti					
47	Thessaloniki	95			Pitesti					
48	Elefsis	96		Midia						
49	Aspropyrgos									
50	Ahghii Theodori									

NB: *In italics*: lubricant and bitumen specialised refineries
* Refinery under 'mothballing' in 2013
Source: [132. O&Gas Journal 2011] reviewed by TWG, 2013

1.3.3 Technical characteristics of European refineries

Compared to other parts of the world, refining configurations of Western European refineries reflect to some extent their technical adaptation to the local demands of middle distillates, in particular diesel and jet fuel: they show proportionally more hydrotreating and hydrocracking capacities and less catalytic cracking capacities than in North America. As shown in Table 1.13, the most complex refinery configurations are observed in North America refineries. As a result, they produce 3 times less heavy residues than in Europe, and 6 times less than in the Russian federation or in Africa.

Table 1.13: Refining configurations as a percentage of crude distillation

World regions	Catalytic cracking	Catalytic reforming	Catalytic hydrocracking	Catalytic hydrotreating
Africa	6.5	14.7	1.9	28.0
Asia	11.9	8.7	3.3	38.5
Eastern Europe	9.0	14.5	3.1	41.6
Middle East	5.1	9.2	8.3	29.2
North America	20.2	31.9	8.4	73.4
South America	19.6	6.4	2.1	28.9
Western Europe	15.0	14.3	7.0	66.7
<i>Source:</i> [20, Gary et al. 2007]				

Table 1.14 shows the number of processes currently operating in the mineral oil refineries in each country. As can be seen, crude and vacuum distillations, catalytic hydrotreatment and catalytic reforming are the most common processes, as they are found in the simplest of refineries. It may be surprising that the number of catalytic hydrotreatment processes is higher than the number of refineries, but the reason is simply that there is, on average, more than one catalytic hydrotreatment in each European refinery. The least common processes in European refineries are coking and polymerisation/dimerisation.

Some of these refining processes have been analysed in order to determine the type of technique or techniques used to perform a certain process. For instance, there are currently two technologies to carry out alkylation, namely sulphuric and hydrofluoric. In this case, these two technologies are competitors but in other cases, such as hydrotreating, one technique does not exclude another. As can be seen in Table 1.14, some techniques are really predominant in particular processes in European refineries. This category includes delayed coking, visbreaking, fluid catalytic cracking, hydrofluoric alkylation, C₅ and C₆ isomerisation, Methyl tert-butyl ether (MTBE) production and steam reforming for the production of hydrogen. Other processes where one technique is less predominant are catalytic reforming, catalytic hydrorefining, catalytic hydrotreating and hydrogen recovery process.

Table 1.14: Number of type of processes per country

Process		EU-27 number	EU+ number	World M barrel/day
1	Fluid coking	2	2	
2	Delayed coking	13	15	
3	Other	1	1	
7	Coking	16	16	4.61
1	Thermal cracking	14	16	
2	Visbreaking	52	57	
22	Thermal ops	66	66	3.82
1	Fluid	58	64	
1	Other	3	4	
5	Catalytic cracking	61	61	14.66
1	Semi-regenerative	58	71	
2	Cyclic	13	13	
3	Continuous regen	34	36	
4	Other	0	0	
6	Catalytic reforming	105	105	11.51
1	Distillate upgrading	24	27	
2	Residual upgrading	6	7	
3	Lube oil manufacturing	5	5	
4	Other	3	3	
c	Conventional	15	17	
m	Mild to moderate	8	8	
13	Catalytic hydrocracking	38	38	5.41
1	Pretreatment of catalytic reformer feeds	81	87	
2	Other naphta desulphurisation	26	26	
3	Naphta aromatics saturation	11	11	
4	Kerosin/jet desulphurisation	35	35	
5	Diesel desulphurisation	65	70	
6	Distillate aromatics saturation	3	3	
7	Other distillates	10	10	
8	Pretreatment cat. crackers feed	20	20	
9	Other heavy GO	13	14	
10	Resid hydrotreating	2	2	
11	Lube oil polishing	15	15	
12	Post hydrotreating of FCC naphta	19	20	
13	Other	9	9	
13	Catalytic hydrotreating	309	309	45.43

Process		EU-27 number	EU+ number	World M barrel/day
19	Crude	110	124	88.22
19	Vacuum	101	110	29.18
	1 Sulphuric acid	7	7	
	2 Hydrofluoric acid	30	30	
2	Alkylation	37	37	2.06
	1 Polymerisation	11	13	
	2 Dimerisation	0	0	
18	Polymerisation/dimerisation	11	13	0.2
	1 BTX	21	22	
	2 Hydrodealkylation	5	5	
	3 Cyclohexane	5	5	
	4 Cumene	3	3	
	Aromatics	34	34	1.34
	1 C4	8	8	
	2 C5	8	8	
	3 C5and6	124	131	
16	Isomerisation	140	140	1.7
	1 MTBE	22	22	
	2 ETBE	12	12	
	3 TAME	4	4	
	4 Other	1	1	
11	Oxygenates	39	39	0.19
	1 Steam methane Reforming	33	34	
	2 Steam naphta Reforming	9	11	
	3 Partial oxidation	5	5	
	4 Pressure swing adsorption	22	25	
	5 Cryogenic	7	7	
	6 Membrane	6	7	
	7 Other	2	2	
14	Hydrogen production	84	84	0.02
3	Lubes	32	34	0.79
7	Coke	17	20	0.2
23	Sulphur	77	83	0.08
4	Asphalt	57	63	1.77

Source: [70, Oil & Gas 2010]

Following the analysis of the type of processes, Figure 1.8 shows the capacity ranges for the different processes found in European refineries, both in thousands of barrels and as a percentage of the worldwide refinery base. As can be seen, the ranges are quite large, explaining again the diversity of type of refineries found in Europe. For instance, there exist huge differences in the capacity of crude units or catalytic hydrotreating. Smaller differences exist in the coking processes and alkylation processes.

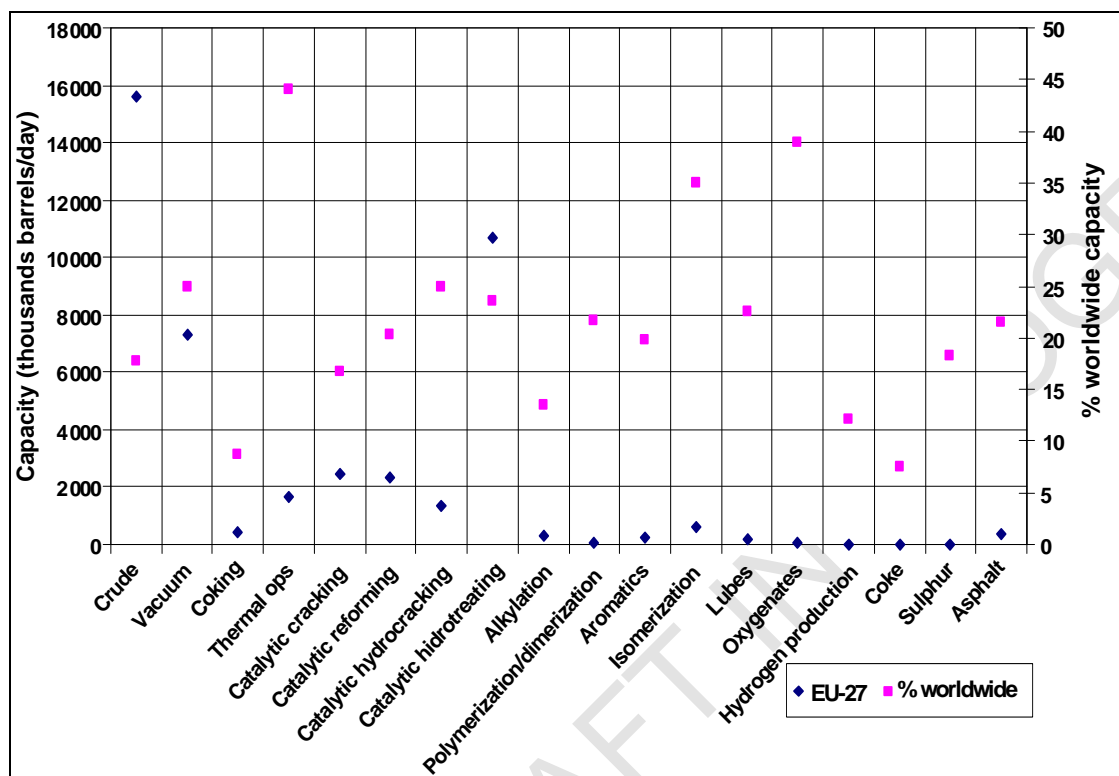


Figure 1.8: Capacity of the various processes in the EU-27 refineries (O&GJ 2011)

There are various approaches to defining a refinery complexity. In some studies it is common to distinguish between several types of refinery configuration according to complexity (see Annex 9.1). The Nelson refinery complexity index was used for the construction of Figure 1.9. This classification is to define five different types of configuration. Other definitions are used in the industry, such as Equivalent Distillation Capacity as used by Solomon Associates.

Figure 1.9 tries to illustrate the variety of complexity of refineries within Europe. The Y axis represents refinery complexity calculated according to the Nelson refinery complexity index [216, Johnston 1996]⁽²⁾. The X axis represents the different EU+ countries. If the Y gap of the EU+ refineries is divided into four categories (less than 3.9, between 3.9 and less than 6.1, between 6.1 and 8.4 and more than 8.4⁽³⁾), it can be seen that 18 % of the refineries belong to the lowest category, 30 % belong to the second category, 41 % to the third and 11 % to the group of more complex refineries. Consequently, seven out of 10 refineries of the EU+ can be considered as refineries with medium complexity.

Even if there are still a number of hydroskimming refineries in operation, the most common configuration in EU+ is the catalytic cracker configuration.

⁽²⁾ Nelson developed a system to quantify the relative cost of components that make up a refinery. It is a pure cost index that provides a relative measure of the construction costs of a particular refinery based on its crude and upgrading capacity. Nelson assigned a factor of 1 to the distillation unit. All other units are rated in terms of their cost relative to this unit.

⁽³⁾ Limits of the categories calculated as average \pm standard deviation.

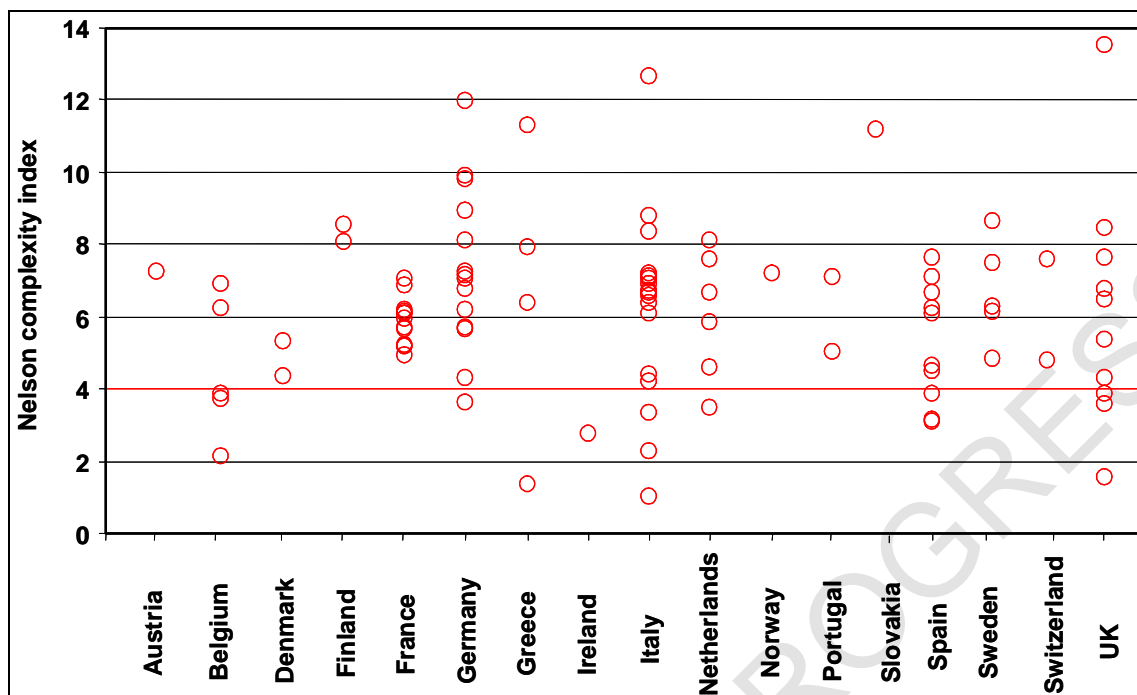


Figure 1.9: Nelson complexity index dispersion for some European refineries per country

Figure 1.10 shows the distribution of the refineries in the EU+ according their complexity (NCI: Nelson complexity index) in 2005 and 2009 [112, CONCAWE 2011].

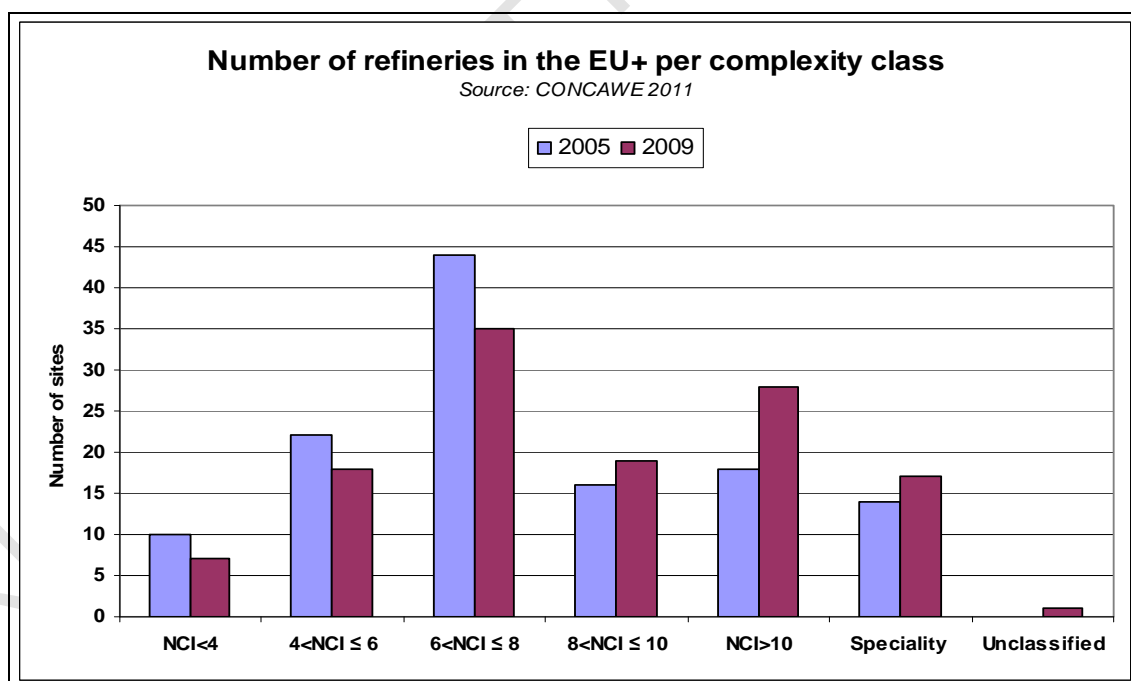


Figure 1.10 Distribution of refineries in the EU+ according Nelson complexity index

1.3.4 Employment in the European refinery sector

According to Eurostat (Manufacture of refined petroleum products -NACE Rev.2 group 19.2), in 2010, the European refining industry employed about 123 000 people in the EU. In addition, it can be considered that as many as 400 000 to 600 000 jobs are directly dependent on the EU refining industry. [72, EC 2010]

1.4 Main environmental issues in the refining sector

Refineries are industrial sites that manage huge amounts of raw materials and products, and they are also intensive consumers of energy and water used to carry out the processes. In their storage and refining processes, refineries generate emissions to the atmosphere, to water and to the soil. Environmental management has become a major factor for refineries. The refining industry is a mature industry, and pollution abatement programmes have been carried out in most refineries for a long time to different extents. As a result, the emissions generated by refineries have declined per tonne of crude processed and are continuing to decline.

It is important to know, with respect to the quality and quantity of refinery emissions, that on a macro scale the crude oils vary only to a limited extent in their composition. Moreover, refineries are often limited to a comparatively narrow range of crude oil diets. Normally, when switching from one crude oil to another within this range, large variations in refinery emissions are not expected. Consequently the type and quantity of refinery emissions to the environment are well known during normal operations. However, from time to time, processing of crude oils previously unknown to the refinery can have unforeseen impacts on the performance of refinery processes; leading to an increase in emissions. This is particularly likely to affect water emissions and to a lesser extent air emissions.

1.4.1 Emissions to the atmosphere

According to available European emission inventories [35, EEA 2009], oil refining is responsible for a significant contribution to air emissions generated by industrial activities. In the particular case of sulphur oxides, this contribution is significant (around 7 %) when even observed at the level of the overall emissions by all human activities.

The following Table 1.15 gives an estimation of the contribution of oil and gas refineries with regard to emissions reported in 2007 and 2009 in the European Union for some main parameters.

Table 1.15: Contribution of oil refining to the EU-27 air emissions (2007 -2009)

Main air pollutants	Overall emissions from industrial activities (kt)	Emissions from the energy production and use ⁽¹⁾ (kt)	Oil refining emissions 2007 ⁽²⁾ (kt) (#sites)	Part of oil refining emissions from the energy production and use (%)	Part of all emissions from all industrial activities (%)	Oil refining emissions 2009 ⁽²⁾ (kt) (#sites)
Greenhouse gases (CO ₂ -equivalent)	4 638 000	2 201 000	158 880 (105)	7.2	3.4	146 745 (100)
Carbon monoxide (CO)	27 921	4 634	58 (27)	1.3	0.2	55 (27)
Fine particulates (PM ₁₀)	1 952	312	8 (44)	2.6	0.4	7 (40)
Fine particulates (PM _{2.5})	1 266	224	11	4.9	0.9	-
Nitrogen oxides (NO _x)	10 939	3 991	193 (110)	4.8	1.8	162 (105)
Sulphur oxides (SO _x)	7 442	6 024	574 (111)	9.5	7.7	426 (103)
Volatile organic compounds (NMVOCs)	8 951	265	180 (98)	67.9	2.0	138 (93)

⁽¹⁾ This sector covers the production of energy from fossil fuels for power and heat generation and industrial manufacturing (NFR Sectors 1A1 and 1A2).
⁽²⁾ Figures given for NFR Sector 1A1b
Source: [EPRTR data]

Power plants, boilers, heaters and catalytic cracking are the main sources of emissions of carbon monoxide and dioxide, nitrogen oxides (NO_x), particulates, and sulphur oxides (SO_x) to the atmosphere.

Refinery processes require a lot of energy; typically more than 60 % of refinery air emissions are related to the production of energy for the various processes.

Sulphur recovery units and flares also contribute to these emissions. Catalyst changeovers and cokers release particulates. Volatile organic compounds (VOCs) are released from storage, product loading and handling facilities, oil/water separation systems and, as fugitive emissions, from flanges, valves, seals and drains. Other emissions to the atmosphere are H₂S, NH₃, BTX, CS₂, COS, HF and metals as constituents of the particulates (V, Ni and others). Table 1.16 shows a very brief summary of the main pollutants emitted by a typical refinery, with their main sources.

Table 1.16: Main air pollutants and their main sources emitted by refineries

Main air pollutants	Main sources
Carbon dioxide	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Flare systems Incinerators LNG plant CO ₂ separation
Carbon monoxide	Process furnaces and boilers Fluidised catalytic cracking regenerators CO boilers Sulphur recovery units Flare systems Incinerators
Nitrogen oxides (NO, NO ₂)	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Coke calciners Incinerators Flare systems
Nitrous oxide (N ₂ O)	Fluidised catalytic cracking regenerators
Particulates (including metals)	Process furnaces and boilers, particularly when firing liquid refinery fuels Fluidised catalytic cracking regenerators CO boilers Coke plants Incinerators
Sulphur oxides	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Coke calciners Sulphur recovery units (SRU) Flare system Incinerators
Volatile organic compounds (VOCs)	Storage and handling facilities Gas separation units Oil/water separation systems Fugitive emissions (valves, flanges, etc.) Vents Flare systems

Carbon dioxide (CO₂) is the greenhouse gas which receives the most attention in the debate about global climate change. The main source of CO₂ emissions is the production of energy. Since the first oil crisis in 1973, refineries have made a concerted effort to enhance energy efficiency. Despite these energy conservation measures, refinery energy demand has increased due to tightened product specifications and a shift over the years from producing heavy fuel oils to transport fuels. The fuel used for petroleum refining increased by about 15 % in the EU-27 between 1990 and 2007, which represents the third largest key source increase during this period, after road transportation, public electricity and heat production. Even if gaseous fuels use has more than doubled since 1990, liquid fuels still represented in 2007 over 90 % of all fuel used. The Netherlands and Italy are, with respectively 5 and 4.5 %, the two Member States with the highest relative importance of CO₂ emissions from petroleum refining in their total greenhouse gas emissions.

Carbon monoxide (CO) always appears as an intermediate product of the combustion processes, in particular in understoichiometric combustion conditions. However, the relevance of CO releases from refineries is not very high compared to CO₂.

Oxides of nitrogen (NO_x), when emitted to the air, can combine with water and form a component of 'acid rain'. Further, NO_x in combination with volatile organic compounds and sunlight, can lead to the formation of ground-level ozone. The source of NO_x is mainly the combustion processes; during the combustion of fuel, nitrogen (mainly originating from the combustion air itself) is transformed to a mixture of NO₂ and NO. Combustion conditions play an important role here. N₂O (laughing gas) is a powerful greenhouse gas that contributes to the stratospheric ozone depletion.

Particulate emissions (PM) have become a focus of attention because of their potential adverse health effects, in particular for the smallest particulate matter with an aerodynamic diameter <10 µm (PM₁₀ - EN12341) and <2.5 µm (PM_{2.5} - EN14907). Particulate emissions are caused by the combustion of fuel oils, especially when there is sub-optimal combustion. Another significant source is the catalytic cracker. The particulate content of hazardous compounds (e.g. heavy metals and polycyclic aromatic hydrocarbons) is of primary interest in a refining context.

Sulphur oxides (SO_x), when emitted to the air, can combine with water and form a component of 'acid rain'. The main source of SO_x is the production of energy; during combustion, the sulphur in the fuel is transformed to a mixture of SO₂ and SO₃. Another source, typically smaller, is the flue-gas from the sulphur recovery units. There is a direct relation between the sulphur in the feed to a combustion process and the sulphur oxides in its flue-gas. Generally speaking the sulphur content of the refinery fuel pool is a careful balance between energy required, the type of crude processed, the emission limits and economic optimisations.

Volatile organic compounds (VOCs), as mentioned above, can react with NO_x in the presence of sunlight to form low-level atmospheric ozone. Furthermore, the emission of VOCs can give rise to odour problems, which may result in complaints from nearby residents. The source of VOC emissions is the evaporation and leakage of hydrocarbon fractions potentially associated with all refining activities, e.g. fugitive emissions from pressurised equipment in process units, storage and distribution losses, and waste water treatment evaporation. Hydrocarbons may also be emitted during non-optimal combustion conditions, but these are only a small contribution.

1.4.2 Emissions to water

Petroleum refineries consume water on a continuous basis to maintain the water balances in the steam, cooling water, utility service water, and emergency fire water supply circuits. Water is also consumed for process and maintenance use purposes.

The losses from the steam and cooling water circuits include, but are not limited to:

- condensate purge;
- consumed steam;
- evaporation;
- cooling water purge, and circuit leaks.

The losses from the emergency fire water supply circuits may include scheduled maintenance purges, water used to test and/or utilise emergency fire fighting equipment, and circuit leaks. Some of the consumed steam that is input into processing systems comes in direct contact with various fractions of hydrocarbons and substances. The condensates resulting from these uses are separated and extracted from the processing system. Condensates may be collected and processed through a steam stripper to separate and extract hydrogen sulphide (H₂S) and ammonia (NH₃) from the water. The stripped water may then be used for other refining processes, such as crude desalting or water washing of process streams.

The water used for process purposes such as crude desalting or water washing will come in direct contact with either crude oil or other various fractions of hydrocarbons and substances. Wash water and/or steam used to clean and purge systems for maintenance activities can also generate waste water that has been in direct contact with these substances.

Other sources of waste water include, but are not limited to:

- water separated and removed from crude oil, intermediate, and product tanks;
- storm water, utility service water, steam condensate and/or emergency fire-fighting water that comes in contact with crude oil, intermediates, products, additives, chemicals, and/or lubricating oils in the drainage area;
- water originating from ballast water tanks of vessels off loading or loading petroleum based materials;
- routine and/or special waste solid-liquid separation activities;
- routine and/or special groundwater extraction activities;
- water discarded from periodic tank and piping system hydro test and metal passivation activities;
- water for sanitary usage.

Rainwater falling onto the site can also come into contact with crude oil and various fractions of hydrocarbons and substances due to entry into some tank systems, secondary containment systems, loading and offloading areas for trucks, railcars, and vessels, production areas that include equipment containing these substances and maintenance work areas.

Rainwater falling onto some non-process areas of the site may have a relatively low risk of coming into contact with materials and substances and therefore may not require treatment technique prior to discharge into the environment.

A refinery site, therefore, generates a collective mix of waste water streams containing insoluble and soluble substances which become pollutants when released.

Waste water treatment techniques are therefore applied to control the amounts of these pollutants. Treatment techniques are typically directed at reducing the amount of pollutants and the oxygen demand exerted by the waste water before it is released.

The main pollutant parameters include:

- total hydrocarbon content (THC);
- total petroleum hydrocarbon index (TPH-index)
- biochemical oxygen demand (BOD);
- chemical oxygen demand (COD) or total organic carbon (TOC);
- ammoniacal nitrogen, total nitrogen;
- total suspended solids (TSS);

- total metals.

Other pollutant parameters include:

- cyanides;
- fluorides phenols;
- phosphates;
- specific metals such as Cd, Ni, Hg, Pb and vanadium;
- benzene;
- toluene, ethylbenzene and xylene (TEX);
- sulfides and other micro-pollutants.

Table 1.17 provides a summary of some of the main water pollutants and their sources within a refinery.

Table 1.17: Main water pollutants (parameters) generated by refineries

Water pollutant	Source
Oil	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain)
H ₂ S (RSH)	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic
NH ₃ (NH ₄ ⁺)	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, sanitary blocks
Phenols	Distillation units, visbreaker, catalytic cracking, spent caustic, ballast water
Organic chemicals (BOD, COD, TOC)	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain), sanitary blocks
CN ⁻ , (CNS ⁻)	Visbreaker, catalytic cracking, spent caustic, ballast water
TSS	Distillation units, visbreaker, catalytic cracking, spent caustic, ballast water, sanitary blocks
Amines compounds	CO ₂ removal in LNG plants
<i>Source: [166, CONCAWE 1999]</i>	

Refinery waste water treatment techniques are mature techniques, and emphasis has now shifted to prevention and reduction of contaminated waste water streams to the final treatment units.

Table 1.18: Evolution of some water pollutants released from refineries

EPRTR data	Tonnes/ year	Number of sites	Tonnes/ year	Number of sites	Tonnes/ year	Number of sites
	2004		2007		2009	
TOC	6475	42	7951	42	6074	41
Phenols	45	56	59	59	42	59
Total Nitrogen	2769	25	2245	20	2103	21
Total Phosphorus	133	10	201	12	99	11
<i>Source: [74, EC 2010]</i>						

1.4.3 Waste generation

The amount of waste generated by refineries is small if it is compared to the amount of raw materials and products that they process. Table 1.20 shows the generation and different waste routes according to the European Pollutant Release and Transfer Register (E-PRTR) declarations.

Oil refinery waste normally covers three categories of materials:

- sludges, both oily (e.g. tanks bottoms) and non-oily (e.g. from waste water treatment facilities);
- other refinery wastes, including miscellaneous liquid, semi-liquid or solid wastes (e.g. contaminated soil, spent catalysts from conversion processes, oily wastes, incinerator ash, spent caustic, spent clay, spent chemicals, acid tar) and;
- non-refining wastes, e.g. domestic, demolition and construction.

Table 1.19 shows a summary of the main types of solid wastes generated in a refinery and their sources.

Table 1.19: Main solid wastes generated by refineries

Type of waste	Category	Source	
Oiled materials	Oily sludges	Tank bottoms, biotreatment sludges, interceptor sludges, waste water treatment sludges, contaminated soils, desalter sludges	
	Solid materials	Contaminated soils, oil spill debris, filter clay acid, tar rags, filter materials, packing, lagging, activated carbon	
Non-oiled materials	Spent catalyst (excluding precious metals)	Fluid catalytic cracking unit catalyst, hydrodesulphurisation/hydrotreatment catalyst, polymerisation unit catalyst, residue conversion catalyst	
	Other materials	Resins, boiler feed water sludges, desiccants and absorbents, neutral sludges from alkylation plants, FGD wastes	
Drums and containers		Metal, glass, plastic, paint	
Radioactive waste (if used)		Catalysts, laboratory waste	
Scales		Leaded/unleaded scales, rust	
Construction/demolition debris		Scrap metal, concrete, asphalt, soil, asbestos, mineral fibres, plastic/wood	
Spent chemicals		Laboratory, caustic, acid, additives, sodium carbonate, solvents, MEA/DEA (mono/diethanol amine), TML/TEL (tetra methyl/ethyl lead)	
Pyrophoric wastes		Scale from tanks/process units	
Mixed wastes		domestic refuse, vegetation	
Waste oils		Lube oils, cut oils, transformer oils, recovered oils, engine oils	
<i>Source:</i> [161, USAEPA 1995]			

Table 1.20: Waste generation declaration

Waste types	Waste routes	2007		2009	
		Thousand tonnes/yr	Number of sites	Thousand tonnes/yr	Number of sites
Hazardous waste in country	Disposal	294	103	405	105
	Recovery	306	98	372	103
Hazardous waste outside the country	Disposal	3	5	4	3
	Recovery	34	30	19	23
Non hazardous waste	Disposal	372	60	262	59
	Recovery	538	61	500	64
TOTAL		1547		1562	

Source: E-PRTR and CONCAWE data 2007-2009

Oil retained in sludges or other types of waste represents a loss of product and, where possible, efforts are made to recover such oil. Waste disposal depends very much on its composition and on the local refinery situation. Because of the high operating costs of waste disposal, much priority has been given to waste minimisation schemes.

Waste generation trends show that oily sludge production is declining, mainly through housekeeping measures, whereas biological sludge generation has increased as a result of increased biotreatment of refinery effluent. Spent catalyst production is also increasing through the installation of new hydrocrackers, hydrotreatment facilities and catalytic cracker dust collectors. For all these waste categories, increased use is made of third party waste contractors for off-site treatment and disposal.

1.4.4 Soil and groundwater contamination

Most refineries have some areas that are contaminated by historical product losses. Current refinery practices are designed to prevent spillages and leaks to the ground. In the past, the awareness of the potential risks of these contaminated areas was low. The two main issues here are the prevention of new spills and the remediation or the remedial control of historic contamination. As mentioned within the scope, soil remediation is not included in the scope of this document.

The main sources of contamination of soil and groundwater by oil are typically those places along the handling and processing train of crude to products where hydrocarbons can be lost to the ground. These are commonly associated with the storage, transfer, and transport of the hydrocarbons themselves or of hydrocarbon-containing water. The possibility of contamination by other substances such as contaminated water, catalysts and wastes also exists.

1.4.5 Other environmental issues

Besides the environmental issues mentioned in the above sections, especially for refineries situated near residential areas, environmental nuisances have become an issue of discussion with both local authorities and with representatives of the local population in so-called neighbourhood councils. Topics such as noise, light, smoke emission (flaring) and odour which directly impact the residents receive much more emphasis in these neighbourhood councils than the above-mentioned 'major' emissions which tended to receive more attention historically.

Aggravation by light can be caused through flaring at night by refineries and petrochemical plants located near densely populated areas.

A potential environmental issue regarding heat discharged by cooling water to the sea or rivers may also be considered.

Occupational health is included in the operational safety procedures aimed at protecting workers from exposure to toxic materials and providing them with all necessary facilities which contribute to their well-being and their sense of security and safety. Instructions, information exchange and the training of personnel, the provision of personal protection equipment, as well as strict adherence to stringent operational procedures, have contributed to a steady decrease in accidents and health incidents. Typical refinery pollutants and products with a health risk include hydrogen sulphide, BTEX (of which benzene is the most prominent), ammonia, phenol, HF, NO_x and SO_x, for which legally binding maximum acceptable concentrations values prevail.

The design of the refinery installations and the process control systems need to include provisions for a safe shutdown with minimum emissions from the unit involved. During unplanned operational upsets, these provisions should guarantee that feed supply is terminated followed by subsequent pre-programmed automated activation of pumps, relief systems,

purging systems, flares and other equipment. Examples of such occurrences are utility failure, the breakdown of equipment, a fire or an explosion. Emergency situations leading to direct spills occurring in parts of the plant which are neither fully contained nor fully automated, such as pipeline and tank bottom rupture, have to be addressed with standing emergency procedures. Such procedures should aim at the minimisation and containment of the spills, followed by the rapid clean-up, in order to minimise the environmental impact.

WORKING DRAFT IN PROGRESS

WORKING DRAFT IN PROGRESS

2 APPLIED PROCESSES AND TECHNIQUES

This chapter describes the major activities and processes that may be found within the natural gas plant sector and the petroleum-refining industry, including the materials and equipment used and the processes employed. This chapter is designed for those interested in gaining a general understanding of the processes and activities that can be found in these two industrial sectors, and for those interested in the interrelationship between the industrial process and the topics described in subsequent chapters of this document, which include emissions, consumptions and best available techniques for the different processes. This chapter does not attempt to replicate published engineering information that is available for this industry in the general literature.

The major production unit operations and activities typically carried out in petroleum refineries are briefly described, in alphabetical order. For many of these production operations, a number of different techniques and/or unit operations are used in the industry. While the major techniques used for each process/activity are described, the intention is not to describe all the different processes currently in use. This chapter specifically describes the purpose and principles of the processes, feed and product streams, and a brief process description of commonly used production processes/activity and operability. This information, coupled with schematic drawings of the identified processes, provides a concise description of the relevant processes/activities.

The first section is dedicated to a general technical description of refineries; the subsequent other sections cover all the processes and activities within the scope of the BREF. The processes related to natural gas plants are included in one independent section (Section 2.17). These sections do not pretend to be of equal importance from the environmental impact point of view. Some sections have more relevance than others, but this approach allows for clearer presentation of the BAT assessment for the mineral oil and gas refinery sectors. No pollution abatement techniques are included in this chapter. However, some of the processes (e.g. hydrotreatments) have an environmental aspect. Environmental implications of production techniques can be found in Chapter 3. Discussions on good environmental practices (prevention techniques) for production techniques can be found in Chapter 4. As a consequence, no information about emissions is generally presented in Chapter 2. Information on, for instance, flares, sulphur recovery units, waste water systems and waste management is not included in this chapter because these activities are not considered production activities. They are security or environmental techniques that are applied in both sectors.

2.1 General overview of refinery processes

Crude oil and natural gas are mixtures of many different hydrocarbons and small amounts of impurities (See Annex 9.2.1). The composition of these raw materials can vary significantly depending on the source. Refineries are complex plants, where the combination and sequence of processes are usually very specific to the characteristics of the raw materials (crude oil and natural gas) and the products to be produced. In a refinery, portions of the outputs from some processes are fed back into the same process, fed to new processes, fed back to a previous process or blended with other outputs to form finished products. One example of this can be seen in Figure 2.1, which also shows that refineries are all different regarding their configuration, process integration, feedstock, feedstock flexibility, products, product mix, unit size and design and control systems. In addition, differences in owner strategy, market situation, location and age of the refinery, historic development, available infrastructure and environmental regulation are among other reasons for the wide variety in refinery concepts, designs and modes of operation. Given these differences, it is hardly surprising that the environmental performance can also vary from refinery to refinery.

The production of a large number of fuels is by far the most important function of refineries and will generally determine the overall configuration and operation. Nevertheless, some refineries also produce valuable non-fuel products, such as feedstocks for the chemical and petrochemical industries. Examples are mixed naphtha feed for a steam cracker, recovered propylene, butylene for polymer applications and aromatics manufacture covered under the Large Volume Organic Chemical Industry BREF [85, EC 2003]. Other speciality products from a refinery include bitumen, lubricating oils, waxes and high grade coke for industrial use. Some refineries may even be dedicated to the production of these products.

The refining of crude oil into usable petroleum products can be separated into **two phases** and a number of **supporting operations**.

The first phase is the desalting of crude oil (Section 2.9) and the subsequent distillation into its various components or ‘fractions’ (Section 2.19). A further distillation of the lighter components and naphtha is carried out to recover methane and ethane for use as refinery fuel, LPG (propane and butane), gasoline-blending components and petrochemical feedstocks. This light product separation is done in every refinery.

The second phase is made up of three different types of ‘downstream’ process: i.e. breaking, combining, and reshaping fractions. These processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher quality molecules. The goal of these processes is to convert some of the distillation fractions into marketable petroleum products (see Section 10.3) through a combination of downstream processes. These processes define the various refinery types, of which the simplest is the ‘hydroskimming’, which merely desulphurises (Section 2.13) and catalytically reforms (Section 2.6) selected cuts from the distillation unit. The amounts of the various products obtained are determined almost entirely by the crude composition. If the product mix no longer matches the market requirements, conversion units can be added to restore the balance.

Market demand has for many years obliged refineries to convert heavier fractions to lighter fractions with a higher commercial value. These refineries separate the atmospheric residue into vacuum gas oil and vacuum residue fractions by distillation under high suction (Section 2.19), and then feed one or both of these cuts to the appropriate conversion units. Thus, by the inclusion of conversion units, the product slate can be altered to suit market requirements, irrespective of the crude type. The number and the possible combinations of conversion units are large.

The simplest conversion unit is the thermal cracker (Section 2.22), by which the residue is subjected to such high temperatures that the large hydrocarbon molecules in the residue convert

into smaller ones. Thermal crackers can handle virtually any feed, but produce relatively small quantities of light products. An improved type of thermal cracker is the coker (Section 2.7), in which all of the residue is converted into distillates and a coke product. In order to increase the degree of conversion and to improve product quality, a number of different catalytic cracking processes have evolved, of which fluid catalytic cracking (Section 2.5) and hydrocracking (Section 2.13) are the most prominent. Recently, residue gasification processes (Section 2.14) have been introduced within refineries, which enable refineries to eliminate heavy residues completely and to convert them into clean syngas for captive use and to produce hydrogen, steam and electricity via combined cycle techniques.

Supporting operations are those not directly involved in the production of hydrocarbon fuels but that serve a supporting role. They may include energy generation, waste water treatment, sulphur recovery, additive production, waste gas treatment, blowdown systems, handling and blending of products and the storage of products.

Table 2.1 summarises the main products obtained from the main refinery processes. As can be seen, many of the products are obtained from different units. This is one aspect of the technical complexity and the variety of modes of operation that can be found in a refinery.

An overview of the general scheme of a complex refinery is provided in Figure 2.1. This figure can be used as a synoptic of Chapters 2, 3 and 4 of this document. For each of the displayed units or processes, it provides, in particular (in red), the corresponding section number which is used over these three chapters, according to the general structure given in the Scope section.

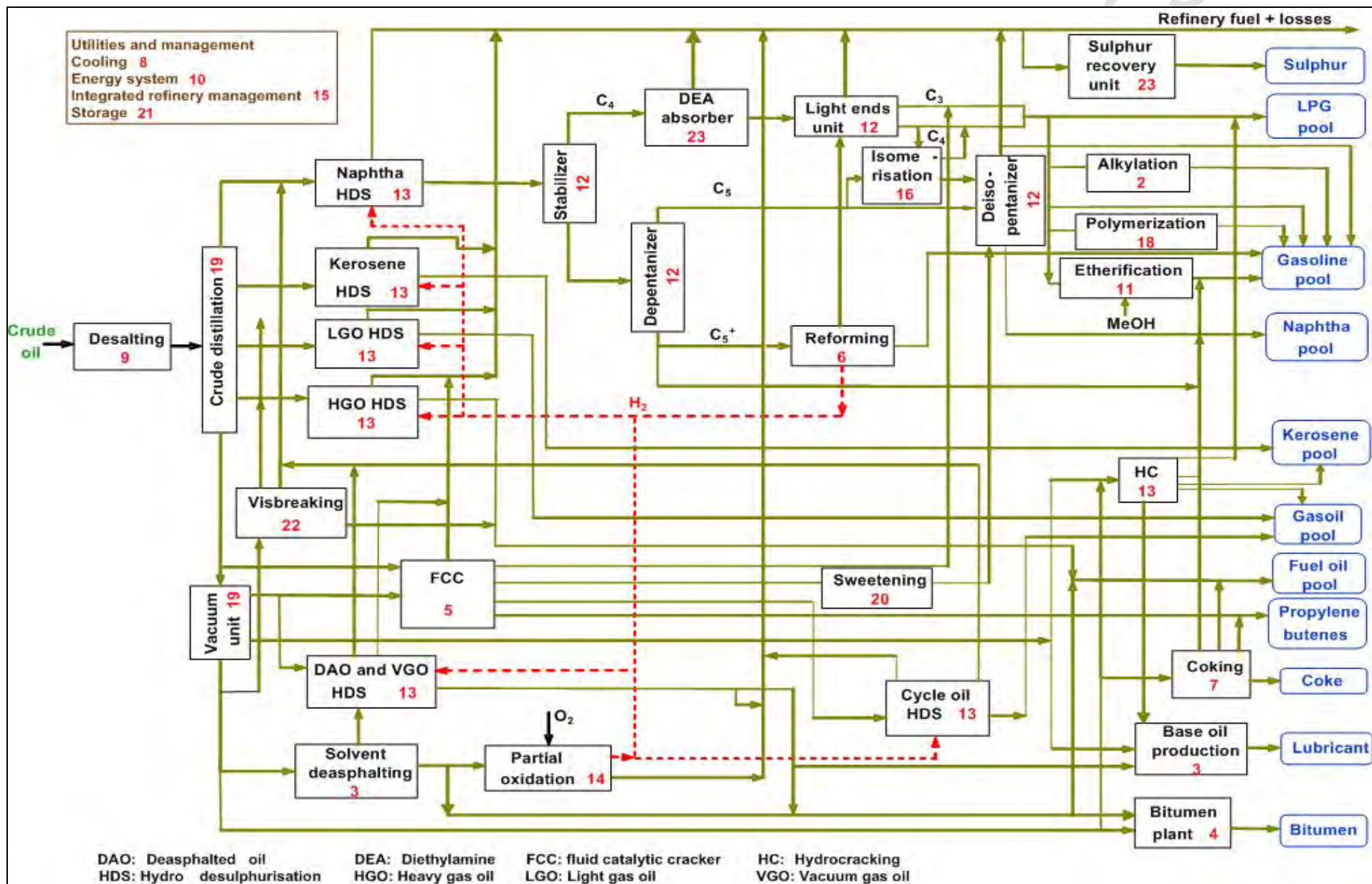


Figure 2.1: General scheme of a complex oil refinery

Table 2.1: Refinery units and their main products

Products → refinery units	Section	LPG	Gasoline	Kero/naphtha	Heating oil/diesel	HFO	Base oil	Coke/bitumen	Special
Carbon number range		C ₃ -C ₄	C ₄ -C ₁₂	C ₈ -C ₁₇	C ₈ -C ₂₅	>C ₈	>C ₁₅	>C ₃₀	
Alkylation	2								
Base oil production	3								Waxes, White Oil, Extracts, Bright Stock
Bitumen production	4								
Catalytic cracker	5								
Residue cracking	5								
Catalytic reforming	6								H ₂
Delayed coking	7								
Flexicoker	7								Low joule gas
Gasification	10								Syngas
Etherification	11								MTBE
Gas separation processes	12								Refinery fuel gas
Hydrogen plant	14								H ₂
Residue hydroconversion	14								H ₂
Hydrocracker	15								
Hydrodesulphurisation	15								
Isomerisation	17								
Crude atmospheric distillation	19								
Vacuum distillation	19								
Thermal cracking/Visbreaking	22								
Sulphur recovery unit	23								S

2.2 Alkylation

Purpose and principle

The purpose of alkylation is to yield high-quality motor fuel after blending. The term alkylation is used for the reaction of olefins with isobutane, to form higher molecular-weight isoparaffins with a high octane number. The process involves low-temperature reaction conditions conducted in the presence of strong acids.

Feed and product stream

Low molecular weight olefins (C₃-C₅) and isobutane are used as alkylation unit feedstocks. The major sources of low olefins are catalytic crackers and cokers. Isobutane is produced by hydrocrackers, catalytic crackers, catalytic reformers, crude distillation and natural gas processing. In some cases, n-butane is isomerised (see Section 2.16) to produce additional isobutane. The product is alkylate (a high-octane gasoline component) with some propane and butane liquids. By proper choice of operating conditions, most of the product can be made to fall within the gasoline boiling range. Dissolved polymerisation products are removed from the acid as thick dark oil.

Process description

Two processes have dominated historically, with hydrofluoric acid (HF) or sulphuric acid (H₂SO₄) used as a catalyst. When the concentration of acid becomes low, some of the acid must be removed and replaced with fresh acid. Safety incidents and accidents in HF units over the years have led to changes:

- Sulphuric acid has dominated in new investments since 1980.
- Additives are now available to reduce the HF volatility and several mitigation systems have been developed to improve safety.
- solid-acid catalyst alternatives have improved in later years but industrial sites have not yet reported successful start-up or operational results. OandG Journal-‘world refinery survey’ january2011. Baku Heydar Aliyev Refinery (Azerbaijan) [75, OandG Journal 2011] selected a solid-acid alkylation unit for their basic design. Several available commercial processes are described in Chapter 6.
- Ionic liquid technology has been subject of new patents and developments. A 65 000 tonnes per year plant in China has been retrofitted and has reported successful results (see Chapter 6). There are also techniques to facilitate the retrofitting of a HF plant into a H₂SO₄ unit.

Safety and environmental concerns are extremely important when choosing an alkylation technology. HF is specifically hazardous due to possible skin penetration and destruction at tissue levels (and pulmonary oedema). In Section 4.2.3, the trade-off between process alternatives is described.

In the hydrofluoric acid process, the acid slipstream is redistilled. The concentrated hydrofluoric acid is recycled and its net consumption is relatively low. In this process (Figure 2.2), the feed enters the reactor and is mixed with the recycled isobutane and HF from the settler. Both the olefin and isobutane feeds are dehydrated first (not shown in Figure 2.2), as this is essential to minimise the potential corrosion. The reactor, operating at 25 - 45 °C and 7 - 10 barg, is cooled to remove the heat generated by the reaction. In the settler, alkylate and excess isobutane are separated from the HF. The HF is recycled to the reactor. A slipstream is regenerated by distillation. The organic phase from the settler, consisting of the alkylate and unreacted isobutane, flows to the isostripper. There, the isobutane and some other light components are stripped from the alkylate. This is routed as product to storage after treating it with potassium hydroxide (KOH). The decomposition of any organic fluoride formed is promoted by the high tube wall temperatures. Saturated butanes are normally distilled outside the alkylation unit to produce a concentrated stream of isobutane, which is fed to the alkylation unit with the olefin feed. The isostripper overhead, essentially isobutane, is returned to the reactor. A small overhead slipstream is sent to a depropaniser, where propane is removed. The

bottoms of the depropaniser (isobutane) are routed to the isobutane circulation stream, while the depropaniser overhead stream (propane) passes through a HF stripper to remove traces of HF and is sent to storage after final KOH treatment. Normal butanes which come in with the unit feedstreams are drawn off as a side-stream from the isostripper, treated with KOH and sent to storage.

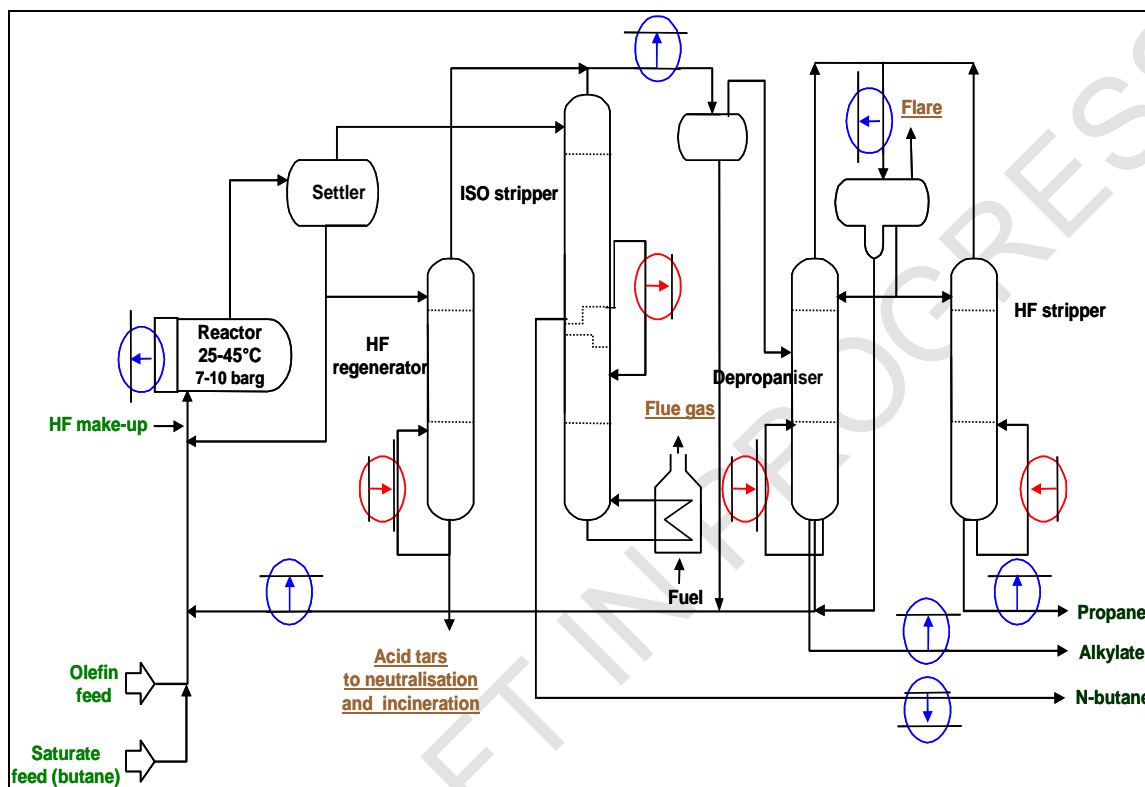


Figure 2.2: Simplified process flow scheme for a HF alkylation unit

In the sulphuric acid process (see Figure 2.3) the aim is to produce high octane branched chain hydrocarbons for the gasoline pool. The process combines olefin and butylene feeds in the presence of strong sulphuric acid. The feed contacts the recycle stream of H_2SO_4 in the reactor. The reactor circulation stream enhances a large interface area at low temperature (4-15 °C). Reaction products are first separated in a flash drum and then through a debutaniser. On-site acid regeneration is also possible (i.e. WSA technique).

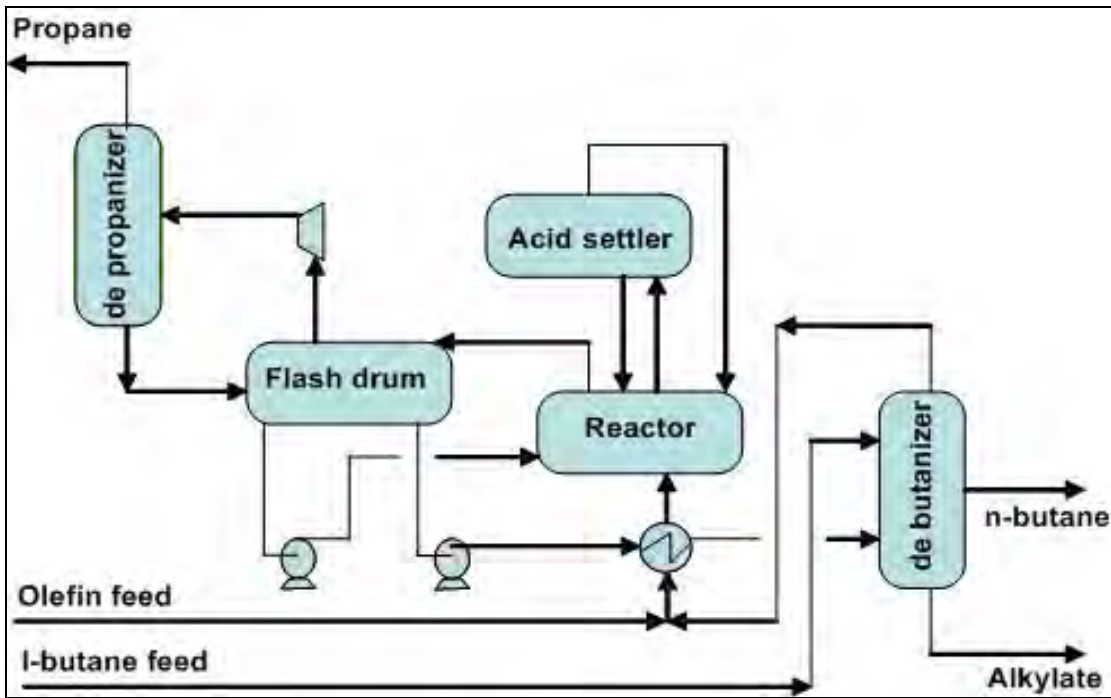


Figure 2.3: Simplified process flow scheme for sulphuric acid alkylation

The AlkyClean solid-acid process is covered as an emerging technique in Chapter 6.

2.3 Base oil production

Although only 20 % of EU refineries produce base oil, some actually specialise in it. Figure 1.7 and the associated Table (in Chapter 1) identify the refineries specialised in the production of lubricant and bitumen. More extensive information about the processes can be found in the general literature (e.g. [231, Sequeira 1998]).

Purpose and principle

Lubricants are a blend of different grades of base oils and special additives. To produce a suitable lubricant, certain properties of the base oil are very important: viscosity, viscosity index (VI : a high VI means that the viscosity changes very little as temperature changes, and vice versa), high resistance to oxidation, low pour point and good dope susceptibility or compatibility.

Base oil is a speciality product and consequently not all crudes are suitable. Heavy crudes are frequently used as feedstock for conventional base oil complexes. New processes based on catalytic hydrogenation reactions enable a wider variety of feeds.

Feed and product stream

The feedstocks of a conventional base oil complex are waxy distillate side-streams from vacuum distillation units (Section 2.19) and the extracts from deasphalting units. Atmospheric residue feedstock to the vacuum distillation unit consists of various types of hydrocarbon compounds with different suitability for base oils, e.g.:

- **aliphatic or paraffinic:** Normal (n-)paraffins and iso (i-)paraffins form this group. The n-paraffins have a high VI and melting points, and at ambient conditions form crystals, which must be removed to reduce the pour point of lubricating. I-paraffins have lower melting points, very high VI but lower viscosity;
- **naphthenic:** The naphthenic rings lend high viscosity, low melting point and a good VI (less than paraffins) to lubricant oils;
- **aromatic:** The aromatic rings lend high viscosity and low melting point to compounds but a low VI to the oils. For this reason, they are considered the least satisfactory type of compounds for lubricants. The ratio in which the three groups are present varies from crude to crude.

New industrial facilities can also use natural gas as feedstock (gas-to-liquid processes).

The American Petroleum Institute (API) has developed a base oil classification system which categorises base oils into five major groups, classified on the basis of the following three criteria:

- The percentage of saturates (the higher the number of saturates, the better the resistance to breakdown or loss of viscosity).
- The sulphur content (the lower the sulphur content, the better the purity: thus the product is less corrosive and there is less potential for oxidation).
- Viscosity index (the VI is an indication of the rate of change of viscosity against temperature, and the higher the VI, the better). The viscosity is the oil resistance to flow and shear. It is the single most critical physical property of the oil, as it affects both the wear rate and the fuel efficiency.

The five groups defined by the API are :

- Group I: Contains less than 90 % saturates and/or greater than 0.03 % sulphur and has a VI between 80 and 120. Demand is around 65 %, with decreasing trend.
- Group II: Contains more than 90 % saturates and less than or equal to 0.03 % sulphur and has a VI from 80 to 120. The demand is around 25 % and tends to go up.
- Group III (Known as unconventional base oils - UCBO): Contains more than 90 % saturates and less than or equal to 0.03 % sulphur and has a VI of more than 120. Group III and II oils are made by the same process, but for group III, the VI is increased by higher temperature in

the hydrocracker or by appropriate crude selection as a feedstock. Group III advantages over group I and II base oils are that it is more fuel efficient, has longer drain intervals, is environmentally friendly and is engine protective. Demand is around 10 % with a growing trend.

- Group IV: Synthetic base oils.
- Group V : all other base oils.

Process description

The marketplace is constantly seeking new lubricants, which in turn require even a higher base oil purity, higher viscosity index, lower volatility, and longer life.

There are many possible routes for improving base oil quality and extending the product variety among the main four following process family including :

Separation by solvent based processes.

Solvent based processes aim to remove the different impurities from the feedstock by extracting the undesired components.

Conversion by hydrogenation based processes [137, Szeitl et al. 2008]

The hydrogen conversion (HC) and catalytic dewaxing (CDW) technology converts undesired components directly into end products. The base oils are hydrofinished at higher pressure (>100 bars) than the around 30 bars pressure applied in conventional manufacturing. This technology has significantly lower operational cost but substantial initial investment. It can process a wider range of feedstock, but has a much narrower product range compared to solvent-based production (e.g. Bright Stock, the upper end of group I base oils specifications). It produces non-carcinogenic naphthenic base oils and removes impurities such as nitrogen, sulphur or oxygenated compounds.

Converting to hydrogen-based processes: Hybrid [252, Ullmann's 2012]

Lower hydrogen usage may lead to lower operational cost. There are many combinations for revamping or debottlenecking existing units. Operators can run the alternative routes in parallel plants or can have upstream units based on hydrogenation together with downstream ones solvents-based. The opposite combination is generally not viable because, the CDW catalyst can only receive low nitrogen and sulphur content (high pressure hydrotreated) feedstock.

Gas to Liquid (GTL)

Liquefaction of natural gas and the chemical reaction route were developed on the basis of the Fischer – Tropsch process. This process creates high-quality liquid products and paraffin wax. High VI oils can then be obtained from natural gas by partial oxidation, polymerisation and isomerisation. The GTL process provides products with high biodegradability and the absence of sulphur, nitrogen, and aromatics compounds. At a global level, GTL is still a new industry with a limited number of commercially operative plants. A number of GTL plants are in operation in South Africa (Sasol: 8 Mt/yr, PetroSA : 1 Mt/yr), in Qatar (Sasol-Qatar Petroleum Oryx: 1.7 Mt/yr), and Malaysia (Shell: 0.6 Mt/yr). Global GTL capacity is expected to increase to more than 25 Mt/yr by 2015. More than 50 % of the global GTL capacity will be in Qatar (new construction units for about 20 Mt/yr additional capacity) [273, O&Gas Journal 2010].

The appropriate options to produce high-quality base oils depend on the refinery's crude oil processing flexibility, the existing units, and the capital-cost tolerance. The new, higher quality base oil refining processes have the lowest cost of production. These new base oil plants are less crude sensitive, offer synergy with fuels strategy, provides high quality and more valueable base oils together with better yield. Their drawback is the lack of heavy cut base stocks, therefore there is a need to keep solvent technologies as well. Many European base oil plants are more than 30 years old, and most of these use solvent based processes.

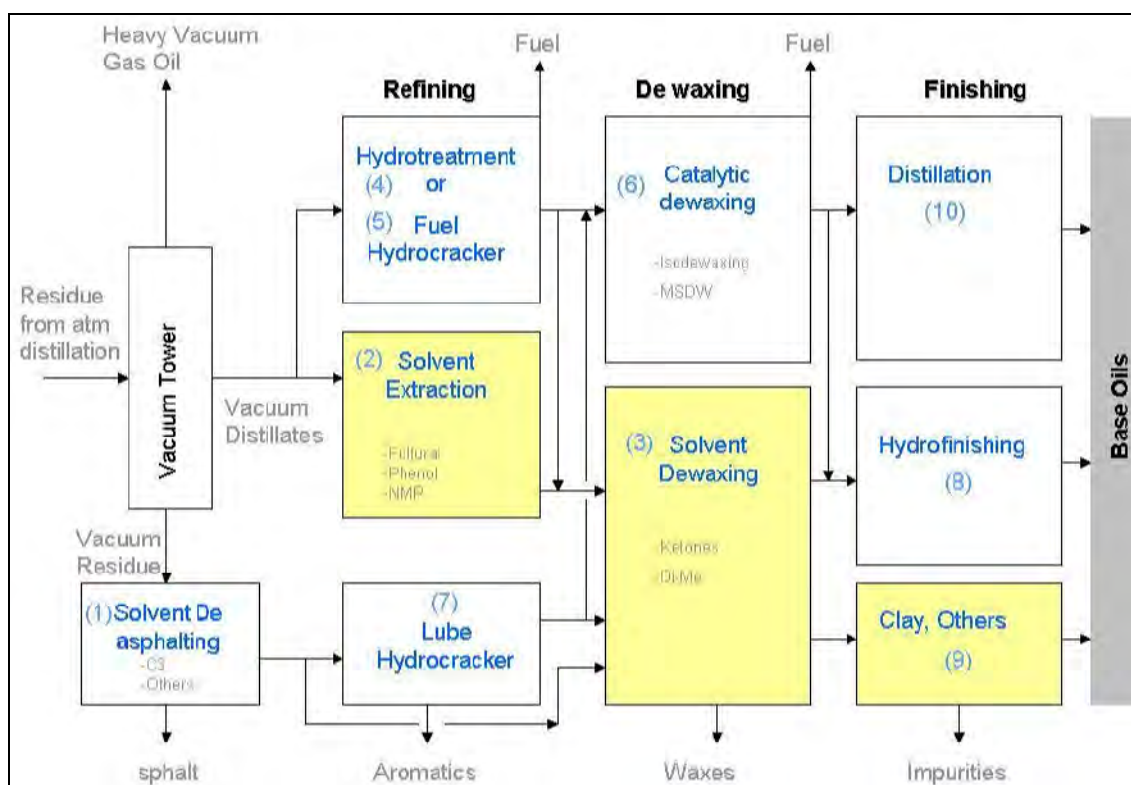


Figure 2.4: Block scheme of a lubricating oil manufacturing plant with a combination of process options units

Each of the process steps shown in Figure 2.4 are described below:

(1) Solvent Deasphalting

- Target: Extracting high-boiling lighter paraffinic and naphthenic hydrocarbons (asphaltenes and resins) from the vacuum distillation unit residue.
- Operations: Propane or propane-butane mixtures are usually used as solvents at specific operating conditions (37 – 40 bar and 40 – 70 °C). A typical extraction process consists of an extractor and recovery sections, flash evaporation and stripping. More recently, solvent deasphalting has been adapted for the preparation of catalytic cracking, hydrocracking, hydrodesulphuriser feeds and hard bitumen (deep deasphalting). For these purposes, heavier-than-propane solvents (butane to hexane mixture) are used, together with higher operating temperatures.
- Features: Propane from the low pressure or stripping section can be recovered within the process by distillation and stripping (with a corresponding energy consumption). Remaining traces of solvent are very often used as a fuel gas.

(2) Solvent based Aromatic extraction [253, CONCAWE 2012]

- Target: Removing aromatics from base oil feedstocks, improving viscosity, oxidation resistance, colour and gum formation.
- Operations: Different solvents can be used (furfural, N-methyl-2-pyrrolidone (NMP), phenol, cresol or liquid sulphur dioxide). These processes are typical extraction processes, consisting of an extractor and recovery sections, flash evaporation and stripping to separate the solvent from the oil-rich raffinate and aromatic-rich extract stream. Typically, feed lube stocks are contacted with the solvent in a packed tower or rotating disc contactor. Solvents are recovered from the oil stream through distillation and steam stripping in a fractionator. The raffinate stream is run down to intermediate storage. The extract, after solvent recovery, is likely to contain high concentrations of sulphur, aromatics, naphthenes and other hydrocarbons, and is often fed to the

hydrocracker or catalytic cracker unit. Depending on the different physico-chemical properties (e.g. boiling and melting points) of the applied solvents the physical design and construction of the aromatic extraction units are different (boiling point for NMP: 202 °C; for furfural: 162°C. Melting point for NMP: -23.6; for furfural: -37 °C).

- Features: Process designs need to consider many factors. When the solvent volume in the process can be reduced, less energy consumption for evaporation is needed. NMP is more corrosive than clean furfural. Furfural tends to degrade and coke within the process, raising solid waste. The waste water from aromatic extraction can be treated separately before leaving the unit. Operating this pre-treatment, the solvents are recovered and kept in the system. In recent years, several furfural extraction plants have been converted into NMP plants, and even phenol plants have a lower priority. NMP is a less toxic solvent and can be used in a low solvent-to-oil ratio with high selectivity. This generates significant energy savings. NMP in new plants generally results in physically smaller units and thus lower capital expenditure.

(3) Solvent Dewaxing [253, CONCAWE 2012]

- Target: Ensuring that the oil has the proper viscosity at lower ambient temperatures Paraffins are removed.
- Operations: Feed is diluted with solvent to lower the viscosity, chilled until the wax is crystallised, and then filtered to remove the wax. Solvents used for the process include propane and mixtures of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK), toluene or chlorinated hydrocarbons, such as a mixture of 1,2-dichloroethane and dichloromethane (Di-Me). The solvents are chosen according to the focus of the dewaxing process:
 - When aiming at removing paraffinic compounds from the feed stock in order to achieve high yields of base oil, a mixture of MEK/Toluene or MEK/MIBK might be chosen.
 - When aiming at producing specific oil and wax qualities with special product requirements, the preferred solvent is a DiMe-mixture. The chlorinated solvents used in the dewaxing/deoiling process usually are 1,2-Dichloroethane (DCE) and Dichloromethane (DCM). The mixture (DiMe) varies from 80/20 to 20/80, according to the feedstock to be treated.
 - When the units are designed to de-oil slack wax of various qualities, a single solvent, 1,2-Dichlorethane, is generally used.
- Features: Solvent is recovered from the oil and crystallised wax through heating, two-stage flashing, followed by steam stripping. The wax is removed from the filters, melted and subsequently fed to a solvent recovery unit to separate the solvent from the wax.

(4) High pressure hydrogenation unit

- Target: Stabilising the most reactive components in the base oil, improve the colour, and increase the useful life of the base oil. This process removes some of the nitrogen and sulphur containing molecules but is not severe enough to remove a significant amount of aromatic molecules.
- Features: Adding hydrogen to the base oil at elevated temperatures in the presence of catalyst Hydrotreating represents only a small improvement in base oil technology.

(5) Hydrocracker

- Target: The molecules of the feed are reshaped and often cracked into smaller ones. A great majority of the sulphur, nitrogen, and aromatics are removed. Molecular reshaping of the remaining saturated species occurs as naphthenic rings are opened and paraffin isomers are redistributed. Produces fuel+base oil; higher purity than solvent based process; lower aromatic content.
- Operations: Add hydrogen to the base oil feed at higher temperatures and pressures than simple hydrotreating. The process is driven by thermodynamics, with reaction rates facilitated by catalysts.
- Features: Since 1995, more than 50 % of new plants use this technology. The return on investment is fairly quick, since the fuels are sold almost immediately.

(6) Catalytic dewaxing

- Target: As an alternative to solvent dewaxing, especially for conventional neutral oils, catalytic dewaxing removed n-paraffins and waxy side chains from other molecules by cracking them into smaller molecules. This process lowered the pour point of the base oil so that it flowed at low temperatures, like solvent dewaxed oils. Since 1995, more than half of all new base oil manufacturing plants have been built or are planned using hydrocracking technology. A number of different catalytic dewaxing processes has been developed and based on appropriate catalysts (generally zeolites) to perform three main classes of chemical transformations, aiming at increasing the VI and good low-temperature characteristics:
 - *Ring conversion*: opening the heterocycle into a more aliphatic structure by the ejection of heteroatoms such as nitrogen or sulphur embedded in structurally hindered rings, ring de-alkylation of multiring hydrocarbons.
 - *Paraffins conversion*: this step can be performed by a family of processes, and involves the boiling point conversion of the paraffin components of waxy feeds by selective hydrocracking or by selective hydroisomerisation.
 - *Saturation*: to ensure the oxidative stability of base stocks a sufficient extent of ring hydrogenation (saturation) is needed.
- Operations: With suitable catalysts, it enables the use of cheaper feeds and produces high value C5 byproducts. Different reaction arrangements are available and subsequent process combinations are possible.
- Features: About 90 refineries in the world use this process.

(7) Lube unit.

- Target: Lube unit converts the vacuum gas oil to low pour point, high VI stable lubricant base oils, mainly by cracking low-VI components and saturating aromatics.
- Operations: The process takes place at high pressure and temperature with hydrogen and a catalyst. The feed is processed over fixed-bed reactors. The products are then fractionated in a distillation section, where columns are reboiled with hot oil.

(8) Hydrofinishing

- Target: In this unit, the colour and colour stability is improved and the organic acid components are removed. Sulphur content is also reduced.
- Operations: The design and operation of this unit is similar to that of a normal hydrotreater unit (Section 2.13).
- Features: In stand-alone base oil refineries, the small amounts of H₂S generated due to hydrotreatment are normally incinerated or burnt as a component of fuel if a Claus unit is generally not available. The need for hydrofinishing depends on the crude oil processed and to a certain extent on the patent owner and the design of the preceding units.

(9) Clay treatment

Instead of hydrotreatment, sulphuric acid and clay treatments may typically be used in old plants. Additional finishing with absorbents (bleaching clays, bauxite) may be used with certain oils specifications (e.g. for transformers, refrigerators, or turbines. The filtration process represents additional complexity and the residues need to be appropriately disposed off).

(10) Distillation

Depending on the upstream process selected, some base oil complex may need a final separation of products with a fractionation train. This is normally done with several distillation columns, potentially under vacuum, that may also withdraw some remaining impurities.

Reference literature

[76, *Hydrocarbon processing* 2011], [137, Szeitl et al. 2008], [251, *Credit Suisse* 2012], [252, *Ullmann's* 2012], [273, *O&Gas Journal* 2010].

2.4 Bitumen production

Bitumen is a residue derived from certain crude oils (e.g. Middle East, Mexico or South America) after vacuum distillation has removed waxy distillates. Bitumen is normally mixed with other components (e.g. gravel) to produce asphalt that is used in road paving, roof coating and pipe sealing or coating. Bitumen production only appears in some refineries (45 % of the EU refineries). There are also some refineries that specialise in producing these components. Figure 1.7 (in Chapter 1) and the associated table identifies the bitumen-specialised refineries.

Purpose and principle

The desired properties of bitumen may be achieved either by adjusting distillation conditions or by 'blowing'. In the latter process, air is blown into hot bitumen causing dehydrogenation and polymerisation reactions and creating a harder product with higher viscosity, higher softening point and a reduced penetration. (The penetration, often used as the main criterion, refers to the depth of penetration by a standard needle in a bitumen sample at standard conditions). The properties of the blown bitumen are determined by the residence time in the oxidation vessel, the air rate and the liquid temperature. If any of these parameters is increased, the penetration is reduced and the softening temperature is raised.

Feed and product streams

In most applications, the hydrocarbon feed stream to a bitumen blowing unit (BBU) is the bottom residue stream from a vacuum unit (Section 2.19) and in some instances the residue (extract) from a deasphalting unit (Section 2.3).

Normally, a number of different grades of bitumen are produced in campaigns and these are further modified by blending with other high-boiling components such as vacuum residue, heavy gas oil or synthetic polymers. In this way, a single blowing unit is able to cater for a wide range of bitumen grades for various applications.

Polymer additives Styrene Butadiene Styrene (SBS), Ethylene Vinyl Acetate (EVA), Natural rubber, etc are used for heavy duty service bitumen production. They do not change the chemical structure of the bitumen but change its mechanical properties. The polymers modify the bitumen's properties such as the softening or brittleness point, and aim at improving longevity.

Process description

The BBU will either operate on a continuous basis or in batch mode depending on the quality of the vacuum residue feedstock and the required bitumen product specification. Continuous processes are the most common in refineries. A simplified process flow diagram of the BBU is shown in Figure 2.5, which represents a typical, continuously-operated BBU receiving its hot feed directly from the vacuum distillation unit. Where the bitumen feed is received from storage, an additional fired heater may be required to preheat the feed to a temperature of about 200 – 250 °C, but it can be up to 550 °C. With a batch-operated BBU, a feed buffer vessel is usually included to store the hot feedstream from the vacuum unit.

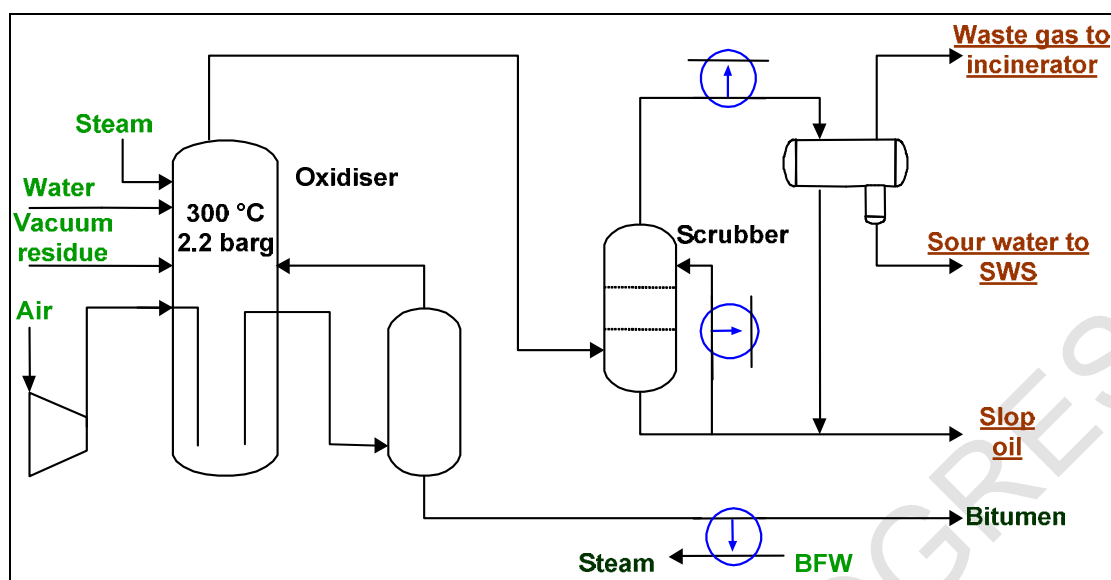


Figure 2.5: Simplified process flow scheme of a bitumen blowing unit

The residue feedstream is pumped into the top of the oxidation vessel. Operating pressure in the top of the oxidation vessel is normally around 1 barg and in the bottom around 2 barg, depending on the height of the vessel. As air is sparged into the base of the vessel, oxidation of the residue takes place, resulting in heat. The temperature in the oxidation vessel, which determines to a certain extent the bitumen grade, is normally controlled between 260 and 300 °C. Different options are applied for adjusting the temperature, which include the addition of colder feed to the oxidation vessel, the recirculation of cooled bitumen product from the bitumen run down cooler, and in older units direct water quenching. The blown bitumen is removed from the bottom of the oxidation vessel and cooled by raising steam, before being sent to storage.

The air rate is normally well in excess of stoichiometric requirements and so a considerable quantity of oxygen is present in the upper vapour space of the oxidation vessel. To avoid an explosion in the vapour space, in most units, steam is injected at a rate necessary to keep the oxygen concentration below the lower flammable limit (5 – 6 % v/v.). In some units, a small amount of water is also injected into the vapour outlet of the oxidation vessel to reduce the vapour temperature. This is sometimes considered necessary to prevent afterburning in the overhead system which could otherwise lead to severe coke formation.

The overhead vapours are first passed through a vent gas scrubber to remove oil and other oxidation products. In most cases, gas oil is used as once-through scrubbing liquid. The vent gas from the scrubber is subsequently cooled to condense light hydrocarbons and sour water, sometimes in a water spray contact condenser or scrubber. The remaining gas, consisting mainly of light hydrocarbons, N₂, O₂, CO₂ and SO₂, is incinerated at high temperatures (~800 °C) to ensure complete destruction of minor components such as H₂S, complex aldehydes and organic acids and phenolics, which have a highly unpleasant odour.

The majority of the BBUs produce the higher grades of bitumen (roof and pipe coatings) and normally operate continuously throughout the year. The BBUs which are used to produce road bitumens operate only when the demand for road asphalt is high.

2.5 Catalytic cracking

Purpose and principle

Catalytic cracking is the most widely used conversion process for upgrading heavier hydrocarbons into more valuable lower boiling hydrocarbons. In 2008, 56 fluid catalytic cracking (FCC) units were installed in the EU-27. It uses heat and a catalyst to break larger hydrocarbon molecules into smaller, lighter molecules. Unlike the hydrocracker process, no hydrogen is used and consequently, limited desulphurisation takes place. Compared to other heavy oil catalytic conversion processes, the fluid catalytic cracking (FCC) process is superior in being able to handle larger quantities of metals, sulphur and asphaltenes. One drawback is the limited flexibility in changing the product yields, even if recent developments in catalysts allow, depending of the catalyst selection, an increase of the LPG yield or a further reduction of the bottom products.

Feed and product streams

Fluid catalytic cracking units can be designed to process heavy vacuum gas oils (HVGO) from the vacuum distillation unit, or bottom streams, also called 'long resid' (LR) from the atmospheric distillation unit. Most often, units designed for HVGO also treat some LR, and vice versa. These two unit types will be referred to as the FCC unit and the RCC unit respectively.

Other process streams may be blended into the catalytic cracker feed such as heavy gas oil from the atmospheric distillation unit, coker or visbroken gas oil, deasphalted oil and extracts from base oil units and sometimes a small quantity of atmospheric residue. These streams may be hydrotreated to adjust the desired product's yields and properties.

Compared to other conversion processes, the catalytic cracker process is characterised by a relatively high yield of good quality gasoline and relatively high quantities of C₃ and C₄. Both products are highly olefinic and therefore are ideal feedstreams for the alkylation, etherification and petrochemical industries. One drawback of this process is the very low quality of the mid-distillate products in terms of sulphur, olefins, aromatics and cetane index. The majority of the products need further treatment prior to storage.

Process description

A number of different catalytic cracking designs are currently in use worldwide, including fixed-bed reactors, moving-bed reactors, fluidised-bed reactors and once-through units. The fluidised- and moving-bed reactors are by far the most prevalent in world refineries.

Fluid catalytic cracking (FCC) units are by far the most common catalytic cracking units. The FCC unit consists of three distinct sections, the reactor-regenerator section including the air blower and the waste heat boiler, the main fractionator section including the wet gas compressor and the unsaturated gas plant section. A simplified flow scheme is shown in Figure 2.6.

In the FCC process, oil and oil vapour preheated to 250 to 425 °C come into contact with hot catalyst at about 680 – 730 °C in the riser reactor. To enhance vaporisation and subsequent cracking, the feed is atomised with steam. The cracking process takes place at temperatures between 500 and 540 °C and a pressure of 1.5 – 2.0 barg. Most catalysts used in catalytic cracking contain zeolites (for more details on zeolites see Annex 9.4) with metals and rare-earths supported by different types of aluminas and clays. The catalyst is in a fine, granular form which mixes intimately with the vaporised feed. The fluidised catalyst and the reacted hydrocarbon vapour are separated mechanically in a (two-stage) cyclone system and any hydrocarbon remaining on the catalyst is removed by steam stripping. The amount of lost catalyst as fines in the reactor and regenerator cyclones is balanced by the addition of fresh catalyst.

The catalytic cracking processes produce coke, which collects on the catalyst surface and diminishes its catalytic properties. The catalyst therefore needs to be regenerated continuously essentially by burning the coke off the catalyst at high temperatures. The method and frequency

with which catalysts are regenerated are a major factor in the design of catalytic cracking units. The catalyst flows into a separate vessel(s) for either single- or two-stage regeneration, done by burning off the coke deposits with air. However, in time, the catalyst deactivates gradually and irreversibly due to high-temperature exposure and metal poisoning (mainly vanadium). The hot regenerated catalyst flows back to the base of the reactor riser, where it is cooled by vaporisation of the feed and by the heat absorption required for cracking reactions.

The cracked hydrocarbon vapours are then fed to a fractionation tower where the various desired fractions are separated and collected. The streams are steam stripped to remove volatile hydrocarbons prior to cooling and sending to storage. Slurry oil is taken from the bottom of the column and is cooled by heat exchange with the reactor feed stream and by steam generation, and is then returned to the column. The recycled slurry oil is used as wash oil and as a quench for the hot reactor overhead vapours to prevent aftercracking. The rest of the slurry oil is filtered or decanted to remove catalyst fines, cooled and sent to storage. The fractionator overhead gas is partly condensed and accumulated in the overhead drum to separate it into three phases: gas, liquid and sour water streams. The liquid and gas streams are both fed to the gas plant (Section 2.12) for further separation and the sour water stream is sent to the sour water stripper for purification (Section 2.25).

Various types of equipment are usually used for recovering energy from this process. The hot flue-gases from the regenerator are cooled by means of steam generation in a waste heat boiler or, in case of partial CO combustion, in a CO boiler. Prior to steam generation, electricity can also be produced by expansion of the flue-gases in a turbo-expander. And, in particular for units processing large quantities of residue, additional heat removal from the regenerator can be achieved with catalyst coolers for steam generation.

Full combustion mode

Full combustion mode is typically applied to vacuum distillate feedstocks. Low Conradson carbon feeds are typically processed in full combustion FCCs.

In the full combustion mode, the following precautions should be taken in order to reduce the emission of pollutants:

- The amount of CO generated can be limited to a range from 35 to 250 mg/Nm³, with an excess of oxygen greater than 2 %, (continuous operations as a daily average). A CO oxidation promoter can be added to the regenerator to catalyse the oxidation of CO. However, this promoter also catalyses the oxidation of the fuel nitrogen in the coke, increasing the NO_x levels (especially NO). A platinum catalyst may promote the generation of N₂O. Consequently, the amount of CO promoter varies the relationship between the NO_x emissions and CO emissions. However, values of 300 - 700 mg/Nm³ of NO_x (3 % O₂) can be achieved.
- For residual feedstock cracking using antimony addition, NO_x emissions can raise to 1000 mg/Nm³ (3 % O₂), if no other reduction technique is used.
- Minimisation of the use of aeration and purge steam can decrease particulate emissions significantly. Aeration/steam rates are based on achieving a stable catalyst circulation in the catalyst lines between the reactor and the regenerator.
- Stripping of the catalyst before reaction or before regeneration reduces the HC content in the coke to be burnt.
- Temperature adjustment in the riser by injection of a recycle stream above the zone of the fresh feed injection.
- Modification of the design and operation of the regenerator, especially to avoid high temperature spots that tend to increase the NO_x formation.

Considering dust emissions, the basic design of an FCC includes two-stage cyclones in the regenerator vessel, which prevent the bulk of the fine catalyst used from escaping from the

system. However, smaller catalyst particles, mostly created by attrition in the circulating system, are not easily retained by the two-stage cyclone system. Consequently, in many cases, other abatement techniques are included to complement the process abatement techniques discussed here.

A reduction of the regeneration temperatures under the usual conditions (700-750 °C) would not have a significant impact in the NO_x emissions but it will increase CO concentration in the flue-gas and coke formation. A change in the design or operation of the regeneration may increase the CO concentration.

When excess O₂ is reduced to around 0.5 %, NO_x production is dramatically reduced. This is due to the increase in CO from less available O₂, which can help reduce NO_x back to N₂. However, many FCC/RCC units cannot operate at these low O₂ levels and still maintain regenerator temperatures within safe operating limits, and low O₂ levels will increase CO emissions. Finally, SO_x production is typically increased at low O₂ when SO_x-additives are being used, since there will not be enough O₂ for the SO₂ to oxidise to SO₃ and be captured by the additive.

Partial combustion mode

In general, feed with a Conradson carbon figure up to 2 – 3 % may be treated in a ‘standard’ FCC without a CO boiler as well as partial-combustion FCC. A Conradson figure from 2 – 5 % would require a CO boiler and from 5 – 10 % a catalytic cooler would be needed. It should be noted that the above figures are only indicative and depend also on the severity of the cracking.

In the partial combustion mode, considerable CO is present in the flue-gas and it is consumed downstream of the regenerator in a CO boiler, both to recover the energy produced in a CO boiler and to meet environmental requirements. This system can be seen as two-stage regeneration in comparison with the full combustion mode, where a single regeneration step is present.

The use of a partial combustion mode together with a CO boiler (COB) generates, in general, less CO and NO_x emissions compared with full combustion. The use of a COB or with a high-temperature regeneration technology can significantly reduce CO emissions. CO achieved emissions are from less than 50 – 400 mg/Nm³ and typically below 100 mg/Nm³ (3 % O₂ daily average). In the COB, refinery fuel gas addition is required to incinerate CO (~900 °C). The advantage of partial combustion coupled with a COB is also to achieve lower NO_x emissions (100 – 500 mg/Nm³ at 3 % O₂, daily average, standard conditions), ammonia and hydrocarbons emissions. Emissions of SO_x and particulates are not affected by this mode of operation.

Residue catalytic cracking (RCC) is basically the same process as FCC. Due to the higher coke laydown on the catalyst as a result of the heavier feeds, the heat balance around the regenerator may require additional measures for catalyst cooling. As the heavier feed normally has a higher metal content, especially Ni and V, the catalyst deactivation rate is so fast that the catalyst needs to be removed continuously, to be replaced by fresh catalyst. Increasing rates of fresh catalyst addition induces higher entrainment rates due to fines present in the fresh catalyst, as well as due to fines produced by attrition. Therefore, higher particulate emissions from the regenerator are expected and should be taken into account in the choice and size of the flue-gas PM abatement technique to be implemented.

Two-stage regenerator processes are tolerant of feedstocks with high Conradson Carbon Residue (CRR) values (3-10 % wt) and containing high levels of metals (Ni, V and Na). The first regenerator burns 30 – 70 % of the coke and essentially all the hydrogen in it. Regeneration conditions are kept mild and vanadium on the catalyst cannot form V₂O₅. In the second regenerator, full catalytic activity is restored by completely removing the remaining coke in a dry atmosphere, as hydrogen has been previously removed. V₂O₅ is now formed at high temperature, but as there is little moisture available to form vanadic acid the catalyst is preserved. The two-stage regeneration system allows a R2R resid cracker RCC to operate at

significantly higher metal levels on the catalyst, thereby reducing the catalyst make up requirements and operating costs.

In the Thermoform Catalytic Cracking (TCC), the preheated feedstock flows by gravity through the catalytic reactor bed. The vapours are separated from the catalyst and sent to a fractionating tower. The spent catalyst is regenerated, cooled, and recycled. The flue-gas from regeneration is sent to a carbon monoxide boiler for heat recovery.

In the moving-bed process, oil is heated to 400 – 700 °C and is passed under pressure through the reactor, where it comes into contact with a catalyst flow in the form of beads or pellets. The cracked products then flow to a fractionating tower where the various compounds are separated. The catalyst is regenerated in a continuous process. Some units also use steam to strip the remaining hydrocarbons and oxygen from the catalyst before the catalyst is fed back to the oil stream. In recent years, moving-bed reactors have largely been replaced by fluidised-bed reactors.

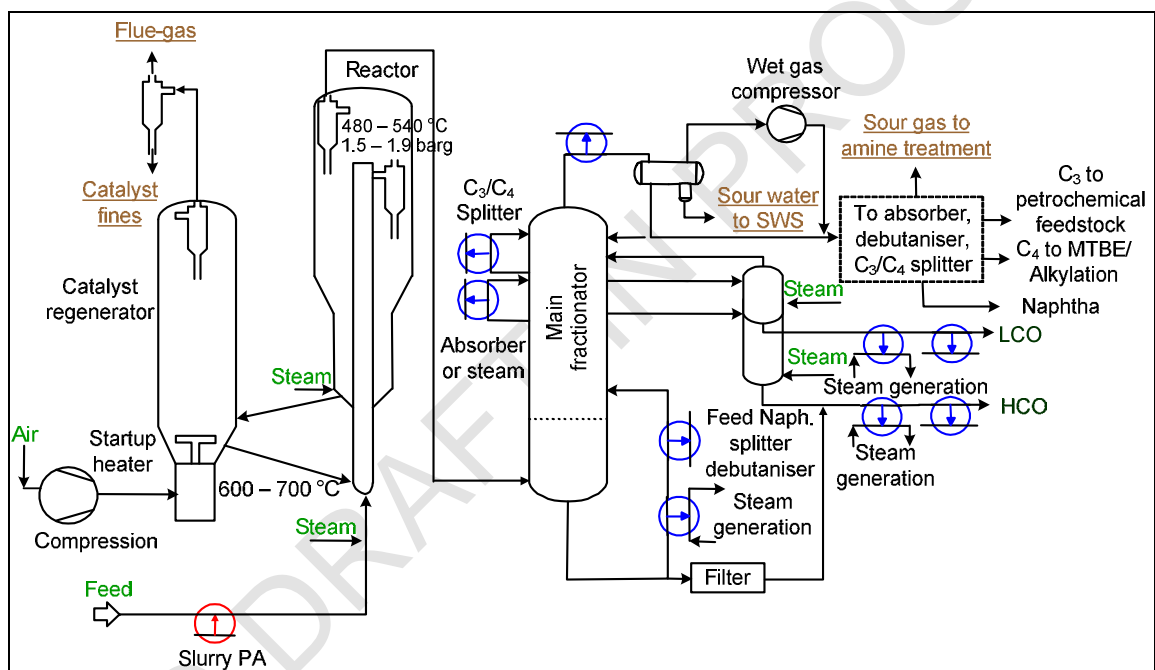


Figure 2.6: Simplified process flow scheme for a fluid catalytic cracker

Reference literature

[76, Hydrocarbon processing 2011], [9, Koottungal 2008].

2.6 Catalytic reforming

Purpose and principle

The heavy naphtha leaving the hydrotreating units is a very poor gasoline blend component due to its low octane. The purpose of a catalytic reformer is to upgrade the octane of these streams for use as a gasoline blendstock. The burning characteristics (octane number) of heavy naphtha are improved significantly by catalytic reforming. The most important characteristic of the reformat product is the octane number. Octane numbers are very low for n-paraffins, slightly better for naphthenes and isoparaffins and are highest for aromatics. There are four major types of reactions which occur during the reforming processes:

- dehydrogenation of naphthenes to aromatics
- dehydrocyclisation of paraffins to aromatics
- isomerisation
- hydrocracking.

Because the EU gasoline market is in decline and reformulated specifications (see Table 1.9) limit the allowable amount of benzene and aromatics in gasoline, catalytic reformer operation is driven more by hydrogen production needs for diesel production than to produce additional aromatics and gasoline blend components, which has traditionally been the case.

Feed and product streams

The typical feedstocks to catalytic reformer units are the hydrotreated straight-run heavy naphtha from the crude distillation unit and, if applicable, the hydrotreated heavy naphtha stream from the hydrocracker unit or coking unit, and the medium catalytically cracked naphtha stream from a FCC unit. A catalytic reformer produces hydrogen, which is essential for use in hydrotreaters (Section 2.13) and may be used in hydrocracking processes. Products from a reformer include, in addition to the hydrogen: refinery fuel gas, LPG, isobutene; n-butane and reformat. The reformat may be blended to gasoline or further separated into components as chemical feedstocks like benzene, toluene, xylene, and naphtha cracker feeds.

Some catalytic reformers operate under more severe conditions, resulting in an increased aromatics content in the reformat product.

Process description

Feedstocks to catalytic reforming processes are usually hydrotreated first to remove sulphur, nitrogen and metallic contaminants. The catalysts used in catalytic reforming processes are usually very expensive (containing platinum [Pt]) and extra precautions are taken to ensure that catalyst is not lost. There are several catalytic reforming processes in use today. In general, they can be classified into three categories: continuous, cyclic or semi-regenerative, depending upon the frequency of the catalyst regeneration. The fixed-bed or moving-bed processes are used in a series of three to six reactors.

Continuous catalyst regeneration (CCR) reforming process

In this process, the catalyst can be regenerated continuously and maintained at a high activity rate. The ability to maintain high catalyst activities and selectivities by continuous catalyst regeneration is the major advantage of this type of unit. Figure 2.7 shows a simplified process flow diagram of a continuous catalytic reformer.

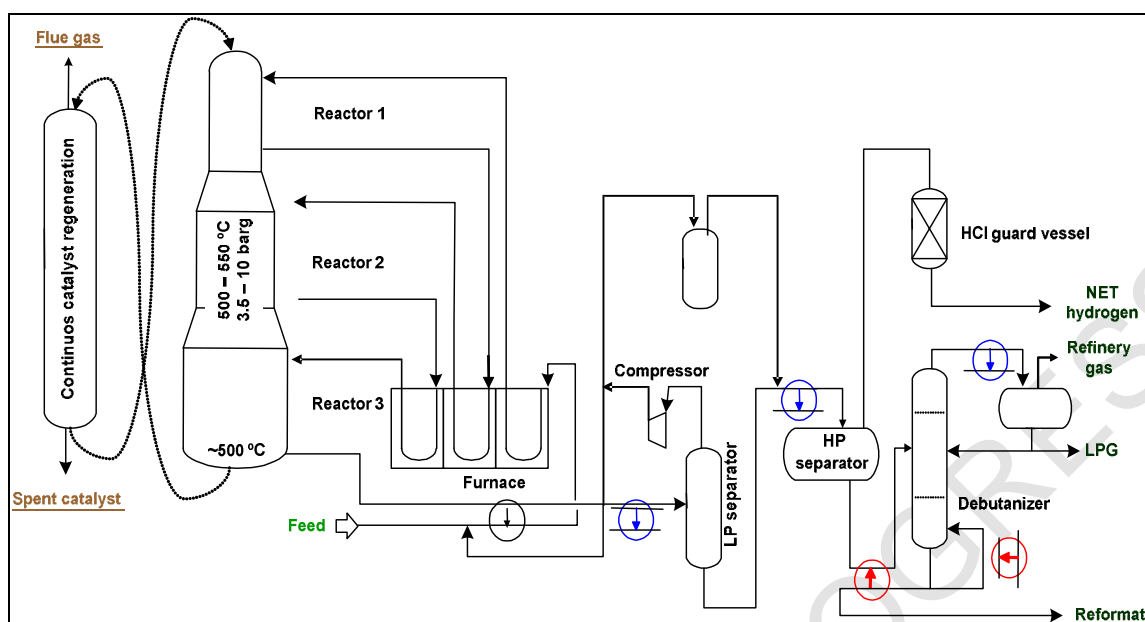


Figure 2.7: Simplified process flow scheme for a continuous catalytic reformer

Interheaters are needed between the reactors to provide the heat required for the endothermic dehydrogenation reaction. As the naphtha feed charge proceeds through the reactors, the reaction rates decrease and the reheat needed lessens. Freshly regenerated catalyst is introduced at the top of the first reactor and flows by gravity from top to bottom. From here it is passed on to the next reactor. Partially-aged catalyst is removed from the bottom of the lowest reactor and sent to an external regenerator, where the carbon is burnt from the catalyst. The catalyst is acidified and reduced before being returned to the lead reactor. The reaction mixture from the last reactor is used to preheat the fresh feed and further cooled down prior to being fed to the low-pressure separator. There the hydrogen-rich gas is separated from the liquid phase. The gas is compressed and partially recycled to the naphtha feed. The remaining vapour is then further compressed, recontacted with the liquid from the low-pressure separator, cooled and fed to the high-pressure separator. The recompression and recontacting is included to maximise recovery of the C₃/C₄ fraction from the hydrogen-rich gas stream. Any excess of this hydrogen-rich gas is routed to the refinery hydrogen system to be used in hydrogen consuming units like hydrotreaters. The selection of the reformer operating pressure and the hydrogen/feed ratio form a compromise between maximum yields and the coking rate.

The CCR reforming process has a higher energy efficiency per tonne of desired product than the semi-regenerative process, due to better yields and improved heat recovery from the products. As the CCR process is the latest and most modern type of catalytic reformer process, it has generally a design with a higher heat integration than the semi-regenerative process and leads to a higher energy efficiency. Appropriate revamping of semi-regenerative units can also achieve higher energy efficiency through the same recovery from products, from pumparounds and from integration with the topping and vacuum.

The use of a CCR generates more dioxins than a semi-regenerative process during the regeneration of the catalyst. For more information, see Section 3.6.

Operational data

This technique operates at lower pressures (3.5 – 10 bar) than, and at the same temperature as, semi-regenerative processes. It uses mono (Pt) or bi-metallic catalysts (Pt-Re, Pt-Sn). Hydrogen is also produced in these processes. A continuous regeneration reformer produces around 350 Nm³ of hydrogen per tonne of feedstock. Since the increased coke laydown and the thermodynamic equilibrium yield of reformat are both favoured by low-pressure operation, the

ability to maintain high catalyst activities and selectivities by continuous catalytic regeneration is the major advantage of the continuous process.

Disadvantages of the CCR reforming process include its ability to make reformates with high aromatic contents >70 vol % and that CCR reformer reformates tend to be higher boiling compared to the semi-regenerative reforming process. These qualities can impact blending CCR reformer reformates into the gasoline pool with gasoline specification of less than 35 % v/v aromatics. Compared to the other reforming technologies, much of the value from CCR reforming is the improved yields at high octanes; however, with bio-fuels blending and decreasing octane demand, the economics for converting other reforming technologies to CCR reforming technology is diminishing.

Economics

As an example, the investment costs based on a 3 975 m³/d continuous octanising unit (battery limits, erected cost, 1998 Gulf Coast) was 10 000 USD per m³/d.

The erected costs of a 3 180 m³/d unit (4Q95, US Gulf Coast) has been USD 48.3 million (USD 15 200 per m³/d). In addition, catalyst costs add another USD 2.6 million.

Example plant(s)

Nowadays, only continuous catalytic reformer units are built. New reforming units larger than 15 000 bpd (2 400 m³/d) are typically designed as continuous catalyst regeneration reformer units. Smaller reformer units may be of continuous catalyst regeneration or semi-regenerative designs, but the cost of the CCR can become prohibitive with smaller scale units.

Reference literature

[183, HP 1998], [175, Meyers 1997], [207, TWG 2001], [77, REF TWG 2010].

Cyclic reforming process

The cyclic reforming process is characterised by having a swing reactor in addition to these on-stream, in which the catalyst can be regenerated without shutting the unit down. When the activity of the catalyst drops below the desired level, this reactor is isolated from the system and replaced by the swing reactor. The catalyst in the replaced reactor is then regenerated by introducing hot air into the reactor to burn the carbon from the catalyst. Typically, one reactor is always being regenerated.

Semi-regenerative reforming process

In this process design, regeneration requires the unit to be taken off-stream. Depending upon the severity of operation, regeneration is required at intervals of three to 24 months. The control of the dosage of a chlorine-containing compound to feed and operating pressures are utilised to minimise coke laydown and the associated loss of catalyst activity. The dosing rate depends on the water content of the feed (actual and potential) and the desired steady-state chloride level on the catalyst.

The reactors operate at temperatures in the range of 400 - 560° C and pressures in the range of 15 – 35 bar. This type of process produces between 130 and 200 Nm³ of hydrogen per tonne of feedstock.

Economics

The erected cost of a semi-regenerative unit of 3 180 m³/d is USD 33 million (USD 10 400 per m³/d). In addition, catalyst costs add another USD 3.4 million (1995 - US Gulf Coast)

Many applications exist in Europe, as well as in the rest of the world.

Cross-media effects

In semi-regenerative reforming, the unit catalyst is regenerated at intervals of three to 24 months, depending on the intensity of the process. The emission factor of dioxins per tonne of feedstock is much lower than with continuous regeneration. For more information, see Section 3.6

2.7 Coking processes

Purpose and principle

Coking is a severe thermal cracking process used primarily to reduce the refinery production of low-value residual fuel oils and transform them into transportation fuels, such as gasoline and diesel. As part of the process, coking also produces petroleum coke, which is essentially solid carbon with varying amounts of impurities. When high-quality coke is required (e.g. to produce anodes for metals industry), green coke needs to be processed in a calciner.

Feed and product streams

As the coking process is a thermal destruction process, the quality of the feed in terms of metal content, Concarbon number and other contaminants is not critical. As a matter of fact, coking is predominantly used when the feed has a high Concarbon number and contains high quantities of impurities which cannot be handled in catalytic conversion processes. All this produces high feedstock flexibility. The feed to a delayed coking unit can consist of atmospheric residue, vacuum residue, shale oils, tar sands, liquid and coal tar, which results in a petroleum coke used for fuel applications. Aromatic oils and residues such as heavy cycle oils from a catalytic cracking unit and thermal tars are suitable feedstocks for the production of needle coke and anode coke. The feed to a fluid coker is the vacuum residue, sometimes mixed with refinery sludges, tar sands, bitumen and other heavy residues.

The products from the coking fractionator are refinery fuel gas, LPG, naphtha and light and heavy gas oils. Petroleum coke is another product, with the type depending upon the process used, operating conditions and feedstock used. Coke produced by the coker is called 'green' coke and still contains some heavy hydrocarbons left from incomplete carbonisation reactions. More information about the properties of the coke can be found in Section 10.3.2.

Process description

Two types of coking processes exist: the delayed and fluid coking processes that produce coke and the flexicoking process that gasifies the coke produced in a fluid coking process to produce coke gas.

Delayed and fluid coking

The basic process is the same as thermal cracking (Section 2.22), except that feed streams are allowed to react for longer without being cooled. Figure 2.8 shows a simplified process flow diagram of the delayed coking unit.

The delayed coking feed stream of residual oils is first introduced to a fractionating tower, where residual lighter materials are drawn off and the heavy ends are condensed (not shown in Figure 2.8). The heavy ends are removed, heated in a furnace and then fed to an insulated vessel called the coke drum, where the cracking takes place. In the case of fluid coking, a fluidised-bed is used. Temperature (440 – 450 °C), pressure (1.5 – 7.0 barg) and recycle ratio are the main process variables which contribute to the quality and yields of delayed coking products. When the coke drum is filled with product, the feed is switched to an empty parallel drum (dotted drum in Figure 2.8).

When the coke drum is full, steam is then injected to remove hydrocarbon vapours. The coke bed is then quenched with water and the cokes are cut out with high pressure water. The cutting water passes to dedicated settlement where coke solids settle out and the clarified water is recycled. The wet green coke is conveyed to designated open stock piles, where water drains out and is recycled. Green coke can already be sold and used for energy production. The yield of delayed coking is usually above 80 % (25-30 % coke, 65 -75 % light products) conversion of feed to products. The production of petroleum coke is of the ratio of 0.13 tonnes of petroleum coke produced per tonne of feedstock

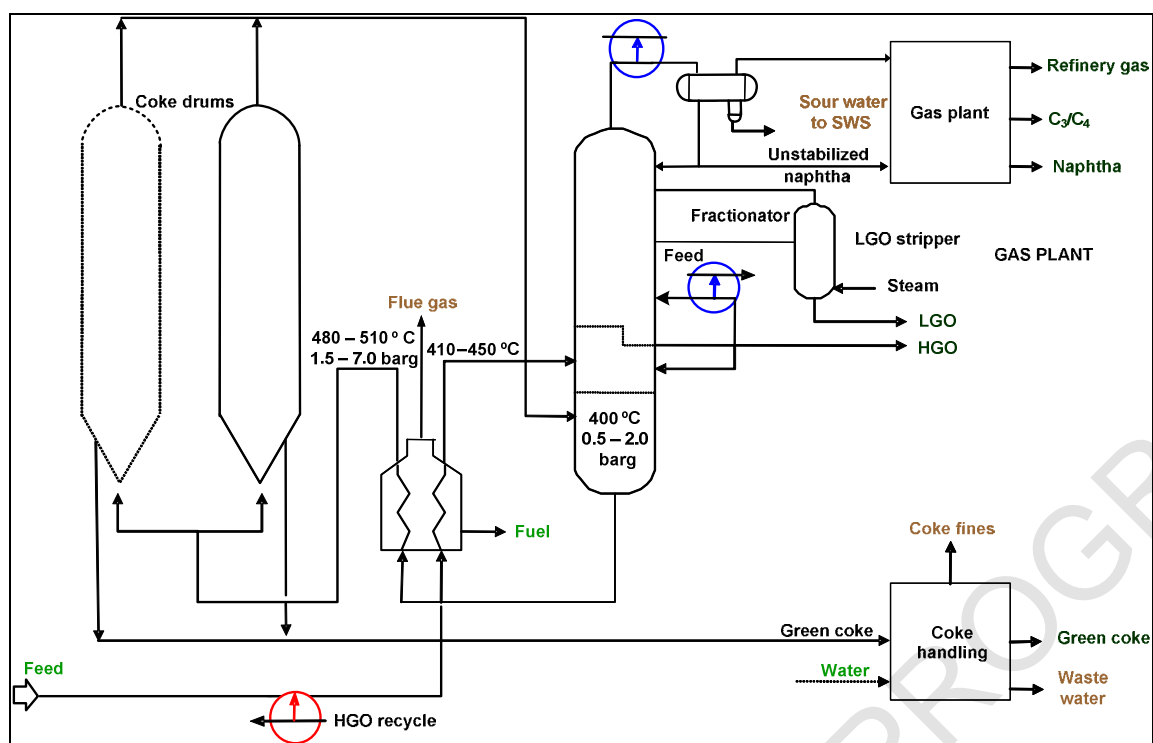


Figure 2.8: Simplified process flow scheme for a delayed coking unit

Hot vapours from the coke drums, containing cracked lighter hydrocarbon products, hydrogen sulphide and ammonia, are fed back to the fractionator where they can be treated in the sour gas treatment system or drawn off as intermediate products. Condensed hydrocarbons are re-processed and collected water is reused for coke drum quenching or cutting. Any remaining vapours commonly pass to the flare system. Normally, products such as naphtha are totally fed to the naphtha hydrotreater for further processing. The heavier products are suitable feedstock for catalytic reforming after proper hydrotreatment. Light oil needs further treatment before being sent to the gas oil blending pool. The heavy gas oil is preferably sent to a hydrocracker unit (Section 2.13) for further conversion into light components. When no cracking units are available, it is blended in the heavy fuel oil pool.

Calciner

For certain applications, green coke should be calcinated before being used or sold. The incinerator kilns are direct fuel gas or coke fine fired at the discharge end. The coke is calcinated at up to 1380 °C, driving off volatile matter and burning it within the kiln. Exhaust gases discharge from the feed end and are incinerated to burn off residuals and coke fines. Hot flue-gases pass through a waste heat boiler and gas cleaning by multi-cyclones. Collected fines from the cyclones are pneumatically conveyed to a silo with exit air filters. The calcinated coke discharges to a rotary direct water injection. Off-gases from the cooler pass to gas cleaning by multi-cyclones and the water scrubber. Collected cyclone fines may be recycled to product, which is oil sprayed as a dust suppressant, or may be incinerated or sold as a fuel.

Flexicoking

The flexicoking process typically converts 84 – 88 % w/w of the vacuum residue to gaseous and liquid products. Virtually all metals in the feed are concentrated in the solids purged from the process (1 – 4 % w/w of the fresh feed). Flexicoking is a very robust process in which coking and gasification are fully integrated. The process is advanced compared to the classic delayed coker in terms of operation and labour intensity. [276, Kamienski et al. 2008]

The flexicoking process uses three major vessels: the reactor, the heater and the gasifier. As auxiliary facilities, the system includes a heater overhead cooling system and a fines removal system, a coke gas sulphur recovery unit and reactor overhead scrubber (Figure 2.9). The

preheated vacuum residue feed is sprayed into the reactor, where it is thermally cracked, typically at 510 – 540 °C. The freshly-formed coke is deposited on the surface of the fluidised recirculated coke particles. In the gasifier, the coke is reacted at elevated temperatures, typically 850 - 1000 °C, with air and steam to form coke gas, a mixture of hydrogen, carbon monoxide and dioxide and nitrogen. Sulphur in the coke is converted in the gasifier primarily to hydrogen sulphide, plus traces of carbonyl sulphide (COS). Nitrogen in the coke is converted to ammonia and nitrogen. Unlike normal gasifiers which are fed with pure oxygen, the flexicoking gasifier is fed with air, resulting in a coke gas with a relatively low calorific value, as it contains a high quantity of nitrogen inerts.

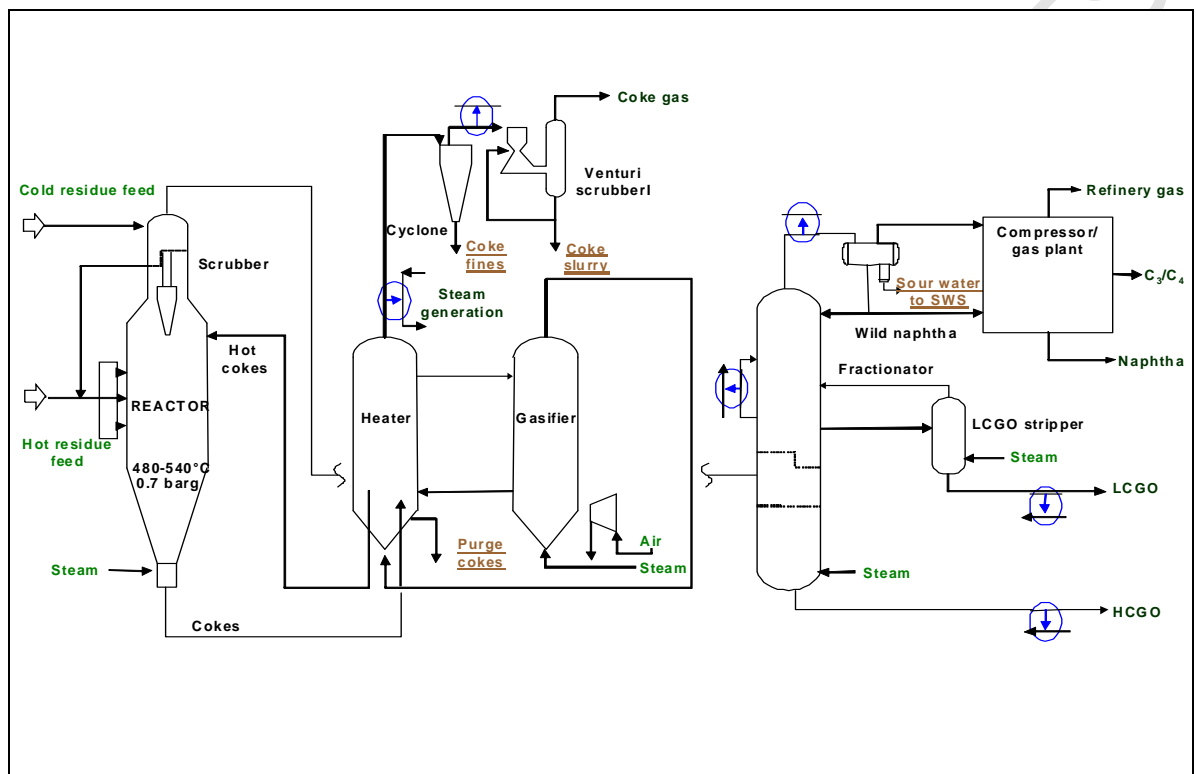


Figure 2.9: Simplified process flow scheme for a flexicoker

The cracked hydrocarbon vapour product from the reactor is passed through cyclones to remove coke particles and is subsequently quenched in a scrubber section located at the top of the reactor. Material boiling above 510 – 520 °C is condensed in the scrubber and recycled to the reactor. The lighter material goes overhead to conventional fractionation, gas compression and light ends recovery sections. The treatments and use of the products are very similar to the ones already described in the delayed coker. Pressure relief from the fractionator of the coking processes passes to flare and from the coke drums to the quench tower system.

2.8 Cooling systems

Under the IPPC process, a horizontal BREF on Industrial Cooling Systems [69, European Commission 2001] has been produced that covers many topics of relevance to the refineries sector. To avoid repetition, therefore, this section on cooling addresses only topics not covered by that horizontal BREF. Moreover, some cooling water pollution issues have already been studied in the OSPAR (North Sea) and HELCOM (Baltic) processes.

Purpose and principle

In a refinery, the cooling of feed and product streams is required to allow refinery process operations to take place at the right temperatures, and to bring products to their appropriate storage temperature. Even though heat integration of process systems ensures that significant cooling can be achieved by exchanging heat between streams to be cooled and streams to be heated, additional cooling is still required. This additional cooling should be provided by an external cooling medium: water and/or air.

Process description

A wide range of techniques is used for cooling purposes in oil refineries. Most refineries use a combination of the techniques available. The selection of a cooling system depends on the required cooling temperature, the cooling capacity, contamination risk (primary or secondary cooling loop) and local circumstances. A simplified diagram of the cooling techniques is shown in Figure 2.10 and briefly described below:

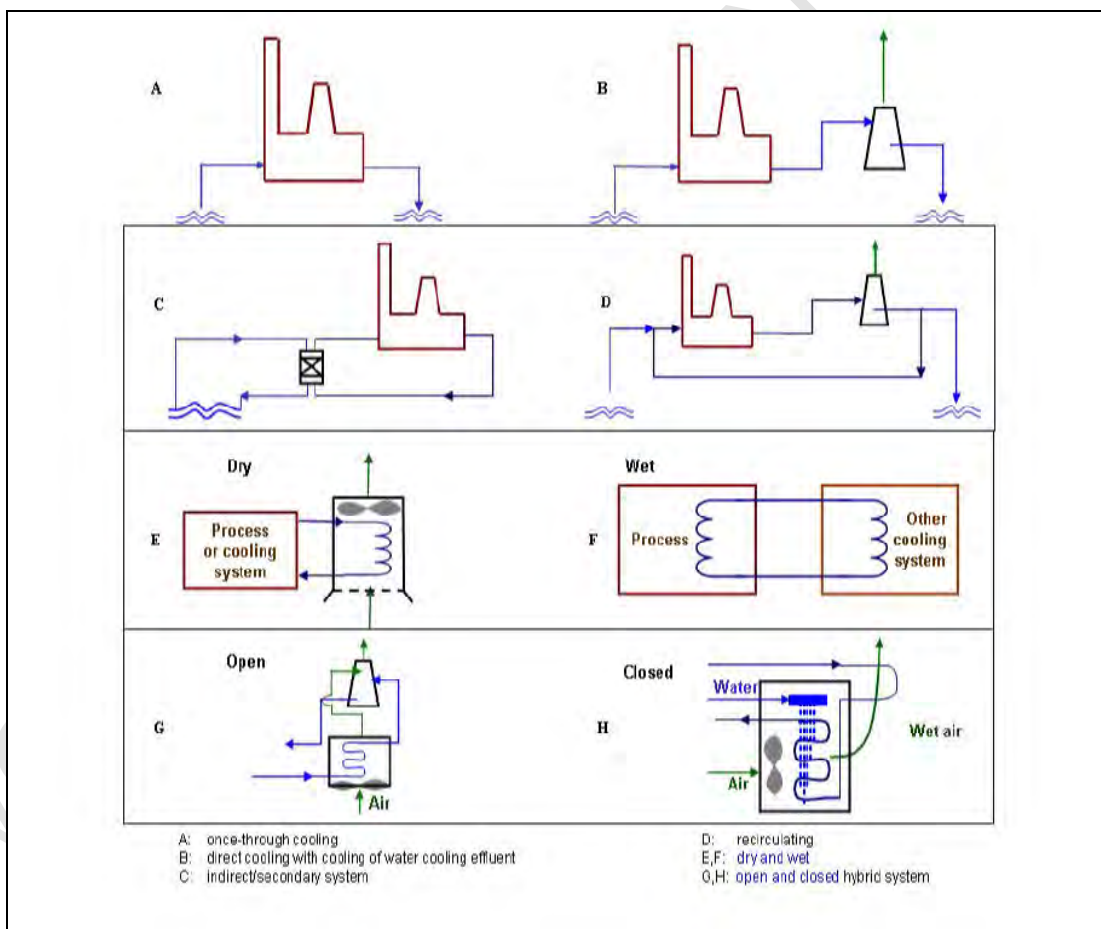


Figure 2.10: Simplified diagrams of the cooling systems used in refineries

Air cooling

In an air cooler (forced or induced draught), the process stream in the tubes is cooled against the air delivered by a fan. An induced draught air cooler is illustrated in Figure 2.10.

Direct water cooling (i.e. quenching)

Because of the high contamination generated by this type of cooling, quenching is only used in cokers (Section 2.7), in gasifiers and in some sludge incinerators.

Once-through system (seawater, river water, etc.)

In a typical once-through cooling system, water is extracted from a surface water body, filtered if necessary and sometimes treated with biocide to inhibit fouling. It is then passed around the refinery to enable cooling through heat exchangers. The cooling water is passed through a process unit once and is then either treated or discharged directly into the receiving environment without treatment. There are several ways to use water for once-through cooling in refineries and that carry a different risk of contamination by process streams as described below:

- Once-through cooling water used for cooling non-polluting streams, e.g. in power generation. A cooling tower system is generally applied when the thermal loading of the surface water is too high (See Figure 2.10 A and B).
- Once-through cooling water used for heat exchange with a recirculating water system which then cools the process streams (Figure 2.10 C).
- Once-through cooling water is used to cool process streams directly (via heat exchangers) (See Figure 2.10 A and B).

Circulation system (tempered water, cooling water)

In this system, most cooling water is repeatedly recycled through cooling towers using ambient air. In order to control the concentration of contaminants and the solids content in the cooling water, a blowdown stream is used, which is sent to the waste water treatment unit, and make-up water is added. A certain amount of water also exits the system through evaporation (Figure 2.10 D).

Wet closed system (normally water)

Tempered water is used when process streams to be cooled should not be exposed to the (low) cooling water temperatures (Figure 2.10 F).

Hybrid systems

In these hybrid systems, both air and water are used as the cooling media. These systems normally maximise the use of air cooling and the rest is done by water cooling. Two types of systems are available and they are shown in Figure 2.10 G and H.

Refrigeration systems

In specific cases where for safety reasons process streams have to be cooled below ambient temperatures, refrigeration systems are applied. This can be either a direct refrigeration system, i.e. using the refrigerant (propane or ammonia) in the process, or an indirect system (Figure 2.10 F) using a circulation system (e.g. brine, glycol) where the refrigerant cools the circulating liquid.

2.9 Desalting

Purpose and principle

Crude oil and heavy residues can contain varying quantities of inorganic compounds, such as water soluble salts, sand, silt, rust and other solids, together characterised as bottoms sediment. The salt in the crude is primarily in the form of dissolved or suspended salt crystals in water emulsified with the crude. These impurities, especially salts, can lead to fouling and corrosion of heat exchangers (crude preheaters) and especially the crude distillation unit overhead system (Section 2.19). Salts are detrimental to the activity of many of the catalysts used in the downstream conversion processes. Additionally, sodium salts stimulate coke formation (e.g. in furnaces). Some inorganic impurities are chemically bound, such as vanadium and nickel, and are often referred to as oil-soluble salts. These cannot be eliminated in a desalter. Moreover, excess water has to be removed from crudes with high water content. Therefore, desalting of the incoming crude oil is generally applied before separation into fractions (See Section 2.19).

The principle of desalting is to wash the crude oil or heavy residues with water at high temperature and pressure to dissolve, separate, and remove the salts and other water extractable components.

Feed and product streams

Crude oil and/or heavy residues (oily feedstock) and reused and fresh water are the feedstreams to the desalter with desalted crude oil and contaminated water (brine) being the outputs of the desalting processes. The water phase from the crude distillation unit overhead and other used water streams are normally fed to the desalter as wash water. Efforts are made in the industry to minimise water content of the desalted crude to less than 0.3 % and bottoms sediments to less than 0.015 %. The concentrations of inorganic impurities in the cleaned stream are highly dependent on the design and operation of the desalter, as well as on the crude source.

Process description

After preheating to 115 – 150 °C, the oily feedstock is mixed with water (fresh and preused water) in order to dissolve and wash out the salts.

Intimate mixing of the oil and wash water takes place in a globe valve mixer, a static mixer or a combination of both. The water must then be separated from the oil feedstock in a separating vessel by adding demulsifier chemicals to assist in breaking up the emulsion and, in addition, by applying a high-potential electric field across the settling vessel to coalesce the polar salt water droplets.

The separation efficiency depends on pH, density and viscosity of the crude oil, as well as on the volume of wash water used per volume of crude. Either AC or DC fields may be used and potentials from 15 to 35 kV are used to promote coalescence. Many refineries have more than one desalter. Multiple-stage desalters also exist. The wash water containing dissolved hydrocarbons, free oil, dissolved salts and suspended solids is further treated in an effluent treatment plant (Section 4.24). Where bottoms sediments are critical in downstream process units, desalters are equipped with a bottom flushing system to remove settled solids. Figure 2.11 shows a simplified process flow diagram of a modern design crude desalter.

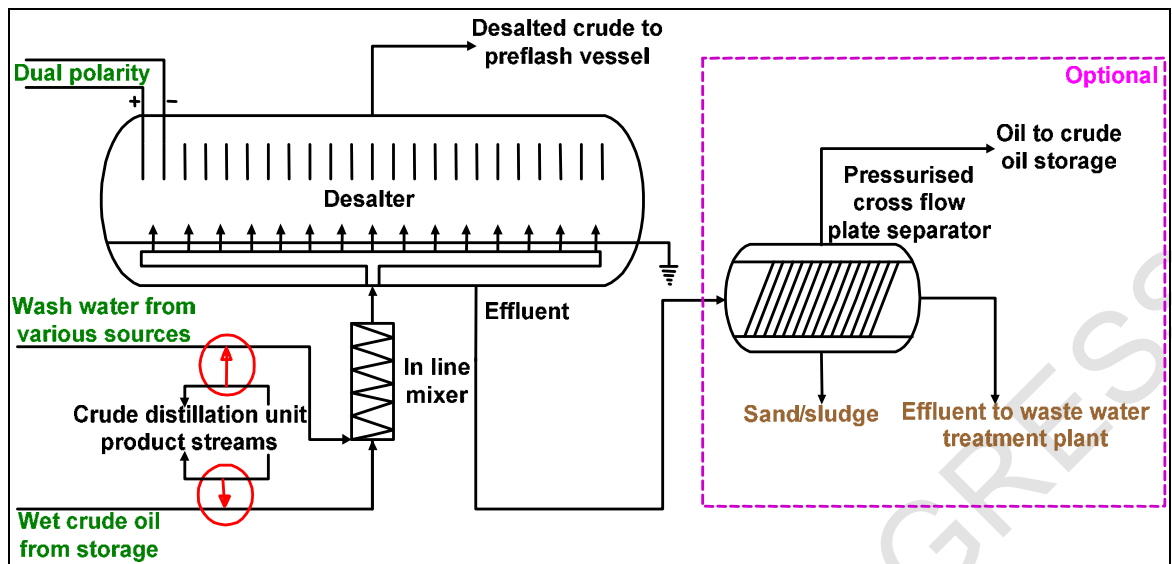


Figure 2.11: Simplified flow diagram of a crude desalter

2.10 Energy system

Heat-producing plants are an essential and integral part of most refining processes/activities. An important aspect of the refining energy system is the effective use of internal residue streams as part of the energy mix. This chapter describes some principles of energy production and management in the context of refinery fuels

Purpose and principle

Heat and electricity are needed to run a refinery. The extensive heat requirement is provided by fuel combustion either directly (by heaters, furnaces) or indirectly via steam. Steam is usually produced inside the refinery. This is increasingly coupled to the generation of electricity in surplus because it can be sold on the external market (as with steam if there is local demand).

An emerging proposition is full commercialisation where (some) steam and electricity production is outsourced to a power company specialist. Some refineries have switched to importing their base load steam and electricity needs from third party companies based locally.

Fuels and fuel systems

The fuel required for the production of steam and power or for the firing of the furnaces originates either from fuels that are produced by the refinery itself (refinery fuels) or from natural gas that is bought outside, or a combination of both. Normally, most or even all of the gaseous and liquid refinery fuels used are by-products of refinery processes. The composition and quality of these fuels vary with the crude oils processed. The refinery fuel pool is a careful balance between energy required, type of crude processed, emission limits and economics.

Refinery fuel gas (RFG)

The majority of the fuel used in a refinery is refinery fuel gas (RFG). This is a mixture of methane, ethane, ethylene and hydrogen and may contain some CO and small amounts of C₃, C₄, N₂ and H₂S. RFG is produced and collected in the refinery gas system, but has to be used quickly and cannot normally be sold as a product. The composition may change over time depending on refinery operations and the feedstock being processed and will be different from site to site, again depending on the feedstock and installed plants, for example if the refinery has a coker that supplies syngas (CO + H₂) to the RFG system.

Most refinery fuel gas systems have alternative sources of supply: refinery gas, imported gas (normally natural gas) and liquefied petroleum gas (LPG). External supplies usually become part of the RFG system, although dedicated units may run on commercial fuel. RFG, if properly treated, is a low-polluting fuel. More information on RFG is provided in Section 4.10.2.

These gases may be sulphur-free at source (i.e. from catalytic reforming and isomerisation processes) or sulphur-containing at source (most other processes, i.e. from crude distillation, cracking, coking and all hydrodesulphurising processes). In the latter case the gas streams are normally treated by amine scrubbing to remove H₂S before being released to the refinery fuel gas system, and dust removal and COS conversion if necessary (Section 4.23). Coke gas forms a main refinery gas source if coking takes place in the refinery. Sulphur content in the form of H₂S is normally below 100 – 220 mg/Nm³, and will strongly depend on the pressure used in the amine treating units. Levels of 4 – 40 mg/Nm³ are possible for gas treated at high pressure (20 bars), and lower levels, 2 – 15 mg/Nm³ can even be reached with very high pressure (50 bars). Residual H₂S concentrations achievable by using a refinery fuel gas treatment are shown in Table 4.80 of Section 4.23.5.1. The nitrogen content is negligible.

Fuel gas system

Figure 2.12 shows a schematic diagram of a typical fuel gas system. The fuel gas is supplied from the different refinery units. In this diagram, backup supply is provided by imported natural gas and by internally-produced LPG, which is vaporised and routed into the fuel gas header. The condensation of heavier hydrocarbons and/or water is critical for the fuel gas system. Normally all units have their own fuel gas knock-out drum, in which condensate formed in the fuel gas distribution system is separated. The fuel gas lines from this drum need to be steam-traced to avoid condensation in the supply lines to the individual burners. Liquids from the fuel gas knock-out drum are drained to a closed slops system.

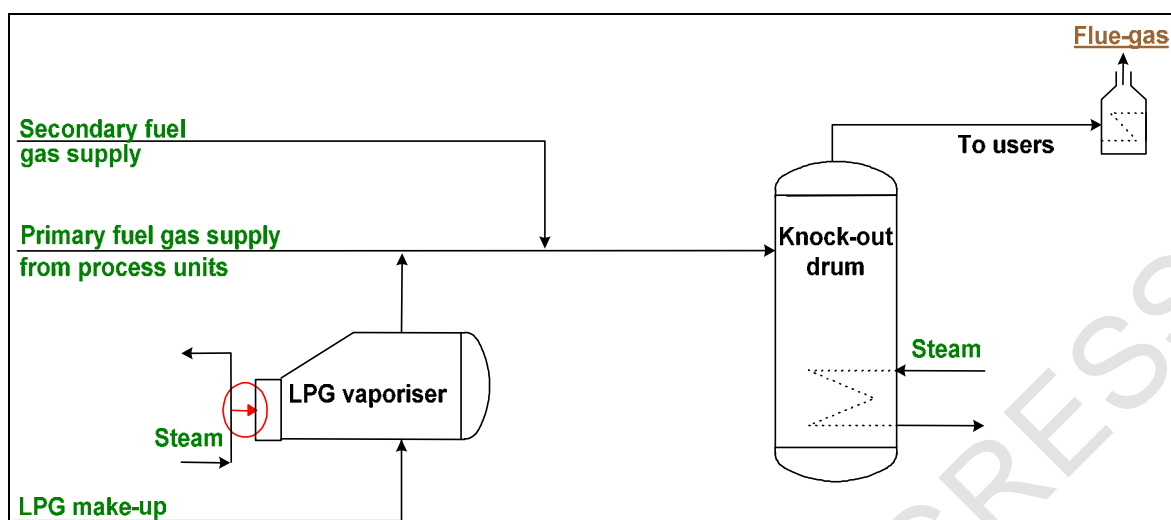


Figure 2.12: Simplified flow diagram of a fuel gas system

Liquid refinery fuel

Heavy fuel oil (HFO) used in the refinery is normally a mixture of the residues from atmospheric and/or vacuum distillation and conversion and cracking processes. Liquid refinery fuels are available in various grades, viscosity being the main parameter. The lower the viscosity, the more expensive the fuel. The heavier (more viscous) grade fuels require heating to reduce their viscosity before combustion. They contain sulphur (<0.1 – 6 %), metals (e.g. V, Ni) and nitrogen (0.1 – 0.8 %) resulting, after direct combustion, in high SO₂, particulates and NO_x emissions. They can also be gasified in the Integrated Gasification Combined Cycle (IGCC) plant, where virtually any refinery residue (e.g. visbroken or thermal tars) can be converted to heat and power.

Provided that the crude oil is properly desalted, the ash content of the fuel will be directly related to the total solids, the amount being proportional to the sum of the nickel and vanadium present (Ni-V value: 0.03 – 0.15 % w/w, depending on the residue source and crude origin). To arrive at the metal content of the HFO, the metal content of the crude is multiplied by a factor of 4 - 5 (dependent on the yield of residue and the residue content of the crude). The metal content of the HFO can vary between 40 and 600 ppm for HFO from a North Sea crude and Arabian Heavy crude, respectively, generating particulate concentrations in the flue-gas of 150 – 500 mg/Nm³. The most prominent metals indigenous to the crude are vanadium and nickel, other metals such as cadmium, zinc, copper, arsenic and chromium have also been detected [150, Dekkers, Daane 1999]. Table 2.2 shows the metal contents of residual fuel oils typically used in refineries.

Table 2.2: Metal content of residual oil

Metal	Concentration range (ppm)	Average concentration (ppm)
V	7.23 – 540	160
Ni	12.5 – 86.13	42.2
Pb	2.49 – 4.55	3.52
Cu	0.28 – 13.42	2.82
Co	0.26 – 12.68	2.11
Cd	1.59 – 2.27	1.93
Cr	0.26 – 2.76	1.33
Mo	0.23 – 1.55	0.95
As	0.17 – 1.28	0.8
Se	0.4 – 1.98	0.75

Source: [234, HMIP UK 1995]

Liquid refinery fuel system

As has already been stated, liquid refinery fuels are heavy residues that should be stored in a separate storage tank at an elevated temperature to reduce the high viscosity. A typical refinery fuel oil system (schematic diagram, see Figure 2.13) includes a dedicated mixing tank (normally off-site), a circulation pump and a heater (when required). The system discharges fuel oil at a constant pressure and at the required conditions of temperature and viscosity, so that atomisation and efficient combustion are possible. If the fuel consumption is low, the cost of installing heated storage, preheating, etc. may not be justified for the use of heavy fuels and so a light fuel oil will be used. Liquid refinery fuels are normally used for process start-ups.

Solid fuels

Solid fuels such as petroleum coke can be gasified as a refinery fuel gas source for refineries (Flexicoking, Section 2.7). Coke is burnt in the catalytic cracking regenerator (Section 2.5) and in the coking process and represents a heat production source in the refinery. Coal, as imported fuel, is not applied in European refineries.

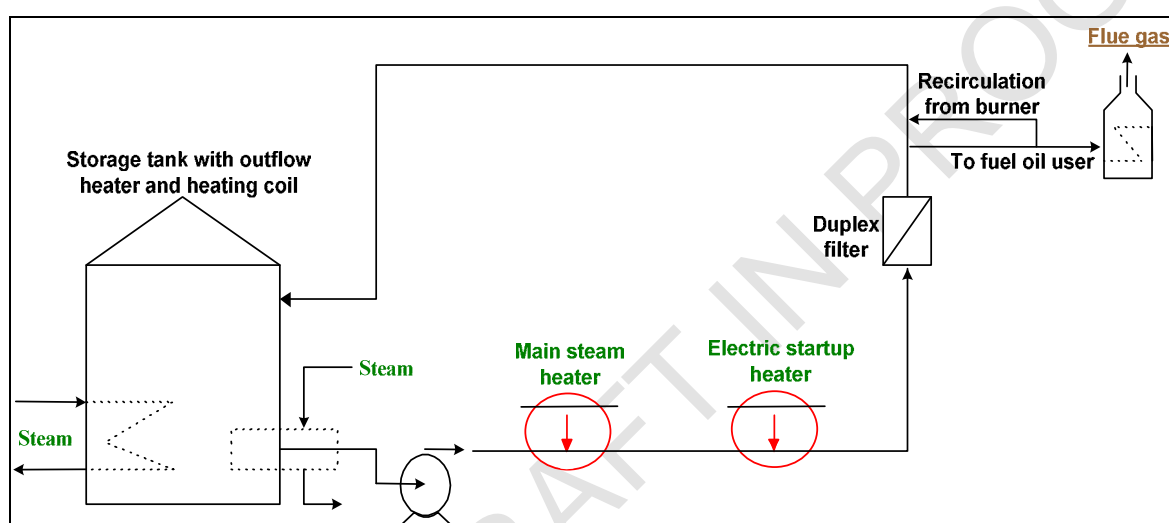


Figure 2.13: Simplified flow diagram of a heavy fuel oil system

Energy production techniques

This section is not intended to include a detailed description of energy production techniques (steam and power), since this is covered in the LCP BREF [7, EC 2006].

Furnaces and boilers

Many of the individual refinery processes and utility systems combust fuel (gas and/or liquid) in dedicated furnaces and boilers to supply the heat necessary for the process. Fired process heaters and boilers are the main heat producers. The former transfer the heat released in the combustion process directly to the process stream and the latter produce steam that will be used somewhere in the refinery. The principle of steam generation is the heating of boiler feed water, under pressure in a specified fuelled boiler or a waste-heat boiler consisting of heat exchanger bundles (economisers and superheaters). In this document, no distinction is made between furnaces and boilers, except when relevant.

A variety of furnaces and burner types are used in refineries, largely determined by the heat-release characteristics required by a particular process. Many but not all furnaces are dual (oil/gas) fired to allow flexibility in the refinery fuel system. Refinery process heaters are typically rectangular or cylindrical enclosures with multiple-fired burners of specialised design using mainly low-combustion intensity. Boilers (fixed or fluidised bed) are generally fairly standard steam-producing units of medium or high-combustion intensity. Waste heat boilers may also be present in the furnaces of stacks. Well maintained and operated direct-fired heaters and boilers achieve thermal efficiencies of over 85%. If air preheat is applied and the

combustion products (flue-gas) are cooled close to their dew point, the thermal efficiency can be as high as 93 %. Boilers consume about 10 - 20 % of refinery energy requirements.

Gas and steam turbines

Gas turbines work as follows: fresh air at ambient conditions is drawn into the compressor where its temperature and pressure are raised. The high-pressure air proceeds into the combustion chamber, where the fuel is burnt at a constant pressure. The resulting high-temperature gases then enter the turbine where they expand to atmospheric pressure, thus producing power. Steam turbines are used to transform the steam pressure to power. Combined-cycle processes combine the gas and steam turbine processes to produce power at higher efficiency than is reached with open-cycle turbines (steam and gas). More information about gas and steam turbines, as well as combined cycles, can be found in the LCP BREF [7, EC 2006].

Cogeneration plants (CHP)

These systems are designed for the co-production of heat and power. The fuel for this type of facility is usually natural gas. It is, however, also possible to fire refinery gas as part of the fuel slate, thus potentially reducing the amount of refinery gas available for combustion in boilers and furnaces. The steam and power cogeneration concept can also be applied to boilers firing, for instance, liquid refinery fuel. They can be designed to generate high pressure steam and to let the pressure down over an expander/turbo-generator. Economisers and the optimisation of air-to-fuel control are also techniques applicable in cogeneration plants.

Integrated gasification combined cycle (IGCC)

Integrated gasification combined cycle is a technique for producing steam, hydrogen (optional) and electrical energy from a variety of low-grade fuel types with the highest conversion efficiency possible. During the gasification of the oil with oxygen and/or air, syngas is also produced and used for energy production, typically in a combined cycle for the production of heat and electricity. Hydrogen can also be separated from the syngas for use in the refinery (Section 2.14).

The principle is based on the high-temperature and high-pressure reaction of organic carbons or coke with steam and understoichiometric amounts of oxygen (partial oxidation) to produce syngas ($\text{CO} + \text{H}_2$). After the combustion chamber, the system contains a number of sophisticated energy recovery systems to produce steam and electricity. Figure 2.14 shows a block flow diagram of an IGCC plant. In the partial oxidation of hydrocarbons, the product gas contains a certain amount of free carbon (soot). The soot particles are removed from the gas together with the ash in a two-stage water wash.

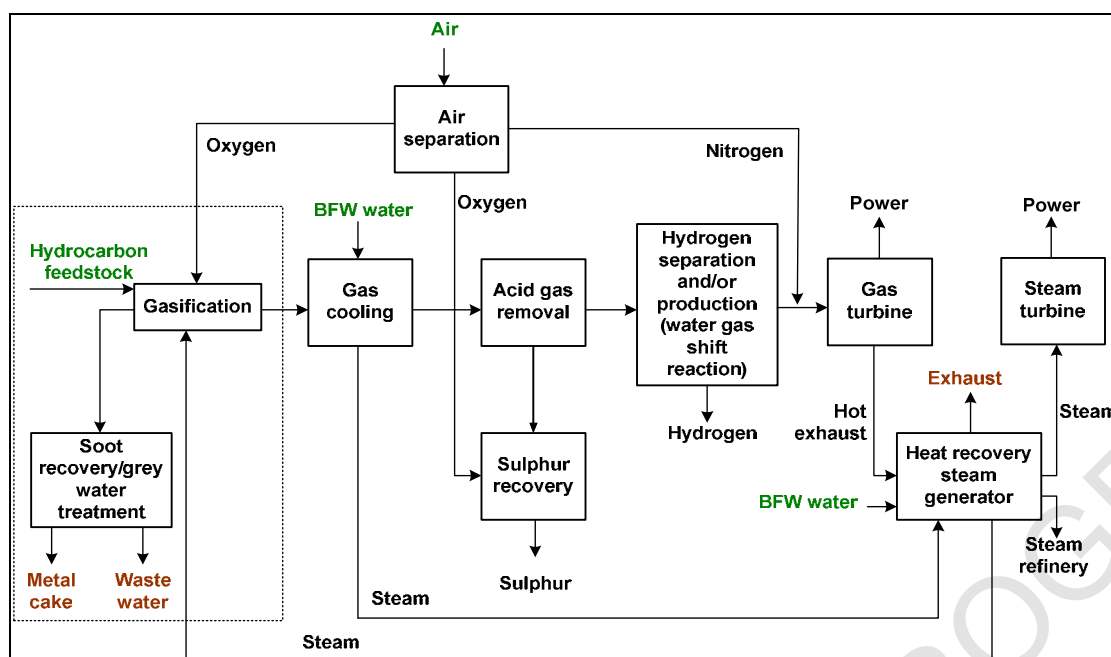


Figure 2.14: Block flow scheme for an IGCC process

The gasification plant consists of two integrated complex units. In the first, syngas manufacturing process plants (SMPP), the gasification of heavy fractions takes place and the syngas is produced and purified. In the second, i.e. the combined-cycle power plants, the syngas is fed to a combined-cycle thermoelectric unit. The SMPP includes the two sections, described below.

- Gasification and carbon extraction:** in the gasification section, the feedstock is gasified through a non-stoichiometric reaction with pure oxygen and water; the reaction occurs in the gasifier, a non-catalytic vessel internally-coated with refractory, operating at a high temperature (about 1300 °C) and pressure (about 65 bar).
- Gas cooling and purification:** in the gas-cooling section, the waste heat from syngas is recovered by the generation of steam at three pressure levels. A small quantity of carbon, formed in the gasifiers is removed from the gas by direct contact with water in a scrubber. Water is then treated in the grey water treatment and then sent to the existing refinery biotreatment plant. A solid effluent in the form of a filter cake is discharged from this unit and sent to external plants for the recovery of the metals. In addition, a COS hydrolysis reactor is provided to convert the small amount of COS produced in the gasifier to H₂S. This section also includes a gas expander for the recovery of the pressure energy of the syngas (pressure in gasifiers is about 65 bar). This system contains an acid-gas removal process which consists of a circulating amine stream used to selectively absorb the H₂S formed in the gasifier and during the COS hydrolysis. It also contains an air separation unit. This unit produces the oxygen required for the gasification and the Claus plant, and the nitrogen for syngas conditioning. It is based on conventional cryogenic air fractionation. And finally, it contains a sulphur recovery unit where Claus units recover elemental sulphur from the H₂S recovered in the acid-gas removal section. This, along with a tail gas treatment section maximise the overall sulphur recovery.

After the cooling and purification sections, the purified syngas is sent to the combined cycle power plant, for power generation. This mainly consists of a conventional cycle with a gas turbine, a heat-recovery steam generator and a steam turbine.

Products from the energy system

As mentioned at the beginning of this section, the energy system of a refinery is there to provide the heat and power necessary to carry out the process. A short description of the types of products produced by the energy system of a refinery (steam and power) is given below.

Steam

The different steam qualities generated in the boilers of the refinery have the general characteristics described below (the heat content ranges from about 2 700 MJ/t for low-pressure steam to 3 200 MJ/t for super heated high pressure steam at 50 bar):

- High-pressure (HP) steam network (>30 bar, 350 – 500 °C), generated in waste heat boilers (cooling of hot off-gases and/or hot products in catalytic processes and hydrocrackers) and in fired boilers. HP-steam is mainly used in turbines to produce electrical power (and medium pressure steam).
- Medium pressure (MP) steam network (7 – 20 bar, 200 – 350 °C), generated by pressure reduction of HP steam, is used within the refinery for stripping, atomisation, vacuum generation and heating (e.g. reboilers, tanks).
- Low pressure (LP) steam network (3.5 – 5 bar, 150 – 200 °C), generated in heat exchangers by cooling of hot products, and by pressure reduction of MP steam. LP steam is used for heating, stripping and tracing.

Steam is produced by heating demineralised water, ‘boiler feed water’ (BFW), under pressure in a steam boiler. Steam-raising plants are normally fuelled with refinery fuel gas or liquid. The refinery is equipped with dedicated steam boilers in virtually all process units, containing a HP-, MP- and LP-steam distribution network and with HP-, MP- and LP-condensate collection networks, which are connected with the BFW preparation unit and the condensate storage tank. (Reference is made to Figure 2.15 and to the LCP BREF [7, EC 2006].

Steam used in turbines and heaters after cooling is usually recovered as condensate. BFW is therefore a mixture of fresh demineralised make-up water (quality dependent on steam pressure) and recovered condensate. BFW make-up can be brought in but can also be prepared at the refinery using drinking water, filtered groundwater, seawater distillation, surface water or even treated effluent by using a combination of treatment operations, such as sand filtration or microfiltration (to remove suspended solids) and demineralisation which is accomplished by subsequent cation and anion exchange (see dotted area in Figure 2.15). Reverse osmosis (to remove ions, colloids and large organic molecules) is usually applied in new plants and is followed in some cases by mixed-bed ion exchange and active carbon filtration for final polishing. The condensate tank is generally equipped with an oil detection system and an oil skimming device. To avoid corrosion in the steam and condensate systems, oxygen and carbon dioxide are removed in deaerators, and oxygen scavengers and corrosion inhibitors are added. After conditioning, the BFW is pumped to the boilers. In boilers, the hot flue-gases and BFW flow countercurrently; BFW is preheated in the economiser and further heated in the first and second superheater. In order to keep the concentration of dissolved compounds and suspended solids in the steam drum constant, a condensate blowdown of 1 – 2 % is normally required.

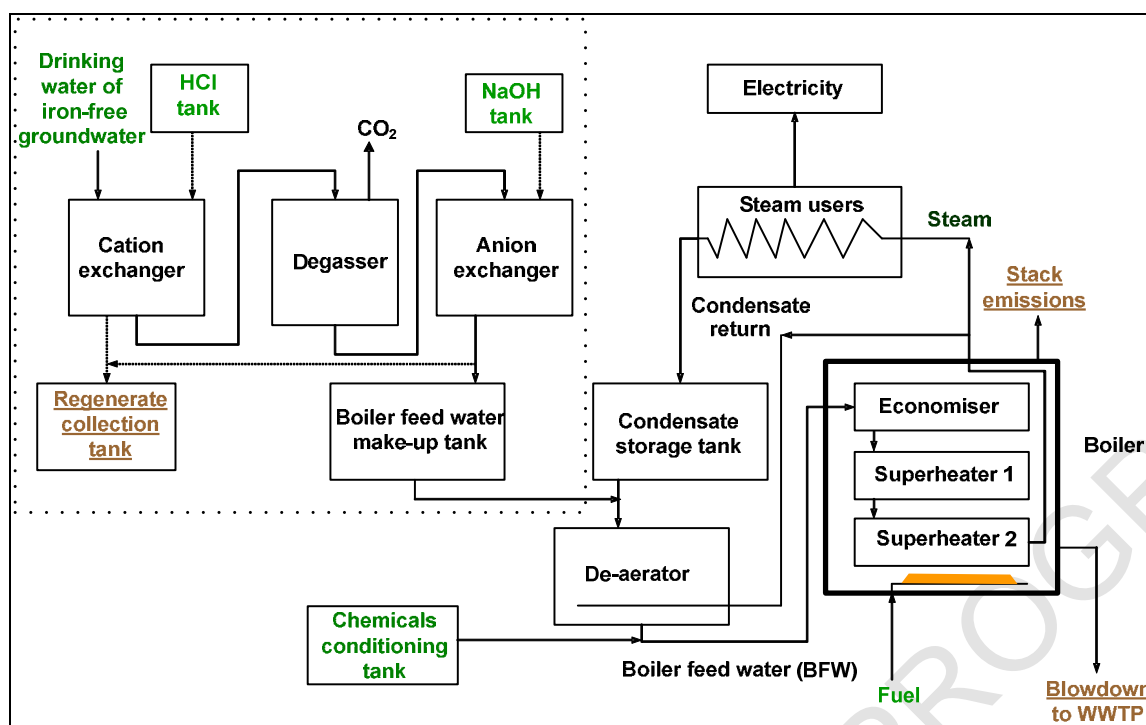


Figure 2.15: Typical layout of a boiler feed water preparation unit and a steam boiler

Electrical power

Power is mainly generated in turbines with high-pressure steam but can also be produced in gas turbines on site and/or bought from the grid (e.g. hydrogenerated power). Electricity is necessary to run pumps, compressors, control systems, valves, etc. Refinery electrical systems are therefore extensive.

Energy management

Good design and management of energy systems are important aspects of minimising the environmental impact of a refinery, bearing in mind the highly integrated and interdependent nature of most processes. The normal aim is to continuously match the variable production and consumption of fuels in processes and utilities at the lowest economic and environmental cost. This issue is also analysed in this document and Section 2.15 examines the integration of all techniques that may be used in a refinery. This section is included here because the energy efficiency of a refinery can be increased not only by improving the energy efficiency of the individual processes (which is addressed in each section) or energy efficiency of the energy production system but also by improving energy management, energy conservation and heat integration/recovery within the refinery as a whole.

Energy management has long been an important issue for refineries. For example, management techniques such as the ISO 14000 system series, the EN 16001 System or EMAS can provide an appropriate framework to develop suitable energy management systems and can increase the energy efficiency of the refinery as a whole. Energy conservation techniques such as reporting and giving incentives for energy savings, carrying out combustion improvements or reviewing the energy integration of the refinery are some of the techniques that may have a great impact on reducing energy consumption and consequently on increasing the energy efficiency of a refinery. Other technical tools to increase efficiency are the heat integration/recovery techniques, of which examples are: the installation of waste heat boilers, the installation of expanders to recuperate power and increasing the insulation of buildings and process units to reduce heat losses. Steam management is another good tool for increasing energy efficiency.

2.11 Etherification

Purpose and principle

A number of chemicals (mostly alcohols and ethers) are added to motor fuels either to improve performance or to meet environmental requirements. Since the 1970s, alcohols (methanol and ethanol) and ethers have been added to gasoline to increase octane levels, reduce carbon monoxide generation and reduce atmospheric ozone due to the lower reactivity of resulting VOC emissions. The octane improvement has been a factor in the phase out of lead as a fuel additive as required by the Auto-Oil I programme. As a result, a number of different ethers are currently added to the gasoline and are better able to meet both the new oxygen requirements and the vapour pressure limits. The most common ethers being used as additives are methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and tertiary amyl methyl ether (TAME). Some refineries manufacture their own supplies of these ethers.

Feed and product streams

Isobutylene and/or isoamylene and methanol (or ethanol) are necessary to produce MTBE (or ETBE) and/or TAME. Isobutylene is obtained from a number of refinery sources including: the light naphtha from the FCC and coking units; the by-product from steam cracking of naphtha processes or light hydrocarbons during the production of ethylene and propylene; catalytic dehydrogenation of isobutane and conversion of tertiary butyl alcohol recovered as a by-product in the manufacture of propylene oxides. These processes are described in the LVOC BREF [85, EC 2003]. Methanol (or ethanol) comes from an external supply.

Process description

Multiple variations of commercial processes are available. Most processes can be modified to react isobutylene or isoamylene with methanol or ethanol to produce the corresponding ether. All use an acidic ion exchange resin catalyst under controlled temperature and pressure conditions. Temperature control of the exothermic reaction is important to maximise conversion and minimise undesirable side effects and catalyst deactivation. The reaction is usually carried out in two stages with a small excess of alcohol to achieve isoolefin conversions of over 99 % and the methanol consumption is essentially stoichiometric. The basic difference between the various processes is in reactor design and the method of temperature control.

MTBE production process

Figure 2.16 shows an example of a simplified process flow diagram of an MTBE plant. The feed stream is cooled prior to entering the top of the primary reactor. The resin catalyst in the primary reactor is a fixed-bed of small beads. The reactants flow down through the catalyst bed and exit the bottom of the reactor. Effluent from the primary reactor contains ether, methanol and unreacted isoolefin and usually some paraffins from the feed. A significant amount of the effluent is cooled and recycled to control the reactor temperature. The net effluent feeds to a fractionator with a section containing catalyst or to a second reactor. Ether is withdrawn as the bottom product, and unreacted alcohol vapour and isoolefin vapour flow up into the catalyst reaction to be converted to ether. The process usually produces an ether stream and a relatively small stream of unreacted hydrocarbons and methanol. The methanol is extracted in a water wash and the resulting methanol-water mixture is distilled to recover the methanol for recycling. The excess methanol and unreacted hydrocarbons are withdrawn as net overhead product, and fed to a methanol recovery tower. In this tower, the excess methanol is extracted by contact with water. The resultant methanol-water mixture is distilled to recover the methanol, which is then recycled to the primary reaction.

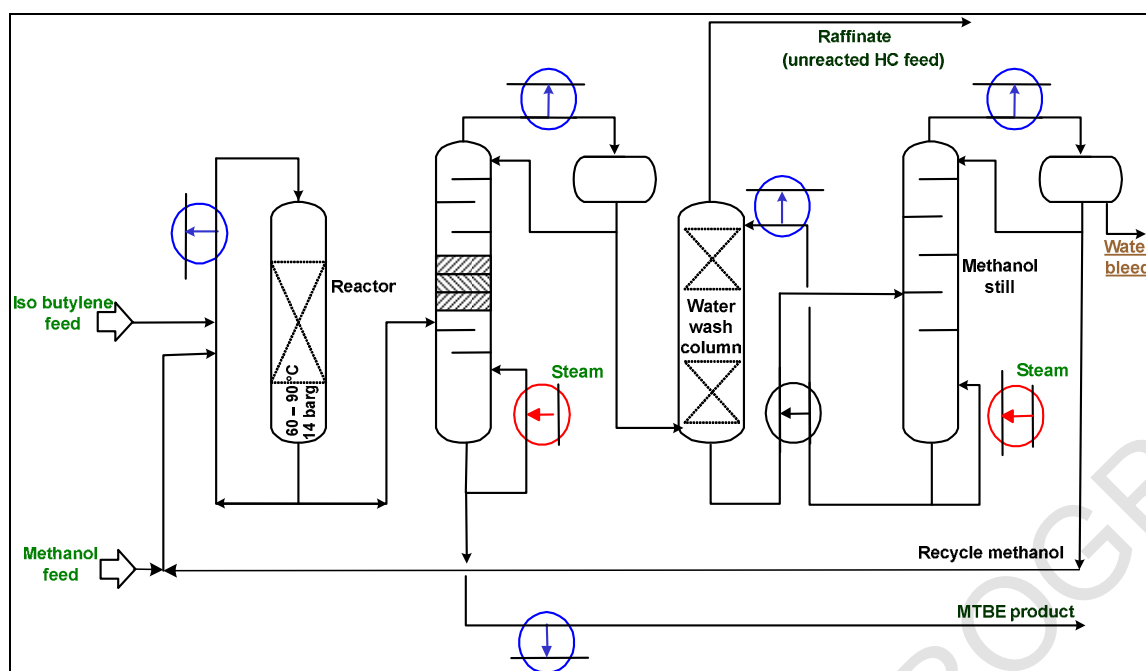


Figure 2.16: Simplified process flow scheme of a MTBE production process

ETBE production process

The MTBE unit is able to produce ETBE with minor modifications and elimination of bottlenecks (increase capacity of the column and cooler, increase bottom temperature on catalytic column, change top and bottom temperature on ethanol/water column).

TAME production process

In this process, C_5 isoamylenes are separated from the light catcracked spirit stream (LCCS) from the FCC unit and catalytically reacted with methanol in the presence of hydrogen to produce TAME. The main stages for TAME production are pentane removal, scavenging, reaction and purification. Figure 2.17 shows a simplified scheme for the TAME production.

C_5 removal is achieved by distillation (depentaniser) of the LCCS feedstock. Overheads are condensed and the hydrocarbons are returned as reflux while gases go to the refinery flue-gas system. A C_5 side-stream is withdrawn from the column as feed to the TAME unit. Column bottom liquids (C_{6+}) are routed to re-blending with the eventual product from the TAME unit.

The C_5 stream is then scavenged to remove catalyst poisons by passing it through an ion exchange resin to remove basic nitrogen compounds, e.g. ammonia, and any metallic contamination. A hydrogen feed is also scavenged to remove any acidic components. The feedstock, containing injected methanol and hydrogen, is fed to the reactor section. Hydrogen is used to convert dienes into monoolefins and prevent gum formation during the reaction. This takes place over a palladium-impregnated ion-exchange resin and the isoamylenes are converted to TAME.

The TAME product stream is purified by fractional distillation, washing and phase separation. Fractionator overheads pass to a reflux drum with the gaseous phase of low-boiling hydrocarbons (C_1, C_2, C_4 , etc.) together with unreacted hydrogen before being vented to refinery fuel gas or flare. The bottom product of TAME gasoline with some methanol is cooled and mixed with recycled water from the methanol recovery plant, then routed to a settler for phase separation. The TAME gasoline fraction from this is blended with the depentaniser bottoms C_{6+} stream and passed to storage. The methanol/water fraction is recycled to the methanol recovery plant feed drum.

Methanol is recovered by distillation in a common still, with the overhead's methanol being condensed and passed to buffer storage for recycling to the TAME plant or other uses. The bottoms are essentially water with some contaminants and are mainly recycled with a purge to effluent treatment to avoid formic acid buildup.

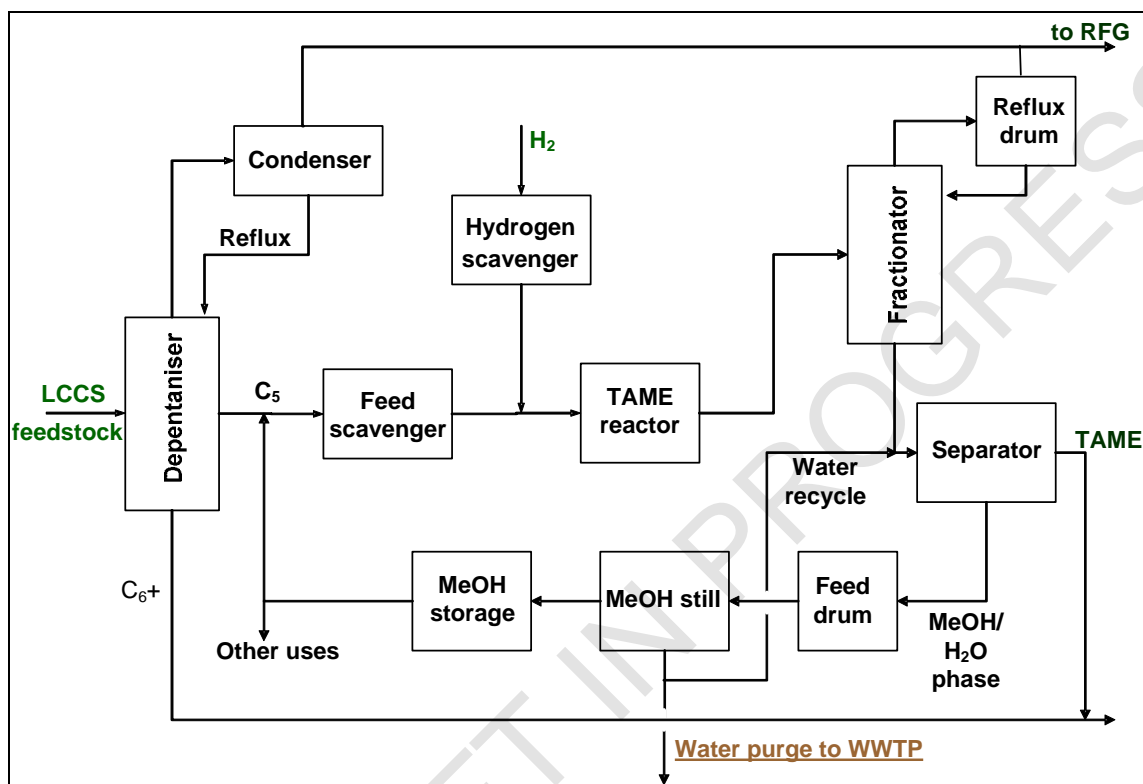


Figure 2.17: Simplified process flow scheme of TAME production

2.12 Gas separation processes

Purpose and principle

Low-boiling hydrocarbons are usually treated in a common separation plant operating at elevated pressures. The purpose of a gas plant is to recover and to separate $C_1 - C_5$ and higher compounds from various refinery off-gases by distillation. In mineral oil refineries, one (or more) gas plant is present to handle different gas streams from different processes. (e.g. cat reformers, catalytic crackers, distillation units). These plants are the core for installations refining natural gas (Section 2.17), where the different components are separated. Depending on application of the products, some refineries remove mercury from LPG, tops and naphtha.

Feed and product streams

The feed of the gas plant consists of gas and liquid streams from crude distillation, cat crackers, catalytic reformers, alkylation, desulphurisation and similar units. Pretreatment of some feedstocks may be necessary, typically by hydro-desulphurisation (Section 2.13) or amine treating (H_2S removal, see Section 4.23.5.1). The compounds recovered depend on the composition of the feed and the market requirements. The gas streams are normally separated into C_1 and C_2 fractions for sale or use as refinery fuel gas, LPG (propane and butane) and a light gasoline (C_5 and higher) stream. Olefins, isoparaffins and n-paraffins can be also separated in the process.

Process description

As a minimum, the gas plant consists of two columns where the first one, an absorber/stripper column (deethaniser) strips all light C_2 -minus components to maximise recovery of C_3 -plus components from the feed streams. Figure 2.18 shows a simplified process flow diagram of a gas plant.

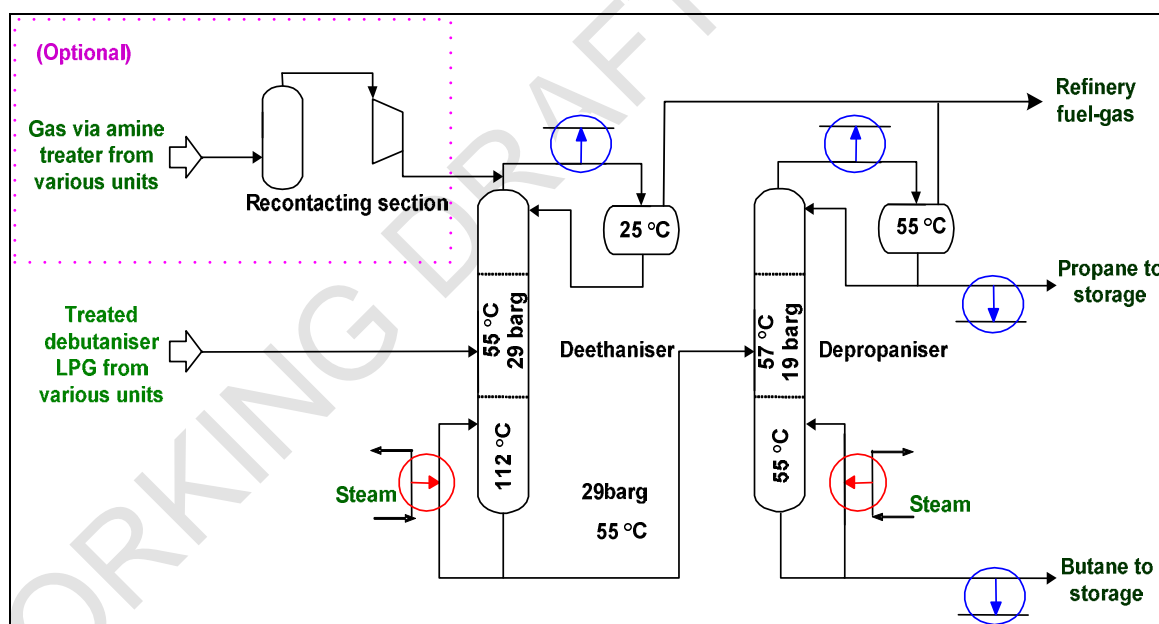


Figure 2.18: Simplified process flow scheme for a part of a gas plant

The feed stream to the gas plant is cooled and chilled, the residual vapour phase from this being routed to a refrigerated absorber, meeting chilled recycled light gasoline absorbent. The absorber overhead is the C_1, C_2 fraction. The bottoms are combined with the liquid stream from chilling, and pass to the first fractionator or de-ethaniser. The first fractionator overheads (essentially C_2 -ethane) are combined with the absorber overheads while the bottoms pass to the second fractionator to produce a C_3/C_4 overheads stream and debutanised gasoline bottoms. A recontacting section, where vapours from various units are compressed and recontacted with the

de-ethaniser overhead can be installed to maximise the C₃/C₄ recovery. The bottoms of the de-ethaniser column, mainly C₃/C₄ compounds, are fed to the depropaniser column. This overheads stream is routed to a third fractionator to split the C₃ and C₄ streams as overheads (propane) and bottoms (butane), respectively. Products pass to pressurised storage via any final sweetening by selective molecular sieve adsorption. Subsequent loading of transport containers is carried out by means such as closed loop systems or by venting and release to the refinery fuel gas system.

The gasoline bottom stream passes to a fourth fractionator to produce a depentanised fraction for use as chilled, recycled gasoline on the absorber. The net output is blended to form the gasoline product. A drying step before sending to storage may be necessary (not shown). Also, a vessel containing a bed of caustic pellets (not shown) can be installed in the butane system as an additional guard, although water and H₂S should have been removed in the top of the de-ethaniser and de-propaniser column. If no (or insufficient) upstream treatment has taken place, this can also be done in the unit itself, e.g. with an amine H₂S absorber followed by a mercaptan oxidation/extraction of the de-ethaniser bottoms with amine H₂S absorption of the de-ethaniser net overhead gas.

If thermal and/or catalytic cracking units are present, recovery of olefinic components may also be worthwhile. It is also possible to separate isobutane from n-butane. The isobutane can be used as feed to an alkylation unit, while the n-butane (or part of it) can be used as a blending component in the gasoline pool or isomerisation.

2.13 Hydrogen-consuming processes

Two types of processes are included in this section: hydrocracking and hydrotreatments. Both processes take place over a metal catalyst in a hydrogen atmosphere. Many of these processes are found in a refinery, normally named according to the type of feed to treat and the reaction conditions. The common denominator to these processes is that all rely on hydrogenation processes and consequently consume hydrogen. Isomerisation processes of alkanes or olefins also consume some hydrogen, but these processes are included in a separate section (Section 2.16).

Purpose and principle

Hydrotreating and hydroprocessing

Hydrotreating and hydroprocessing are similar processes used to remove impurities such as sulphur, nitrogen, oxygen, halides and trace metal impurities that may deactivate process catalysts. Hydrotreating also upgrades the quality of fractions by converting olefins and diolefins to paraffins for the purpose of reducing gum formation in fuels. Hydroprocessing, which typically uses residuals from the crude distillation units, also cracks these heavier molecules to lighter, more saleable products. Both processes are usually placed upstream of these processes in which sulphur and nitrogen could have adverse effects on the catalyst, such as catalytic reforming and hydrocracking units. The processes use catalysts in the presence of substantial amounts of hydrogen under high pressure and temperature to react the feedstocks and impurities with hydrogen.

Hydrotreating

Hydrotreating can be divided into a number of reaction categories: hydrodesulphurisation, hydrodenitrification, saturation of olefins and saturation of aromatics. A hydrotreater unit specifically employed to remove sulphur is usually called a hydrodesulphurisation unit (HDS). In this section the standard hydrotreating of naphtha, mid-distillate and residue-type feed streams is discussed and includes the items described below.

- A naphtha hydrotreater unit normally serves three purposes: desulphurisation, denitrogenation and stabilising the naphtha feed stream to the downstream isomerisation and reformer units. Stabilising the naphtha streams usually requires the conversion of unsaturated hydrocarbons produced in thermal and catalytic cracking processes into paraffins. The selective hydrogenation of light dienes that are contaminants of many light olefin streams may also be partially hydrogenated. Hydrogenation of aromatics is a variant of either naphtha or of processed distillate. Gasoline desulphurisation is dominated by sulphur removal from FCC naphtha, which accounts for about 35 % of gasoline pool but over 90 % of the sulphur in gasoline. Deep reduction of the gasoline sulphur (to below 10 ppm) must be made without decreasing the octane number or losing gasoline yield. The problem is complicated by the high olefins contents of FCC naphtha, which contributes to octane number enhancement but can be saturated under HDS conditions.
- A mid-distillate hydrotreater unit normally has two purposes: desulphurisation and hydrogenation of the mid-distillate stream. Stabilising mid-distillate streams is required when large quantities of cracked components are blended to the mid-distillate pool, and usually requires partial saturation of aromatics and olefins and a reduction of the N-content. The full saturation of aromatics may be required to prepare naphtha, kerosene, and diesel feedstocks. Among the applications of this process are smoke-point improvements in aircraft turbine fuels, reduction of the aromatic content of solvent stocks to meet requirements for air pollution control, production of cyclohexane from benzene (LVOC) and cetane number improvement in diesel fuels.
- Diesel oil deep desulphurisation (Hydrofining) is normally done to heating and diesel oils to meet product sulphur specifications. Large decreases of diesel sulphur require a high

desulphurisation of 4,6-dimethyldibenzothiophene, as this is the least reactive sulphur compounds that have substitutions on both 4- and 6-positions. The deep HDS problem of diesel streams is exacerbated by the inhibiting effects of co-existing poly-aromatics and nitrogen compounds in the feed, as well as H₂S in the product.

- Residue hydrotreating is mainly applied to improve the residue feed quality (normally atmospheric residue) to a residue catalytic cracker (RCC) unit. RCCs are restricted to process residue streams by their metal content and Concarbon number.

Hydroprocessing

Hydroprocessing may also be designed to remove low-levels of metals from the feed. The metals to be removed include nickel and vanadium, which are native to the crude oil, as well as silicon and lead-containing metals that may be added elsewhere in the refinery.

Hydrocracking

Hydrocracking is one of the most versatile of all refining processes, capable of converting any fraction, from atmospheric gas oils to residual (deasphalted) oil into products with a lower molecular weight than the feed. The hydrocracking reactions occur under high hydrogen partial pressure in the presence of a catalyst with a two-fold function: hydrogenation and cracking. Hydrocracking may also be used for the cracking of superior fuels and the production of lubricants (dewaxing is discussed in Section 2.3). The type of catalyst maximises the production of naphtha, mid-distillates or lube production. The presence of hydrogen suppresses the formation of heavy residual material and increases the yield of gasoline by reacting with the cracked products, giving net products, which are a mixture of pure paraffins, naphthenes and aromatics. Hydrocracking produces mid-distillates with outstanding burning and cold flow properties as follow:

- kerosene with low freezing points and high smoke points;
- diesel fuels with low pour points and high cetane numbers;
- heavy naphthas with a high content of single-ring hydrocarbons;
- light naphthas with a high isoparaffin content;
- heavy products that are hydrogen-rich for feed FCC units, ethylene plants (LVOC), or lube oil dewaxing and finishing facilities (Section 2.3).

When hydrocracking is applied to heavy residues, a pretreatment is needed to remove high metal contents before the hydrocracking reaction is produced. Residue hydroconversion is a type of hydrocracking applied to convert low-value vacuum residue and other heavy residue streams into lighter low-boiling hydrocarbons by reacting them with hydrogen.

Feed and product streams

Hydrotreating and hydroprocessing

These processes are applied to a wide range of feedstocks, from LPG up to heavy residue and mixtures thereof. Table 2.3 summarises the feeds, products and process objectives for each type of hydrotreatment.

Table 2.3: Feedstocks, desired products and process objectives of hydrotreatments

Feedstocks	Desired products	For the removal of:
LPG	Clean LPG	S, olefins
Naphthas	Catalytic reformer feed (S: 0.05 – 0.5 % w/w)	S (<0.5 ppm), N, olefins
LPG, naphthas	Low diene contents	Dienes (25 – 1 ppm) in product
Cat. cracked naphtha	Gasoline blending component	S
Atmospheric gas oils	Ethylene feedstock (LVOC)	S, aromatics
	Jet	S, aromatics
	Diesel	S, aromatic and n-paraffins
Vacuum gas oils	Ethylene feedstock	Aromatics
	Kerosene/jet (S: 0.05 to 1.8 % w/w)	S, aromatics
	Diesel (S: 0.05 to 1.8 % w/w)	S, aromatics
	FCC feed	S, N, metals
	Low-sulphur fuel oil	S
	Lube oil base stock	Aromatics
Atmospheric residue	FCC feedstock	S, N, CCR ^(*) , and metals
	Low-sulphur fuel oil	S
	Coker feedstock	S, CCR, and metals
	RCC feedstock	CCR, and metals
(*) CCR=Conradson carbon residue.		

Hydrocracking

Hydrogen in substantial quantities is consumed in these processes, making the hydrogen manufacturing unit mandatory (Section 2.14) in refineries that contain hydrocracking. In addition to the treated products, these processes produce a stream of light fuel gases containing hydrogen sulphide, ammonia and water.

As is reflected in Table 2.4, the main feed stream to a hydrocracker is the heavy vacuum distillate stream from the high vacuum distillation unit. These feedstocks are fractions which are very difficult to crack and cannot be cracked effectively in catalytic cracking units. Other process streams such as heavy cycle oil from the catalytic cracker unit, heavy gas oils from the coker or visbreaker unit, extracts from lube oil units, mid-distillates, residual fuel oils and reduced crudes may be blended to the main heavy vacuum distillate stream. The main products are LPG, gasoline, jet fuel and diesel fuel, all practically sulphur-free. The production of methane and ethane is very low, normally less than 1 %.

Table 2.4: Feedstocks and desired products of hydrocracking processes

Feedstocks	Desired products
Naphthas	LPG
Atmospheric gas oils	Naphtha
Atmospheric residue	Diesel
Vacuum gas oils	LPG
	Naphtha
	Ethylene feedstock (LVOC)
	Kerosene/jet
	Diesel
	Lube oil base stock
Vacuum residues	LPG
	Naphtha
	Kerosene
	Gas oil
	Fuel oil
Tars and derived bitumens (metal content <500 ppm)	Diesel

Process description

Types of reactor technologies applied in hydroconversion and hydrotreatment

There are several residue hydrotreating and hydroconversion technologies in use today. They can be classified into four categories: fixed-bed; swing reactor; moving-bed and ebullated-bed. The selection of the type of process is predominantly determined by the metal content in the feed. Fixed-bed residue hydroconversion is applied for 'low' metal-containing feeds (100 ppm) and the required conversion is relatively low, moving bed or ebullated bed technology is used for 'high' metal-containing feeds. To overcome metal poisoning of the catalyst in fixed-beds and to maintain the concept, some licensors propose the swing reactor concept: one reactor is in operation whilst the other one is off-line for catalyst replacement. The concept and layout of the fixed-bed hydroconversion technology is identical to long residue hydrotreating. Moving bed technology or ebullated bed technology is selected when the metal content in the residue feed is typically above 100 ppm but below 500 ppm. Normally this concentration of metals in the feed is found in vacuum residue streams from heavier crudes, bitumen streams from tar sands and heavy atmospheric residue streams. Both technologies allow withdrawal and replacement of the catalyst during operation, the main difference is the reactor configuration.

Hydrotreating and hydroprocessing

Naphtha hydrotreater. Naphtha feed is mixed with a hydrogen-rich gas stream, heated and vaporised in the reactor feed/effluent exchanger and the furnace, and fed into the hydrotreater reactor with a fixed-bed cobalt/nickel/molybdenum catalyst. The reactor conditions can vary but are typically 30 to 40 bar and 320 to 380 °C. The reactor effluent is cooled in the feed/effluent exchanger and reactor cooler and flashed into the high-pressure separator. The flashed vapours, consisting mainly of unreacted hydrogen, are compressed and recycled to the reactor. The fractionation part is very similar to the one explained in the hydroconversion process. (See also hydrofining below in this section)

Catalytic distillation. (CD HDS)

This process aims to selectively desulphurise (to ultra low sulphur) FCC gasoline with minimum octane loss. Hydrogen and full range FCC gasoline are fed to the reactive distillation column where light naphtha is distilled from the top. Bottoms containing the reacted mercaptans are fed to the CD HDS, where heavy and mid naphtha are catalytically desulphurised. Catalytic distillation eliminates catalyst fouling because fractionation removes heavy coke precursors from the catalyst zone. The lifetime of CD HDS is similar to FCC (4-5 year cycles). Milder temperature and pressure diminishes octane losses.

Distillate hydrodesulphurisation

Figure 2.19 provides a simplified flow diagram of a typical distillate HDS unit. The distillate feed may range from kerosene up to long vacuum gas oil or mixtures thereof. The reactor system is in principle the same as for the naphtha hydrotreater. The main difference is that the feed does not fully vaporise and the reactor operating conditions are more severe, 40 – 70 barg and 330 – 390 °C. Furthermore, it is normal practice that wash water is injected into the reactor effluent stream when nitrogen-rich feedstocks are desulphurised.

Solid deposits like ammonium sulphides $(\text{NH}_4)_2\text{S}$ and chlorides NH_4Cl are formed in the cooler parts of the unit and must be removed by water wash. The liquid from the low-pressure separator is fed to a stripper column to stabilise and strip off the light hydrocarbons and H_2S . The stripping steam and light hydrocarbons are taken overhead, condensed and separated into a sour water phase and a hydrocarbon phase. The water phase is sent to the sour water stripper, and the light hydrocarbon phase is normally recycled to the crude unit or naphtha hydrotreater distillation section for further fractionation. Any water dissolved and dispersed in the distillate should be removed to avoid the formation of haze and ice when stored.

The wet distillate is therefore either fed to a vacuum column, where the total water content is lowered to 50 ppm, or sometimes a combination of coalescer and molecular sieve beds is used, where water is selectively adsorbed on the bed.

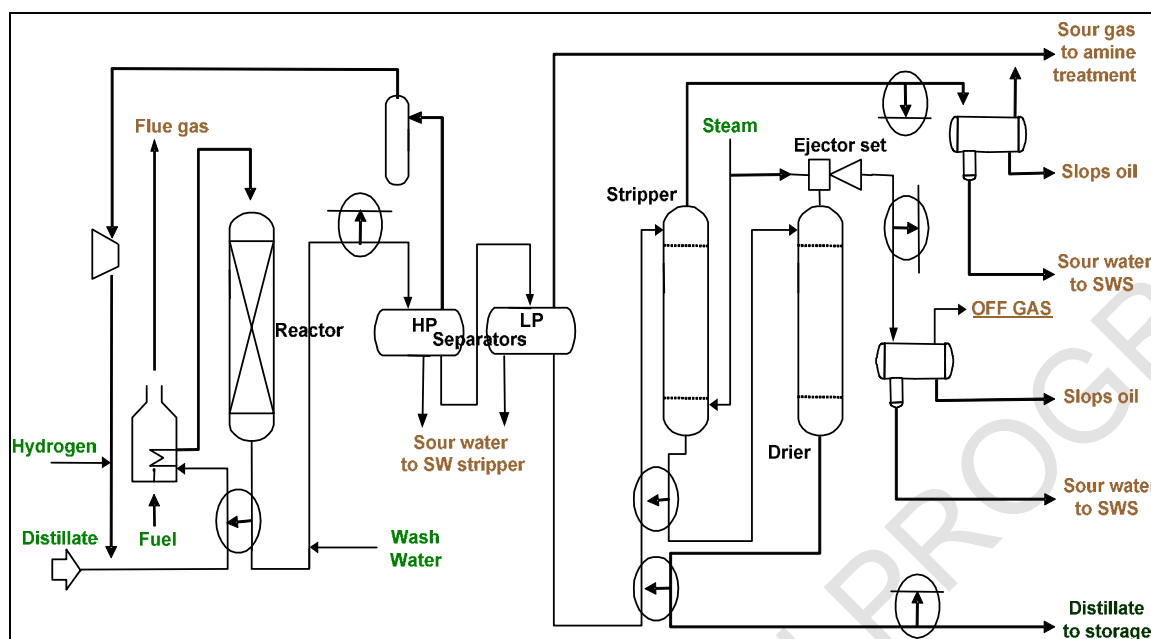


Figure 2.19: Simplified process flow scheme of a distillate hydrodesulphurisation unit

Diesel oil deep desulphurisation (hydrofining)

Because this technique operates at low pressures, efficient hydrogen utilisation can be achieved within an overall refinery context. Very low sulphur contents can be achieved (8 ppm) in the raffinate. The unit usually operates at 45 bar and consumes very small amounts of hydrogen. Equivalent deep desulphurisation techniques for gasoline with a comparatively low hydrogen consumption are currently under development.

Research on this process has gained considerable importance in recent years (further information can be found in Sections 3.13, 4.13 and Chapter 6 of this document). Development is taking place both at the research and industrial levels to deliver a wider process option. Approaches can be grouped depending on whether the technique is applied before, after or during FCC; whether it uses a large, a medium or no H_2 to remove sulphur species; whether it targets solely reduction of sulphur content or combines other improvement processes; and whether it is a new process or an optimisation (revamping) of HDS design or conditions.

Lower sulphur content can be achieved by revamping existing HDS units by means of replacing the catalyst type, increasing catalyst volume, enhancing operating severity (temperature and H_2 pressure), removing H_2S from recycle gas, and using high efficiency distribution trays. Commercially available catalyst are numerous and evolving, such as new catalyst preparation method that increases active Co-Mo-S phase.

The following tables show examples on revamping process data:

Table 2.5: Revamping process examples from 500 ppm to 30 ppm sulphur

	Current	UOP	IFP	Akzo	Criterion	Topsoe
LHSV(*)	2	1.5	1.45	1.08	0.5	1
Amine scrubber installed	no	yes	yes	yes	yes	yes
Mol % purity of H_2	75	90	91.3	75	75	75
Ratio of circulating H_2	1	1.9	3.649	1	1.6	1.16
Catalyst packing method	Sock	Dense	Sock	Sock	Sock	Sock
(*) Liquid Hourly Space Velocity						
Source: [79, Fayruzov et al. 2009]						

Table 2.6: Revamping process examples from 30 ppm to 10 ppm sulphur

	UOP	IFP	Akzo	Criterion	Topsoe
LHSV(*)	1.5 to 0.9	1.45 to 1	1.08 to 0.45	0.5 to 0.4	1 to 0.7
Ratio of circulating H ₂	1.9 to 2	3.649 to ?	1	1.6 to 1.85	1.16
Partial pressure (kg/cm ²)	46	58	46	46	46
(*) Liquid Hourly Space Velocity Source [79, Fayruzov et al. 2009]					

New deep HDS processes focus on process and reactor design configuration as well as addressing other steps. Some examples are octane recovery, cetane increases, dearomatisation, eliminating Nitrogen compounds. These new techniques are based on other principles like reactive distillation, adsorption, reactive adsorption at high temperature or polar adsorption in countercurrent approach. Some of them consume significantly low H₂ such as the reactive adsorption principle.

There has been intensive development in non-H₂ desulphurisation techniques. Most of them are mentioned in Chapter 6 of this document. Some oxidative desulphuration processes (like SulphCo) have reached commercialisation with substantially lower operating costs.

Table 2.7 illustrates some process of deep desulphurisation of gas oil and naphtha:

Table 2.7: Examples of process for deep gas oil and naphtha desulphurisation

Process	Key Features	Industrial application	H ₂ -consumption	Octane loss	Name of process	Licensors
Naphtha hydro-treating (NHT)	Conventional	yes	high	high	various	a number of firms
NHT+ octane increase	Zeolite + isomerisation	yes	high	low	Octgain, Isal	ExxonMobil, UOP
Selective NHT	RT-225	yes	medium	low	SCANfining	ExxonMobil
	Dual catalyst	yes	medium	low	Prime-G+	IFP
	Catalytic distillation	yes	medium	low	CDHydro/CDHDS	CDTech
Selective NHT + octane increase	Combination	yes	medium	low	SCANfining II	ExxonMobil
Adsorption	Zn adsorbent	yes	low	low	S Zorb	Philips
	Alumina adsorbent	pilot	low	low	Irvad	Alcoa
Extractive distillation	Selective solvent sys.	yes	none	low	GT-DeSulf	GTC
Oxidation	Peroxyacid	pilot	none	low	CED	Petrostar
	Ultrasound	pilot	none	low	SulphCo	Bechtel
Alkylation	Solid acid	pilot	low	low	OATS	BP
Bio processing	Bio catalysis	no	none	low		Enchira
Source: [80, Stanislaus et al. 2010]						

Residue hydrotreating

The principle process scheme for residue hydrotreating is the same as normal distillate. The main difference is the reactor system, which normally consist of two or three reactors in series. Removal of the metals from the residue feed normally occurs in the first reactor(s) and uses a low-activity coarser Co/Mo catalyst. Further hydrotreating and hydrogenation occur in the tail reactor(s), resulting in a higher hydrogen-to-carbon ratio and a lower Concarbon number of the

residue. Since the catalysts operate in a H₂S and NH₃-rich environment the nickel/molybdenum or nickel/tungsten catalysts are usually applied in the tail reactors. Table 2.8 shows the typical hydrotreatment operating conditions for the different feedstocks:

Table 2.8: Typical hydrotreating operating conditions

Operating conditions	Naphtha	Mid distillate	Light gas oil	Heavy gas oil	Residuum
Liquid hourly space velocity	1.0 – 5.0	1.0 – 4.0	1.0 – 5.0	0.75 – 3.0	0.15 – 1
H ₂ /HC ratio, Nm ³ /m ³	50	135	170	337	300
H ₂ partial pressure, kg/cm ²	14	28	35	55	55
Reactor temperature, °C	260 – 380	300 – 400	300 – 400	350 – 425	350 – 425
Source: [175, Meyers 1997]					

Hydrogenation of light dienes

This process is a highly-selective catalytic process that can hydrogenate acetylenes and dienes to the corresponding monoolefin without affecting the valuable olefin content of the feedstock. In addition, this process can be designed to provide hydroisomerisation of some of the olefins (e.g. conversion of 1-butene to 2-butene). Hydrogenation takes place in a liquid-phase fixed-bed reactor. Unless the hydrogen purity is low, no separation step is required for the removal of the light ends from the product. Thus, reactor effluent can be charged directly to downstream units.

Saturation of aromatics

The use of highly-active noble-metal catalysts permits the reactions to take place under mild conditions. Because of the mild conditions and the very selective catalyst, the yields are high, and hydrogen consumption is largely limited to just the desired reactions. The process is carried out at moderate temperatures (205 – 370 °C) and pressures (3 500 to 8 275 kPa) over a fixed catalyst bed in which aromatics are saturated and in which hydrogenation of olefins, naphthenic ring openings and the removal of sulphur and nitrogen occur.

Hydrocracking

Hydrocracking normally uses a fixed-bed catalytic reactor with cracking occurring under substantial pressure (35 to 200 kg/cm²) in the presence of hydrogen at temperatures between 280 and 475 °C. This process also breaks the heavy, sulphur-, nitrogen- and oxygen-bearing hydrocarbons and releases these impurities to where they could potentially foul the catalyst. For this reason, the feedstock is often first hydrotreated and dewatered to remove impurities (H₂S, NH₃, H₂O) before being sent to the hydrocracker. If the hydrocracking feedstocks are first hydrotreated to remove impurities, sour water and sour gas streams will contain relatively low-levels of hydrogen sulphide and ammonia in the fractionator.

Depending on the products desired and the size of the unit, hydrocracking is conducted in either single-stage or multi-stage reactor processes. Hydrocrackers can be classified into three categories: single-stage once-through; single-stage recycle and two-stage recycle. These categories are described below:

Only fresh feed is processed in the single-stage once-through hydrocracker. The conversions achieved are around 80 – 90 %, depending on the catalyst and reactor conditions. The heavy residue is either sent to the fuel oil pool or further processed in a catalytic cracker or coking unit.

In the single-stage recycle configuration, the unconverted oil is recycled to the reactor for further conversion, increasing the overall conversion to around 97 – 98 %. A small bleed stream of about 2 – 3 % on fresh feed is required to avoid a buildup of polyaromatics (PAH) in the recycle loop. Figure 2.20 shows a simplified process flow diagram of the single-stage hydrocracker with recycle configuration. In the first reactor beds, conversion of N and S

compounds, saturation of olefins and partial saturation of PAH takes place. In the subsequent beds, the actual cracking will take place. The vapour from the low-pressure (LP) separator is used as refinery fuel after amine treating. Many different fractionation section configurations are found. A common fractionation section is illustrated in Figure 2.20. The product stream is fed to the debutaniser column to separate the LPG. The LPG stream is washed in an amine wash and then fractionated into a propane and a butane stream. The bottom stream from the debutaniser column is fed to the first fractionator. In this column, a light naphtha stream is taken as overhead product, heavy naphtha and kerosene are taken as side-streams and the bottom stream is fed to a second fractionator. In the second fractionator, operating at mild vacuum, the diesel product is taken as the overhead product and the bottom stream and the unconverted oil is recycled to the reactor section.

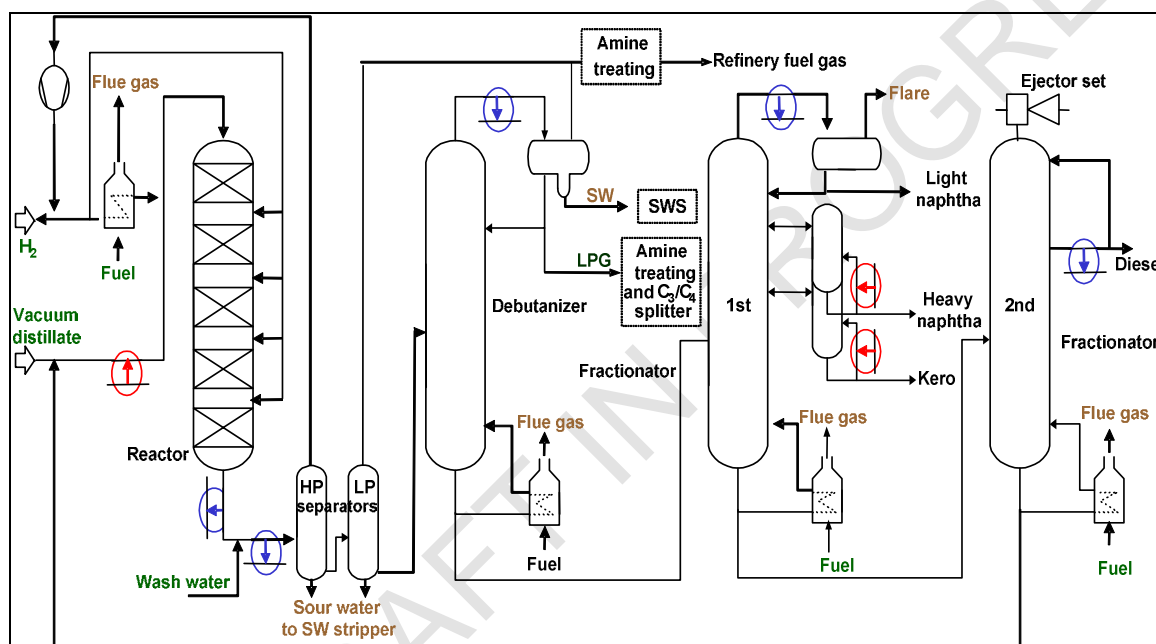


Figure 2.20: Simplified process flow scheme of a hydrocracker (single stage with recycling)

In the two-stage recycle configuration, the first hydrocracker reactor operates in a once-through mode with a typical conversion of around 50%. The unconverted oil from the first hydrocracker reactor is fed to a second hydrocracker reactor for further conversion. The unconverted oil from the second stage hydrocracker is recycled to achieve an overall conversion of around 97 – 98%. A small bleed stream of about 2 – 3% on fresh feed is also required here. This concept is normally applied when a very heavy high refractory feed stock such as deasphalted oil is processed. Two-stage configurations are usually more cost effective for large capacity units, and more flexible and efficient for processing difficult feedstocks. By adjusting specific catalysts for each stage, most ammonia and hydrogen sulphide can be generated at the first stage, allowing to settle down a cleaner second stage reaction environment with improved middle distillate production yield and product quality. Table 2.9 shows the typical operating conditions of hydrocrackers

Table 2.9: Typical hydrocracker operating conditions

Parameters	High-pressure hydrocracking	Moderate-pressure hydrocracking
Conversion, % w/w	70 – 100	20 – 70
Pressure, barg	100 – 200	70 – 100
Liquid hourly space velocity	0.5 – 2.0	0.5 – 2.0
Average reactor temperature °C	340 – 425	340 – 425
Hydrogen circulation, Nm ³ /m ³	650 – 1700	350 – 1200

Source: [175, Meyers 1997.]

Hydroconversion

In principle, three reactions take place: hydrodemetallisation, hydrotreating/hydrogenation and hydrocracking. Removal of the metals from the residue feed predominantly occurs in the first reactor(s) and uses a low activity cobalt and molybdene (Co/Mo) catalyst. Hydrotreating, hydrogenation and hydrocracking occur in the following reactor(s) where the quality is mainly improved by increasing the hydrogen/carbon ratio. Conversion levels to products in a hydroconversion process are typically 50 – 70 %, but depend significantly on the type of hydroconversion process and the quality of the feedstock.

Figure 2.21 shows a simplified process flow diagram of a moving bed process. The process comprises five reactors in series, catalyst handling facilities and a work-up section. The reactors operate at high pressure and relatively high temperatures.

The first three reactors are bunker hydrodemetallisation (HDM) reactors. The nickel-vanadium (Ni+V) conversion typically exceeds 60 % for the first 60 days of operation and then gradually trends towards the expected equilibrium conversion level, 50 to 70 %. This way, high-metal feeds can be treated.

The last two reactors are fixed-bed desulphurisation and conversion reactors. The moving bed technology employs a bunker flow/moving bed technology to replenish the HDM catalyst continuously. Catalysts are transported through a slurry transport system in which the rate of catalyst replenishment is controlled in accordance with the rate of metal deposition. The catalyst in the HDM reactors flows concurrently downward with the process fluids. Screens separate the catalysts from the process fluids before leaving the reactor. Sluice systems are present at the top and the bottom of the reactors to enable catalyst addition and withdrawal.

The following conversion section consists of two fixed-bed reactors in series, containing catalysts, that are highly active for sulphur removal and conversion. The ebullated-bed reactor operates as a fluidised-bed three-phase system with back mixing of the unconverted liquid and the catalyst.

The concept of the fractionation section is also very licensor-dependent as it depends on the configuration of the separator system and the resulting temperatures. Typically, it consists of a main fractionator, a vacuum distillation column, and some form of a gas plant to fractionate and stabilise the lighter fractions. Products from the fractionation section are normally refinery fuel gas, LPG, naphtha, kerosene, light gas oil, vacuum distillate and a low-sulphur/metal vacuum residue (bottoms) stream. The refinery fuel gas and LPG streams are amine washed to remove H₂S. The naphtha product is normally fed to a naphtha hydrotreater for further processing, identical to the straight run naphtha product. The kerosene and light gas oil products are normally fed to a hydrotreater for further purification. The vacuum distillate is converted further in a hydrocracker or FCC unit. The bottom stream is normally blended into the heavy fuel oil pool or used as delayed coker feedstock.

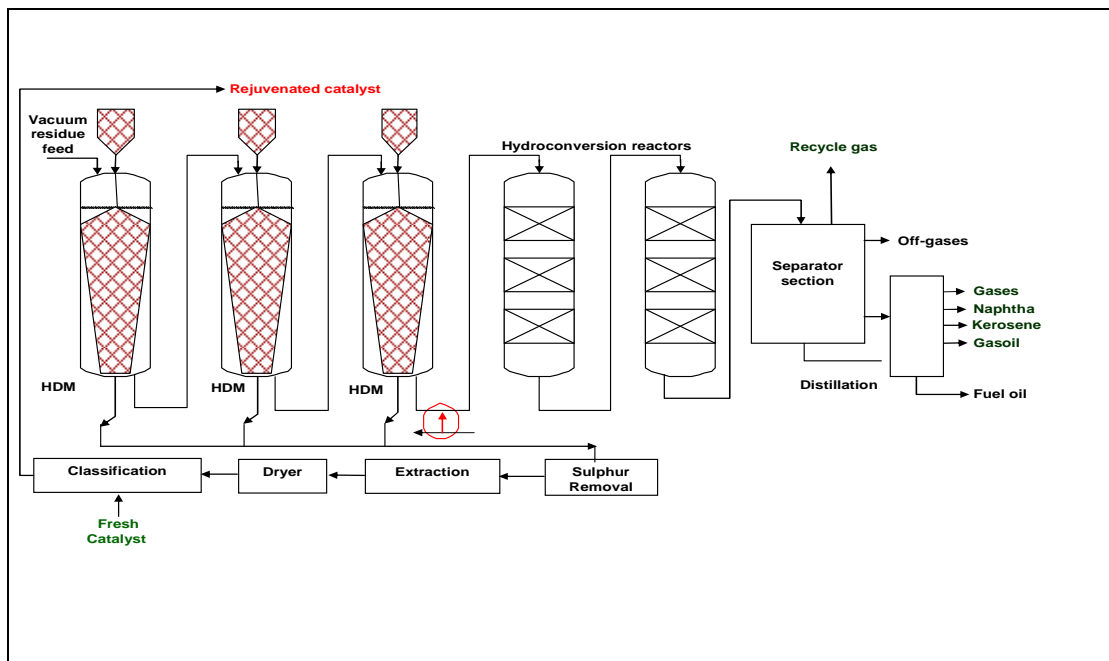


Figure 2.21: Simplified process flow scheme of a hydroconversion process (moving bed)

2.14 Hydrogen production

Purpose and principle

There is an increasing demand for hydrogen in European refining, due to an increased use of hydrocracking and hydrotreating. More hydrodesulphurisation is needed to achieve legislative requirements for lower sulphur content in fuels.

In such a context, the purpose of a hydrogen plant is to produce hydrogen for use in hydrocracking and other hydrogen-consuming refinery process units (Sections 2.13 and 2.16). Hydrogen can be provided by one of the following processes:

- reforming operations (Section 2.6) for hydrotreating (refineries with the simplest configuration may produce sufficient quantities);
- steam reforming of light ends or natural gas;
- partial oxidation (gasification) of heavy oil fractions (IGCC in Section 2.10) to produce syngas where hydrogen can be separated.

Complex plants with extensive hydrotreating and/or hydrocracking operations typically require more hydrogen than is produced by their catalytic reforming units. The reliable operation of a hydrogen plant is critical for the hydrogen-consuming processes. Reactions that may occur in these processes are listed in Table 2.10.

Feed and product streams

The feed of the hydrogen plant consists of hydrocarbons in the range from natural gas to heavy residue oils and coke. The conventional steam reforming process produces a hydrogen product of a maximum of 97–98 % v/v purity and higher if a purification process is applied (99.9–99.999 % v/v). The partial oxidation process requires oxygen if oxygen-blown gasification is used instead of air-blown gasification.

Table 2.10: Main chemical reactions occurring in hydrogen production processes

Steam reforming process	
$C_nH_m + n H_2O \rightleftharpoons n CO + (n+m/2) H_2$	Generic for steam reforming (endothermic)
$CH_4 + H_2O \rightleftharpoons CO + 3 H_2$	Steam methane reforming ($\Delta H = -206 \text{ kJ/mol}$ at 15°C)
$CO + H_2O \rightleftharpoons CO_2 + H_2$	Shift (exothermic) ($\Delta H = + 41.2 \text{ kJ/mol}$ at 15°C)
$CO + 3 H_2 \rightleftharpoons CH_4 + H_2O$ $CO_2 + 4 H_2 \rightleftharpoons CH_4 + 2 H_2O$	Methanation (exothermic)
Partial oxidation	
$C_nH_m + n/2 O_2 \rightleftharpoons n CO + m/2 H_2$	Generic for partial oxidation (endothermic)
$CO + H_2O \rightleftharpoons CO_2 + H_2$	Shift (exothermic) ($\Delta H = + 41.2 \text{ kJ/mol}$ at 15°C)
Gasification	
$C + H_2O \rightleftharpoons CO + H_2$	Coke gasification ($\Delta H = -132 \text{ kJ/mol}$ at 15°C)
$CO + H_2O \rightleftharpoons CO_2 + H_2$	Shift (exothermic) ($\Delta H = + 41.2 \text{ kJ/mol}$ at 15°C)

In steam reforming, only light hydrocarbons are reacted with steam to form hydrogen. However, all products of a refinery could be used for hydrogen production by partial oxidation. The most interesting option from the economic point of view is to use products with a low market value. In some refineries, heavy oil residues are transformed to petroleum coke and subsequently gasified (Section 2.7) to produce syngas.

Hydrogen production strategy

Both reforming and gasification can lead to a reduced environmental impact at the overall site scale. The choice between these two approaches primarily depends on two factors:

- the availability and nature of excess hydrocarbon streams which may be used as feedstocks;
- the quantity of hydrogen required.

The primary advantage of a gasification strategy is that useful products are generated as raw synthesis gas containing carbon monoxide and hydrogen (see Table 2.11). It does so from heavier refinery hydrocarbon streams that would not otherwise have been used. Therefore, the implementation of gasification technology has an environmental and economic benefit on the overall refinery conversion performance. However, one clear limitation is that the hydrogen produced from gasification can only be considered a by-product. The heavier the feedstock, the lower the H₂/CO ratio: the most common solid and liquid refinery streams are going to yield a molar ratio less than 2 (see Figure 4.40 in Chapter 4.14.1). The economic and environmental viability of the gasification technology depends primarily on having a productive use of the resulting syngas/CO primary product. The second limitation arises from the availability of hydrogen within the refinery. More specifically, the heavier refinery hydrocarbon (waste) streams that would be gasified simply may not have enough hydrogen in them to produce the required quantity. In case of a very large hydrogen requirement (as is often the case), then an additional hydrogen supply (usually by light hydrocarbon steam reforming) would be needed.

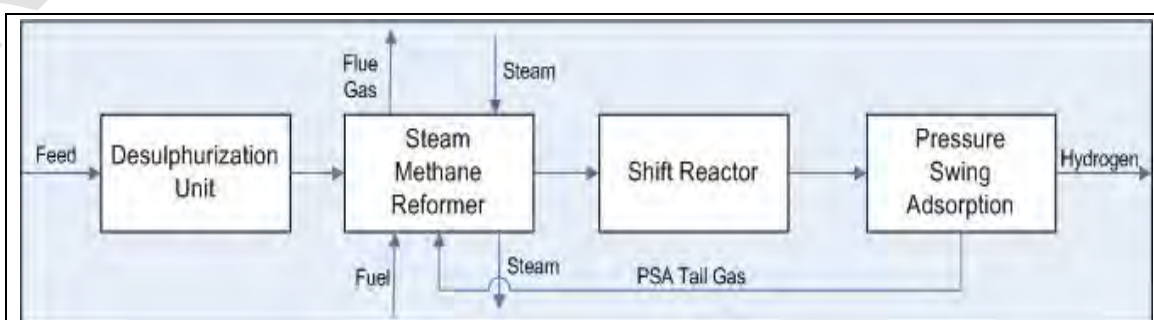
By using a steam reforming strategy, the yield is much higher. As such, hydrogen can be truly considered the primary product. However, the main limitation of this process is that it requires a light feedstock (natural gas, naphtha or other light hydrocarbon cuts), which is also a potential high value feedstock for other refinery or petrochemical applications, or a favourable fuel source for reducing the site PM, NO_x and SO_x emissions.

In all cases, hydrogen purification is necessary to meet the downstream desulphurisation process requirements. This is true for steam reforming, gasification, or any other already existing streams within the refinery.

Process description

Steam reforming

This is the most commonly used method for hydrogen production. The best feedstocks for steam reforming are light, saturated, and low in sulphur; this includes natural gas (the most common), refinery gas, LPG, and light naphtha. In its simplest form, as shown in Figure 2.22, the steam methane reforming process for pure hydrogen production consists of four stages: a desulphurisation unit, a steam methane reformer, shift reactor(s), and finally pressure swing adsorption.



Source: [56, EIGA 2009]

Figure 2.22: The four main steps of H₂ production by steam methane reforming

The reaction is typically carried out at 750 – 1 000°C and a pressure of 20 – 40 barg over a fixed catalyst bed, which is very sensitive to poisoning. Desulphurisation of the feedstock is required in order to protect the catalyst in the reformer furnace against deactivation.

It is common practice to operate at excess steam/hydrocarbon ratios to prevent carbon formation. Heat for the endothermic reforming reaction is provided by the furnace burners. The reformed gas, a mixture of hydrogen, carbon dioxide, carbon monoxide, methane and steam, is cooled down to about 350 °C by rising steam. After reforming, the CO in the gas is reacted with steam to form additional hydrogen (shift reaction).

The oxidation of the CO to CO₂ can be done in a one-step (low, medium or high temperature) converter in a two-step shift (high followed by low temperature) converter, reducing the CO content to less than 0.4 %. The product gas passes to a PSA which delivers ultra-pure hydrogen. The PSA tail gas is recycled to the steam-methane reformer burners as shown on Figure 2.22.

More information on hydrogen production can be found in the LVIC-AAF BREF [92, EC 2007].

Gasification of coke

The processes used for the gasification of petroleum coke are the same as those used in the gasification of coal and they are integrated in the Flexicoker (See Section 2.7). In an oxygen-blown operating mode of a gasifier, the gas produced can be processed to recover hydrogen or synthesis gas, or can be used as a medium-calorific value fuel. The gasifier product gas (syngas, CO, H₂, CO₂, CH₄ and H₂O), after it has passed the cyclones, contains hydrogen sulphide (H₂S) and carbonyl sulphide (COS). With a sulphur adsorbent such as limestone (CaCO₃) or dolomite (Mg, CaCO₃) in the gasifier, the sulphur content of the gas can be drastically reduced. If no sorbent is used, the sulphur content of the gas will be in proportion to the sulphur in the feed. The particulates in product gas are removed in the barrier filter. Volatile metals and alkali tend to accumulate on the particulate as the gas is cooled. The particulates contain a high percentage of carbon and are usually sent with the ash to a combustor, where the remaining carbon is burnt and the calcium sulphide is oxidised to sulphate. In this hot-gas clean-up system, there is no aqueous condensate produced, although some may be produced in subsequent processing of the gas.

Table 2.11: Example of composition of petroleum coke used and the composition of the syngas produced in a oxygen-blown fluidised-bed gasification process

Analysis of petroleum coke used in gasification		Composition of gas produced by gasification at 980 – 1135 °C	
Ultimate analysis	% w/w		% v/v
Carbon	87.1 – 90.3	CO	34.3 – 45.6
Hydrogen	3.8 – 4.0	CO ₂	27.3 – 36.4
Sulphur	2.1 – 2.3	Hydrogen	13.5 – 16.8
Nitrogen	1.6 – 2.5	Water	8.7 – 13.9
Oxygen	1.5 – 2.0	Methane	0.1 – 0.9
Proximate analysis		Nitrogen	0.4 – 0.7
Fixed carbon	80.4 – 89.2	H ₂ S	0.3 – 0.6
Volatiles	9.0 – 9.7		
Moisture	0.9 – 10.2		
Ash	0.2 – 0.4		

Source: [175, Meyers 1997]

Gasification of hydrocarbons (partial oxidation)

In partial oxidation, hydrocarbon feed reacts with oxygen at high temperatures to produce a mixture of hydrogen and carbon monoxide (also covered in IGCC in Section 2.10). Since the high temperature takes the place of a catalyst, partial oxidation is not limited to the light, clean feedstocks required for steam reforming.

Hydrogen processing in this system depends on how much of the gas is to be recovered as hydrogen, and how much is to be used as fuel. Where hydrogen production is a relatively small part of the total gas stream, a membrane is normally used to withdraw a hydrogen-rich stream. That stream is then refined in a purification unit.

Purification of hydrogen

A wide variety of processes are used to purify hydrogen streams. Since the streams are available at a wide variety of compositions, flows, and pressures, the method of purification will vary. They include wet scrubbing, membrane systems, cryogenic separation and pressure-swing adsorption (PSA). This last technique is the most commonly used. In the PSA plant, most impurities can be removed to any desired level. Several layers of adsorbents (molecular sieves) remove carbon dioxide, water, carbon monoxide, methane and nitrogen from the out-stream. Nitrogen is the most difficult to remove of the common impurities, and removing it completely requires additional adsorbent. Since nitrogen acts mainly as a diluent, it is usually left in the product if the hydrogen is not going to be used in a very high-pressure system such as a hydrocracker or a common network. Hydrogen purity is 99.9 – 99.999 % v/v after the PSA unit. The residual constituent of the product gas is usually less than 10 ppm CO. Several adsorber beds are used, and the gas flow is periodically switched from one vessel to another to allow regeneration of the adsorbent by pressure reduction and purging, thus releasing the adsorbed components. The desorbed gas is used as fuel at a convenient location.

2.15 Integrated refinery management

All refinery process units, systems and activities are typically operated in an integrated way, aimed at optimising production in a way that is economic, sustainable and acceptable to society. This requires a concerted well-managed approach in the execution and planning of all activities likely to impact on the site environmental performance.

Sections 15 of Chapters 2, 3, 4 aim at describing general management activities related to the environment, with a focus on several aspects of housekeeping, soil and groundwater protection, and utility management which are particularly relevant to the refining sector. These Sections have been structured according to the two following categories.

- Refinery management activities including environmental management tools and good housekeeping techniques. Within this section, activities such as maintenance, cleaning, good design, production planning (including start-ups and shutdowns), training, information system process supervision/control systems and safety systems have been included.
- Utilities management within a refinery not covered by other sections, such as water management, blowdown systems, compressed air generation and distribution and electricity distribution systems.

Refinery management activities

Environmental management tools

An environmental management system (EMS) is a system for managing all activities (including energy) in a refinery that presents the purpose of the refinery as a whole, the responsibilities of employees/management and procedures to be followed. An intrinsic aim of EMS is to achieve continuous improvement, with a refinery learning, in particular, from its own operational experience, as well as that of others. See also Section 4.15.1.1 on EMS.

The development of EMS started by building upon the experience gained by other business parameters. Quite often, management responsibility for the environment is placed on the same person with the management responsibility for safety, health, and sometimes quality. Environmental management is also named environmental care. In this section the importance of good housekeeping and management is highlighted. It is remarked that systems exist for improving performance in many fields, such as safety, maintenance and product quality. Environmental Management Systems have also been developed for the improvement of refinery performance in environmental matters.

Good housekeeping.

Good housekeeping techniques refer to the proper handling of the day-to-day aspects of running a refinery. Many daily refinery activities undertaken in various domains like maintenance, cleaning, new process and process modification development, production planning (including start-ups, shutdowns), information systems process supervision/control, and training and safety are likely to have an impact on environmental performance and should be managed properly in that respect. Other European regulatory schemes, like the Council Directive 96/82/EC on the control of major-accident hazards, underline the importance of proper housekeeping and the obligation to plan and control activities efficiently within the refinery EMS.

Heat exchanger cleaning

Heat exchangers are widely used throughout petroleum refineries to heat or cool petroleum process streams. The heat exchangers consist of bundles of pipes, tubes, plate coils, or steam coils enclosing heating or cooling water, steam, or oil to transfer heat indirectly to or from the oil process stream. The bundles are cleaned periodically to remove accumulations of scale, sludge and any oily wastes. Therefore, heat exchanger cleaning is one issue of particular importance to be addressed within refinery management activities.

Utilities management

Energy management including steam management and cooling are included in other Sections 8 and 10.

Water management

Water is used within a refinery as process water, boiler feed, fire-fighting preparedness and cooling water and these require adequate management before discharge into receiving environment. Besides these, any precipitation like in rainwater (clean or contaminated) is another type of water that should be also considered. In addition, sanitary waste water, ballast water and blowdown water are other sources of waste water that may require treatment before discharge.

Water master plans are normally applied to refineries in order to optimise the consumption of water. Water inventories are sometimes a great help in the management of water, matching the quantity and quality of the effluents. Water integration and management is dependent on the refinery configuration, the crude quality and the level of desalting required, the cost of potable water, the availability of rainwater and the quality of the cooling water.

Within a refinery, a number of standard process-integrated effluent/water treatment provisions are available, as well as a number of standard possibilities for water reduction and reuse. In most refineries, a number of these options have already been implemented to some extent, either in the original design or by retrofit. Segregation of process water discharges and other types of water are also points to consider in the water management system. Ballast water is relevant to these refineries that have crude receipt facilities from ships or handle big product tankers or inland barges. This ballast water can be high in volume and salt content (seawater), and contaminated with oil and will require appropriate treatment. However, volumes of ballast water to be treated are declining with the gradual introduction of segregated ballast tankers.

Water and drainage applies to any industrial site. It entails the complete system of fresh water supply, rainwater, ballast water, process water, cooling water and groundwater, as well as effluent collection, storage and the various waste water treatment systems. The design is based on local factors (rainfall, receiving water bodies, etc.), effluent segregation, source reduction, first flush approach, flexible routing and reuse options.

Recirculated process water streams and cooling water streams are often manually purged to prevent the continued build-up of contaminants in the stream (blowdown system).

Purge/vents systems

Most refinery process units and equipment are arranged into a collection unit, called the purge/vent system. These systems provide for the safe handling and disposal of liquid and gases, as well as for shutdown, cleaning and emergency situations. Purge/vent systems are either automatically vented from the process units through pressure relief valves, or are manually drawn from units. Part or all of the contents of equipment can also be purged prior to shutdown before normal or emergency shutdowns. Purge/vent systems use a series of flash drums and condensers to separate the blowdown into its vapour and liquid components.

Compressed air generation

Compressed air is necessary as a utility within a refinery. It is normally generated by electric compressors and is distributed around the refinery.

Heating of pipes

Current practices are to apply steam heating (low-pressure steam), electric heating or hot oil heating of lines, if it is required. Electric heating normally generates less corrosion and consequently is easier to maintain compared with heating using steam. Hot oil heating is used when high temperatures are needed.

2.16 Isomerisation

Purpose and principle

Isomerisation is used to alter the arrangement of a molecule without adding or removing anything from the original molecule. Typically, low-molecular-weight paraffins (C_4 - C_6) are converted to isoparaffins with a much higher octane index. The isomerisation of olefins is also included in this section.

Feed and product streams

Typical feedstocks to isomerisation units are any butane, pentane or hexane-rich feedstream. These streams are hydrotreated naphtha, straight run light naphtha, light naphtha from hydrocrackers, light reformate, coker light naphtha and the light raffinate stream from an aromatic extraction unit. The feedstream to C_5/C_6 isomerisation unit is normally fractionated so that it includes as much of the C_5/C_6 as possible, while minimising heptanes and heavier compounds.

Process description

Figure 2.23 shows a simplified process flow diagram of a low-temperature isomerisation unit with hydrogen and hydrocarbon recycle. The isomerisation reactions occur in the presence of hydrogen and catalyst. The atmosphere of hydrogen is used to minimise carbon deposits on the catalyst, but with a low hydrogen consumption. The reactions normally take place in two reactors in a series. An advantage of the two-reactor scheme is that the first reactor may operate at higher temperatures to kinetically drive the reactions, while the tail reactor may be operated at lower temperatures to push the desired products closer to equilibrium conversion.

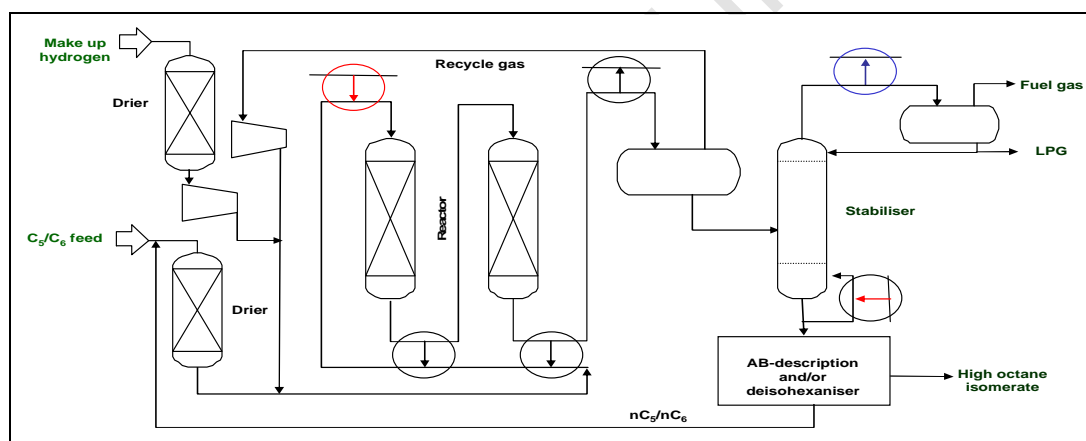


Figure 2.23: Simplified process flow scheme of an isomerisation unit

There are several isomerisation process designs based on three isomerisation catalyst technologies that can be further designed to operate with or without hydrogen recycle and with or without hydrocarbon recycle. In general, they can be classified into two categories, 'hydrocarbon once-through' or 'hydrocarbon recycled'.

- In 'once-through' isomerisation designs, only fresh feed is processed in the isomerisation unit. The octane number which can be achieved is only around 77 – 80 RON when using a zeolite-based catalyst, and 82 – 85 RON using a chloride-promoted catalyst. Conversions of 80 % can be expected.
- In hydrocarbon recycle isomerisation designs, the unconverted, lower octane paraffins are recycled for further conversion. Depending on the recycle option, the recycle may be normal paraffins or methylhexanes and n-hexane. The octane number obtained can be up to 92 RON, dependent on the feedstock composition, configuration and catalyst used. The

yield in the isomerate is around 95 – 98 %, depending on the targeted octane number of the final stream.

There are three distinctly different types of isomerisation catalysts currently in use:

- chloride-promoted
- zeolitic
- sulphated-zirconia catalysts.

The zeolite catalyst operates at significant higher temperatures (250 - 280 C and 15-25 barg) and is more tolerant to contaminants, though the resulting octane improvements are lower. The zeolite catalyst is mainly used when higher octane isomerate product does not justify the additional capital required to reduce feed contaminants for the chlorided-alumina catalyst or is a better match for a retrofit unit. The highly active chloride-promoted catalyst operates at a relatively low temperature (130-180 °C and 30 barg) and gives the highest octane improvement. This type of catalyst requires the addition of small amounts of organic chlorides which are converted to hydrogen chloride in the reactor to maintain the high activity. In such a reactor, the feed must be free of oxygen sources including water to avoid deactivation and corrosion problems. Furthermore, this catalyst is very sensitive to sulphur, so deep desulphurisation of the feed to less than 0.5 ppm is required. Lower reaction temperatures are preferred to higher temperatures because the equilibrium conversion to the desired isomers is enhanced at lower temperatures.

After isomerisation, the light ends are fractionated from the product stream leaving the reactor and are then sent to refinery fuel gas or to the light ends recovery unit. In a hydrocarbon once-through isomerisation unit, the bottom stream from the stabiliser is, after product cooling, sent to the gasoline pool. In a hydrocarbon recycle isomerisation design, the bottom stream from the stabiliser is fed to a separation unit, which is either a deisohexaniser column or an adsorption system.

In the deisohexaniser column, a split can be made between the higher octane dimethylbutanes and the lower octane methylpentanes. The dimethylbutanes and lower boiling C₅ components (isomerate product) are taken overhead from the column and are sent to the gasoline pool. The methylpentanes and normal hexane are taken as a side-stream close to the bottom, and are recycled to the isomerisation reactor. The bottom stream from the deisohexaniser is a small quantity of heavy by-product which is sent with the isomerate product to the gasoline pool or to a catalytic reformer if the refinery recovers benzene as chemical feed. The principle of adsorption is that the unconverted normal paraffins are adsorbed on the molecular sieve whereas the isoparaffins pass the adsorbent. Desorption takes place with heated hydrogen-rich gas from the separator or a butane mixture. The desorbent is separated from the net hydrogen-rich recycle stream in a separator vessel and returned to the isomerisation reactor for further conversion.

2.17 Natural gas plants

Natural Gas refined in Europe has been largely up to this point in time from the North Sea basin. Natural gas is also obtained from a small number of on-shore oil fields, where it is co-produced with crude oil and separated at local facilities before being treated, brought up to specification and finally exported. Off-shore gas production consists of a number of central platforms with satellite platforms and is sent via pipeline systems to coastal refining terminals. However, off-shore platforms are not included in the scope of this document.

Descriptions

The following processes are generally in place at a gas refinery:

- gas Dewpointing;
- inlet Reception Facilities;
- glycol Recovery, Reuse and storage;
- gas Heating and Pressure Reduction;
- H₂S Removal;
- gas Metering and Export;
- condensate Separation and Stabilisation;
- condensate Storage, Metering and Export;
- propane Refrigeration System.

The extent to which the initial gas refining is completed off shore is dependent on the type of facility available and the nature of the gas from the wells. At some well head facilities the process involves the removal of all condensate and water, which are removed to shore via other routes. For the rest of the gas streams the condensate fraction is removed and then re-injected back into the system. It is also at this stage that glycol (commonly mono-ethylene glycol) is injected for the purpose of anti-freeze. The gas stream may also have scale inhibitors added at this stage to prevent hydrate formation within the pipelines.

Gas reception facilities usually includes sphere pig receivers and slug catchers. The slug catchers are large volume low pressure sections of pipeline, which are there to knock down the water and dust entrained with the gas.

Gas Dewpointing is part of the the true refining section of the process. The gas is cooled usually using propane heat exchangers (the propane will freeze during this process and is subsequently recycled through re-boilers). It is through this process that the final gas stream quality is achieved, in combination with a final metering and mixing stage to achieve sales gas quality.

H₂S Removal: The majority of the gas wells in the North Sea are sweet and the number of sour wells has fallen over the past few years, but most terminals will have the ability to deal with feed stocks which have small percentages of sour gas. The main principles used are amine gas treatment or catalysed bed system.

Condensate Separation and Stabilisation: The usual method is to remove the lighter fractions in the refining process and some of the more volatile elements. Condensate is then either refined on site or shipped to a refining site, which will produce kerosene and naphtha for sale as an important economic by-product.

Glycol system : This is a re-circulation system, with the glycol being pumped off shore injected into the feed gas stream, and then removed early in the process It is re-boiled and cleaned up via filters and prepared to be re-injected into the system.

Purpose and principle

The overall objective of natural gas processing is to remove the treatment chemicals and to remove any contaminants from the well-head stream, in order to produce a methane-rich gas

which satisfies statutory and contractual specifications. The main contaminants to be removed fall into the following categories:

- solids: sands, clay, sometimes scale like carbonates and sulphates (including naturally-occurring radioactive metals (e.g. lead or radium), mercury);
- liquids: water/brine, hydrocarbons, chemicals added at well-head;
- gases: acid gases, carbon dioxide, hydrogen sulphide, nitrogen, mercury and other gases (e.g. mercaptans).

Feed and product streams

The feedstock is natural gas and the products that may be separated within the natural gas plants are methane rich gas, C₂, C₃, C₄ fractions and condensates (C₅₊).

Process description

As shown in Figure 2.25, the purification plant consists of an acid gas treatment (sweetening plant) where acid gases such as CO₂, H₂S, SO₂ are separated. Natural gas is considered 'sour' when it contains significantly greater amounts of hydrogen sulphide than those required to comply with the pipeline quality specifications or when it contains such amounts of SO₂ or CO₂ to make it impractical to use without purification. The H₂S must be removed (called 'sweetening' the gas) before the gas can be utilised. If H₂S is present, the gas is usually sweetened by absorption of the H₂S in an amine solution. Amine processes are the most common process used in the United States and Europe.

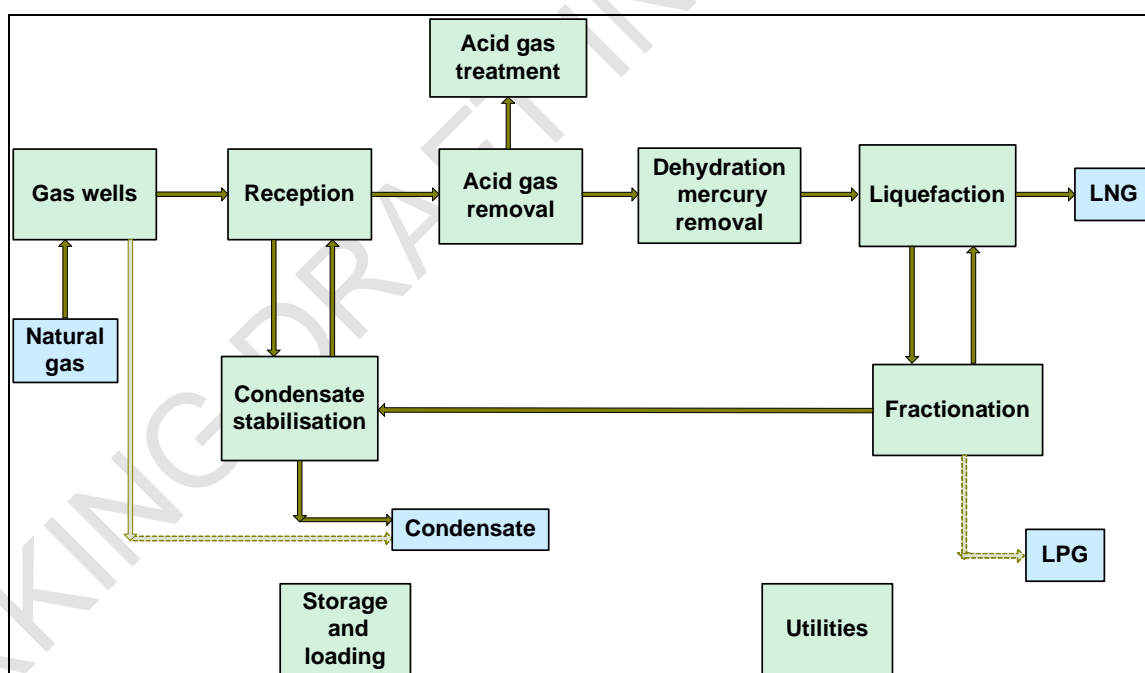


Figure 2.24: General block diagram of a natural gas plant

Other methods, such as carbonate processes, solid bed absorbents, and physical absorption, are employed in other sweetening plants.

Natural gasoline, butane and propane are usually present in the gas, and gas processing plants are required to recover these liquefiable constituents (see Figure 2.25). The type of processes found are very similar to those described in Section 2.12. As a summary, these processes are physical separations at very low temperatures (typically distillation). The following figures describe two of the main steps of the natural gas separation process.

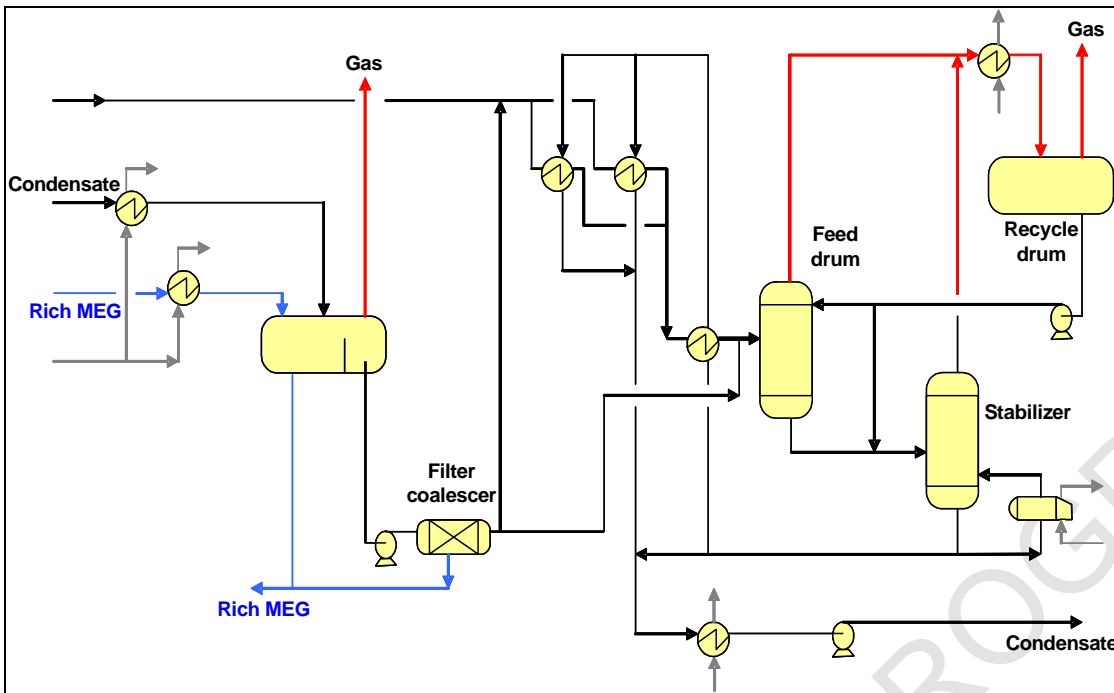


Figure 2.25: Condensate separation in a natural gas plant

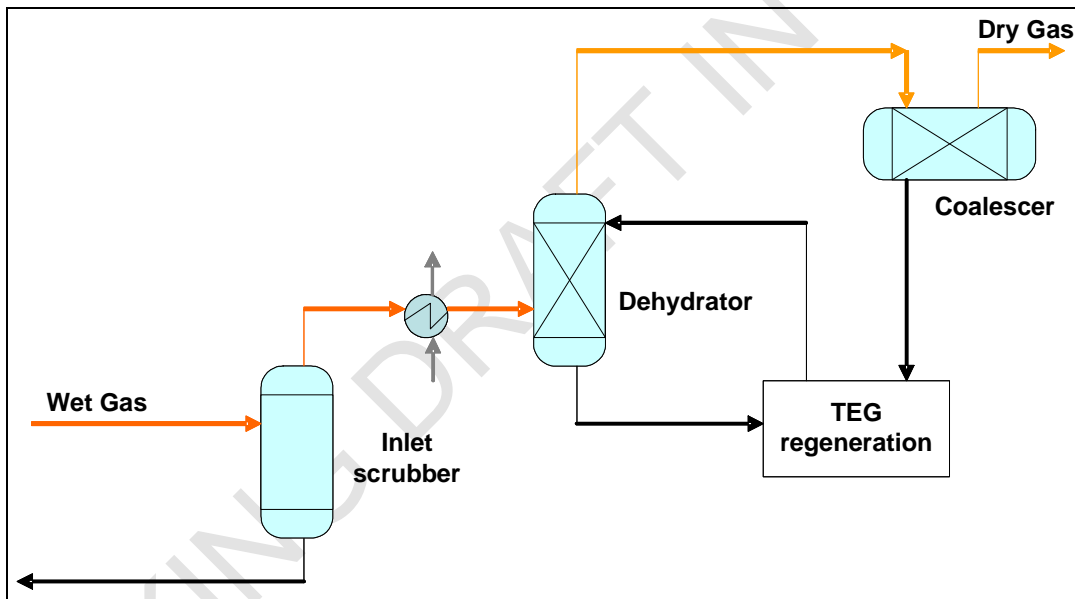


Figure 2.26: Gas dehydration in a natural gas plant

2.18 Polymerisation

This section covers the polymerisation, dimerisation and condensation of olefins.

Purpose and principle

Polymerisation is occasionally used to convert propene and butene to high octane gasoline blending components. The process is similar to alkylation in its feed and products, but is often used as a less expensive alternative to alkylation. Prevailing chemical reactions may vary according to olefin type and concentration but can be described in general terms shown below:

$2 \text{ C}_3\text{H}_6$	\rightarrow	C_6H_{12}	(dimerisation)
$2 \text{ C}_4\text{H}_8$	\rightarrow	C_8H_{16}	(dimerisation)
$\text{C}_3\text{H}_6 + \text{C}_4\text{H}_8$	\rightarrow	C_7H_{14}	(condensation)
$3 \text{ C}_3\text{H}_6$	\rightarrow	C_9H_{18}	(polymerisation)

Feed and product streams

Propene and butene contained in the LPG stream from the FCC are the most common feedstreams for this unit.

Process description

The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst adsorbed onto natural silica and extruded in pellets or in small cylinder forms. All reactions are exothermic, and therefore the process requires temperature control. The feed must be free of: sulphur, which poisons the catalyst; basic materials, which neutralise the catalyst and oxygen, which affects the reactions. The propene and butene feed is washed first with caustic to remove mercaptans, then with an amine solution to remove hydrogen sulphide, then with water to remove caustics and amines, and finally dried by passing through a silica gel or molecular sieve dryer. A simplified scheme of a polymerisation unit is shown in Figure 2.27.

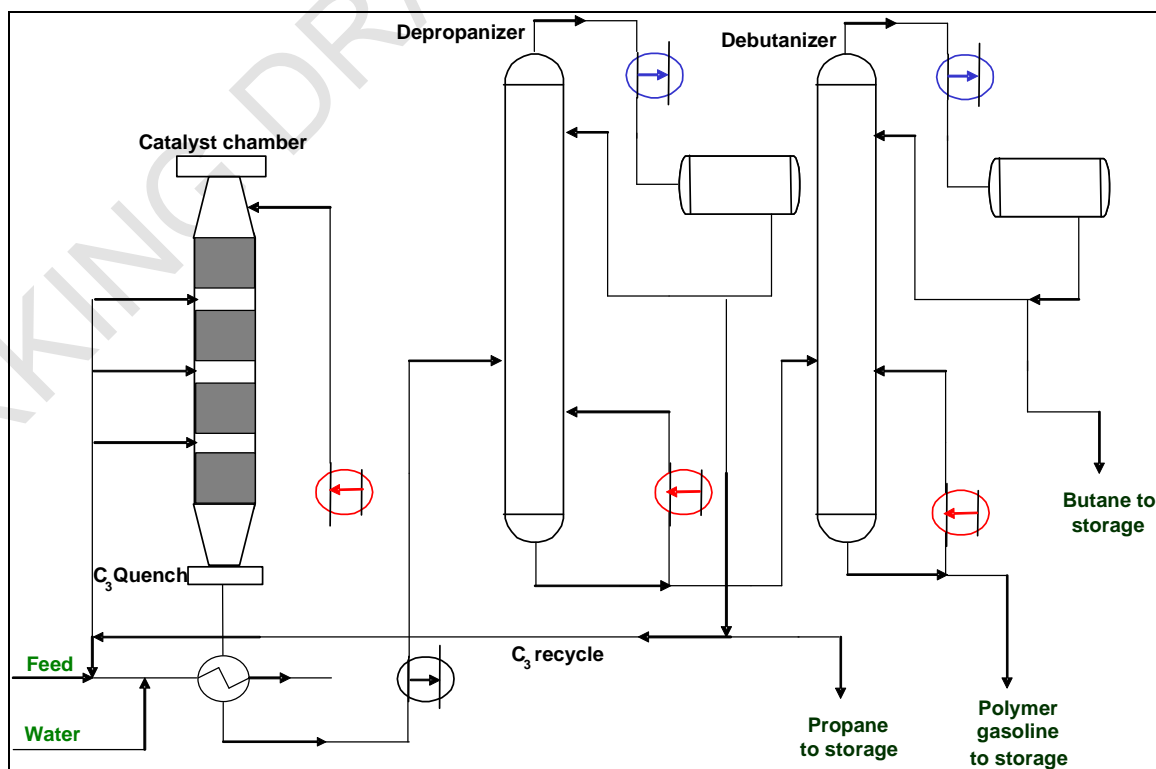


Figure 2.27: Simplified scheme of a polymerisation unit

When the polymerisation yield drops, the catalysts need to be replaced. After nitrogen purging, the polymerisation unit is opened and the catalyst removed by means of a high-pressure water jet. It can also be removed using steam (compression dumping). The phosphoric acid goes in the water medium, while the natural silica pellets break down to form a slurry, which is usually pumpable.

WORKING DRAFT IN PROGRESS

2.19 Primary distillation units

This section includes atmospheric and vacuum distillation. These two primary distillations are preceded by crude oil desalting and they are the first and fundamental separation processes in a refinery.

Purpose and principle

The Atmospheric Crude Oil Distillation Unit (CDU) is the first important processing step in a refinery. Crude oil is heated to elevated temperatures and then generally subjected to distillation under atmospheric pressure (or slightly higher), separating the various fractions according to their boiling range. Heavier fractions from the bottom of the CDU, which do not vaporise in this column, can be further separated later by vacuum distillation.

Increased demand for light products and a reduced demand for heavy fuel oil have resulted in refiners upgrading the atmospheric residue into more valuable lower boiling fractions such as naphtha, kerosene and mid-distillates. Vacuum distillation is simply the distillation of petroleum fractions at a very low pressure to increase volatilisation and separation whilst avoiding thermal cracking. The high vacuum unit (HVU) is normally the first processing step in upgrading atmospheric residue, followed by downstream refining units. HVU produces feedstocks for cracking units, coking, bitumen and base oil units. The contaminants from the crude oil stay predominantly in the vacuum residue.

Feed and product streams

The crude oil feed to the crude distillation unit is supplied from the crude oil storage tanks after desalting. Normally all crude oil entering a refinery passes through a crude distillation unit. In addition to that, it is common practice that off-specification product streams are reprocessed in the CDU. The products from the crude distillation unit, ranging from the lightest to the heaviest cut are; naphtha and light components (boiling $<180\text{ }^{\circ}\text{C}/\text{C}_1\text{-C}_{12}$ - lights, naphtha and gasoline), kerosene (boiling range $180 - 240\text{ }^{\circ}\text{C} - \text{C}_8\text{-C}_{17}$), light gas oil (boiling range approximately $240 - 300\text{ }^{\circ}\text{C}/\text{C}_8\text{-C}_{25}$), heavy gas oil (boiling range approximately $300 - 360\text{ }^{\circ}\text{C}/\text{C}_{20} - \text{C}_{25}$) and atmospheric residue (boiling $>360\text{ }^{\circ}\text{C}/>\text{C}_{22}$). The overhead of this column is the light fraction, non-condensable refinery fuel gas (mainly methane and ethane). Typically, this gas also contains hydrogen sulphide and ammonia gases. The mixture of these gases is known as 'sour gas' or 'acid gas'. A certain amount of it passes through the condenser to a hot well, and is then discharged to the refinery sour fuel system or vented to a process heater, flare or other control device to destroy hydrogen sulphide.

The main feed stream to the HVU is the bottom stream of the crude oil distillation unit, referred to as atmospheric or long residue. In addition, the bleed stream from the hydrocracker unit (if applicable) is normally sent to the HVU for further processing. The products from the HVU are light vacuum gas oil, heavy vacuum gas oil, and vacuum residue. Light vacuum gas oil is normally routed to the gas oil hydrotreater(s), heavy gas oil is normally routed to a fluid catalytic cracker and/or hydrocracker unit. The vacuum residue can have many destinations, such as visbreaking, flexicoking or delayed coking, residue hydroprocessing, residue gasification, bitumen blowing or it may go to the heavy fuel oil pool.

Process description

Atmospheric distillation

Distillation involves the heating, vaporisation, fractionation, condensation, and cooling of feedstocks. The desalted crude oil is heated to about $300 - 400\text{ }^{\circ}\text{C}$ and fed to a vertical distillation column at atmospheric pressure, where most of the feed is vaporised and separated into its various fractions by condensing on 30 to 50 fractionation trays, each corresponding to a different condensation temperature. The lighter fractions condense and are collected towards the top of the column.

The overhead hydrocarbon vapours are condensed and accumulated in the overhead reflux drum of the main fractionator. In this drum, sour water, light fractions (about 0.5 % on crude charge) and stripping steam (1.5 % on crude) are separated from the hydrocarbon liquid. The overhead hydrocarbon liquid, the naphtha minus stream, is commonly fed directly to the downstream naphtha treater.

Within each atmospheric distillation tower, a number of side-streams of low-boiling point components are removed from different trays in the tower. These low-boiling point mixtures are in equilibrium with heavier components which must be removed. The side-streams are each sent to a different small stripping tower, containing four to ten trays with steam injection under the bottom tray. The steam strips the light-end components from the heavier components and both the steam and light-ends are fed back to the atmospheric distillation tower above the corresponding side-stream draw tray.

Most of these fractions generated in the atmospheric distillation column can be sold as finished products after a hydrotreatment, or blended with products from downstream processes. In Figure 2.28, a simplified process flow diagram of a crude distillation unit is shown. Many refineries have more than one atmospheric distillation unit.

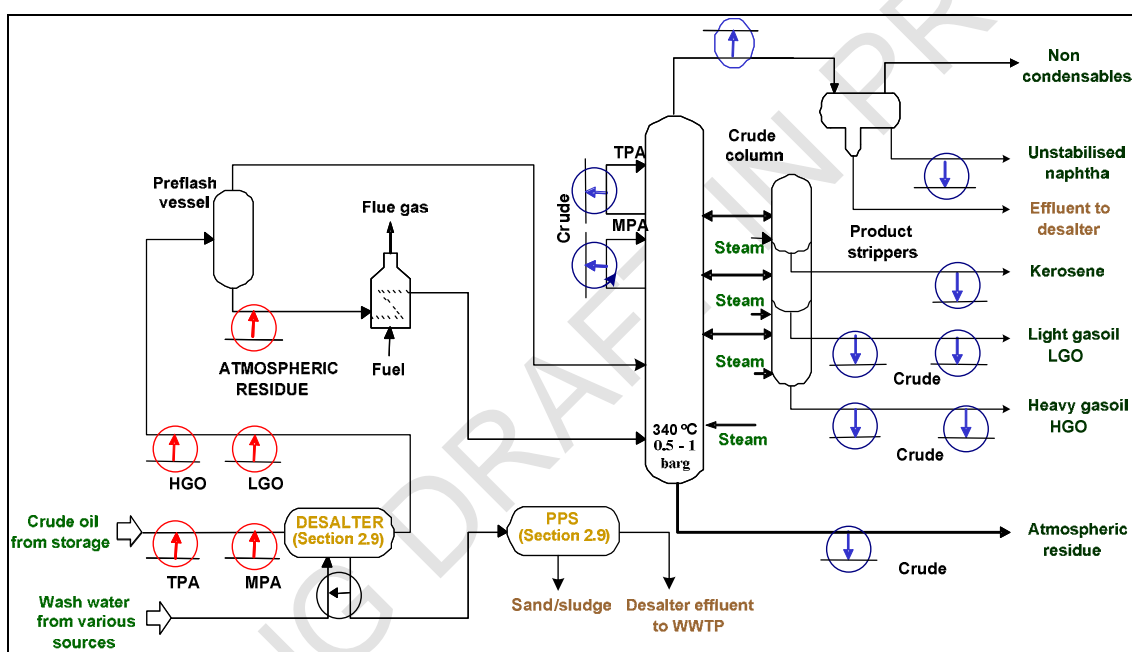


Figure 2.28: Simplified process flow diagram of a crude distillation unit

The operating conditions of the tower are based on the properties of the crude oil and the desired product yields and quality. To maximise the yield of distillates, the pressure is minimised, but the temperature is increased to the maximum. Every refinery has a crude distillation unit designed for a selected crude (mix). There are therefore many different crude distillation configurations with varying product cuts and heat integration.

Vacuum distillation

Figure 2.29 shows a simplified process flow diagram of the high vacuum unit. Atmospheric residue is heated up to 400 °C, partially vaporised (30 – 70 % by weight), and flashed into the base of the vacuum column at a pressure between 40 and 100 mbar (0.04 to 0.1 kg/cm²). The vacuum inside the fractionator is maintained with steam ejectors, vacuum pumps, barometric condensers or surface condensers. The injection of superheated steam at the base of the vacuum fractionator column further reduces the partial pressure of the hydrocarbons in the tower, facilitating vaporisation and separation.

The unvaporised part of the feed forms the bottom product and its temperature is controlled at about 355 °C to minimise coking. The flashed vapour rising through the column is contacted with wash oil (vacuum distillate) to wash out entrained liquid, coke and metals. The washed vapour is condensed in two or three main spray sections. In the lower sections of the column, the heavy vacuum distillate and optional medium vacuum gas oil are condensed.

In the upper section of the vacuum column, the light vacuum distillate is condensed. Light (non-condensable) components and steam from the top of the column are condensed and accumulated in an overhead drum for separating the light non-condensables, the heavier condensed gas oil, and the water phase.

The most important operational aspect of a vacuum unit is the quality of the heavy vacuum gas oil, especially when this is fed to a hydrocracker unit. The Concarbon level and/or metal content is very critical for a hydrocracker unit and depends on the operation and performance of the wash oil section in the vacuum distillation unit, as well as the desalter in the crude distillation unit.

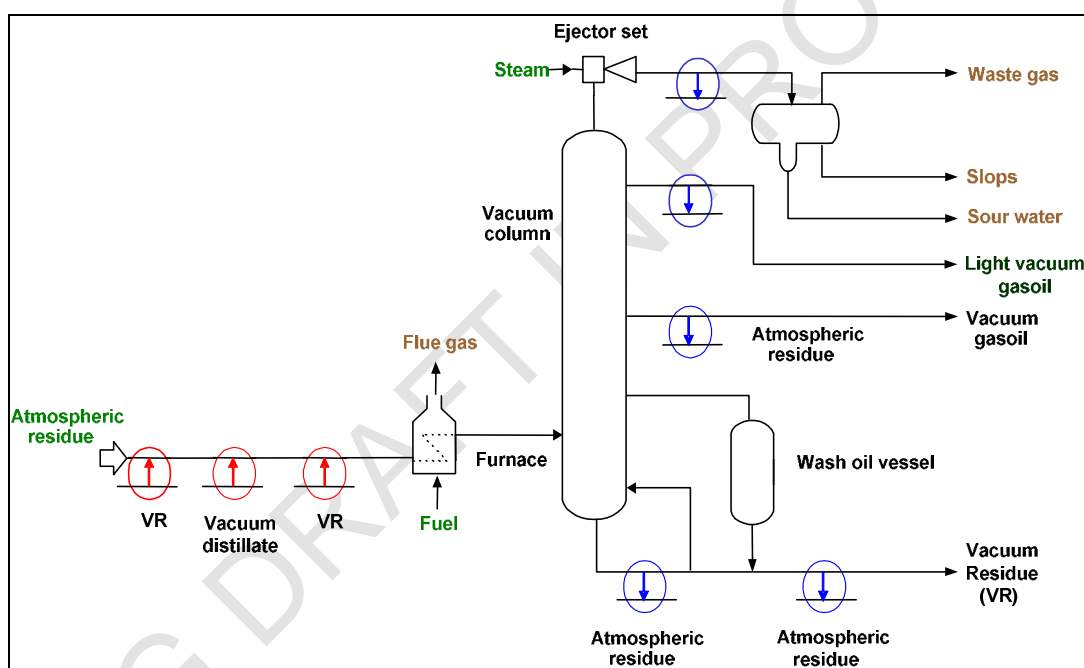


Figure 2.29: Simplified process flow scheme of a high vacuum distillation unit

2.20 Product treatments

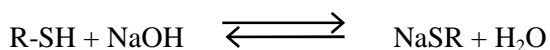
The treatments used in a refinery to achieve certain product specifications are included in this section, in which two types of processes can be identified:

- The first group of processes corresponds to extraction or removal techniques where the component to treat is removed from the stream to be treated. Under this category, mention can be made of molecular sieve extraction for the removal of carbon dioxide, water, hydrogen sulphide or mercaptans (Section 4.23.5.3), amine scrubbing for the removal of hydrogen sulphide (included in Section 4.23.5.1), and caustic washing for the removal of acids or mercaptans.
- The second group is composed of these systems where the chemical to be treated is not removed from the stream to be treated e.g. by catalytic dewaxing process .

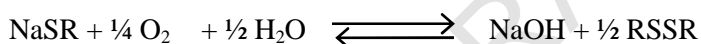
Extraction processes

Purpose and principle

In petroleum refining, chemical treatment is used to remove or change the undesirable properties associated with sulphur, nitrogen, or oxygen compound contaminants contained in petroleum products. Some of these systems (i.e. 'mercaptan oxidation') are designed to reduce the mercaptan content (organic sulphur compounds) of hydrocarbon streams to improve product odour and to reduce corrosivity. These treatments are accomplished by either extraction or oxidation (also known as sweetening), depending upon the product. The extraction process removes the mercaptans by caustic extraction, resulting in a lower sulphur content. The following reaction takes place at low temperatures:



Mercaptan oxidation-sweetening is another version of the mercaptan oxidation process in which the mercaptans in the hydrocarbon products are converted to less odorous and less corrosive disulphides which remain in the product. The reaction is:



As a result no reduction in the total sulphur content takes place during sweetening and consequently, it is only applied to these streams where the sulphur content is not a problem.

Feed and product streams

The mercaptan oxidation-extraction process entails the removal of mercaptans from LPG, naphtha, gasoline and kerosene streams. Oxidation or 'sweetening' is used on gasoline and distillate fractions. It should be stressed that mercaptans are also removed by hydrotreatment (Section 2.13).

Process description

Mercaptans are removed from light hydrocarbon streams by a concentrated alkaline wash in an extraction column under elevated pressure (5 barg). If H₂S or acids are present, a caustic prewash is required. The treated and odour-free hydrocarbon stream leaves the reactor as an overhead stream.

The aqueous bottom phase is heated to 50 °C, mixed with air, and fed to the oxidation reactor. The dissolved NaSR is now converted into disulphides (which are insoluble in caustic soda water solution) at 4.5 barg. By using an excess of air and adding catalyst, a high rate of reaction is maintained. In this way, the alkaline solution is regenerated. The liquid from the reactor is routed to a vessel where spent air, the disulphide fraction insoluble in the caustic solution and the caustic solution are separated. The spent air is routed to an incinerator or process furnace, the disulphides are usually recycled to the crude, and the regenerated caustic is circulated to the

extraction column. Figure 2.30 shows a simplified process flow diagram of an extraction process.

Another oxidation process is also a mercaptan oxidation process that uses a solid catalyst bed. Air and a minimum amount of alkaline caustic ('mini-alky' operation) are injected into the hydrocarbon stream and the caustic cannot regenerate. As the hydrocarbon passes through the mercaptan oxidation catalyst bed, sulphur mercaptans are oxidised to disulphide.

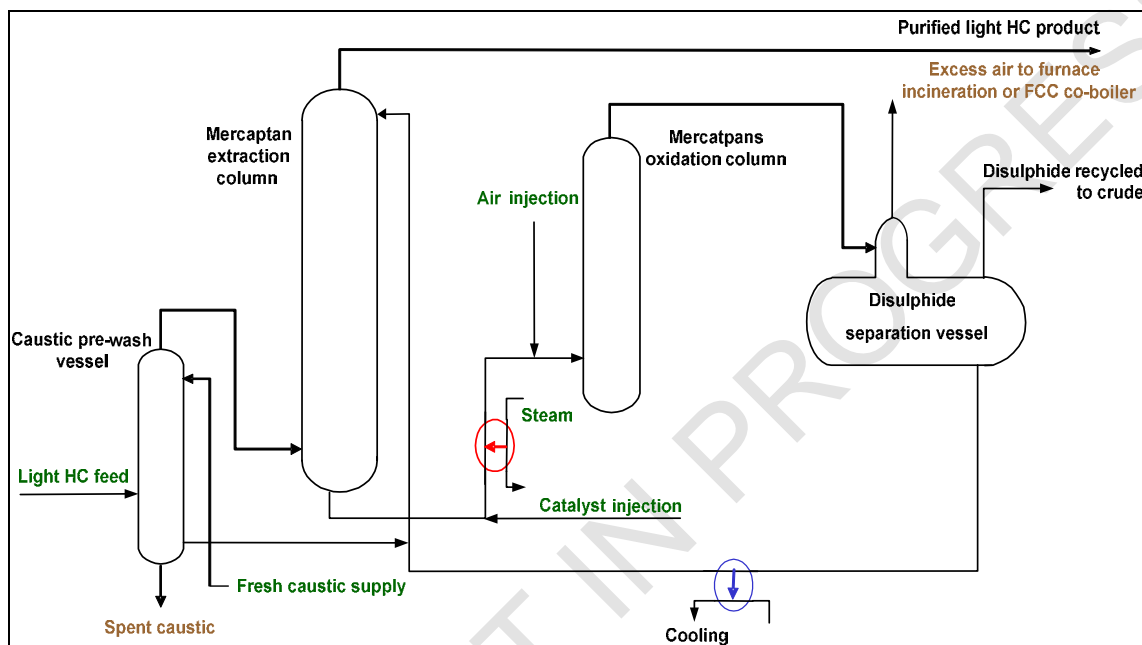


Figure 2.30: Simplified process flow diagram of the mercaptan oxidation extraction process

Both processes can be integrated in a caustic cascading system to achieve the desired product quality improvements at minimum caustic make-up and spent caustic disposal costs.

Figure 2.31 shows a simplified process flow diagram of the mercaptan oxidation extraction process.

Catalytic dewaxing

Another process that can be found in refineries is the selective hydrocracking (hydrofiner), where one or two zeolite catalysts are used to selectively crack the wax paraffins (n- and near-to-n-paraffins). This technique can be used for the dewaxing of mid-distillate components that may be blended into products for extreme winter conditions. A variation of this, is the use of isodewaxing catalyst that isomerises the n-paraffin wax to desirable isoparaffin lube molecules, while co-producing low-quality mid-distillate transportation fuels. The design and operation of this unit is similar to that of a normal hydrotreater unit (Section 2.13).

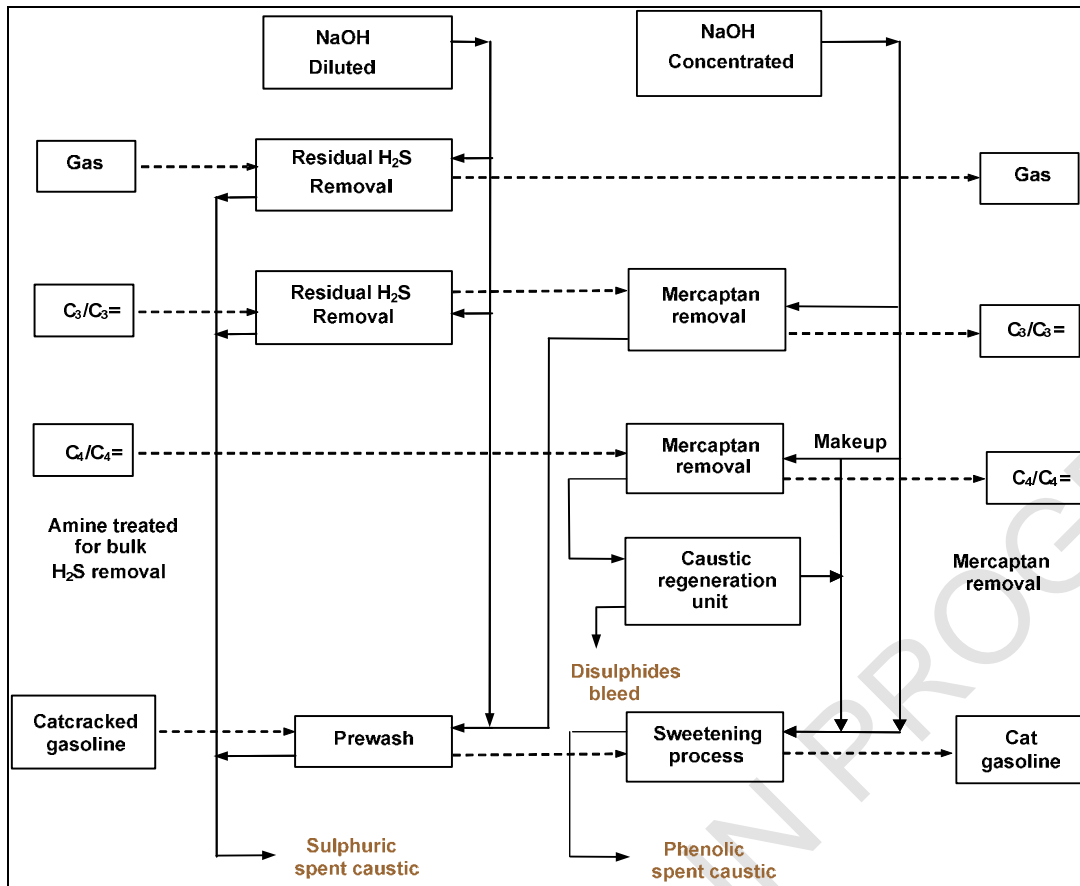


Figure 2.31: Simplified process flow diagram of the caustic cascading system (mercaptan oxidation extraction and sweetening)

2.21 Storage and handling of refinery materials

Storage and handling of refinery materials are not covered exhaustively in this document, because the storage and handling of oil products are within the scope of the horizontal BREF on storage [5, EC 2006], to which reference will be made as appropriate. This section also covers activities related to feed and product blending, piping and other small techniques used for the handling of materials. Storage of specific products, such as base oils, bitumen and petroleum coke, is included in the respective production sections.

Purpose and principle

Crude oil, petroleum intermediates and final products are transferred to, in, and from refineries through marine terminals via pipeline or rail/road vehicles. Between these movements, the products are stored in tanks. Storage tanks or caverns are used throughout the refining process to store crude oil, other raw materials and intermediate process feeds. Finished petroleum products are also kept in storage tanks before transport off site. Tanks are also needed to accommodate the blocked-out operation of processing units and to link continuous refinery processes with discontinuous ones. Consequently, storage is an essential part of a refinery. Blending systems are also used in refineries to prepare feed streams to individual refinery units and to produce finished products to be sold.

Feed blending may be applied to prepare the optimum feed stream to a refinery unit, thereby ensuring the optimum performance of the refinery unit. For example, a refiner processes a mixture of four different low-sulphur crudes in an atmospheric distillation unit. The feed blend is selected so that the throughput in the distillation unit and further downstream units are optimised/maximised, with the objective of maximising overall profit. Alternatively, the different quality crudes may be processed separately for a short period (a few days) in 'blocked-out' operations.

Product blending is applied to produce the optimum mix of finished refinery products. The majority of the product streams produced in different refinery units, normally identified as an intermediate product stream, can be blended into more than one finished product stream. For example, (hydrotreated) kerosene product is normally blended into diesel oil, light heating oil and even heavy fuel oil, with the remainder blended into jet fuel oil. The amount of kerosene allocated to the different products is selected so that product demands and specifications are met, with the objective of maximising overall profit. Blending products involves mixing the products in various proportions to meet specifications such as vapour pressure, specific gravity, sulphur content, viscosity, octane number, cetane index, initial boiling point and pour point, and to add distinctive smells (LPG).

Process description

The crude oil storage systems can be located either at a separate oil terminal or within the refinery complex. A large part (often more than 50 %) of the refinery area is occupied by oil movement facilities. Storage tanks can be divided into four main types: pressure vessels, fixed roof tanks, fixed roof tanks with floating covers, and floating roof tanks. Figure 2.32 shows the different types of storage systems found in a refinery.

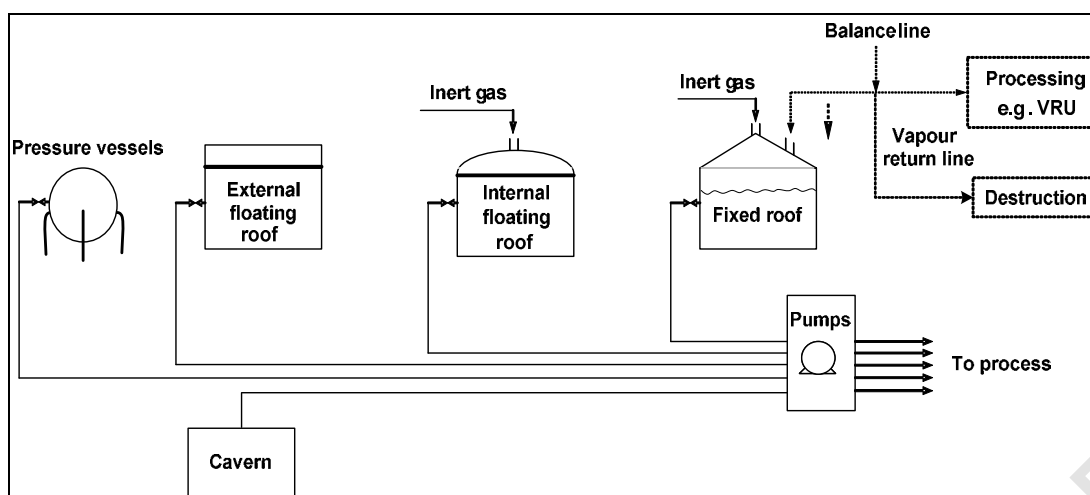


Figure 2.32: Examples of some types of storage tanks

Pressure vessels are normally used to store high pressures material (>91 kPa), most typically LPG. Fixed-roof tanks can hold a wide range of materials. For very low vapour pressure liquids, they can be open to the atmosphere. They can also be designed to hold volatile liquids with several classes of permitted pressure build-up, from 20 mbarg (low pressure) to 60 mbarg (high pressure). In these situations, measures to prevent the occurrence of flammable atmospheres, such as inerting and vapour loss (e.g. floating roof and vapour recovery), are required. Such tanks are necessarily provided with pressure/vacuum relief valves. Fixed roof tanks may also be fitted with internal floating covers. Floating covers float upon and move with the liquid and act as a barrier to evaporation. External floating roof tanks are generally larger and are extensively used for crude oil and product storage.

Above-ground storage tanks (ASTs) are used at refineries for holding either the raw feedstock (crude oil) or end-products generated by the refinery processes (gasoline, diesel, fuel oils, etc.). Underground storage tanks are used much less frequently (if at all) at refineries, primarily for storing fuel for onsite boilers and vehicles, or for capturing liquids at low-level drain points. The storage of crude oil and products in caverns is also applicable in some European countries.

Blending can be carried out in-line or in batch blending tanks. An in-line blending system consists of a manifold where individual streams are blended on flow control, and the blend ratio is normally controlled and optimised by a computer. When a certain volume of a given quality product is specified, the computer uses linear programming models to optimise the blending operations to select the blending components to produce the required volume of the specified product at the lowest cost. To ensure that the blended streams meet the desired specifications, in-line stream analysers for flash point, RVP, boiling point, specific gravity, research and motor octane number (RON and MON), sulphur, viscosity, cloud point and others are inserted to provide feedback to the computer, which in turn corrects blending ratios where necessary.

Batch blending involves mixing the feed streams in a blend tank, from where the relevant process units are fed. The same applies to intermediate product streams, which are first sent to intermediate storage tanks, where they are batch blended into the final product tanks.

Additives and odorants.

The odorant is stored as a liquid, normally in fixed tanks. The odorant is not added to the gas stream prior to liquefaction but is usually added to the LPG whilst the LPG is being loaded into the delivery tankers, although in-tank odorising is also carried out. Allowance may be made for any residual mercaptans already present in the LPG. The pump addition rate is carefully controlled. In the case of liquid propane, methanol may be added with the odorising agent in order to prevent hydrate icing in propane evaporators.

Odouring plants are designed to minimise the potential for leaks, e.g. by having the minimum number of pumps/valves/filters/tank connections, etc, by using welded, not flanged, connections wherever possible and by protecting the plant from possible impact damage. All such items used need to be designed to a very high standard of sealing efficiency. Devices such as automatic self-sealing couplings for loading lines are preferred.

Pipes, valves and auxiliary systems, such as vacuum recovery units are found throughout a refinery. Gases, liquids and even solids are transferred from unit operation to unit operation by pipes. Process pipes are normally above ground but some pipes are underground. [147, Irish EPA 1992]

WORKING DRAFT IN PROGRESS

2.22 Visbreaking and other thermal conversions

2.22.1 Visbreaking

Purpose and principle

Visbreaking is a well-established non-catalytic thermal process that converts atmospheric or vacuum residues to gas, naphtha, distillates and tar. It uses heat and pressure to break large hydrocarbon molecules into smaller, lighter molecules.

When vacuum residue is directly blended with the heavy fuel oil pool, significant quantities of cutter stock (normally high-value gas oil) need to be blended to the residue to meet the viscosity specifications of the heavy fuel oil. By thermally cracking the vacuum residue at relatively mild conditions, about 10 – 15 % of the feed is cracked to lighter fractions and, more importantly, the viscosity of the vacuum residue is reduced significantly. For this reason, the thermal cracker unit is normally called the ‘visbreaker’ gas oil unit.

Feed and product streams

The atmospheric residue from the crude distillation unit, the vacuum residue from the high vacuum unit, and heavy gas oils or vacuum gas oils or mixtures are typically the feedstocks. In this process, only part of the feedstock is converted and a large amount of residue remains unconverted. As no catalyst is involved in the thermal cracking process, the quality of the feedstock, in terms of metals and sulphur, is not critical. A significant quantity of gas is produced and all distillate products need further treatment and upgrading prior to running them to storage.

Process description

Thermal cracking is one of the oldest conversion processes to upgrade heavy oil fractions. At present, it is mainly used to upgrade vacuum residue. Figure 2.33 shows a simplified process flow diagram of the visbreaker unit. The most important factor in controlling the cracking severity should always be the stability and viscosity of the visbroken residue fed to the fuel oil pool. In general, an increase in the temperature or residence time results in an increase in severity. Increased severity produces higher gas-plus-gasoline yield and at the same time a cracked residue (fuel oil) of lower viscosity. Excessive cracking, however, leads to an unstable fuel oil, resulting in sludge and sediment formation during storage. Thermal cracking converts a maximum 20 % of the feed. Thermal cracking units to upgrade atmospheric residue have conversion levels significantly higher (35 – 45 %) and the viscosity of the atmospheric residue is reduced.

The feedstock is heated above 500 °C and then fed to a reaction chamber, which is kept at a pressure of about 9.65 barg. Following the reactor step, the process stream is mixed with a cooler recycle stream, which stops the cracking reactions. The product is then fed to a flasher chamber, where pressure is reduced and lighter products vaporise and are drawn off. The lighter products are fed to a fractionating tower, where the various fractions are separated. The bottoms consist of heavy residue, part of which is recycled to cool the process stream leaving the reaction chamber; the remaining bottoms are usually blended into residual fuel.

There are two types of visbreaker operations, ‘coil or furnace cracking’ and ‘soaker cracking’. Coil cracking uses higher furnace outlet temperatures (470 – 500 °C) and reaction times from one to three minutes, while soaker cracking uses lower furnace outlet temperatures (430 - 440 °C) and longer reaction times. The product yields and properties are similar. Run times of three – six months are common for furnace visbreakers and six – 18 months for soaker visbreakers.

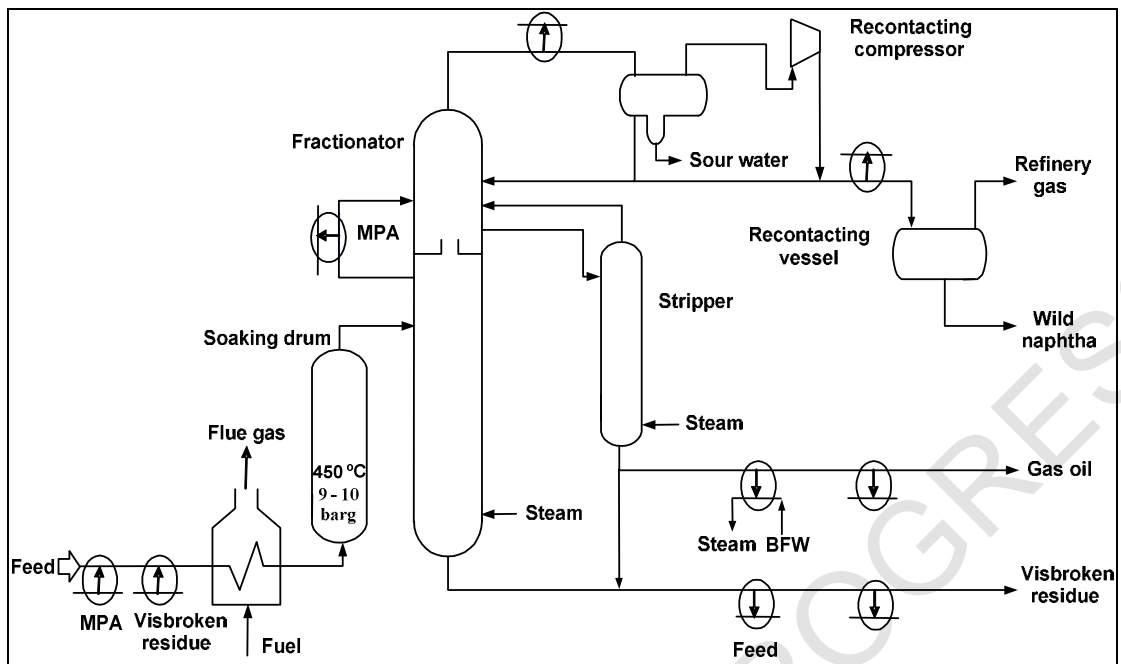
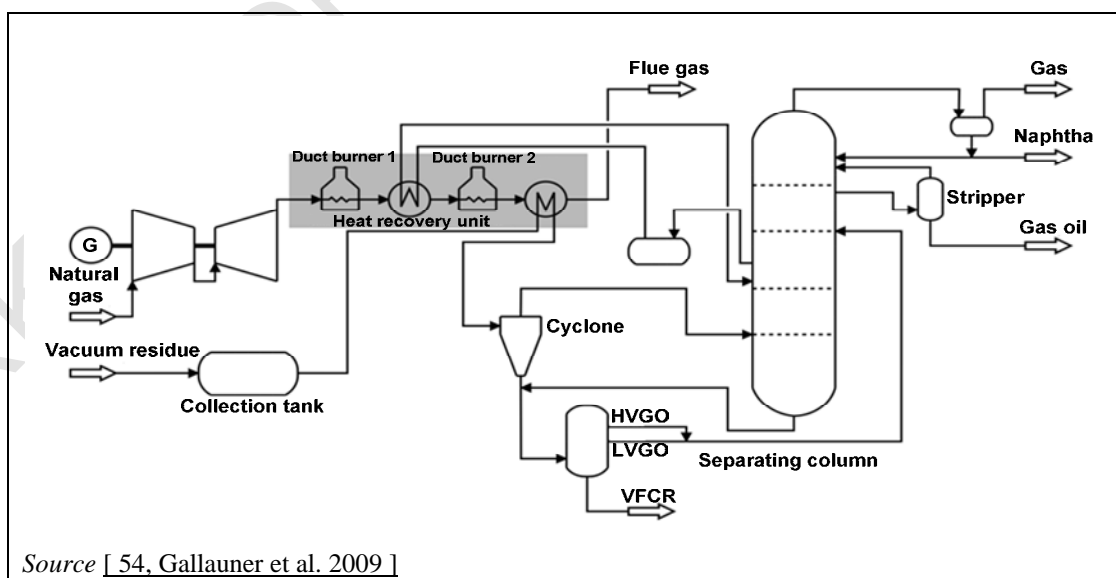


Figure 2.33: Simplified process flow scheme for a visbreaking unit

2.2.2.2 Thermal gas oil unit

The thermal gas oil unit (TGU) allows the conversion of the vacuum distillation residue by using a two-step thermal cracking and subsequent distillative separation into the gas oil and naphtha cuts produced. As shown in Figure 2.34, after a first thermal cracking, the resulting products are separated in a cyclone. The gaseous phase is introduced in the flash zone of the main distillation column and separated according to the desired boiling intervals. The heavy gas oil (HVGO) and the vacuum gas oil from the flash column (LVGO) are treated in a second thermal cracker and reintroduced into the column.



Source [54, Gallauer et al. 2009]

Figure 2.34: Simplified process of a thermal gas oil unit

The resulting vacuum flashed cracked residue (VFCR) has a high sulphur content and can only be used as fuel in the refinery power plant if equipped with an efficient and appropriately sized flue-gas cleaning system.

2.23 New high conversion techniques

Residue upgrading has great importance among refiners due to a continued decrease in demand for high sulphur fuel oil (HSFO) and a great demand for higher volumes and quality of middle distillates. In addition, the price differential between light/sweet and heavy/sour crudes is driving operators to process larger volumes of heavy crudes.

Refiners and engineering firms aim to minimise fuel oil production at minimum investment and operating costs. The technology options available for residue upgrading depend on the difficulty of the feed to be processed, whether it is atmospheric (AR) or vacuum residue (VR), the metal contents and the level of conversion desired.

There has not been any technology breakthrough, only marginal improvements on proven technologies. Final results will depend on how the integration within units is done.

The following tables summarise those processes that have experienced recent improvements regarding residue conversion and/or valorisation:

Table 2.12: Conversion techniques grouped by feed and chemical engineering approach

Feed	Carbon rejection	H ₂ addition	Partial Oxidation
Vacuum GO	FCC	H ₂ Cracking	
Vacuum Residue	Coking Visbreaking SDA RFCC	ARDS/VRDS H-Oil HCK HDHplus	Gasification
<i>Source: [EIPPCB review]</i>			

Table 2.13: Examples of recent improvements made by several conversion techniques

BREF Section	Technique names	Technical description	Advantage	Drawbacks
3	Solvent Deasphalting	Separates by molecular weight	Separates residue from deasphalted oil	High post treatment
5	FCC upgrade	Better catalysts enable heavier/wider feedstocks		
	Residue FCC/Deep C.C	Fluidised process, 2 stage regenerator	Cost effective	
7	Delayed Coker	Low pressure low recycling, low coke	High flexibility and high conversion to lighter	Uses much water; Harder to sell coke at fair price and high capital cost
10	IGCC/Gasification		Valorisation of waste to Syngas	
10	Circulating Fluid Bed Boiler (CFB)	Coke valorisation at low emission	Cogen possible	Solid handling
13	Atmospheric residue DS	Optimised catalyst combination		High investment and Ops cost
13	Vacuum residue DS	Higher ppH ₂		High investment and Ops cost
13	Slurry HC.	Disperse phase catalyst and elevated temp	Selective conversion, minimum residue	
13	Residue HC./ebullated bed HC	Fixed bed+HT catalysts	Reduces metals, sulphur, CCR, produces high distillates	
22	Visbreaking	Rapid heat in furnace and cracked for a specific residence time in a soaking zone	Reduce viscosity, lower capital cost	High post treatment, low conversion to light
22	Thermal GO/deep thermal conversion	Lower temp, special internal for backmixing	Selective cracking, lower investment cost	

2.24 Techniques for the elimination and the valorisation of external waste used as a secondary raw material

There is an increasing role played by the refineries in recycling waste oil, not only managing their own residues but also valorising external waste.

The following wastes are partly use as feedstock in the EU refineries:

- Re-refining of waste oil:

Used oil from different applications is first collected and then part of it is sent back to refineries. In 2006, in the EU, this recycling effort represented only a 0.1 % of the crude oil feedstock, however this initiative is growing.

The largest group of end users that are recycling oil are auto repair shops, large industrial consumers of lubricants (e.g. ironworks, mines, power plants and electricity distribution networks), and large transportation fleets. Table 2.14 shows the order of magnitude by quantities by country.

- Recycling of waste rubber of asphalt grades

There is a large volume of spent tyres in EU. In some processes, tyres are converted into powder and then mixed with asphalt grades.

- Waste oil hydrogenated in refineries:

For more in depth description, see Chapter 6, (hydro)Isomerisation. There are some examples of the recycling of animal and vegetable oil (waste) by using retrofitted desulphurisation units: e.g. Cepsa (Spain) started in 2011 and plan a 100 000 m³/year production. Oil is hydrogenated and then mixed in diesel gasoline grades.

Table 2.14: Re-refining waste oil in Europe

Member state	Collected waste oil in 2006 (tonnes)	Distillation of waste oil (tonnes)			
		Re-refining (base oil)	Burning (replacing coal)	Burning (replacing heavy fuel oil)(*)	Other/ unknown
Austria	39 596	12 396	24 700	2 500	
Belgium	60 000	15 000	500	25 000	19 500
Bulgaria	17 000			1 200	15 800
Cyprus	4 300			4 300	
Czech Republic	32 867	986	4 800	27 081	
Denmark	20 000	15 500	2 000	2 500	
Estonia	5 400		11 250	2 700	
Finland	22 500		39 130	11 250	
France	224 759	99 403	70 000	61 439	24 787
Germany	525 000	135 000		295 000	25 000
Greece	36 000	36 000			
Hungary	27 823		6 000	7 823	14 000
Ireland	20 000				20 000
Italy	216 300	172 600		34 600	9 100
Latvia	11 000		5 500	5 500	
Lithuania	14 000		7 000	7 000	
Luxembourg	5 364	5 364		0	
Malta	1 200				1 200
Netherlands	50 000	18 000		32 000	
Poland	76 500	63 500	3 000	10 000	
Portugal	28 700	6 800	3 550	13 550	4 800
Romania	27 663		9 500	16 147	2 016
Slovenia	3 967			3 499	468
Slovakia	15 000		6 000	9 000	
Spain	216 045	140 084		74 362	1 599
Sweden	45 000	8 000	37 000		
United Kingdom	350 000			270 000	80 000
Total:	2 095 984	728 633	232 630	916 451	218 270
Percentage (%)	100 %	35 %	11 %	44 %	10 %

(*) Including direct burning and simple treatment
Source: GEIR 2008 quoted by Oköpol – 2008

2.25 Techniques for the abatement of emissions

There are many non-production techniques in use in a refinery. Particularly relevant, for this document, are those techniques used to control and abate emissions to air, water and soil. Descriptions of many of these techniques can be found in the CWW BREF [6, EC 2003]. These techniques are not described in this chapter because they are typically techniques that might be considered in the determination of BAT and consequently are extensively described and analysed in Chapter 4 (See Sections 4.23 and 4.24).

Even if some preventive techniques or primary measures can also be implemented, pollutants such as NO_x, particulates, H₂S, SO₂, other sulphur compounds and VOC, among others, are typically abated by end-of-pipe techniques. One of the largest systems within a refinery is the abatement of H₂S produced on-site. These systems typically contain an amine scrubbing system and a sulphur-recovery unit to convert H₂S into sulphur, a by-product produced within refineries.

Flares are another technique used within the refinery for safety and environmental reasons. Techniques for the abatement of odour and noise are also relevant for refineries. Specific information on flare systems can be found in the CWW BREF [6, EC 2003].

Most refineries treat waste water on-site using end-of-pipe waste water treatment facilities prior to discharge. However, several refineries utilise off-site waste water treatment services. Both on-site and off-site waste water treatment facilities reduce the amounts of pollutants that are discharged into the receiving environment.

Refineries also generate solid wastes. Some of them are recycled within the refinery, others (e.g. catalysts) are recycled by specialist companies and others are disposed of. Soil contamination prevention techniques are also relevant to the whole refinery.

WORKING DRAFT IN PROGRESS

3 CURRENT EMISSION AND CONSUMPTION LEVELS

This chapter provides data and information about current emission and consumption levels in existing installations at the time of writing (2009 – 2013). Because it covers many types and sizes of refineries, the data are very wide-ranging. The goal of the chapter is to bring together, the emission and consumption levels of the refinery as a whole and for each specific process. The data cited will, in most cases, enable an estimate of the concentration and load of emissions, in turn enabling a competent authority issuing a permit to verify the information provided in the permit application.

Section 3.1 gives an overview of the main emissions and consumptions of European refineries as a whole. It is not a simple aggregation of the emissions and consumptions in the other sections: most of them cannot be aggregated because of the varying integration of processes in refineries.

Sections 3.2 to 3.22 cover the emissions and consumptions from the various processes/activities covered by this document. Sections 3.23 to 3.25 cover the emissions generated by the techniques used to abate emissions, including the emissions from sulphur recovery units. The chapter ends with a section on monitoring, which covers the monitoring systems typically applied in refineries and provides some discussion on their application.

3.1 Current emission and consumption levels in refineries as a whole

Refineries are industrial sites that manage huge amounts of raw materials and products and are also intensive consumers of energy and water. From storage and the refining process they generate emissions to the atmosphere and to water and they may also potentially pollute the soil.

This chapter addresses these three media, and the pollutants that affect them, and is a summary of the emissions from all refinery processes. The main environmental problems were mentioned in Chapter 1 (Section 1.4), but without figures. This section aims to quantify refinery emissions.

Although the principal raw material input to petroleum refineries is crude oil, refineries use and generate a large number of chemicals, some of which leave the facilities as discharges of air emissions, waste water or solid waste. Pollutants generated typically include ammonia (NH₃), carbon dioxide (CO₂), carbon monoxide (CO), hydrogen sulphide (H₂S), metals, nitrogen oxides (NO_x), particulates, spent acids (e.g. HF, H₂SO₄), sulphur oxides (SO_x), volatile organic compounds (VOC) and numerous other organic compounds.

Figure 3.1 shows a simplified example of what is consumed and emitted by a refinery. This figure only focuses on the main typical pollutants, among more than 90 specific compounds that have already been identified as likely to be generated by refining processes and activities [161, USAEPA 1995]. The great majority are pollutants to air. In this figure, low values in the ranges normally correspond to refineries with abatement techniques and good environmental performance and practises, whereas high values typically correspond to refineries without abatement techniques.

Table 3.1 shows the environmental accounts of refinery processes, and provides a summary of the impact on the different media from the different activities found within refineries.

Table 3.1: Environmental accounts of refinery processes

Process/Functional unit	Environmental item						
	Air	Waste water	Waste	Substances and energy	Waste heat	Noise	Safety
Fundamental processes							
Delivery	—	—	—	—	—	0	X
Loading	X	—	—	—	—	X	X
Storage	X	0	X	0	0	—	X
Process furnaces	X	—	0	X	X	X	X
Separation processes							
Crude oil atmospheric distillation unit	X	X	0	X	X	0	X
Vacuum distillation unit	X	X	0	X	X	0	X
Gas separation unit	X	0	0	0	0	0	X
Conversion processes							
Thermal cracking, visbreaking	X	X	0	X	X	0	X
Delayed coking	X	X	X	X	X	X	X
Catalytic cracking	X	X	X	X	X	0	X
Hydrocracking	X	X	X	X	X	0	X
Bitumen blowing	X	X	X	X	X	0	X
Reforming	X	X	X	X	X	0	X
Isomerisation	X	X	X	X	X	0	X
MTBE production	X	X	X	X	0	0	X
Alkylation	X	0	X	X	0	0	X
Refining processes							
Hydrosulphurisation	X	X	X	X	X	0	X
Sweetening	X	X	X	X	0	0	X
Gas washing	X	0	X	X	0	0	X
Lubricating oil production	X	X	X	X	0	0	X
Extractions							
- with solvents	X	0	0	X	0	—	X
- with molecular sieves	X	—	X	X	0	—	X
Other processes							
Sulphur plant	X	X	0	0	0	0	X
Flare	X	X	0	0	0	X	X
Cooling tower	X	X	0	0	0	0	0
Waste water treatment	X	X	X	X	0	—	0
Blending units	X	X	0	0	0	—	X
Off-gas clean up (Exhaust gas recovery unit)	X	X	X	0	0	0	X
NB: X: high impact 0: small impact —: very small or no impact							
Source: [222, UBA 2000]							

3.1.1 Present consumption levels in refineries

3.1.1.1 Energy

General information

Petroleum refining is one of the most energy-intensive industries. In a country like the US, refining activities account for 28 % of the energy consumed by industry.

Energy is required by the combustion systems and process units. The largest energy use is of internal or external fuels in a combustion plant, which can be up to 200 MW thermal input in size. Some refineries use Combined Heat and Power (CHP) units to raise some of their steam and electricity. Such units may be operated by third parties and export some of their energy. Also they may use commercial rather than internal refinery fuels. Processes such as catalytic cracking can provide energy from the burn off of coke, usually supplemented by internal fuel for efficient heat recovery. Sulphur removal from products is energy intensive as it requires hydrogen production.

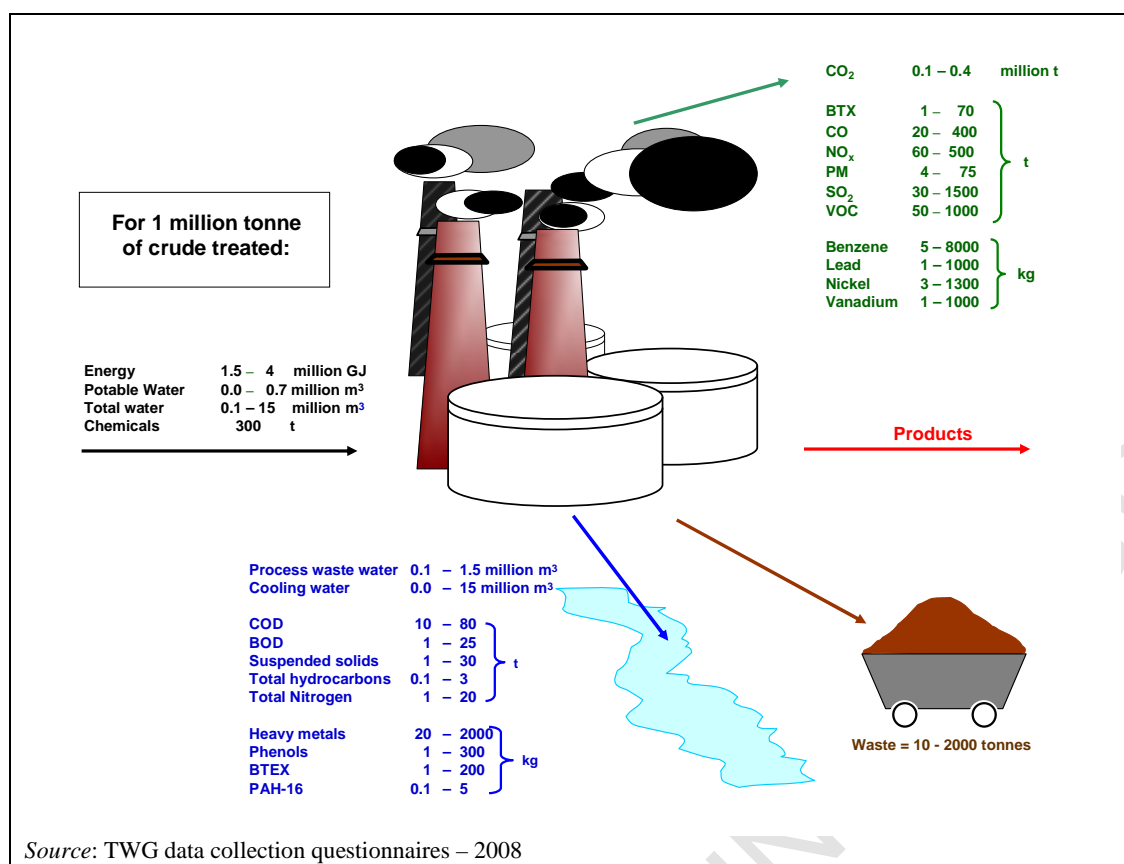


Figure 3.1: Example of specific emissions and consumptions in European refineries

The actual specific consumptions of a sample of European refineries in recent years are shown in Table 3.2., ranging from 1.5 – 4.0 GJ/t of crude, with an average of 2.75. Around 3 – 9 % of the crude feedstock received is burnt in the refinery. As shown on Figure 3.3, the site's overall CO₂ emissions are rather narrowly correlated to specific consumption.

Growing impact of desulphurisation processes

Processes that have the greatest throughput dominate energy consumption; atmospheric distillation and, to a lesser extent, vacuum distillation units represent together 35 to 40 % of the total process energy consumed in a refinery. However, it can be noted from Figure 3.2 that energy consumption is also clearly related to the sulphur input recovered from the overall refinery feedstock, linked to the fact that, on average, another 20 – 25 % of this energy is spent in hydrotreating.

Figure 3.2 gives the distribution of energy consumption for each main process typically operated in US refineries, calculated as an average from the 146 refineries that were operated in 2001 [68, Worrell et al. 2005]. In this graphic, all data are expressed in primary energy (see the graphic footnotes).

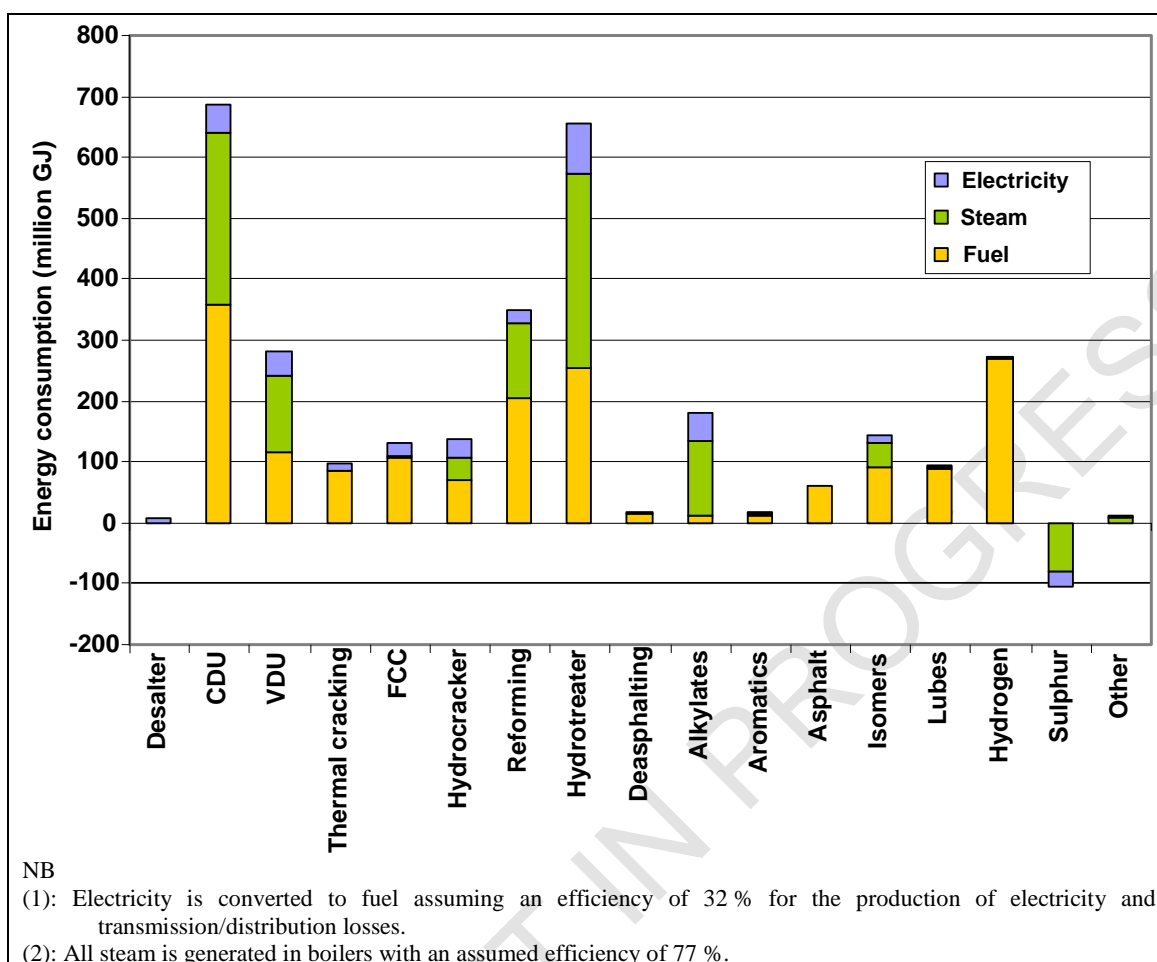


Figure 3.2: Estimated primary energy consumption distributed by refining process in the US

Impact of site complexity

It is interesting to notice on Figure 3.3 that, despite quite a large dispersion of values, there is also a clear general trend for most complex sites to be associated with highest specific energy consumptions.

Use of natural gas

A growing part of necessary energy comes from the supply of external fuels, especially natural gas which is used in 31 out of these 48 refineries (64.5 % of the sample). Natural gas represents on average 17 %, and up to 82 % of the overall consumption of the sites concerned. As shown in Figure 3.4, there is no obvious correlation between the part of total gaseous fuels (RFG + eventual external supply of natural gas) and the specific energy consumption. However, refineries where natural gas is the most intensively used are usually operating recent CHP power plants for their steam delivery; it is then not surprising that the largest natural gas use closely correlates with the best specific energy consumptions.

Table 3.2: Specific energy consumption and other relevant data for a selection of EU refineries

	Questionnaire label	Nelson index	Total feedstock refined	Net thermal energy used	Specific energy consumption	Specific CO ₂ emission	Natural gas/total energy	Total gaseous fuels/total energy	S emitted/S input (%)
	N°		kt	10 ⁶ GJ	GJ/t	t/t	%	%	%
	1	6.2	9096	42.04	4.6	0.31	7 % ^(*)	52 % ^(*)	NA
	2	11.2	606	NA	NA	0.28	1 %	6 %	3.8 %
	3	5.7	3483	5.85	1.7	0.13	0 %	92 %	5.3 %
	4	3.1	4900	8.37	1.7	0.10	0 %	100 %	0.8 %
	5	6.8	2772	5.75	2.1	0.15	0 %	100 %	2.0 %
	6	13.5	12400	43.26	3.5	0.24	82 %	89 %	2.2 %
	7	6.4	3268	7.05	2.2	0.15	0 %	96 %	5.9 %
	8		953	3.25	3.4	0.27	35 %	35 %	5.9 %
	9	6.6	5727	12.11	2.1	0.14	3 %	86 %	4.9 %
	10	6.8	8852	22.13	2.5	0.16	8 %	67 %	7.5 %
	11	6.2	9350	20.41	2.2	0.16	10 %	68 %	4.9 %
	12	9.0	6412	20.77	3.2	0.22	0 %	61 %	13.4 %
	13	6.0	5303	16.45	3.1	0.25	3 %	74 %	11.2 %
	14	9.3	16552	60.95	3.7	0.24	41 %	85 %	5.2 %
	15	6.9	4858	12.09	2.5	0.15	0 %	73 %	10.8 %
	16	8.7	7153	21.01	2.9	0.17	9 %	78 %	6.2 %
	17	4.0	728	1.94	2.7	0.23	0 %	63 %	10.2 %
	18	12.9	8272	19.05	2.3	0.17	28 %	100 %	0.8 %
	19	5.1	3359	NA	NA	0.11	NA	NA	NA
	20	12.9	9243	28.92	3.1	0.22	13 %	71 %	4.9 %
	21	13.1	5627	43.05	7.7	0.69	1 %	29 %	3.5 %
	22	7.2	8635	25.71	3.0	0.25	4 %	89 %	3.0 %
	23	8.4	NA	NA	NA	NA	0 %	92 %	NA
	24	4.9	8653	5.84	0.7	0.10	0 %	54 %	2.7 %
	25	9.7	3613	7.84	2.2	0.14	34 %	97 %	0.5 %
	26	10.8	10193	28.10	2.8	0.23	2 %	84 %	1.1 %
	27	10.8	19151	68.50	3.6	0.29	29 %	78 %	2.5 %
	28	9.4	14251	50.25	3.5	0.26	41 %	54 %	2.6 %
	29	9.4	3817	13.80	3.6	0.27	0 %	41 %	13.9 %
	30	6.3	10490	24.07	2.3	0.20	2 %	50 %	4.4 %
	31	6.7	12087	31.34	2.6	0.17	0 %	64 %	3.7 %
	32	11.4	5886	14.23	2.4	0.20	29 %	74 %	4.5 %
	33	4.6	4610	9.43	2.0	0.14	0 %	46 %	3.0 %
	34	8.6	10462	28.81	2.8	0.23	7 %	58 %	3.8 %
	35	5.7	3624	9.74	2.7	0.18	27 %	51 %	7.0 %
	36	10.1	5622	17.63	3.1	0.24	0 %	46 %	4.1 %
	37	9.5	7293	22.02	3.0	0.22	17 %	67 %	3.3 %
	38	7.3	8183	20.44	2.5	0.17	4 %	59 %	7.4 %
	39	8.2	10098	22.98	2.3	0.18	0 %	99 %	0.2 %
	40	6.2	5668	9.45	1.7	0.10	7 %	89 %	0.6 %
	41	6.5	3942	9.10	2.3	0.13	0 %	100 %	0.3 %
	42	12.0	10916	28.64	2.6	0.17	3 %	100 %	6.2 %
	43	8.7	15474	46.57	3.0	0.20	22 %	70 %	7.9 %
	44	1.6	4410	NA	NA	0.59	0 %	1 %	5.2 %
	45	8.4	10050	37.80	3.8	0.27	0 %	59 %	18.9 %
	46	6.2	9712	24.42	2.5	0.18	20 %	82 %	8.6 %
	47	11.6	11871	25.19	NA	0.20	0 %	76 %	11.6 %
	48	8.4	6900	10.85	1.6	0.53	0 %	44 %	1.7 %
	49	5.7	15000	32.00	2.1	0.14	25 %	100 %	3.2 %
	50	10.5	4620	13.88	3.0	0.20	0 %	95 %	4.5 %
	51	8.4	4400	14.40	3.3	0.22	6 %	95 %	8.4 %
	52	10.9	4990	9.77	2.0	0.26	3 %	89 %	4.7 %
	53	3.8	NA	6.20	NA	NA	0 %	91 %	NA
	54	5.4	10794	NA	NA	0.15	NA	NA	NA
	55	5.1	940	NA	NA	NA	0 %	25 %	0.7 %
	56	12.4	6276	11.81	1.9	0.18	3 %	48 %	3.0 %
Number of values	56	55	54	50	48	53	53	53	51

		Total feedstock refined	Net thermal energy used	Specific energy consumption	Specific CO ₂ emission	Natural gas/total energy	Total gaseous fuels/total energy	S emitted/S input (%)
		kt	10 ⁶ GJ	GJ/t	t/t	%	%	%
Minimum		606	2	0.67	0.10	0.0 %	0.9 %	0.2 %
Maximum		19 151	69	7.65	0.69	82.3 %	100 %	18.9 %
Average		7 436	22	2.75	0.22	9.8 %	70.5 %	5.1 %
Sum		401 544	1 075					
5th Percentile				1.67	0.106	0.0 %	27.4 %	0.6 %
95th Percentile				3.73	0.395	37.1 %	100 %	12.5 %

NA: these data have not been made available to the TWG
 Source: TWG data collection for 2008 except (*) 2009

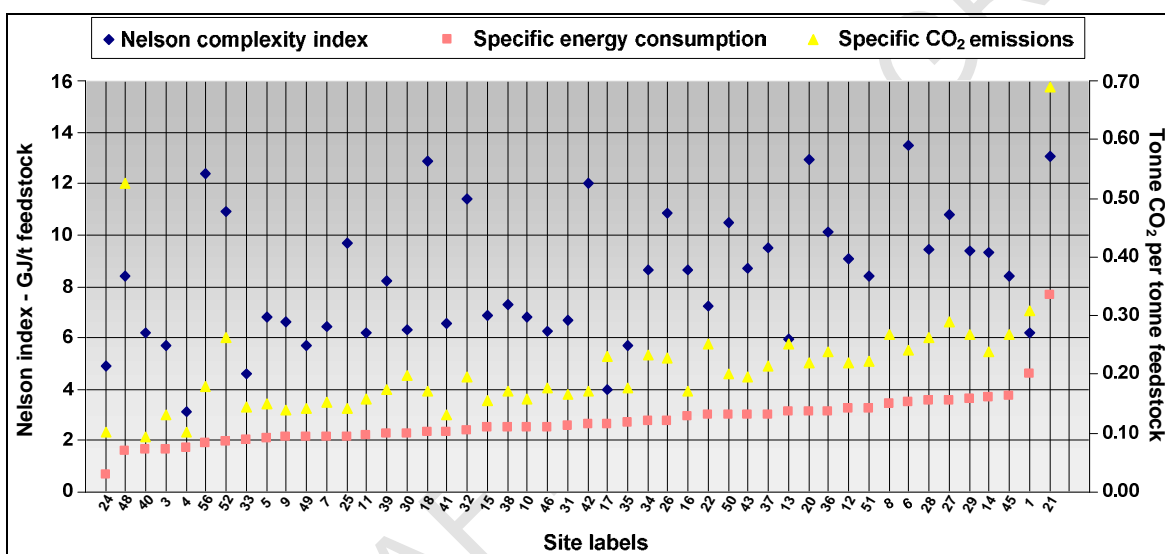


Figure 3.3: Specific energy consumption compared to CO₂ emissions and site complexity for a sample of EU refineries

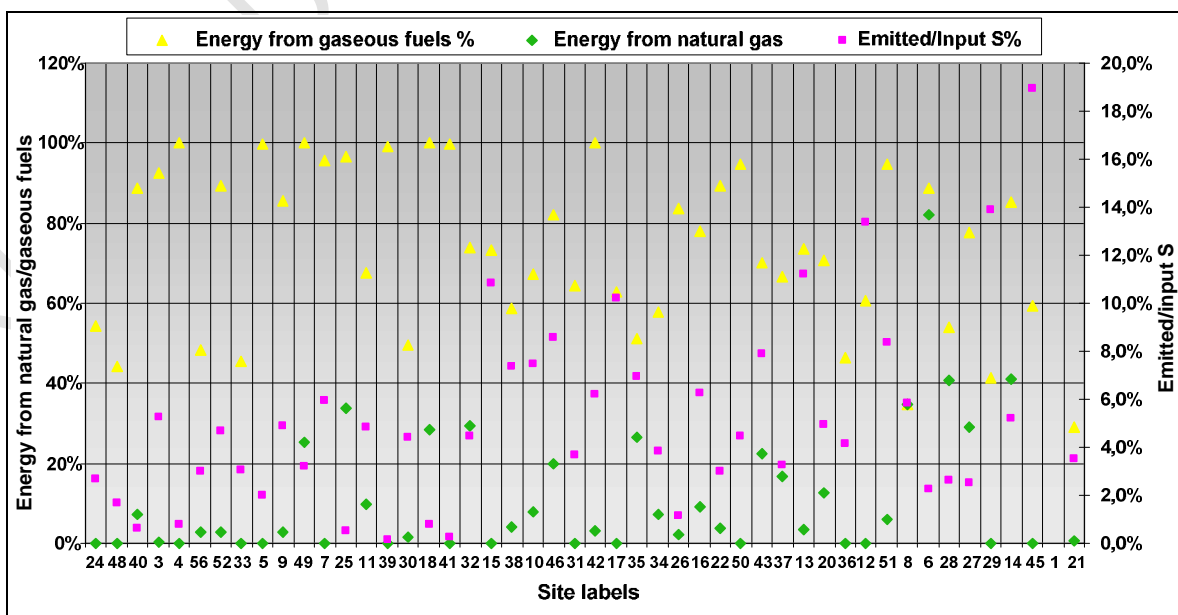


Figure 3.4: Use of gaseous fuels and emitted part of sulphur input for a sample of EU refineries sorted by ascending order of specific energy consumption

3.1.1.2 Water

Water and steam are mainly used:

- in the various refinery processes, to assist the distillation process or the cracking of hydrocarbons, in overhead systems, and for washing, scrubbing, quenching or (steam) stripping. The desalter is the biggest user, and the main producer of waste water in oil refineries (with the exception of base oil refineries);
- for tank and flare seal drains;
- for cleaning operations;
- for steam generation as a feedstock for boilers and CHPs;
- for cooling systems.

From a qualitative point of view, the first three categories of use generate the main part of the organic load which must be abated in the WWTP, since the water will have been in direct contact with hydrocarbons and is usually contaminated. This type of water is typically referred to as process water. On the other hand, from a quantitative point of view, the amount of water used depends primarily on the type of refinery and, especially, on the cooling systems used: closed, open recirculating, or once-through systems.

Actual specific usage of water of a sample of European refineries are displayed in Table 3.3. Most of it (90 % of the data - from the 5th to 95th percentiles) ranged between 0.2 and 25 m³/t of feedstock refined. The largest part (more than 50 % on average) is still used for cooling. As well, as shown in Figure 3.5, the highest specific usage (above 1 m³/t) at the site level are always determined by the highest cooling usage. They relate to sites where the greatest proportion of once-through cooling circuits are still used.

Potable water from public supply represents, on average, 3 % of the overall usage of these refineries, but its use varies greatly. Some sites do not use any potable water, while other sites fully rely upon it, including for purposes other than sanitary use.

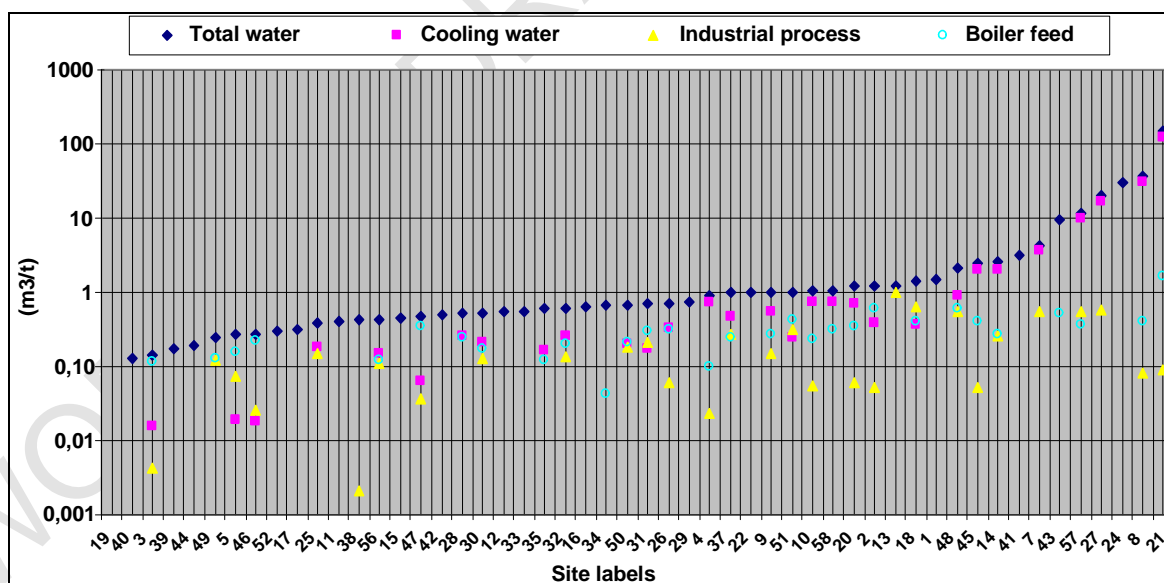


Figure 3.5: Specific water usage data for a selection of European refineries

Table 3.3: Water consumption data for a set of European refineries

Site label	Nelson Index	Total water consumed	Specific water consumption	Water for industrial processes			Water for boilers feed			Water for cooling systems			Proportion of use of fresh water		
		Mm ³ /yr	m ³ /t	m ³ /yr	%	m ³ /t	m ³ /yr	%	m ³ /t	m ³ /yr	%	m ³ /t	m ³ /yr	%	m ³ /t
1	6.2	13.50	1.48	NA			NA			NA			NA		
2	11.2	0.74	1.22	31 000	4.2 %	0.05	360 000	49 %	0.59	235 000	32 %	0.39	41 750	5.6 %	0.07
3	5.7	0.50	0.14	15 000	3.0 %	0.004	412 000	83 %	0.12	55 000	11 %	0.02	495 500	100 %	0.14
4	3.1	4.42	0.90	117 000	2.6 %	0.02	500 000	11 %	0.10	3 780 000	86 %	0.77	25 000	0.6 %	0.01
5	6.8	0.74	0.27	204 000	27.5 %	0.07	432 000	58 %	0.16	54 000	7 %	0.02	743 000	100 %	0.27
7	6.4	13.65	4.18	1 802 816	13.2 %	0.55	NA			11 808 517	86 %	3.61	41 200	0.3 %	0.01
8	NA	35.81	37.56	79 504	0.2 %	0.08	383 091	1 %	0.40	34 845 753	97 %	36.55	463 677	1.3 %	0.49
9	6.6	5.79	1.01	873 560	15.1 %	0.15	1 581 120	27 %	0.28	3 162 240	55 %	0.55	0	0.0 %	0.00
10	6.8	9.20	1.04	477 856	5.2 %	0.05	2 030 890	22 %	0.23	6 649 878	72 %	0.75	40 308	0.4 %	0.00
11	6.2	3.77	0.40	NA			NA			NA			3 766 686	100 %	0.40
12	9.0	3.46	0.54	NA			NA			NA			70 208	2.0 %	0.01
13	6.0	6.58	1.24	5 384 185	81.8 %	1.02	NA			NA			50 904	0.8 %	0.01
14	9.3	42.47	2.57	4 351 435	10.2 %	0.26	4 457 867	10 %	0.27	33 576 647	79 %	2.03	81 020	0.2 %	0.00
15	6.9	2.16	0.44	NA			NA			NA			274 169	12.7 %	0.06
16	8.7	4.66	0.65	NA			NA			NA			55 787	1.2 %	0.01
17	4.0	0.23	0.31	NA			NA			NA			226 180	100 %	0.31
18	12.9	11.90	1.44	5 306 385	44.6 %	0.64	3 297 800	28 %	0.40	3 038 516	26 %	0.37	255 746	2.1 %	0.03
20	12.9	11.02	1.19	574 218	5.2 %	0.06	3 232 352	29 %	0.35	6 552 703	59 %	0.71	0	0.0 %	0.00
21	13.1	842.09	149.65	497 281	0.1 %	0.09	9 447 040	1 %	1.68	831 672 535	99 %	147.80	474 469	0.1 %	0.08
22	7.2	8.62	1.00	NA			NA			NA			0	0.0 %	0.00
23	8.4	17.97	NA	NA			NA			NA			12 881	0.1 %	NA
24	4.9	266.18	30.76	NA			NA			NA			435 714	0.2 %	0.05
25	9.7	1.40	0.39	547 000	39.0 %	0.15	NA			653 000	47 %	0.18	547 000	39.0 %	0.15
26	10.8	7.19	0.71	623 664	8.7 %	0.06	3 162 240	44 %	0.31	3 408 192	47 %	0.33	7 194 096	100 %	0.71
27	10.8	388.84	20.30	11 028 626	2.8 %	0.58	NA			377 541 509	97 %	19.71	11 294 307	2.9 %	0.59
28	9.4	7.38	0.52	NA			3 510 671	48 %	0.25	3 722 846	50 %	0.26	0	0.0 %	0.00
29	9.4	2.89	0.76	NA			NA			NA			67 035	2.3 %	0.02
30	6.3	5.54	0.53	1 358 440	24.5 %	0.13	1 824 770	33 %	0.17	2 274 000	41 %	0.22	82 580	1.5 %	0.01
31	6.7	8.35	0.69	2 595 498	31.1 %	0.21	3 604 606	43 %	0.30	2 144 738	26 %	0.18	28 1000	3.4 %	0.02
32	11.4	3.51	0.60	799 098	22.8 %	0.14	1 158 205	33 %	0.20	1 509 710	43 %	0.26	0	0.0 %	0.00
33	4.6	2.56	0.55	NA			NA			NA			1 465 000	57.3 %	0.32
34	8.6	6.90	0.66	NA			441 049	6 %	0.04	NA			6 902 700	100 %	0.66
35	5.7	2.15	0.59	NA			451 435	21 %	0.12	600 219	28 %	0.17	551 648	25.6 %	0.15

Site label	Nelson Index	Total water consumed	Specific water consumption	Water for industrial processes			Water for boilers feed			Water for cooling systems			Proportion of use of fresh water		
		Mm ³ /yr	m ³ /t	m ³ /yr	%	m ³ /t	m ³ /yr	%	m ³ /t	m ³ /yr	%	m ³ /t	m ³ /yr	%	m ³ /t
37	9.5	7.14	0.98	1952263	27.3 %	0.27	1760370	25 %	0.24	3415251	48 %	0.47	4799449	67.2 %	0.66
38	7.3	3.46	0.42	17000	0.5 %	0.002	NA			NA			142000	4.1 %	0.02
39	8.2	1.75	0.17	NA			NA			NA			0	0.0 %	0.00
40	6.2	0.72	0.13	NA			NA			NA			721000	100 %	0.13
41	6.5	12.41	3.15	NA			NA			NA			1171395	9.4 %	0.30
42	12.0	5.41	0.50	NA			NA			NA			125681	2.3 %	0.01
43	8.7	148.39	9.59	NA			8201500	6 %	0.53	NA			450000	0.3 %	0.03
44	1.6	0.85	0.19	NA			NA			NA			14100	1.6 %	0.00
45	8.4	24.87	2.47	530000	2.1 %	0.05	4016000	16 %	0.40	20260000	81 %	2.02	35000	0.1 %	0.00
46	6.2	2.69	0.28	252957	9.4 %	0.03	2200270	82 %	0.23	175800	7 %	0.02	59697	2.2 %	0.01
47	11.6	5.52	0.46	431427	7.8 %	0.04	4076298	74 %	0.34	748275	14 %	0.06	262800	4.8 %	0.02
48	8.4	14.85	2.15	3861846	26.0 %	0.56	4214512	28 %	0.61	6140076	41 %	0.89	8713325	58.7 %	1.26
49	5.7	3.70	0.25	1795317	48.5 %	0.12	1909028	52 %	0.13	NA			3704345	100 %	0.25
50	10.5	3.10	0.67	859919	27.7 %	0.19	984095	32 %	0.21	934425	30 %	0.20	0	0.0 %	0.00
51	8.4	4.50	1.02	1402658	31.2 %	0.32	1837388	41 %	0.42	1074965	24 %	0.24	2337675	52.0 %	0.53
52	10.9	1.48	0.30	NA			NA			NA			34124	2.3 %	0.01
53	3.8	0.96	NA	557000	58.2 %	NA	400000	42 %	NA	NA			450000	47.0 %	NA
56	12.4	2.70	0.43	680236	25.2 %	0.11	768017	28 %	0.12	928026	34 %	0.15	0	0.0 %	0.00
57	8.2	68.84	11.91	3109536	4.5 %	0.54	2073024	3 %	0.36	63572370	92 %	11.00	84802	0.1 %	0.01
58	10.2	12.15	1.06	NA			3613982	30 %	0.32	8284316	68 %	0.72	248923	2.0 %	0.02
Number of values:	57	53	51	31	31	30	31	31	30	30	30	30	52	52	50
Minimum:		0.23	0.13	15000	0.06 %	0.002	360000	1 %	0.04	54000	7 %	0.02	0	0.0 %	0.00
Maximum:		842	149.65	11028626	81.8 %	1.02	9447040	83 %	1.68	831672535	99 %	147.80	11294307	100 %	1.26
Average:		39	5.89	1681185	19.7 %	0.22	2462633	32 %	0.33	47760617	51 %	7.69	1140267	23.3 %	0.16
5th percentile		0.73	0.18	24000	0.36 %	0.013	391546	2 %	0.110	109360	9 %	0.019	0	0.0 %	0.000
95th percentile		196	25.53	5345285	53.3 %	0.612	6329684	78 %	0.603	236255396	97 %	28.97	7033828	100 %	0.659

Source: [TWG data collection questionnaires]

Figure 3.6 shows in more detail, and with a linear scale instead of the logarithmic one used in Figure 3.5, a breakdown of the main water usages for the sub-sample of European refineries for which this information was fully available. What appears is the rather constant water use related to the boiler feed in all of these sites, regardless of their increasing total site usage. Furthermore, this figure clearly displays the beneficial effect of the closed-loop cooling system on the site's overall specific usage.

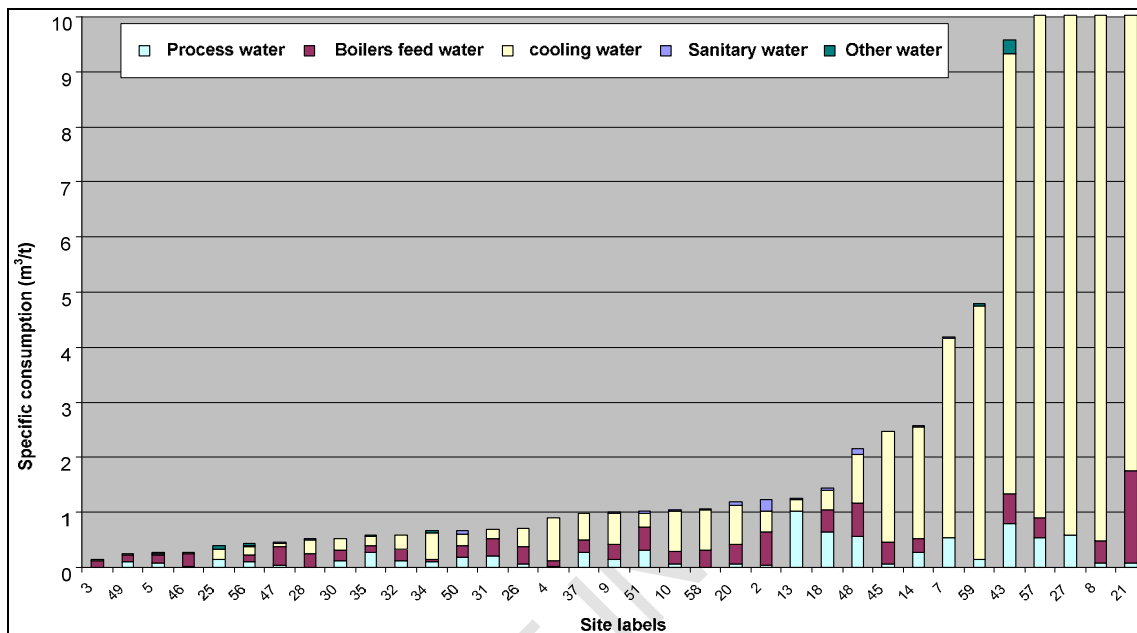


Figure 3.6: Water specific consumption breakdown for a sample of European refineries

3.1.2 Emissions to air

The main air emissions from a refinery are CO₂, SO_x, NO_x, VOC and particulates (dust, soot and associated heavy metals (mainly V and Ni)). However, noise, odour, H₂S, NH₃, CO, CS₂, benzene, toluene, dioxins, HF and HCl also contribute to the air emissions. They emerge typically from sources such as stacks of process furnaces and boilers, regenerators (FCC), individual items such as valves and pump seals, and to a lesser extent from flares and incinerator stacks. Some documents establish emissions factors for the calculation of air emissions from refineries. [181, USAEPA 1996], [172, MRI 1997] The E-PRTR regulation [74, EC 2010] required refineries to make inventories and report annual emissions of a large number of substances since 2007.

3.1.2.1 Carbon dioxide emissions

Almost all of the carbon present in crude oil, once produced from the oil well, will be converted into CO₂. A small portion (<3 – 10 %) of the CO₂ will be converted in the refinery during the processing of crude oil into marketable products. The remainder will be converted into CO₂ once the refined oil products are sold and subsequently consumed by the various sectors of industry and private consumers.

In 2007, oil refineries in the EU-27 (Romania and Bulgaria excluded) emitted around 135 Mt of CO₂. In 1990 these figures were respectively 115 Mt of CO₂ and 91 %. The 15 % increase of CO₂ emissions between 1990 and 2007 is mainly linked to the increasing average site complexity, the diversification of refining processes and the significant increase of hydrotreatment capacities for deeper product desulphurisation and conversion.

The share of CO₂ emissions from oil refining in the total greenhouse gas emissions was, in 2007, around 3 % at the EU-15 level. At the individual Member State level, it ranged from around 0.5 % (for Ireland) to 5 % (for the Netherlands).

Actual specific emissions of a sample of European refineries for recent years are displayed in Table 3.2 in Section 3.1.1.1. The largest part (90 % of them from the 5th to 95th percentiles) range within 0.11 – 0.39 t/t of feedstock processed, with an average of 0.22. As shown in Figure 3.3, highest values are often associated with the most complex sites.

At the individual site level, CO₂ emissions by themselves ranged from 0.168 to 5.547 million tonnes per year. However, the lowest and highest emissions originate from two refineries with nearly the same CO₂ specific emissions (0.28 – 0.29 t/t), which is close to the European average.

The main emission sources for CO₂ are the process furnaces and boilers, gas turbines, FCC regenerators, flare systems and incinerators.

3.1.2.2 Nitrogen oxides emissions

The term NO_x, by convention, only refers to NO (nitrogen monoxide) and NO₂ (nitrogen dioxide). N₂O can be also found in flue-gases from FCCs and some SCR. In most combustion processes NO contributes to over 90 % of the total NO_x. However, as it is rapidly oxidised to NO₂ in the atmosphere, emissions of NO are expressed as NO₂.

Contributing processes and units

Based on the information gathered by the TWG, the following Figure 3.7 and Figure 3.8 display site-level data on the NO_x specific emissions and the main NO_x contributing units and processes within a sample of European refineries. The main emission sources of NO_x are combustion processes, i.e.: process furnaces and boilers, CHP and gas turbines, FCC regenerators, and to a lesser extent, eventual waste gas incinerators and the flare system. However, the respective weights of these units in the overall site emissions are highly variable, as shown in the same figures.

In the case of refineries without an FCC unit, the major NO_x contribution obviously comes from furnaces and boilers, which account most often for about 60 – 90 % of emissions, as shown in Figure 3.7. Gas turbines and CHP, when they are operated on such plants, are responsible for a significant part (30 – 50 %) of NO_x emissions, and are associated with the highest specific emissions at the site level. SRU and flare systems usually account for less than 5 – 10 % of emissions.

In the case of a refinery configuration including an FCC unit, furnaces and boilers remain the major NO_x contributors and generate 50 – 80 % of site emissions, while the FCC by itself may only represent 15 – 25 % of them. As displayed in Figure 3.8, most of the remainder is emitted by CHP and gas turbines which, as stated above, are clearly related to highest specific emissions reported.

When operating a coker, coking emissions can also represent a very significant contribution (up to 40 %) which appear here in the ‘Other’ category.

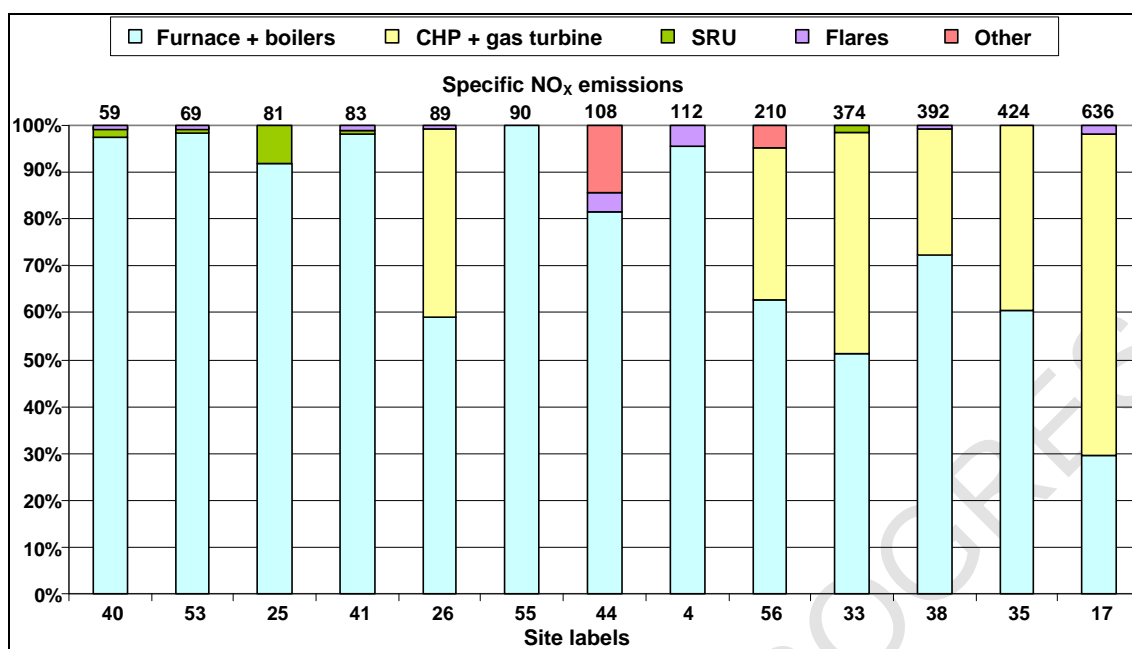


Figure 3.7: Respective weights of the main NO_x-contributing processes for 12 European refineries not operating an FCC unit as a function of their specific emissions (g/t of feed)

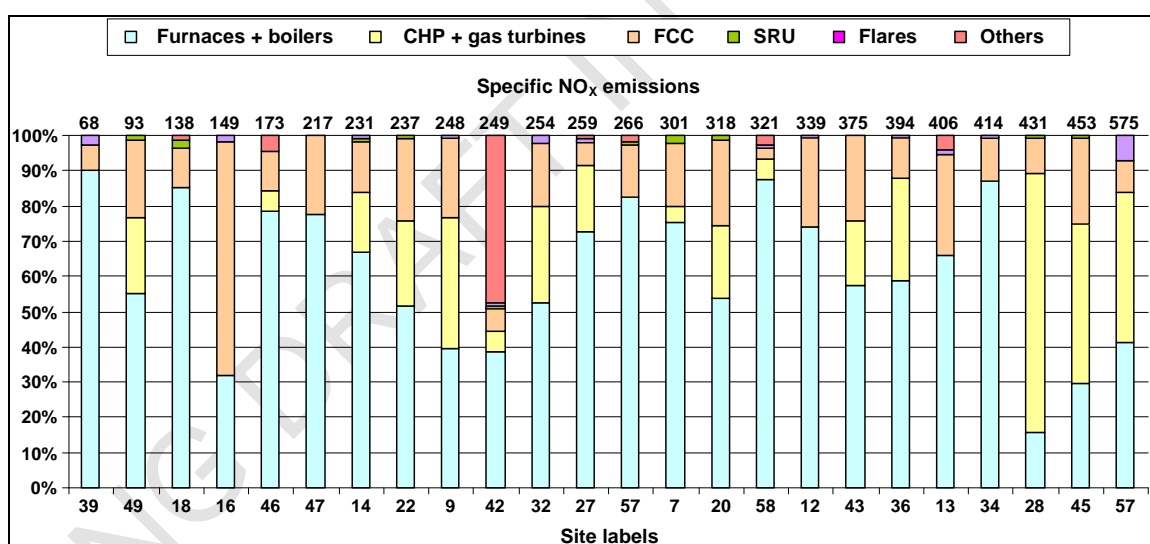


Figure 3.8: Respective weights of the main NO_x-contributing processes for 24 European refineries operating an FCC unit as a function of their specific emissions (g/t of feed)

Influence of the overall site configuration on NO_x emissions

The range of NO_x emissions reported for the site sample displayed in Figure 3.9 within the period 2007 – 2008 is approximately 100 – 6000 tonnes per year. The specific emission range of NO_x varies from 68 – 575 tonnes of NO_x per million tonnes of crude oil processed, with most of these refineries (80 % of data – from the 10th to 90th percentiles) emitting within the range of 100 – 450 g/t. The average specific emissions achieved within the particular subgroup of refineries without an FCC is 258 g/t processed. This average only increases to up to 269 g/t processed (+4 %) for the subgroup operating an FCC. Therefore, FCC configurations should not be considered noticeably increasing NO_x emissions at the site level.

Figure 3.9 displays the distribution of the Nelson index and the specific energy consumption for these two subgroups of European refineries, each of them ordered by ascending specific NO_x

emission. No obvious correlation can be seen as far as the Nelson index is concerned, and the specific NO_x emissions of non-FCC sites and FCC sites evolve basically in the same range of 60 – 600 g/t of feedstock processed. And, for both categories of refineries, the highest specific NO_x emissions are clearly associated with the highest specific energy consumptions.

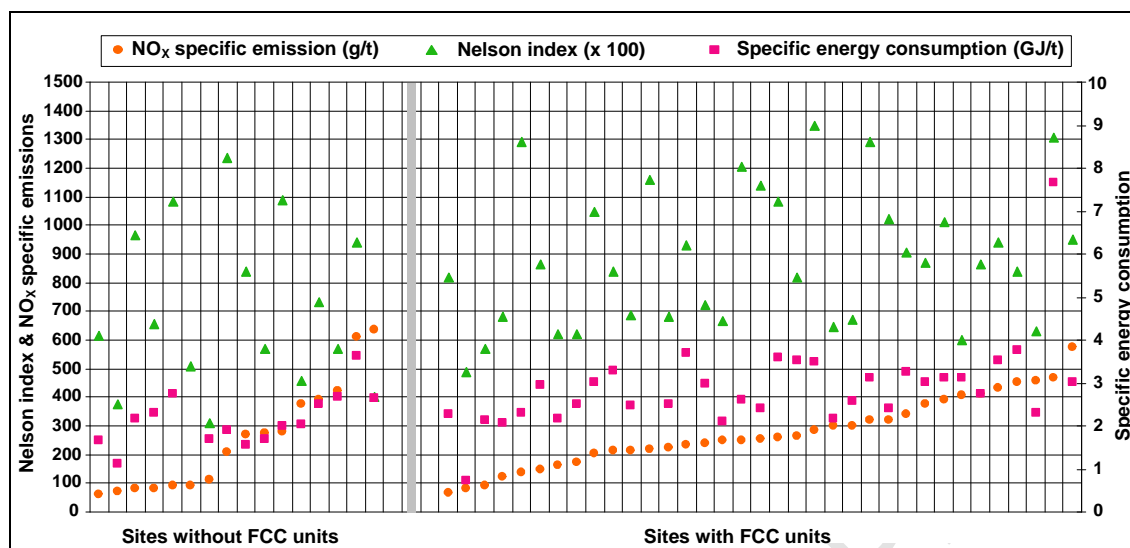


Figure 3.9: Influence of the configuration, complexity and specific energy consumption on NO_x emissions

Influence of the refinery fuel mix on NO_x emissions

NO_x emissions from refineries depend on the fuel type (nitrogen or hydrogen content of fuel), combustor equipment design, NO_x control system, and operating conditions. In the particular case of FCC regenerator flue-gas, NO_x emissions are, in general, not thermal NO_x produced by the interference of air-contained nitrogen in high temperature combustion, but are directly linked to the nitrogen content in the feedstock. Accordingly, large differences in the NO_x emission levels can be expected between refineries and even between different combustion installations at the same refinery at different times. Nevertheless, general trends can be observed showing a rather clear correlation between NO_x emissions and the use of gaseous fuels for energy system firing: as shown in Figure 3.10, the highest values of NO_x specific emissions recorded within a sample of 51 European refineries are associated with the lowest percentages of energy coming from gaseous fuels in the fuel mix used at these sites (regardless of the part taken by the eventual natural gas external supply in these gaseous fuels).

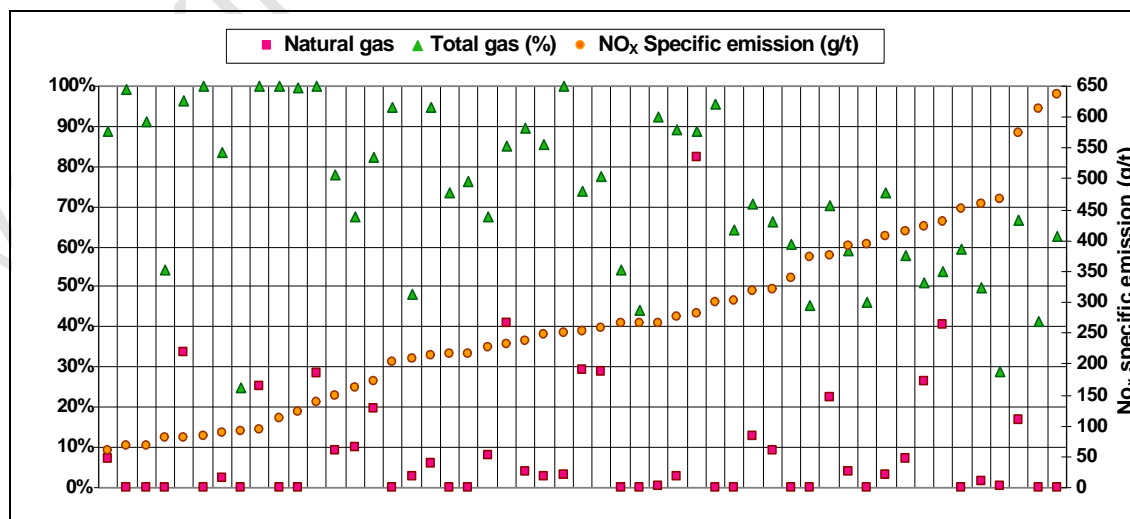


Figure 3.10: Influence of the gaseous fuels used for energy supply on the site NO_x emissionsTable 3.4: NO_x emissions and main contributing unit data for 58 European refineries

Questionnaire	Nelson Index	FCC (yes=1)?	Year	Total NO _x		NO _x specific emission		Furnace + boilers		CHP + stand alone gas turbines		FCC		SRU		Flares		Others	
				t/yr	g/t	t/yr	%	t/yr	%	t/yr	%	t/yr	%	t/yr	%	t/yr	%	t/yr	%
40	6.2	0	2008	337	59	328	97 %	-	-	-	-	7.7	2.3 %	0.8	0.2 %	0	-		
53	3.8	0	2008	380	69 ⁽¹⁾	375	99 %	-	-	-	-	3	0.8 %	2	0.5 %	0	-		
25	9.7	0	2007	294	81	270	92 %	-	-	-	-	24.2	8.2 %	NA	-	0	-		
41	6.5	0	2008	329	83	323	98 %	-	-	-	-	2	0.6 %	4	1.2 %	0	-		
26	10.8	0	2008	910	89	536	59 %	366	40 %	-	-	1.66	0.2 %	5.75	0.6 %	0	-		
55	5.1	0	2008	85	90	85	100 %	NA	-	-	-	NA	-	NA	-	NA	-		
44	1.6	0	2007	476	108	389	82 %	-	-	-	-	0	-	18	3.8 %	69	14.5 %		
4	3.1	0	2008	548	112	523	95 %	-	-	-	-	0	-	25	4.6 %	0	-		
56	12.4	0	2008	1317	210	824	63 %	431	33 %	-	-	0	-	NA	-	61	4.6 %		
19	5.1	0	2008	773	230	NA	-	NA	-	-	-	NA	-	NA	-	NA	-		
48	8.4	0	2007	1842	267	NA	-	NA	-	-	-	NA	-	NA	-	NA	-		
3	5.7	0	2006	931	267	NA	-	NA	-	-	-	NA	-	NA	-	NA	-		
2	11.2	0	2007	165	272	NA	-	NA	-	-	-	NA	-	NA	-	NA	-		
52	10.9	0	2008	1384	277	NA	-	NA	-	-	-	NA	-	NA	-	NA	-		
33	4.6	0	2008	1725	374	887	51 %	814	47 %	-	-	24	1.4 %	NA	-	0	-		
38	7.3	0	2008	3208	392	2316	72 %	870	27 %	-	-	0	-	22	0.7 %	0	-		
35	5.7	0	2008	1535	424	927	60 %	609	40 %	-	-	0	-	NA	-	0	-		
8	NA	0	2008	477	500	476	100 %	-	-	-	-	-	-	NA	-	0	-		
29	9.4	0	2007	2337	612	NA	-	NA	-	-	-	NA	-	NA	-	NA	-		
17	4.0	0	2008	463	636	136	29 %	318	69 %	-	-	-	-	9	1.9 %	0	-		
23	8.4	0	2007	1030	(²)	NA	-	NA	-	-	-	NA	-	NA	-	NA	-		
39	8.2	1	2008	687	68	620	90 %	-	-	48	7 %	0	-	19	2.8 %	0	-		
24	4.9	1	2007	694	80	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-		
49	5.7	1	2008	1400	93	760	54 %	300	21 %	300	21 %	20	1.4 %	NA	-	0	-		
5	6.8	1	2008	343	124	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-		
1	6.2	1	2008	1203	132	NA	-	564	47 %	53	4 %	NA	-	NA	-	NA	-		
18	12.9	1	2007	1144	138	959	84 %	-	-	127	11 %	20.7	1.8 %	NA	-	17.65	1.5 %		
16	8.7	1	2008	1064	149	340	32 %	-	-	702	66 %	0	-	21.28	2.0 %	0	-		
11	6.2	1	2008	1512	162	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-		
46	6.2	1	2008	1685	173	1322	78 %	101	6 %	187	11 %	-	-	NA	-	75	4.5 %		
54	5.4	1	2007	1930	179	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-		
50	10.5	1	2008	944	204	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-		
51	8.4	1	2007	939	213	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-		
15	6.9	1	2007	1049	216	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-		
47	11.6	1	2008	2577	217	2002	78 %	-	-	575	22 %	-	-	NA	-	0	-		
10	6.8	1	2007	2002	226	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-		
14	9.3	1	2008	3831	231	2554	67 %	661	17 %	540	14 %	34	0.9 %	42	1.1 %	0	-		
22	7.2	1	2007	2047	237	1052	51 %	498	24 %	481	23 %	17.4	0.8 %	NA	-	0	-		
9	6.6	1	2008	1418	248	557	39 %	532	38 %	324	23 %	0	0.0 %	4.9	0.3 %	0	-		
42	12.0	1	2008	2723	249	1056	39 %	154	6 %	178	7 %	21	0.8 %	21	0.8 %	1293	47.5 %		
32	11.4	1	2008	1494	254	783	52 %	410	27 %	265	18 %	-	0.0 %	36	2.4 %	0	-		
27	10.8	1	2006	4959	259	3608	73 %	920	19 %	357	7 %	14	0.3 %	16	0.3 %	44	0.9 %		
57	8.2	1	2008	1535	266	1261	82 %	-	-	229	15 %	13	0.8 %	0.8	0.1 %	28	1.8 %		
6	13.5	1	2008	3508	283	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-		
7	6.4	1	2008	984	301	742	75 %	43	4 %	177	18 %	22	2.2 %	NA	-	0	-		
31	6.7	1	2008	3654	302	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-		

Questionnaire	Nelson Index	FCC (yes=1)?	Year	Total NOx		Furnace + boilers		CHP + standalone gas turbines		FCC		SRU		Flares		Others		
				t/yr	g/t	t/yr	%	t/yr	%	t/yr	%	t/yr	%	t/yr	%	t/yr	%	
20	12.9	1	2007	2942	318	1589	54 %	607	21 %	706	24 %	40	1.4 %	NA	-	0	-	
58	10.2	1	2008	3667	321	3201	87 %	218	6 %	122	3 %	-	-	29	0.8 %	98	2.7 %	
12	9.0	1	2008	2175	339	1608	74 %	-	-	561	26 %	-	-	NA	-	5.89	0.3 %	
43	8.7	1	2008	5803	375	3339	58 %	1068	18 %	1396	24 %	0	0.0 %	NA	-	0	-	
36	10.1	1	2008	2213	394	1304	59 %	644	29 %	252	11 %	0	0.0 %	14	0.6 %	0	-	
13	6.0	1	2008	2155	406	1419	66 %	-	-	618	29 %	NA	-	27.6	1.3 %	89	4.1 %	
34	8.6	1	2007	4333	414	3785	87 %	-	-	542	13 %	NA	-	22.27	0.5 %	0	-	
28	9.4	1	2008	6147	431	968	16 %	4523	74 %	626	10 %	30	0.5 %	-	-	0	-	
45	8.4	1	2008	4550	453	1340	29 %	2080	46 %	1125	25 %	10	0.2 %	4	0.1 %	0	-	
30	6.3	1	2007	4826	460	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-	
21	13.1	1	2007	2634	468	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-	
37	9.5	1	2008	4197	575	1728	41 %	1792	43 %	381	9 %	1.2	0.03 %	294.2	7.0 %	0	-	
Number of values:			58	58	58	57	38	34	24	24	25	25	21	21	22	22	10	10
Sum (kt):			-	-	111.5	-	46292	-	18523	-	10873	-	306	-	639	-	1781	-
Minimum:			-	-	85	59	85	16 %	0	0 %	48	3 %	0	0 %	0.8	0.1 %	6	0.3 %
5th Percentile:			-	-	369	78	250	29 %	52	5 %	67	5 %	0	0.0 %	0.9	0.2 %	11	0.5 %
50th Percentile:			-	-	1923	249	943	69 %	548	27 %	357	15 %	14	0.8 %	19	0.8 %	65	3.4 %
95th Percentile:			-	-	4238	515	3379	99 %	2037	65 %	1041	28 %	34	2.3 %	42	4.5 %	755	32.6 %
Maximum:			-	-	6147	636	3785	100 %	4523	74 %	1396	66 %	40	8 %	294	7 %	1293	47 %

(¹) Based on 90 % of the production capacity.
(²) The annual feedstock refined has not been made available to the TWG.
NA These data have not been made available to the TWG.
(-) Not applicable.
Source: TWG data collection questionnaires

3.1.2.3 Particulate emissions

The concern with particulate emissions (including heavy metals) stems from health effects. The main emission sources are process furnaces/boilers (mainly these fired with (liquid) heavy fuel oil), catalytic cracker regenerators, coke plants, incinerators, decoking and soot blowing of furnaces and flares. As shown, the range of emissions found in most European refineries (5th to 95th percentiles within a sample of 43 plants) is approximately from 20 to 700 tonnes of particulates emitted per year, which correspond with a specific emission range from 4 to 75 tonnes of particulates per million tonnes of crude oil processed. The lower emission value can be achieved in refineries burning substantial amounts of gas or when effective dedusting devices (e.g. ESP) are used.

Table 3.5: Specific emission ranges of PM, PM₁₀ and PM_{2.5} for 43 European refineries

Type of particulates	Unit	Specific load		No
		5th – 95th percentile	50th percentile	
PM (total)	g/t	4 – 75	181	43
PM ₁₀	g/t	0.1 – 45	15	25
PM _{2.5}	g/t	0.01 – 12	4	4

Important heavy metals in crude oils are arsenic, mercury, nickel and vanadium. Nickel and vanadium are enriched in the residues during distillation (see Table 3.55 in Section 3.10.2) and are removed with the particulate matter by ESP or fabric filters after combustion in the furnaces or after the regeneration of catalysts by burning off. Data on metal emissions collected from a sample of European refineries are available in Table 3.12.

3.1.2.4 Sulphur oxides emissions

Sulphur emissions to the atmosphere have long been an issue for refineries. All crude oils contain sulphur compounds. Consequently, when firing non- or partially desulphurised refinery fuels, SO_2 and SO_3 are emitted. There is a direct relation between the sulphur content of the fuel and the amount of SO_x emitted (for example, a fuel with 1 % sulphur generates a flue-gas with around 1700 mg/Nm^3 of SO_x). The sulphur, which is not extracted from the products in the refinery, will remain in the various products and will be burnt to SO_x by the various end-users. The refinery, as a consumer of fuel for its energy use, similarly emits SO_x . However, natural gas, as a growing external energy supply in oil refining, normally contains only traces of sulphur compounds.

Sulphur input/output mass balance

The sulphur output distribution can vary greatly depending on FCC unit, furnace and boiler operation modes, SRU and hydrotreater performances and the overall share of products not for combustion.

According to a 2006 investigation by CONCAWE based on 67 European refineries (accounting for 68 % of the crude and intermediate feedstock refined in the OECD), 156 kt of sulphur have been emitted to air (i.e. 312 kt of SO_2 after oxidation) out of a 4183 kt total sulphur intake, representing 3.73 % of sulphur emitted and 45.1 % of sulphur recovered, as shown in Figure 3.11. A similar survey based on 2010 data from 61 refineries shows an increase in the percentage of the recovered sulphur to 55.4 %.

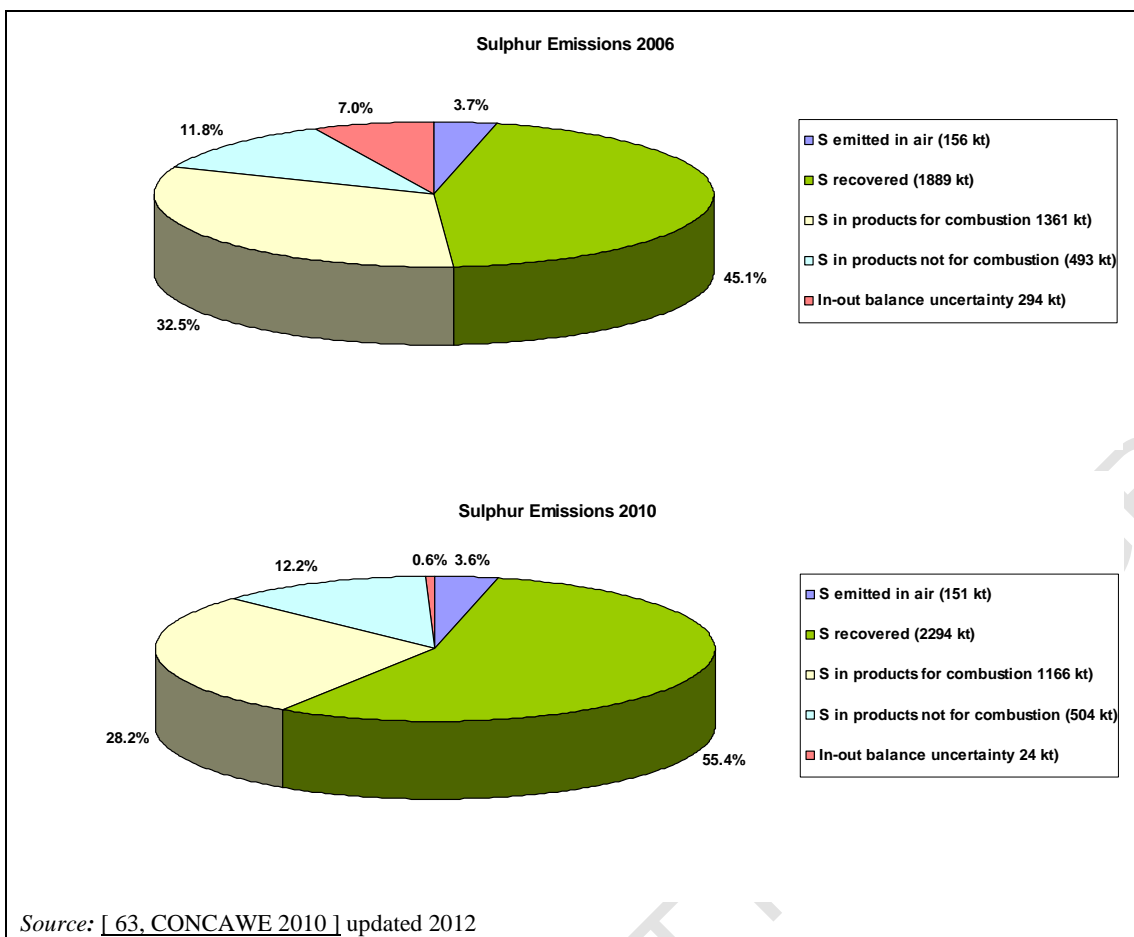


Figure 3.11: Average sulphur output distribution from a sample of European refineries

Moreover, based on the information gathered by the TWG, the following Table 3.6 displays site-level data on the sulphur input, specific emissions and the fuels used in a set of 49 European refineries. Within this sample, the median percentage of sulphur emitted in the air is 4.4 % and the median percentage of sulphur recovered by the SRUs is 44.7 % of the refinery sulphur input (see Section 3.23.2 on emissions from SRU). These two values are very close to the ratios displayed in Figure 3.11. It means that this European sample is representative of the European global situation as reflected in the CONCAWE survey.

Table 3.6: Sulphur balance and specific emissions to air for a sample of 49 European refineries

Questionnaire (1)	Specific SO ₂ (g/t crude treated) (2)	Sulphur in crude (%)	Sulphur in intermediate products (%)	Sulphur input in feedstock (t) (3)	Sulphur input in external fuels (t)	Total Sulphur input (t)	Sulphur in RFG (ppm)	Sulphur in liquid fuel (%)	RFG/total fuel burnt (%)	Natural gas/Total fuel burnt (%)	Total gas/Total fuel burnt (%)	Sulphur emitted in air/input (%)
41	12	0.22	-	8672	0	8672	15	0.68	100	0	100	0.3
40	29	0.24	NA	12984	0	12984	19	0.40	82	7	89	0.6
39	34	1.10	NA	106458	0	106458	24	0.002	99	0	99	0.2
4	79	0.50	-	24500	0	24500	100	-	100	0	100	0.8
18	161	1.22	0.05	86856	0	86857	647	0.09	72	28	100	0.8
25	225	2.16	0.50	75685	0	75685	3200	1.87	63	34	97	0.5
24	254	0.62	0.13	40517	0	40517	288	0.81	54	0	54	2.7
44	259	0.25	-	11025	0	11025	6	0.49	1	0	1	5.2
55	266	2.00	-	18800	0	18800	NA	0.35	25	0	25	0.7
3	268	0.25	0.30	8816	0	8816	168	0.40	92	0	92	5.3
26	304	1.30	-	132506	3522	136027	516	-	81	2	84	1.1
49	322	0.50	-	75000	0	75000	950	-	75	25	100	3.2
6	428	1.00	0.80	118020	19	118039	20	0.80	6	82	89	2.2
48	435	1.30	-	89700	0	89700	20	NA	44	0	44	1.7
52	441	0.50	0.20	23480	0	23480	400	0.10	86	3	89	4.7
42	466	0.40	0.30	41086	0	41086	87	-	97	3	100	6.2
51	502	0.30	-	13200	0	13200	20	NA	89	6	95	8.4
5	514	1.30	-	36036	0	36036	500	1.00	100	0	100	2.0
33	518	0.85	-	39185	0	39185	1300	0.67	46	0	46	3.0
22	540	0.90	-	77715	0	77715	100	1.60	85	4	89	3.0
50	639	0.70	1.20	32940	0	32940	500	0.96	95	0	95	4.5
15	667	0.30	0.50	14946	0	14946	500	0.37	73	0	73	10.8
28	678	1.30	NA	184874	1	184874	10	1.08	13	41	54	2.6
7	724	0.61	-	19935	0	19935	5	0.63	96	0	96	5.9
9	741	0.74	1.50	43262	0	43262	44	1.60	83	3	86	4.9
11	777	0.80	-	74800	0	74800	100	1.12	58	10	68	4.9
47	789	0.32	0.45	40390	0	40390	47	0.8	76	0	76	11.6
27	870	1.68	2.50	331841	0	331841	652	1.28	49	29	78	2.5
32	908	1.10	0.60	59569	0	59569	1177	1.80	45	29	74	4.5
46	960	0.46	2.00	54408	0	54408	49	0.96	62	20	82	8.6
14	966	0.86	2.00	153941	0	153941	800	1.28	44	41	85	5.2
31	980	1.36	0.50	161135	0	161135	800	0.86	64	0	64	3.7
16	999	0.80	-	57226	0	57226	2000	1.00	69	9	78	6.2
13	1037	0.47	0.03	24497	0	24497	393	0.69	70	3	74	11.2
20	1045	1.00	1.70	97730	0	97730	10	0.87	58	13	71	4.9
30	1062	1.15	1.50	125595	0	125595	0	1.50	48	2	50	4.4
45	1117	0.30	0.10	29650	0	29650	350	1.2	59	0	59	18.9
2	1119	1.40	-	8484	327	8811	1000	1.00	5	1	6	3.8
43	1162	0.74	0.05	113959	0	113959	2123	1.79	48	22	70	7.9
10	1183	0.80	0.70	69905	0	69905	NA	1.90	60	8	67	7.5
36	1210	1.65	0.50	82303	0	82303	0.76	1.0	46	0	46	4.1
37	1242	1.91	-	139304	0	139304	49	1.46	50	17	67	3.3
12	1271	0.30	1.85	30474	0	30474	50	1.30	61	0	61	13.4
17	1370	0.67	-	4878	0	4878	16300	1.12	63	0	63	10.2
35	1443	1.04	NA	37551	0	37551	0	1.71	25	27	51	7.0
34	1530	1.99	-	208188	0	208188	50	1.95	51	7	58	3.8
38	1589	1.09	NA	88233	0	88233	4900	1.40	55	4	59	7.4
21	2417	3.10	2.30	157588	34220	191807	380	1.26	29	1	29	3.5
29	2564	1.05	NA	35244	0	35244	0	2.28	41	0	41	13.9

Questionnaire ⁽¹⁾	Specific SO ₂ (g/t crude treated) ⁽²⁾	Sulphur in crude (%)	Sulphur in intermediate products (%)	Sulphur input in feedstock (t) ⁽³⁾	Sulphur input in external fuels (t)	Total Sulphur input (t)	Sulphur in RFG (ppm)	Sulphur in liquid fuel (%)	RFG/total fuel burnt (%)	Natural gas/Total fuel burnt (%)	Total gas/Total fuel burnt (%)	Sulphur emitted in air/input (%)
Number of values	49	49	26	49	49	49	47	43	49	49	49	49
Average	798	0.95	0.86	71900		72677	865	1.06	61	9.8	71	5.2
5th percentile	52	0.25	0.035	8729	0	8813	0.228	0.125	9	0.0	27	0.5
50th percentile	741	0.85	0.5	54408	0	54408	100	1	61	3.0	74	4.4
95th percentile	1565	2	2	175378	204	189034	2877	2	100	38.2	100	12.7

(¹) Refineries with no atmospheric distillation are excluded.
(²) The feedstock is calculated as the sum of crude oil and eventual intermediates, with no specific ponderation.
(³) When not available (3 sites), the sulphur content of intermediates has been assumed equal to the site crude oil.
NA These data have not been made available to TWG .
(-) Not applicable.
Source: [TWG data collection questionnaires]

Main contributing processes and units

The main emission sources of SO₂ are the process furnaces/boilers, sulphur recovery units, FCC regenerators, flares, waste water stripping and incondensable off-gas incinerators, decoking operations and coke calcination. The CONCAWE 2006 investigation already referred to in this section gives an average distribution of the SO_x emissions from the 67 refineries studied, as shown in Table 3.7.

Table 3.7: SO₂ breakdown by main contributing units as an average from a sample of 67 European refineries

SO ₂ emitted by:	Percentage of the sulphur refinery intake	Approximate percentage of refinery SO ₂ emissions
Fuel fired in furnaces/boilers	1.8 %	48 %
FCC units	0.4 %	11 %
Sulphur recovery units	0.6 %	16 %
Flares	0.7 %	20 %
Miscellaneous	0.2 %	5 %
Total:	3.7 %	100 %

For further details, site-level individual data collected through TWG questionnaires have been summarised in Table 3.8 for 57 European refineries. The first part of the table corresponds to the group of sites which do not operate an FCC unit, while FCC sites are gathered in the second part of this table (next page). These data show the distribution of SO₂ emissions according to the main contributing units or processes.

Table 3.8: SO₂ emissions and main contributing units for a sample of 57 European refineries

Site label	Nelson Index	FCC (yes=1)	Year	Total SO ₂		Furnaces + boilers		CHPs + standalone gas turbines		FCC		SRU		Flares		Other	
				t/yr	%	t/yr	%	t/yr	%	t/yr	%	t/yr	%	t/yr	%	t/yr	%
41	6.5	0	2008	49	0.3 %	5	10 %	NA	-	-	-	36	73 %	8	16 %	0	0 %
25	9.7	0	2007	812	0.5 %	568	70 %	-	-	-	-	244	30 %	0	0 %	0	0 %
40	6.2	0	2008	162	0.6 %	158	98 %	0	0 %	-	-	4	2 %	0.02	0 %	0	0 %
55	5.1	0	2008	250	0.7 %	111	44 %	NA	-	-	-	142	57 %	NA	-	0	0 %
4	3.1	0	2008	386	0.8 %	76	20 %	0	0 %	-	-	0	0 %	310.2	80 %	0	0 %
26	10.8	0	2008	3101	1.1 %	2639	85 %	289	9.3 %	-	-	5	0.2 %	169	5 %	0	0 %
48	8.4	0	2007	3000	1.7 %	NA	-	NA	-	-	-	NA	-	NA	-	NA	-
56	12.4	0	2008	5022	3.0 %	3603	72 %	1351	27 %	-	-	NA	-	NA	-	68	1 %
33	4.6	0	2008	2386	3.0 %	1746	73 %	188	8 %	-	-	452	19 %	NA	-	0	0 %
2	11.2	0	2007	678	3.8 %	NA	-	-	-	-	-	NA	-	NA	-	NA	-
52	10.9	0	2008	2199	4.7 %	NA	-	NA	-	-	-	NA	-	NA	-	NA	-
44	1.6	0	2007	1144	5.2 %	429	37 %	0	0 %	-	-	NA	-	4.6	0 %	711	62 %
3	5.7	0	2006	932	5.3 %	NA	-	NA	-	-	-	NA	-	NA	-	NA	-
35	5.7	0	2008	5228	7.0 %	3980	76 %	2	0.04 %	-	-	278	5 %	870	17 %	98	2 %
38	7.3	0	2008	13002	7.4 %	9737	75 %	80	0.62 %	-	-	2006	15 %	1179	9 %	0	0 %
17	4.0	0	2008	997	10.2 %	866	87 %	49	4.9 %	-	-	0	0 %	82	8 %	0	0 %
29	9.4	0	2007	9789	13.9 %	9637	98 %	NA	-	-	-	0	0 %	0	0 %	0	0 %
19	5.1	0	2008	981	NA	NA	-	NA	-	-	-	NA	-	NA	-	NA	-
23	8.4	0	2007	4818	NA	NA	-	NA	-	-	-	NA	-	NA	-	NA	-
53	3.8	0	2008	675	NA	50	7 %	0	0 %	-	-	575	85 %	50	7 %	0	0 %
39	8.2	1	2008	346	0.2 %	38	11 %	0	0 %	68	20 %	102	29 %	138	40 %	0	0 %
18	12.9	1	2007	1331	0.8 %	304	23 %	0	0 %	42	3 %	941	71 %	0	0 %	39	3 %
5	6.8	1	2008	1424	2.0 %	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-
6	13.5	1	2008	5302	2.2 %	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-
27	10.8	1	2006	16653	2.5 %	8337	50 %	32	0.19 %	2630	16 %	312	2 %	4955	30 %	388	2 %
28	9.4	1	2008	9668	2.6 %	152	2 %	8424	87 %	251	3 %	841	9 %	0	0 %	0	0 %
24	4.9	1	2007	2195	2.7 %	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-
22	7.2	1	2007	4665	3.0 %	1621	35 %	131	2.8 %	1110	24 %	1802	39 %	NA	-	0	0 %
49	5.7	1	2008	4823	3.2 %	NA	-	NA	-	3200	66 %	200	4 %	NA	-	NA	-
37	9.5	1	2008	9055	3.3 %	4706	52 %	0	0 %	303	3 %	3430	38 %	616	7 %	0	0 %
21	13.1	1	2007	13602	3.5 %	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-
31	6.7	1	2008	11847	3.7 %	5098	43 %	143	1.2 %	896	8 %	5710	48 %	NA	-	0	0 %
34	8.6	1	2007	16008	3.8 %	11587	72 %	0	0 %	2137	13 %	2283	14 %	0.2	0 %	0	0 %
36	10.1	1	2008	6801	4.1 %	3470	51 %	241	3.5 %	941	14 %	2018	30 %	NA	-	131	2 %
30	6.3	1	2007	11138	4.4 %	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-
50	10.5	1	2008	2951	4.5 %	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-
32	11.4	1	2008	5347	4.5 %	4193	78 %	3	0.06 %	708	13 %	340	6 %	103	2 %	0	0 %
57	8.2	1	2008	8402	4.6 %	2781	33 %	0	0 %	2243	27 %	2142	25 %	244	3 %	993	12 %
11	6.2	1	2008	7263	4.9 %	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-
9	6.6	1	2008	4245	4.9 %	1560	37 %	0	0 %	986	23 %	1688	40 %	11	0 %	0	0 %
20	12.9	1	2007	9658	4.9 %	3537	37 %	0	0 %	4911	51 %	976	10 %	231	2 %	0	0 %
14	9.3	1	2008	15991	5.2 %	9475	59 %	0	0 %	2121	13 %	2604	16 %	1791	11 %	0	0 %
7	6.4	1	2008	2365	5.9 %	733	31 %	0	0 %	658	28 %	943	40 %	31	1 %	0	0 %
42	12.0	1	2008	5089	6.2 %	113	2 %	2	0.04 %	970	19 %	1535	30 %	449	9 %	2020	40 %
16	8.7	1	2008	7148	6.2 %	2525	35 %	0	0 %	864	12 %	1771	25 %	336	5 %	1652	23 %
10	6.8	1	2007	10469	7.5 %	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-
43	8.7	1	2008	17979	7.9 %	9218	51 %	194	1.1 %	3779	21 %	4632	26 %	156	1 %	0	0 %
51	8.4	1	2007	2210	8.4 %	NA	-	NA	-	NA	-	NA	-	NA	-	NA	-
46	6.2	1	2008	9326	8.6 %	1784	19 %	0	0 %	1929	21 %	1331	14 %	1475	16 %	2807	30 %

Site label	Nelson Index	FCC (yes=1)	Year	Total SO ₂	S emitted/S input (%)	Furnaces + boilers	CHPs + standalone gas turbines	FCC	SRU	Flares	Other					
15	6.9	1	2007	3 239	10.8 %	1 328 41 %	0 0 %	543 17 %	582.9 18 %	32.4 1 %	753 23 %					
13	6.0	1	2008	5 499	11.2 %	1 591 29 %	0 0 %	602 11 %	1 527 28 %	167 3 %	1 611 29 %					
47	11.6	1	2008	9 365	11.6 %	3 061 33 %	0 0 %	1 712 18 %	1 096 12 %	20 0 %	3 477 37 %					
12	9.0	1	2008	8 151	13.4 %	5 903 72 %	0 0 %	1 652 20 %	421 5 %	166 2 %	9 0 %					
45	8.4	1	2008	11 230	18.9 %	6 874 61 %	0 0 %	3 595 32 %	760 7 %	0 0 %	0 0 %					
54	5.4	1	2007	729	NA	NA -	NA -	NA -	NA -	NA -	NA -					
1	6.2	1	2009	539	NA	23 -	454 -	62 -	NA -	NA -	NA -					
58	10.2	1	2008	13 127	NA	11 264 88 %	0.8 0.01 %	262	724 6 %	877 7 %	0 0 %					
No of values:	57	-	57	51	39	39	35	35	27	25	38	38	33	33	39	39
Minimum:	-	-	49	0.2 %	5	2 %	0	0 %	42	3 %	0	0 %	0	0 %	0	0 %
5th Percentile:	-	-	327	0.6 %	49	7 %	0	0 %	64	3 %	0	0 %	0	0 %	0	0 %
Average:	-	-	4 832	5.1 %	4 050	49 %	318	4 %	1 451	20 %	1 170	23 %	438	9 %	378	7 %
95th Percentile:	-	-	15 994	12.5 %	9 890	89 %	608	15 %	3 724	47 %	3 610	71 %	1 601	34 %	2 099	37 %
Maximum:	-	-	17 979	18.9 %	11 587	98 %	8 424	87 %	4 911	66 %	5 710	85 %	4 955	80 %	3 477	62 %

NA These data have not been made available to TWG.
(-) Not applicable.
Source: [TWG data collection questionnaires]

As shown in Figure 3.12 and Figure 3.13, no obvious correlation can be graphically observed, neither for the first group of sites (non-FCC operated) nor for the second one (including FCC), between the sulphur emitted/input ratio calculated for these refineries and the respective weight of their different main contributing units or processes. In both cases, furnaces and boilers appear most often as the main contributors, which confirms the trend shown in Table 3.7. It is even truer if emissions from the entire energy system, including eventual CHPs and stand-alone, gas turbines are considered.

For the selected refineries operating an FCC, this unit generates a rather stable proportion, most often within 15 – 30 %, of the SO₂ site emissions. It should also be noted the important role played, by sources involved in the 'Other' category, when they exist. Even if their average weight reported to the overall European refining emissions is low (around 5 %, as shown in Table 3.7), they most often represent a major part of the individual site-level SO₂ emissions for the refineries concerned. These emissions come from:

- the incineration of waste water stripping and/or process incondensable off-gases, when they are eventually not recycled into the RFG treating system;
- the eventual coke plants, and especially the green coke calcination;
- the contribution of flares, which can be very significant, notably for refineries experiencing other than normal operating conditions, such as technical difficulties or major start-up/shutdown episodes.

Influence of crude sulphur content and the site refining overall configuration

An overview of the historic development of the distribution of sulphur output in European refineries is given in Table 3.9. It also presents the average sulphur recovery percentage in the western European refineries that has grown from about 10 % in the late 70s to more than 45 % now. This table shows the reductions of sulphur content achieved in the oil products destined for combustion (so called S in fuels) sold to customers. It can be noted that these reductions were achieved while direct sulphur emissions from the refineries have shown a decrease since 1995.

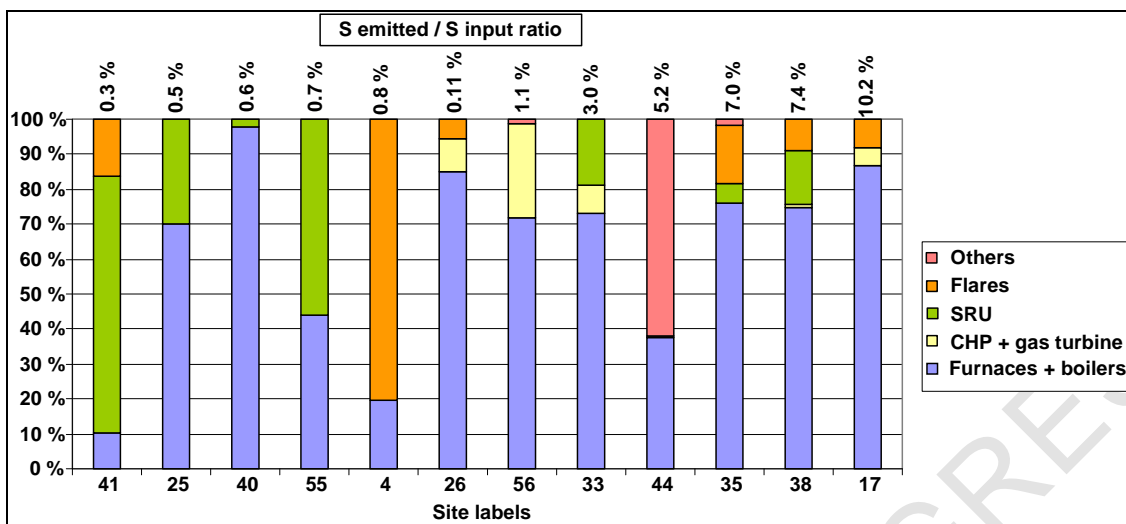


Figure 3.12: Respective weight of main SO₂ contributing processes for 12 European refineries not operating a FCC unit as a function of their sulphur emitted/input ratio

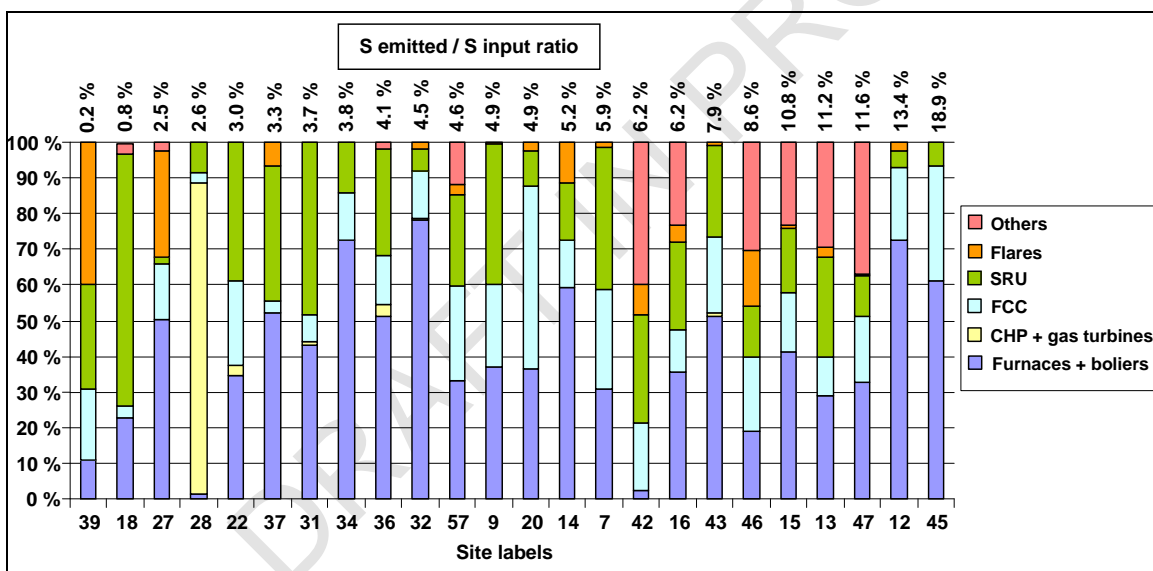


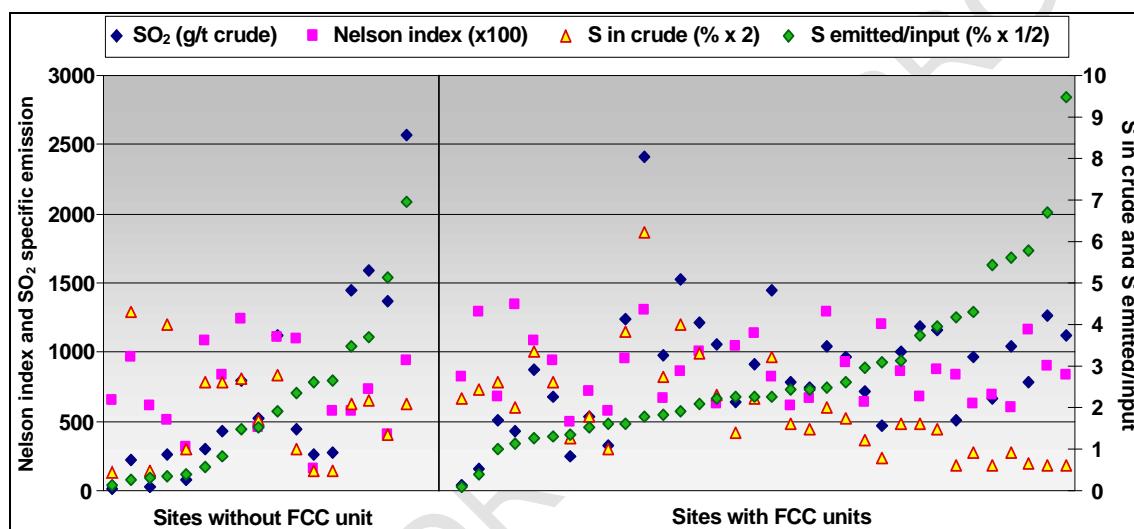
Figure 3.13: Respective weight of main SO₂ contributing processes for 24 European refineries operating an FCC as a function of their sulphur emitted/input ratio

Table 3.9: Trends of sulphur distribution in western European refineries (data in kt/yr)

Year	1979	1982	1985	1989	1992	1995	1998	2002	2006
Crude intake ⁽¹⁾	680 000	494 000	479 000	527 000	624 000	637 000	635 000	684 000	696 000
S in crude % ⁽²⁾	1.45	1.28	0.98	1.10	1.06	1.03	0.97	0.91	0.91
S in crude ⁽¹⁾	9 860	6 323	4 694	5 797	6 615	6 561	6 159	6 224	6 334
S recovered % ⁽²⁾	10.4	17.5	23.2	30.5	26.9	36.1	39.4	47.6	45.0
S emitted in air %	9.0	12.2	11.2	9.1	7.9	8.6	7.2	5.5	3.7
S in fuels % ⁽²⁾	90.7	75.7	73.3	58.3	50.9	40.0	37	29.8	32.5

⁽¹⁾. For all OECD Europe.
⁽²⁾. From the CONCAWE refinery site sample covered by the annual survey.
Source: [152, CONCAWE 1998] [63, CONCAWE 2010]

Figure 3.14 shows, for 51 European refineries, the interaction between various parameters related to the crude quality (% of sulphur), the site complexity (measured with the Nelson Index), and the specific emissions reported to the amount of feedstock treated (SO₂ g/t) and to the sulphur total intake (% of sulphur emitted/input ratio). Available data is displayed for two site groups according to the presence of an FCC unit (34 sites) or not (17 sites).

**Figure 3.14: Influence of the configuration, complexity and crude quality on SO₂ emissions**

Several points can be derived from this graphic.

- The highest SO₂ specific emissions are not necessarily associated with the most complex sites.
- As mentioned in the beginning of this section, FCC units contribute to around 11 % of the SO₂ European refining emissions, and represent on average 20 % (up to 66 %) of the individual emissions of the sites concerned. However, as shown on Figure 3.14, refineries with FCC do not tend to emit more SO₂ than refineries without FCC.
- Another important variable that is typically referred to for explaining the behaviour of SO₂ emissions in refineries is the content of sulphur in the crude oil processed. However, once again, data displayed in Figure 3.14 shows that, within this site sample, refineries with similar sulphur content in the treated crude oil can have very high differences in specific emissions, and many sites achieving very high specific emissions are actually those treating the most favourable crudes.

Influence of the refinery fuel mix

Another parameter which could be expected to strongly influence the refinery SO₂ emissions is the ratio of gaseous fuels (including the eventual supply of external natural gas) and residual

liquid fuels in the site energy supply. As shown in Figure 3.15, there is a clear correlation within this site sample between the SO₂ specific emissions and the weight of residual fuel oils in the fuel mix, even if some sites with very high liquid fuel ratios can achieve very good SO₂ performance

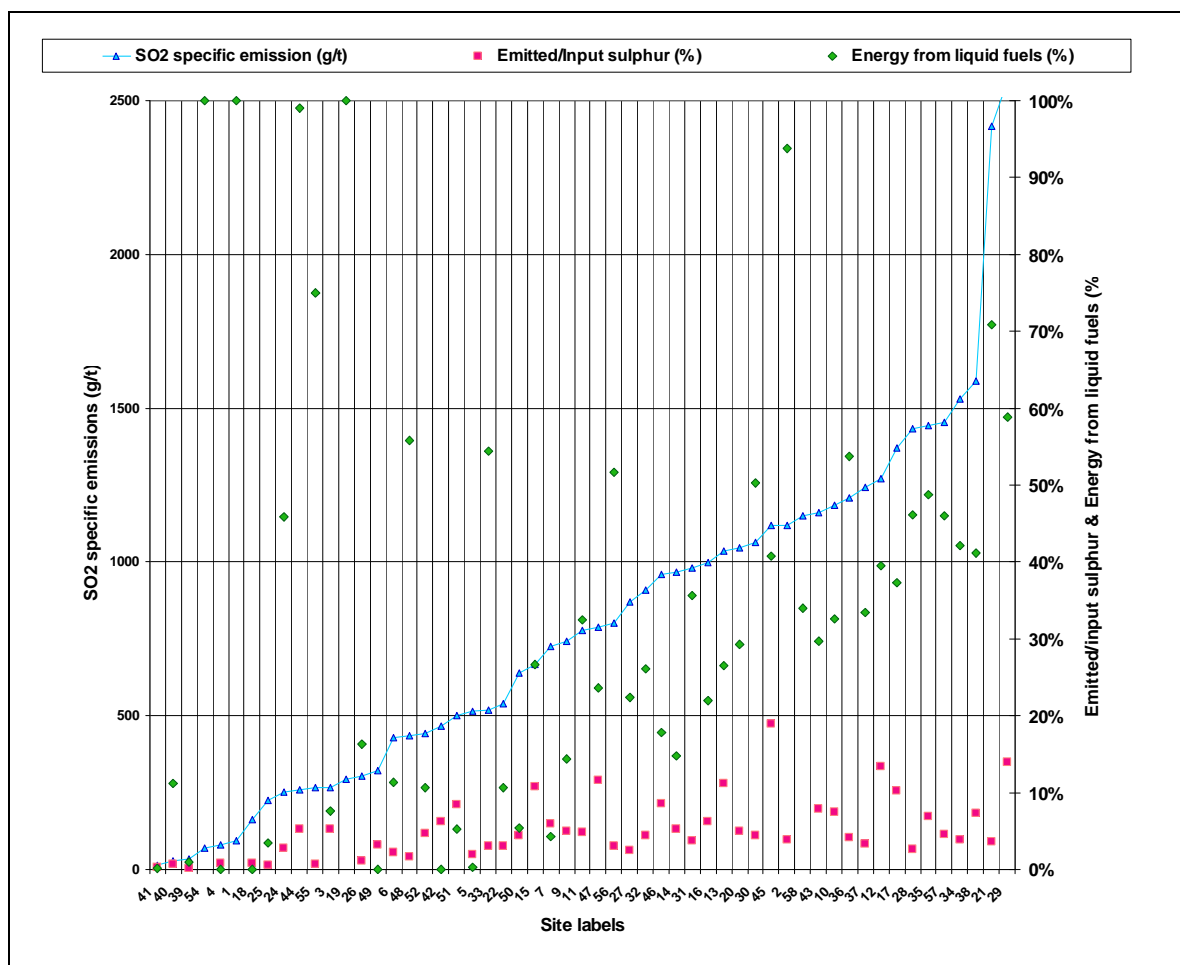


Figure 3.15: Influence of the gaseous fuels used for energy supply on the site SO₂ emissions

3.1.2.5 Volatile organic compounds emissions

Volatile organic compounds (VOCs) is the generic term applied to all compounds containing organic carbon, which evaporate at ambient temperature and contribute to the formation of odour nuisance, ‘summer smog’ and, with sufficient sunshine, tropospheric ozone. VOC losses can be calculated through various methods based on emission factors or directly measured. Extensive information on this issue can be found in Section 3.26.1.3 related specifically to VOC monitoring.

The main sources of VOCs from refineries are, fugitive emissions from piping systems, waste water systems, fixed roof storage tanks (tank breathing), loading and unloading systems, other storage, handling, and blowdown systems. Fugitive VOC emission sources such as (single) seals from pumps, compressors, valves and flanges and leaks in pipelines and equipment may contribute significantly to the total VOC emissions. Most of the European refineries (from 5th to 95th percentiles based on the 53 sites gathered by the TWG) emit from 150 to 6500 tonnes of VOCs per year; the related specific emission range is from 50 to 1000 tonnes of VOCs per million tonnes of total feed processed. Almost all of these results have been achieved using emission factor estimates. All available data are displayed in Table 3.10. For more details on the diffuse VOC monitoring, see Section 3.26.1.3.

Table 3.10: Data on volatile organic compounds emitted by a sample of 53 European refineries

Site label	Nelson index	Total VOCs		NMVOCs		Diffuse VOCs		Benzene	
		t/yr	g/t	t/yr	g/t	t/yr	g/t	kg/yr	g/t
44	1.6	1621	368	NA	NA	1563	354	48642	11.03
4	3.1	6882	1404	4792	978	NA	NA	NA	NA
17	4.0	282	387	NA	NA	NA	NA	3585	4.92
33	4.6	NA	NA	1170	254	NA	NA	NA	NA
24	4.9	NA	NA	NA	NA	3825	442	NA	NA
19	5.1	2825	841	NA	NA	NA	NA	NA	NA
55	5.1	NA	NA	435	463	435	463	NA	NA
54	5.4	NA	NA	6161	571	NA	NA	NA	NA
35	5.7	2388	659	2012	555	NA	NA	416	0.11
49	5.7	956	64	913	61	758	51	6742	0.45
3	5.7	1231	353	1192	342	NA	NA	NA	NA
13	6.0	NA	NA	1176	222	NA	NA	31710	5.98
40	6.2	NA	NA	3000	529	3000	529	34000	6.00
1	6.2	NA	NA	503	55	NA	NA	NA	NA
11	6.2	NA	NA	1390	149	233	25	11697	1.25
46	6.2	NA	NA	NA	NA	1021	105	NA	NA
30	6.3	NA	NA	2103	200	2040	194	41130	3.92
7	6.4	513	157	NA	NA	NA	NA	12983	3.97
41	6.5	1071	272	NA	NA	905	230	14000	3.55
9	6.6	1077	188	795	139	94	16	14649	2.56
31	6.7	NA	NA	806	67	NA	NA	6490	0.54
5	6.8	NA	NA	NA	NA	923	NA	NA	NA
10	6.8	997	113	967	109	897	101	16177	1.83
15	6.9	558	115	NA	NA	NA	NA	6000	1.24
22	7.2	NA	NA	3095	358	3022	350	33346	3.86
39	8.2	NA	NA	3910	387	3910	387	38000	3.76
57	8.2	1175	203	1123	194	1019	176	NA	NA
45	8.4	4300	428	4270	425	4100	408	40000	3.98
23	8.4	NA	NA	2900	NA	NA	NA	24008	NA
48	8.4	32000	4638	1000	145	NA	NA	17835	2.58
51	8.4	666	151	646	147	NA	NA	2034	0.46
34	8.6	1750	167	1537	147	NA	NA	NA	NA
16	8.7	NA	NA	768	107	NA	NA	NA	NA
43	8.7	2056	133	2006	130	NA	NA	35000	2.26
12	9.0	NA	NA	677	106	NA	NA	13889	2.17
14	9.3	NA	NA	2252	136	2355	142	25251	1.53
29	9.4	NA	NA	780	204	738	193	17000	4.45
28	9.4	1110	78	NA	NA	774	54	1003	0.07
37	9.5	5651	775	4862	667	4490	616	1660	0.23
25	9.7	236	65	NA	NA	236	65	NA	NA
36	10.1	152	27	151	27	NA	NA	NA	NA
58	10.2	2227	195	NA	NA	2086	183	NA	NA
50	10.5	2552	552	2376	514	2271	492	4216	0.91
27	10.8	3070	160	2757	144	207	11	10000	0.52
26	10.8	2103	206	2082	204	1958	192	43752	4.29
52	10.9	807	162	783	157	NA	NA	9600	1.92
2	11.2	151	249	NA	NA	NA	NA	NA	NA
32	11.4	742	126	709	120	67	11	5300	0.90
47	11.6	4949	417	NA	NA	NA	NA	64320	5.42
42	12.0	6044	554	5971	547	5850	536	302000	27.67
56	12.4	NA	NA	123	20	NA	NA	NA	NA
20	12.9	NA	NA	3655	395	NA	NA	32894	3.56
21	13.1	3326	591	NA	NA	3288	584	NA	NA
No of values		32	32	38	37	28	27	34	33
5th percentile		198	65	392	50	134	13	1430	0.2
50th percentile		1426	205	1291	194	1292	193	15413	2.6
95th percentile		6421	1095	5029	590	4353	570	54129	8.0

Figure 3.16 has been constructed from the 39 refineries in this sample for which the full distribution of VOC (Total VOC or NMVOCs) per contributing processes has been made available.

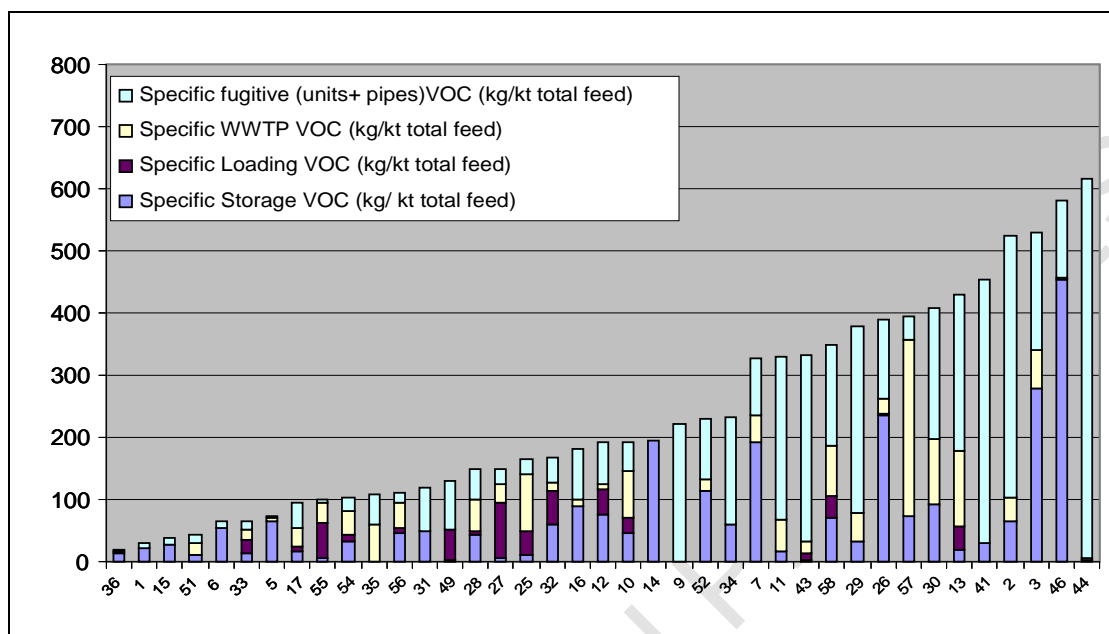


Figure 3.16: VOC specific emission range and breakdown for 39 European refineries

As it appears in Figure 3.16, the highest specific VOC emissions at the site level are mainly driven by fugitive emissions (leakages from units and pipes) and storage emissions. For the lowest ones, the waste water treatment is the most significant.

Some accidental spillages can be of a continuous nature, such as leaking pump seals, leaking valve glands and leaks from pipework. Others which are of a one-off nature, can occur from sources such as equipment failures, overfilling of tanks and overfilling of road and rail cars. As shown in Figure 3.16 from the TWG 2008 data collection, the fugitive emissions from process equipment are one of the largest single sources of VOCs emitted to the atmosphere in a refinery and can account for 50 % of the total emissions. Fugitive emissions include the emissions that occur from items such as valves, pump and compressor seals, flanges, vents and open ends. Valves are considered to account for approximately 50 - 60 % of fugitive emissions. Furthermore, a major portion of fugitive emissions comes from only a small fraction of the sources (e.g. less than 1 % of valves in gas/vapour service can account for over 70 % of the fugitive emissions of a refinery). Some valves are more likely to leak than others, e.g.:

- Valves that are operated frequently, such as control valves, may wear down more quickly and allow emission paths to develop. However, newer, low-leak control valves provide good fugitive emissions control performance.
- Valves with rising stems (gate valves, globe valves) are likely to leak more frequently than quarter-turn type valves such as ball and plug valves.

Factors driving these releases of hydrocarbons are equipment design, quality of the sealing system, maintenance programme and properties of the line contents. Poor designs (with wider tolerances), poor sealing systems (e.g. leak-prone valve packings) and limited maintenance will lead to higher emissions. These emissions can be estimated using the factors in

Table 3.11.

For example emission factors can be estimated, using the US EPA stratified method as presented in Table 3.15, taking into account they are derived from short term measurements. Other methods have been applied to calculate the fugitive emissions from refineries, the adsorption method and DIAL method (see Section 3.26).

Table 3.11: Emission factors according to the stratified US EPA-method for the assessment of fugitive emissions

Emission source	Emission factor in (g/(h.source)) for measured values in ppm v/v in the following three ranges		
	0 – 1000	1001 – 10000	>10000
Emission range (ppm v/v)			
Valves for gas or vapour	0.14	1.65	45.1
Valves for liquids with Vp>0.3 kPa (light liquid)	0.28	9.63	85.2
Valves for liquids with Vp<0.3 kPa (heavy liquid)	0.23	0.23	0.23
Pumps for light liquids	1.98	33.5	437
Pumps for heavy liquids	3.80	92.6	389
Compressors	11.32	264	1 608
Safety valves for gases	11.4	279	1 691
Flanges	0.02	8.75	37.5
Open-end valves	0.13	8.76	12.0
<i>Source: [160, Janson 1999] [77, REF TWG 2010]</i>			

3.1.2.6 Other emissions to air

Other pollutants considered are carbon monoxide (process furnaces/boilers, gas turbines, FCC regenerators, flare system, incinerators, cold vents) and methane (storage and handling (loading), cold vents and leaks). Noise, H₂S, NH₃, CS₂, dioxins and HF also contribute to the air emissions from a refinery.

Mercury and components of arsenic are volatile and are emitted to some extent with the clean gas. A part of these compounds react with plant material or deposit on the catalysts in the reactors of the conversion plants. Therefore, protective layers are used for the interception of the catalyst poisons.

Flares, compressors, pumps, turbines and air coolers require particular attention as regards sources of noise.

Finally, odours in a refinery are mainly created by sulphur compounds such as H₂S, mercaptans but also by some hydrocarbons (e.g. aromatics). The main sources of odour in refineries are storage (e.g. sour crudes), bitumen production, desalter water, sewers, uncovered dissolved air flotation, oil/water/solid separation and biotreatment units and flaring.

Table 3.12 gathers a set of data illustrating the performance of European refineries, made available from the 61 site-level questionnaires provided by the TWG in charge of the revision of the present document.

Table 3.12: Specific air emission ranges for various substances from European refineries

Substance	Specific load (g/t of feed)		No of values
	5th – 95th percentile	50th percentile	
Carbon monoxide	10 – 415	53	43
Ammonia	0.1 – 22	1.1	17
Hydrogen sulphide	0.15 – 1.1	0.3	4
Hydrofluoric acid ⁽¹⁾	0.01 – 1.6	0.1	6
Benzene	0.18 – 8	2.5	33
BTEX	1 – 70	17	7
PAH-16	0.001 – 0.4	0.005	17
PCDD/F	NA	NA	
As	<0.001 – 0.014	0.002	28
Cd	<0.001 – 0.034	0.002	25
Cr	<0.001 – 0.18	0.007	29
Cu	<0.001 – 0.07	0.009	24
Hg	<0.0001 – 0.038	0.001	23
Mn ⁽¹⁾	0.002 – 0.007	0.004	3
Ni	0.002 – 1.3	0.16	37
Pb	0.001 – 0.1	0.009	27
Se ⁽¹⁾	0.002 – 0.007	0.004	3
V	0.001 – 1.1	0.15	23
Zn	0.001 – 0.62	0.04	33
Metals ⁽²⁾	0.01 – 3.4	0.38	⁽²⁾

⁽¹⁾ For these parameters, only min, max and average are provided given the limited number of available values

⁽²⁾ Sum of individual percentile data for the following metals:
Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, Zn.

3.1.2.7 Expression of full or partial site air emissions using ‘bubbles’

The ‘bubble’ approach for the evaluation and monitoring of refinery air emissions

In the context of this BREF and for the purpose of expressing meaningful site or partial site level, the bubble determination should always be based on concentration and specific emission ranges expected at all concerned installations when BAT is applied, and should involve the following steps (regardless of their order):

1. exhaustive identification and geographical mapping of all included sources;
2. determination of the off-gas volumetric contributions expected from all included sources;
3. determination of the mass contributions expected from all included sources;
4. determination of the bubble-associated monitoring regime.

The actual details of the calculation and additional information on each of these steps are given in Annex 9.6. More details on this approach are available in section 4.15.4.7.

The total emissions of one substance released by all the stacks on site can therefore be expressed as a single value using this approach based on available data provided through TWG data collection.

Actual NO_x emissions from European refineries: bubble-expressed examples

Site individual sets of NO_x data collected by the TWG for each site have been gathered in Table 3.13. These data have been processed in order to calculate the annual average equivalent concentration of NO_x in the sum of flue-gases emitted by the four categories of contributing units as listed below. These calculations are based on actual emissions reported for the year 2007 or 2008. Two examples of bubble-expressed emission levels, which correspond respectively to Figure 3.17 and Figure 3.18, are presented for the set of sites concerned.

In the first case, as shown in Figure 3.17, which corresponds to column (e) in Table 3.13, the full list of contributors has been used, which includes:

- furnaces and boilers
- CHPs and gas turbines
- FCC units
- sulphur recovery units.

Mass and volumetric contribution terms from each of these four categories were fully available for a sample of 25 sites, among which seven were non-FCC sites and 18 were FCC sites; Figure 3.17 shows the range of equivalent concentrations obtained. The unit for which less data was available, in particular as far as volumetric contributions are concerned, is SRU and is mainly responsible for the limited size of this refinery set.

In the second case, illustrated by Figure 3.18, the small NO_x contribution of sulphur recovery units have not been taken into account, and contributors only include:

- furnaces and boilers
- CHPs and gas turbines
- FCC units.

Mass and volumetric contribution from each of these three categories were fully available for a total of 30 sites, among which 10 were non-FCC sites and 20 were FCC sites. The results obtained for the whole group of refineries are very close to the results obtained in the first case.

In both cases, as shown in Figure 3.17 and Figure 3.18, an information summary is provided for each refinery on the part taken by the refinery fuel gas and an eventual additional natural gas supply in the refinery energy mix, together with the main NO_x abatement techniques implemented on the FCC unit and the energy system.

Table 3.13: Equivalent concentrations of NO_x emissions for a sample of European refineries

Questionnaire	Configuration with FCC	Specific NO _x emission	Furnace + boilers		CHP + gas turbines		FCC		SRU		Bubble CP (a)	Bubble CP+ CHP (b)	Bubble CP+CHP+ SRU (c)	Bubble FCC (d)	Full bubble (e)
			t/yr	GNm ³ /yr	t/yr	GNm ³ /yr	t/yr	GNm ³ /yr	t/yr	GNm ³ /yr					
yes=1	g/t	t/yr	GNm ³ /yr	t/yr	GNm ³ /yr	t/yr	GNm ³ /yr	t/yr	GNm ³ /yr	mg/Nm ³ @ 3 % O ₂					
40	0	59	328	3.48	0	0.00	-	-	7.7	0.09	94	94	94	-	94
53	0	69	375	2.09	0	0.00	-	-	3	0.02	179	179	179	-	179
25	0	81	270	2.16	0	0.00	-	-	24.2	0.10	125	125	130	-	130
26	0	89	536	6.15	366	1.51	-	-	1.66	0.06	87	118	117	-	117
44	0	108	389	0.88	0	0.00	-	-	NA	NA	442	442	NA	-	NA
56	0	210	824	2.64	431	0.98	-	-	NA	NA	312	347	NA	-	NA
33	0	374	887	1.73	814	0.86	-	-	24	0.03	512	655	656	-	656
38	0	392	2316	4.73	870	1.32	-	-	NA	0.16	490	527	513	-	513
35	0	424	927	1.75	609	0.27	-	-	0.00	0.35	529	757	645	-	645
8	0	500	476	2.20	0	0.00	-	-	NA	NA	216	216	NA	-	NA
39	1	68	620	6.03	0	0.00	48	0.73	0	0.19	103	103	100	66	96
1(f)	1	92	221	3.03	454	5.61	88	0.76	NA	NA	73	78	78	116	78
49	1	93	760	5.60	300	0.60	300	2.00	20	0.08	136	171	172	150	167
18	1	138	959	6.20	0	0.00	127	0.84	20.7	0.11	155	155	155	151	155
46	1	173	1322	4.00	101	0.66	187	1.70	NA	NA	331	305	NA	110	NA
47	1	217	2002	7.81	0	0.00	575	1.98	0	0.02	256	256	256	290	263
14	1	231	2554	10.12	661	5.55	540	0.94	34	0.37	252	205	203	574	223
22	1	237	1052	4.25	498	5.95	481	1.74	17.4	0.14	247	152	151	276	169
9	1	248	557	2.26	532	0.60	324	0.70	0	0.03	246	380	376	467	394
42	1	249	1056	4.74	154	0.56	178	1.13	21	0.06	223	255	256	158	238
32	1	254	783	3.13	410	1.15	265	0.71	NA	NA	250	279	NA	373	NA
27	1	259	3608	11.91	920	7.58	357	1.43	14	0.65	303	232	226	250	227
57	1	266	1261	5.61	0	0.00	229	0.90	13	0.17	225	225	220	254	225
7	1	301	742	1.54	43	NA	177	0.38	22	0.05	482	NA	NA	466	NA
20	1	318	1589	6.40	607	3.10	706	1.90	40	0.10	248	231	233	372	256
12	1	339	1608	5.03	0	0.00	561	1.31	0	0.05	320	320	317	428	339
43	1	375	3339	7.20	1068	1.00	1396	2.51	0	0.10	464	537	531	556	537
36	1	394	1304	8.24	644	2.62	252	1.40	0	NA	158	179	NA	180	NA
13	1	406	1419	3.39	0	0.00	618	1.24	0	0.08	418	418	408	497	431
28	1	431	968	5.45	4523	11.58	626	0.85	30	0.34	177	322	318	735	337
45	1	453	1340	3.68	2080	3.71	1125	3.95	10	0.05	364	463	461	285	400
37	1	575	1728	4.85	1792	1.79	381	1.25	1.2	0.08	356	530	524	305	489
No of values		32	32	32	32	31	22	22	25	26	32	31	25	22	25
Average		263	1191	5	559	1.84	434	1.38	12	0	274	299	293	321	294
Minimal		59	221	0.88	0	0.00	48	0.38	0	0.00	73	78	78	66	78
5th percentile		69	302	1.65	0	0.00	127	0.70	0	0.02	91	99	95	110	94
50th percentile		252	964	4.49	366	0.63	357	1.25	10	0.09	249	255	233	288	238
95th percentile		474	2907	9.09	1922	6.77	1125	2.51	33	0.37	499	596	622	574	624
Maximal		575	3608	11.91	4523	11.58	1396	3.95	40	0.65	529	757	656	735	656
(a) Equivalent concentration calculated for off-gases emitted by all furnaces and boilers															
(b) Equivalent concentration calculated for off-gases emitted by all furnaces, boilers, and CHP and stand-alone gas turbines if any															
(c) Equivalent concentration calculated for off-gases emitted by all furnaces and boilers, CHP and stand-alone gas turbines if any, and SRUs															
(d) Equivalent concentration corresponding to the FCC alone															
(e) Equivalent concentration corresponding to the sum of (c) and off-gases emitted by the FCC UNITS if any															
(f) NB: Site 1 data made available for 2009 emissions- tail gas of SRU treated in SNO _x of CHP plant															
NB: NA This data has not been made available to the TWG															
Source: [TWG data collection questionnaires]															

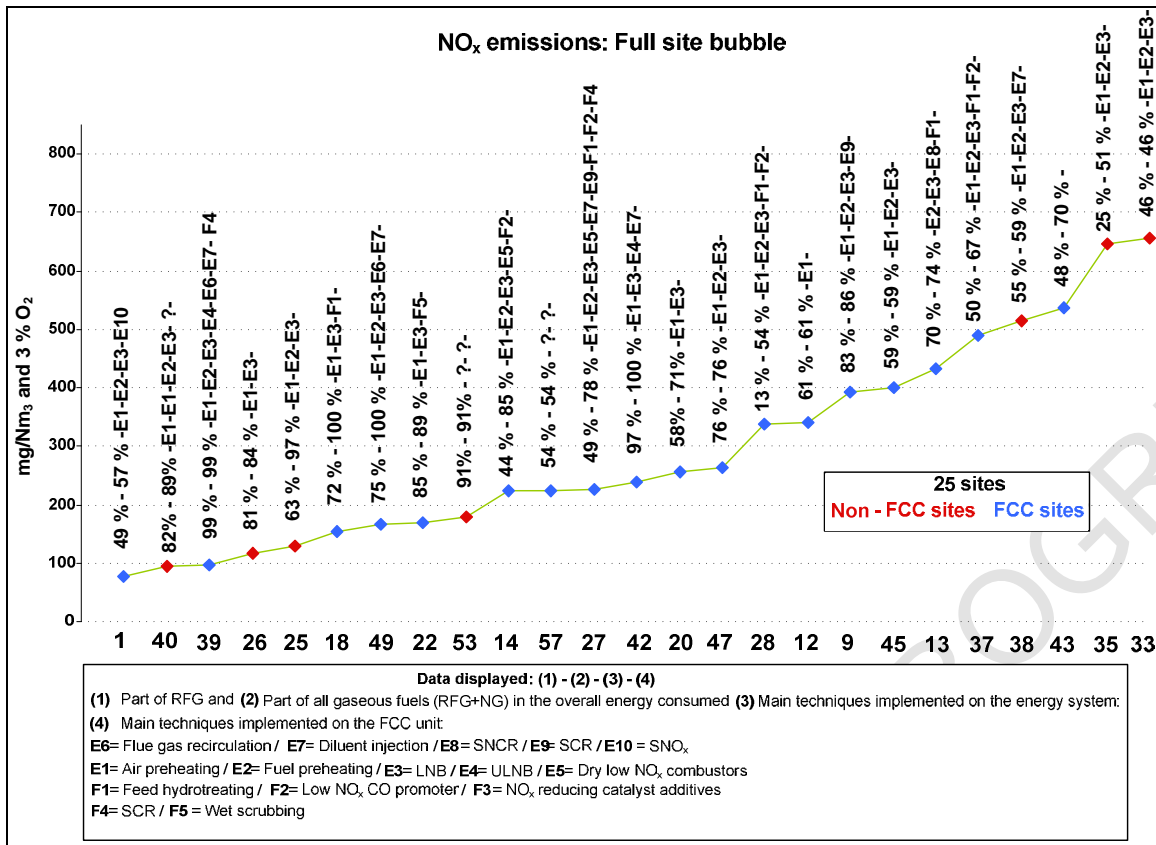


Figure 3.17: Equivalent concentration of the NO_x emissions from the whole energy system, FCC and SRU units of 24 European refineries

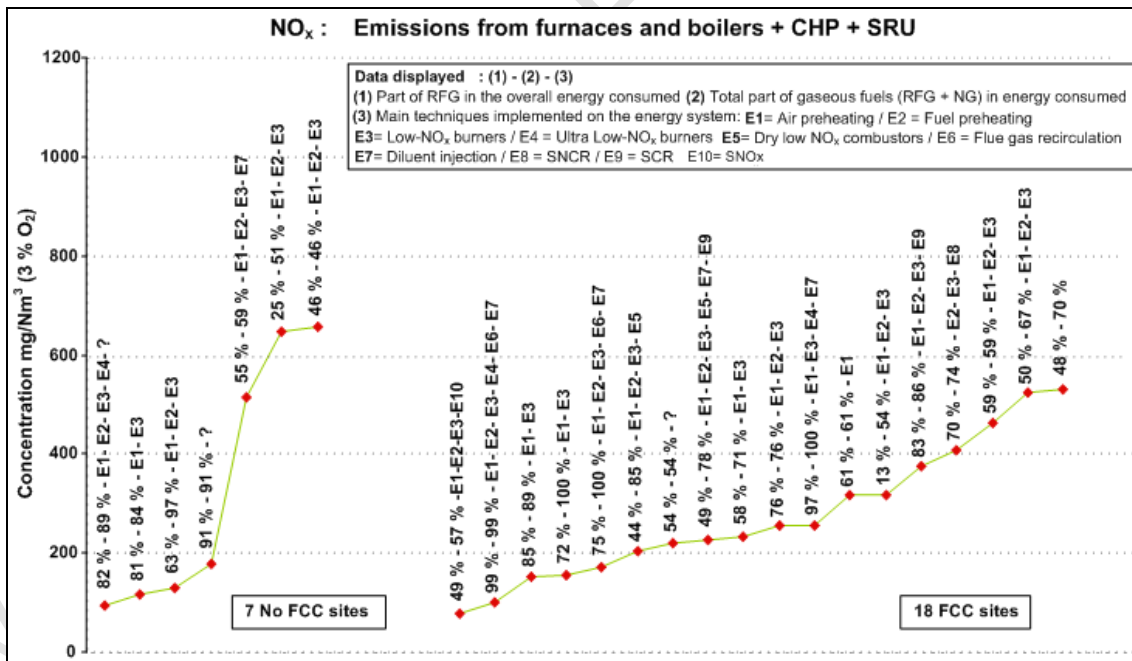


Figure 3.18: Equivalent concentration of the NO_x emissions from the whole energy system and the FCC unit of 30 European refineries

Actual SO₂ emissions from European refineries: a bubble-expressed example

Similar to what has been presented above for the NO_x emissions, individual site sets of SO₂ data collected by the TWG have been gathered in Table 3.14. These data have been processed in order to calculate the annual average equivalent concentration of SO₂ in the sum of the flue-

gases emitted by the four categories of contributing units as listed below. These calculations are based on actual emissions reported for the year 2007 or 2008.

An example of bubble-expressed emission levels is displayed in Figure 3.19, which corresponds to Column (e) in Table 3.14. The full selection of contributors has been used, which includes:

- furnaces and boilers
- CHPs and gas turbines
- FCC units
- Sulphur recovery units.

Mass and volumetric contribution terms from each of these four categories were fully available for a sample of 29 sites, among which 10 were non-FCC sites and 19 were FCC sites, and Figure 3.19 shows the range of equivalent concentrations obtained. The contributing unit category for which the data was available, in particular as far as volumetric contributions were concerned, was once again SRUs, mainly responsible for the limitation of this refinery data-set.

As shown in Figure 3.19, an information summary is provided for each refinery on the part taken by the refinery fuel gas and an eventual additional natural gas supply in the refinery energy mix, together with the main NO_x abatement techniques implemented on the FCC unit and the energy system.

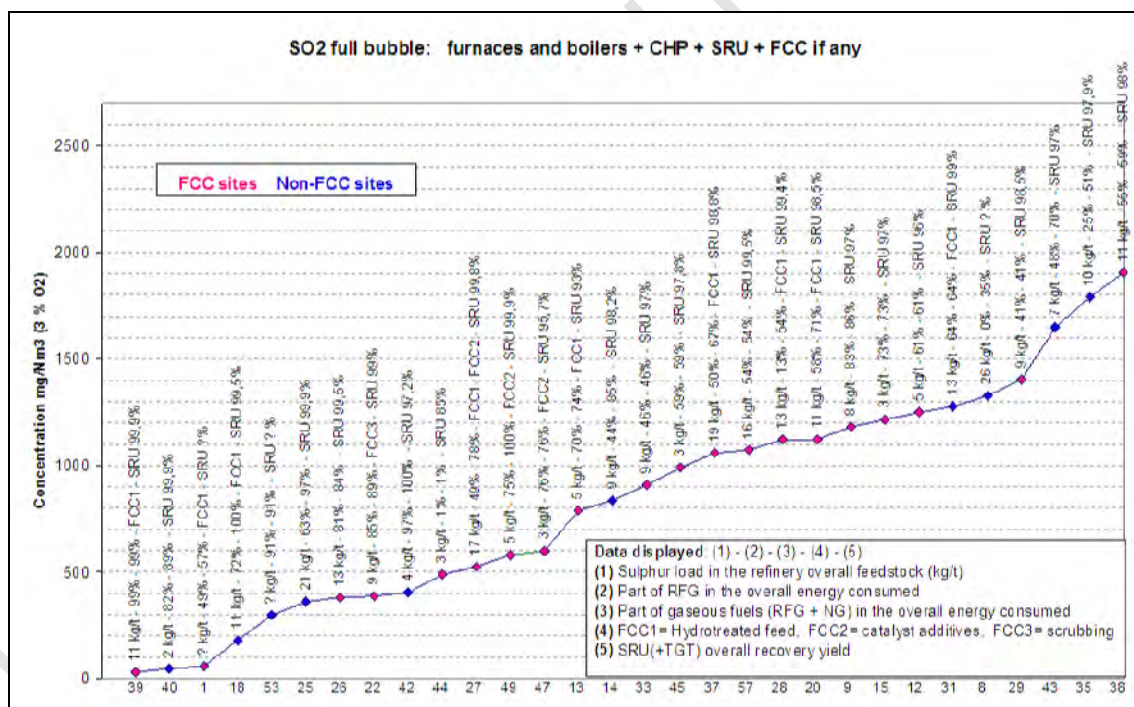


Figure 3.19: Equivalent concentration of the SO₂ emissions from the whole energy system and the FCC and SRU unit of 30 European refineries

Table 3.14: Equivalent concentrations of SO₂ emissions for a sample of European refineries

questionnaire	Configuration with FCC?	Furnaces+boilers		CHP+gas turbines		FCC		SRU		Bubble CP (a)	Bubble CP+CHP (b)	Bubble CP+CHP+SRU(c)	Bubble CP+CHP+SRU+ FCC if any (d)	Bubble CP+CHP 'enriched' SRU ^(e)	Bubble CP+CHP+SRU 'enriched' SRU ^(e)
		yes=1	SO ₂ (t)	GNm ³ /yr	SO ₂ (t)	GNm ³ /yr	SO ₂ (t)	GNm ³ /yr	SO ₂ (t)	GNm ³ /yr	mg/N m ³	mg/N m ³	mg/N m ³	mg/N m ³	mg/N m ³
53	0	50	2.09	0	0.00	-	-	575	0.02	24	24	296	296	299	299
40	0	158	3.48	0	0.00	-	-	4	0.09	46	46	45	45	47	47
25	0	568	2.16	0	0.00	-	-	244	0.10	263	263	360	360	376	376
26	0	2639	6.15	289	1.51	-	-	5	0.06	429	382	380	380	383	383
44	0	429	0.88	0	0.00	-	-	NA	NA	487	487	487	487	487	487
33	0	1746	1.73	188	0.86	-	-	452	0.03	1007	745	908	908	919	919
8	0	2918	2.20	0	0.00	-	-	NA	NA	1326	1326	1326	1326	1326	1326
56	0	3603	2.64	1351	0.98	-	-	NA	NA	1365	1369	NA	NA	NA	NA
29	0	9637	6.86	NA	NA	-	-	0	0.003	1405	1405	1404	1404	1405	1405
38	0	9737	4.73	80	1.32	-	-	2006	0.16	2059	1623	1905	1905	1954	1954
35	0	3980	1.75	2	0.27	-	-	278	0.35	2269	1963	1790	1790	2100	2100
39	1	38	6.03	0	0.00	68	0.73	102	0.19	6	6	23	30	23	31
1	1	23	3.03	454	5.61	62	0.76	NA	NA	8	55	55	57	55	57
42	1	113	4.74	154	0.56	970	1.13	1535	0.06	24	22	308	404	311	407
28	1	258	5.45	18044	11.58	640	0.85	1498	0.34	47	1075	1140	1122	1163	1143
18	1	304	6.20	0	0.00	42	0.84	941	0.11	49	49	197	180	201	183
49	1	1400	5.60	NA	0.60	3200	2.00	200	0.08	250	226	255	580	258	585
45	1	1110	3.68	5800	3.71	3600	3.95	760	0.05	302	935	1031	989	1038	994
22	1	1621	4.25	131	5.95	1110	1.74	1802	0.14	381	172	344	386	348	391
47	1	3061	7.81	0	0.00	1712	1.98	1096	0.02	392	392	531	598	532	599
36	1	3470	8.24	241	2.62	941	1.40	2018	NA	421	342	NA	NA	528	544
46	1	1784	4.00	0	0.66	1929	1.70	1331	NA	446	383	NA	NA	668	793
13	1	1591	3.39	0	0.00	602	1.24	1527	0.08	469	469	897	788	919	802
7	1	733	1.54	0	NA	658	0.38	943	0.05	476	NA	NA	NA	NA	NA
57	1	2781	5.61	0	0.00	2243	0.90	2142	0.17	496	496	852	1072	878	1100
20	1	3537	6.40	2	3.10	4911	1.90	976	0.10	553	553	694	1122	705	1135
9	1	1560	2.26	0	0.06	986	0.70	1688	0.03	689	545	1124	1181	1136	1191
27	1	8337	11.91	32	7.58	2630	1.43	312	0.65	700	429	431	524	445	541
31	1	5098	6.07	143	1.87	896	1.09	5710	0.23	839	659	1338	1278	1378	1311
14	1	9475	10.12	0	5.55	2121	0.94	2604	0.37	936	605	753	836	771	855
37	1	4706	4.85	0	1.79	303	1.25	3430	0.08	970	708	1210	1058	1225	1069
12	1	5903	5.03	0	0.00	1652	1.31	421	0.05	1174	1174	1245	1248	1257	1258
43	1	9218	7.20	194	1.00	3779	2.51	4632	0.10	1280	1148	1692	1649	1713	1664
32	1	4193	3.13	3	1.15	708	0.71	340	NA	1340	980	NA	NA	1060	1051
15	1	1328	0.75	0	0.00	543	1.21	583	0.06	1760	1760	2351	1215	2533	1251
Number of values		35	35	32	32	24	24	33	30	35	34	30	20 ⁽¹⁾	33	23 ⁽¹⁾
Average		3060	4.63	842	1.81	1513	1.36	1217	0.13	705	671	846	816 ⁽¹⁾	862	824 ⁽¹⁾
Min value		23	0.75	0	0.00	42	0.38	0	0.00	6	6	23	30 ⁽¹⁾	23	31 ⁽¹⁾
5th perc.		46	1.34	0	0.00	63	0.70	0	0.00	19	23	50	56 ⁽¹⁾	52	70 ⁽¹⁾
50th perc.		1784	4.73	0	0.76	978	1.23	941	0.08	487	521	802	913 ⁽¹⁾	771	855 ⁽¹⁾
95th perc.		9524	8.80	3553	6.68	3752	2.43	3911	0.36	1850	1671	1853	1296 ⁽¹⁾	2013	1306 ⁽¹⁾
Max value		9737	11.91	18044	11.58	4911	3.95	5710	0.65	2269	1963	2351	1649 ⁽¹⁾	2533	1664 ⁽¹⁾
(a) Equivalent concentration calculated for off-gases emitted by all furnaces and boilers															
(b) Equivalent concentration calculated for off-gases emitted by all furnaces, boilers, and CHP and stand-alone gas turbines if any															
(c) Equivalent concentration calculated for off-gases emitted by all furnaces and boilers, CHP and stand-alone gas turbines if any, and SRUs															
(d) Equivalent concentration corresponding to the sum of (c) and off-gases emitted by the FCC UNITS if any															
(e) Equivalent concentration calculated as for (c) and (d) but neglecting the volumetric contribution from SRUs															
(f) NB: Site 1 data made available for 2009 emissions- tail gas of SRU treated in SNO _x of CHP plant – NA: data not available to the TWG															
⁽¹⁾ These values are calculated only for the FCC-refinery sample.															
Source: [TWG data collection questionnaires]															

However, flue-gases emitted by sulphur recovery units are typically highly concentrated, representing, at the site level, small volumetric contributions which are rarely measured and often estimated with rather significant uncertainty. As an alternative - which corresponds to Column (f) in Table 3.14 - these small volumetric contributions could be neglected. The equivalent concentration would then be calculated with the mass contributions from the four categories of sources above-mentioned, but only divided into the volumetric contributions from:

- furnaces and boilers
- CHPs and gas turbines
- and FCC units.

With this option, data necessary for the calculation are available for a wider sample of 32 sites, among which 10 are non-FCC sites and 22 are FCC sites. The site equivalent concentrations obtained for the whole group of refineries are, on average, slightly higher than those obtained in the first case, due to their artificial 'enrichment' related to the decrease of the overall flue-gas volume.

3.1.3 Emissions to water

Waste waters consist of cooling water, process water, sanitary sewerage water and storm water. The quantity of waste waters generated and their characteristics depend on the process configuration. This can vary over time and can vary from one refinery site to another, depending on refinery complexities, variability of feed stocks, integration with petrochemical facilities, techniques, etc.

Waste waters are generally treated in on-site waste water treatment facilities or sometimes by external Waste Water Treatment Plants (WWTP) and then discharged. Depending on the origin of the waste water, these can be contaminated with hydrocarbons, inorganics, metals and salts that may have the potential to impact the receiving environment. Nearly all refinery processes have steam injection to enhance the distillation or separation processes. This leads to the production of sour water (containing ammonia, hydrogen sulphide and hydrocarbons). Sour water needs stripping prior to further treatment or reuse as wash water. When off-gases are generated in this pre-treatment step these should be properly routed and treated before release (see Section 4.24.2).

Depending on the prevailing climate and the location's housekeeping, storm or rainwater can also generate a significant effluent stream in refineries. When rainwater may come into contact with potentially oil-polluted surfaces ('surface water run-off'), this requires treatment.

The effect of rainwater on both the amount and the quality of the effluent water and the problems that the water discharges to either fresh continental waters or to the sea are issues to consider. Furthermore, sanitary waste water and firefighting water are waste water streams which need attention and quality control prior to deciding on treatment, direct discharge and/or potential reuse.

The water effluent quality parameters to be considered relevant for refining activities are mainly the pH, total suspended solids (TSS), total organic carbon (TOC) or COD, total nitrogen and its various forms (organic R-NH₂, ammonium NH₄⁺, reduced or Kjeldahl NTK, nitrite NO₂, and nitrate NO₃), total phosphorus, BOD, Total Petroleum Hydrocarbons (TPH), aromatics (BTEX), phenols, PAH, metals, temperature. Based on the data collected (see Section 3.1.1.2), an average of 5 – 6 m³ is used (process waste water, cooling water and sanitary waste water) per tonne of feed. This value is strongly dependent on the type of cooling system in use on site, driving the level of water recycling. Water from processes account for around 0.1 – 1.6 m³/tonne of feed (see Section 3.24).

The resulting discharge of the aforementioned substances depends on the 'in-process' preventive measures (knowledge of all streams, reduction at source, good housekeeping, reuse) and the presence and technical standards of waste water treatment facilities. The typical process water pollutants and/or waste water parameters relevant to the overall refining process and prior to any purification steps are as stated in Table 3.15.

Table 3.15: Representative concentrations of pollutants in typical refinery effluents before treatment

Source	Oil	H ₂ S (RSH)	NH ₃ (NH ₄ ⁺)	Phenols	BOD COD TOC	CN ⁻ (CNS ⁻)	TSS
Distillation Units	XX	XX	XX	X	XX	-	XX
Hydrotreatment	XX	XX(X)	XX(X)	-	X(X)	-	-
Visbreaker	XX	XX	XX	XX	XX	X	X
Catalytic Cracking	XX	XXX	XXX	XX	XX	X	X
Hydrocracking	XX	XXX	XXX	-	X	-	-
Lube oil	XX	X	X	-	XX	-	-
Spent caustic	XX	XX	-	XXX	XXX	X	X
Ballast water	X	-	-	X	X	X	X
Utilities (Rain)	-(x)	-	-	-	X	-	-
Sanitary/Domestic	-	-	X	-	X	-	XX
Key: X = <50 mg/l XX = 50 – 500 mg/l XXX = >500 mg/l							
Source: [166, CONCAWE 1999]							

Table 3.16 summarises the annual average range of the water effluents from European refineries. Most data were gathered in 2009 – 2010 by the Technical Working Group set up for the revision of the present BREF document, and relate to a sample of 44 sites, all equipped with a dedicated WWTP. These data reflect a annual period of continuous emissions between years 2006 – 2008.

The details on the various treatment steps in operation at the refinery sites are shown in Section 4.24.

More detailed data on the main parameters used for characterising organic and nitrogen compounds are shown in Table 3.17 and Table 3.18. The actual range and distribution shape of annual average concentrations and their eventual correlation with related specific emissions are displayed in following Figure 3.20 to Figure 3.25, respectively for parameters TOC, COD, BOD₅, TSS and Total Nitrogen. These particular figures only concern data relating to refineries where aqueous effluents are treated in a single dedicated waste water treatment plant.

The amount of oil discharged is usually expressed in grams of Total Hydrocarbon Content (THC) per tonne of refinery throughput. According to CONCAWE, nearly 90 % of the European refineries meet the standard of the Oslo/Paris Commission of 3 grams THC/tonne of refinery throughput since the early 1990's.

Table 3.16: Typical refinery influent/effluent annual average composition and load

Parameter	Composition after pretreatment by API, CPI and SWS		Annual effluent composition downstream WWTP		Specific load (g/t feedstock)		No ⁽²⁾	
	Average	Max.	Min - Max					
pH (pH unit)	7	10	6 – 9					
Temperature (°C)	25	45	10 – 35					
			5th – 95th Percentile	50th Percentile	5th – 95th Percentile	50th Percentile		
Concentration in mg/l	TOC	100	250	4 – 50	14	1 – 15	5.5	22
	COD	300 – 500	1 000	19 – 125	66	9 – 85	27.2	38
	BOD5	80 – 150	300	2 – 30	10	0.5 – 25	4.4	31
	HOI ⁽³⁾	40 – 50	100	0.05 – 6.3	1.5	0.1 – 3	0.4	15
	HOI ⁽⁴⁾	NA	NA	0.3 – 5	1.2	0.03 – 10	0.6	11
	TSS	20 – 60	200	4 – 35	15	1 – 30	6.3	37
	AOX ⁽¹⁾	NA	NA	0 – 6	0.2	0 – 0.5	0.06	14
	Ammonium-N	12 – 15	30	0.3 – 15	2.7	0.1 – 10	1.2	19
	Nitrites-N	NA	NA	0.03 – 1.5	0.2	0.05 – 0.7	0.1	13
	Nitrates-N	NA	NA	0.4 – 12	1.7	0.2 – 3	1.4	15
	Kjeldahl nitrogen	25	50	2 – 20	5.4	1 – 6	2.3	13
	Total Nitrogen	25	50	3 – 22	8	1 – 20	4	38
	Phosphate	5	20	0.1 – 1.5	0.3	0.05 – 1	0.13	7
	Total Phosphorus	NA	NA	0.05 – 4	0.6	0.05 – 2	0.3	26
	Anionic agents	NA	NA	0.2 – 0.3	0.25	0.1 – 0.2	0.15	2
	Cyanide ⁽¹⁾	0 – 3	5	0.003 – 0.1	0.015	0.001 – 0.03	0.004	16
	Sulphide	5	10	0.005 – 0.2	0.05	0.002 – 0.25	0.025	16
	Phenols	12	25	0.01 – 0.4	0.1	0.001 – 0.3	0.02	29
	MTBE ⁽¹⁾	0 – 3	15	0.003 – 0.1	0.02	0.001 – 0.03	0.005	3
	Fluoride ⁽¹⁾	0 – 30	60	0.2 – 3	0.8	0.3 – 2	0.6	7
	Benzene	NA	10	<0.001 – 0.1	0.001	<0.001 – 0.05	0.002	10
	Toluene	NA	NA	<0.001 – 0.6	0.003	<0.001 – 0.1	0.004	10
	Ethylbenzene	NA	NA	<0.001 – 0.005	0.001	<0.001 – 0.007	0.004	9
	Xylenes	NA	NA	<0.001 – 0.2	0.001	<0.001 – 0.15	0.004	7
	BTEX	5	10	<0.001 – 1	0.005	<0.001 – 0.2	0.01	10
	PAH-16	0.1	0.5	<0.0001 – 0.01	0.0007	<0.0001 – 0.005	0.0003	11
	Arsenic-As	NA	NA	<0.001 – 0.02	0.003	<0.001 – 0.02	0.0007	21
	Boron-B	NA	NA	0.2 – 0.6	0.4	NA	NA	4
	Cadmium-Cd	NA	NA	<0.001 – 0.05	0.001	<0.0001 – 0.005	0.001	18
	Chromium-Cr	NA	100	<0.001 – 0.05	0.003	<0.0001 – 0.005	0.001	23
	Chromium VI	NA	NA	<0.001 – 0.02	0.002	<0.0001 – 0.002	0.001	7
	Cobalt-Co	NA	NA	<0.001 – 0.003	0.001	NA	NA	3
	Copper-Cu	NA	NA	0.01 – 0.1	0.05	<0.001 – 0.03	0.002	27
Iron-Fe	NA	NA	0.15 – 3	0.4	0.01 – 0.6	0.15	14	
Mercury-Hg	NA	NA	<0.0001 – 0.003	0.0002	<0.0001 – 0.002	0.0001	21	
Manganese-Mn	NA	NA	0.02 – 0.5	0.08	0.001 – 1.8	0.04	9	
Molybdenum-Mo	NA	NA	0.004 – 0.02	0.01	NA	NA	4	
Nickel-N	NA	NA	0.002 – 0.1	0.01	<0.001 – 0.03	0.006	22	
Lead-Pb	NA	10	<0.0001 – 0.01	0.001	<0.0001 – 0.02	0.005	25	
Selenium-Se	NA	NA	0.003 – 0.08	0.04	NA	NA	5	
Stain-Sn	NA	NA	<0.001 – 0.02	0.01	<0.0005 – 0.005	0.004	6	
Vanadium-V	NA	NA	0.005 – 0.1	0.02	<0.001 – 0.01	0.003	10	
Zinc-Zn	NA	NA	0.005 – 0.12	0.03	<0.001 – 0.1	0.015	29	
Heavy metals ⁽⁵⁾	1	2	0.05 – 1.0	0.2	0.02 – 2	0.1	-	

(¹) dependent on whether or not relevant units are part of the refinery.
(²) Number of available site yearly concentration values provided to the TWG .
(³) Hydrocarbon Oil Index measured according to method EN 9377-1.
(⁴) Hydrocarbon Oil Index measured according to method EN 9377-2: 2000 (GC-FID).
(⁵) Sum of individual percentile data for the following metals: Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, Sn; V, Zn..
(-) Not appropriate .
Source: [TWG data collection questionnaires]

Table 3.17: Emissions of main organic pollutants and suspended solids from a sample of 48 European sites

Site label	Total feed refined kt	Dedicated WWTP yes=1	TOC			BOD5			COD			TSS		
			mg/l	g/t	kg/yr	mg/l	g/t	kg/yr	mg/l	g/t	kg/yr	raw	final	kg/yr
38	8 183	0	50.0	5.4	44 000	60	6.5	53 000	170	18.3	150 000		49.0	43 000
1	9 096	0	10	7.4	67 000	5	3.9	35 510	28	20.3	184 920			
6	12 400	0								21.5	266 897			
26	10 193	0				14	7.8	79 967	115	54.3	553 019	71	62.8	350 232
58	11 430	0					6.9	78 937		61.3	700 976			157 515
30	10 490	0				102	16.9	176 843	374	61.7	647 501		72.8	125 970
27	19 151	0				15			115			200	25.0	
31	12 087	0	29.2	10.6	128 406							127	76.9	377 678
48	6 900	0		94.6	652 522									
51	4 400	0		138.4	608 808									
35	3 624	1	20.4	1.3	4 630	8	0.5	1 774	74	4.6	16 771		14.2	3 211
56	6 276	1	20.6	2.4	14 919	4	0.4	2 818	55	6.3	39 701	56	8.6	6 235
11	9 350	1				13	2.2	20 983		9.1	84 684		7.3	11 571
39	10 098	1	9.0	2.5	25 600	3	0.9	9 000	33	9.3	94 000	9	9.0	25 600
40	5 668	1	11.7	3.0	16 900	8	2.1	11 700	42	10.6	60 000	24	4.2	6 000
41	3 942	1					4.3	16 900		11.4	44 900			10 800
4	4 900	1				2	0.7	3 524	37	11.5	56 397		6.5	9 770
19	3 359	1				31	4.4	14 782	82	11.9	39 936			
17	728	1				24	3.0	2 184	112	13.9	10 115		29.7	2 679
47	11 871	1	4.0	1.0	11 857				65	14.8	175 364	72	17.0	45 043
15	4 858	1	18.0	4.1	19 959	10	2.2	10 881	88	16.5	80 365	25	20.0	20 395
42	10 916	1	22.0	5.6	61 139				66	17.1	186 463	36	10.0	29 352
59	3 513	1				9.27	1.5	5 331	95.88	18.6	65 333		22.6	13 007
12	6 412	1	12.8	5.5	35 100	5	2.1	13 329	44	18.8	120 274		7.9	21 569
50	4 620	1	12.5	5.4	25 162	27	11.6	53 508	45	19.7	91 085		17.2	34 557
52	4 990	1	18.1	7.6	38 000				53	22.4	112 000		4.8	10 000
34	10 462	1	1.3	0.5	5 293					23.3	243 508			
28	14 251	1							55	26.2	372 765	100	6.4	43 509
9	5 727	1				2	3.2	18 300	21	26.7	152 838		8.5	61 319
16	7 153	1	15.2	5.6	40 020	8	2.9	21 031	73	27.6	197 587		12.0	32 967
46	9 712	1	12.0	3.7	36 397				98	29.5	286 809		13.0	37 792
36	5 622	1				13	6.8	38 002	59	31.4	176 436		13.5	40 716
7	3 268	1				4	17.9	58 390	8	31.4	102 758		6.3	86 301
10	8 852	1				24	5.5	48 444	136	31.7	280 318	80	32.0	67 095
22	8 635	1	10.0	8.2	70 985	18	14.2	122 237	41	33.0	284 850		19.9	138 938
32	5 886	1	46.8	14.9	87 834				111	35.4	208 325	178	22.4	42 040
25	3 613	1							48	35.9	129 597		21.8	59 375
57	5 778	1				8	5.6	32 318	53	36.3	209 729		23.5	92 272
37	7 293	1							109	38.9	283 706			
5	2 772	1				6	3.5	9 800	90	49.8	138 000		14.8	22 700
49	15 000	1				32	10.7	16 0810	149	49.9	748 772		19.0	95 481
13	5 303	1				13	8.3	43 989	76	50.1	265 582		16.3	57 490
18	8 272	1				13	15.3	126 700	47	55.7	460 640			
14	16 552	1				14	9.1	151 450	95	56.2	930 051		10.7	104 707
29	3 817	1	10.7	6.9	26 213	20	13.0	49 733	121	77.3	295 211		22.2	54 387
8	953	1				25	37.7	35 939	80	110.7	105 561		14.0	18 637
33	4 610	1	65.5	18.6	85 800									
53		1	16.0		21 000	10		12 000	40		48 000		15.0	36 000
54	10 794	1	20.3	7.7	82 706								47.0	199 780
60		1	8.2		18 253	2.53		5 256	40.23		83 353		10.3	21 425
61		1	15.0		157 701	15		162 733	97		1 028		23.3	246
No of values	48	51	24	23	26	34	32	35	41	42	45	12	39.0	41
5th percentile ⁽¹⁾			3.9	0.9	11 528.8	2.4	0.8	3 100	29.4	9.2	35 263	15	5.7	5 004
50th percentile ⁽¹⁾			13.9	5.5	30 656.5	11.3	4.3	20 983	65.0	26.7	133 799	56	14.0	34 557
95th percentile ⁽¹⁾			47.7	15.7	91 327.4	29.7	17.2	157 066	125.2	62.5	503 860	147	30.6	114 976

⁽¹⁾ Only for sites with a dedicated WWTP.

Source: [TWG data collection questionnaires]

Table 3.18: Emissions of nitrogen compounds from a sample of 51 European sites

Site label	WWTP	Total feed	Ammonium (NH ₄ - N)			Nitrites (NO ₂ - N)			Nitrates (NO ₃ - N)			Nitrogen Kjeldahl			Total nitrogen (as N)					
			(¹)	kt	(²)	mg/l	g/t	kg/yr	mg/l	g/t	kg/yr	mg/l	g/t	kg/yr	mg/l	g/t	kg/yr	(²)	mg/l	g/t
1	0	9096		0.9														10.70		
6	0	12400																	6.51	80721
26	0	10193								12.52	127639	9.80	4.63	47170	27			17.15	174808	
27	0	19151					0.60			1.60				11.00				13.00		
30	0	10490																71.00	11.71	122856
31	0	12087		7.3	2.64	31950												16.80	4.67	56400
38	0	8183		12.0	1.34	11000				16.00	1.71	14000						24.00	2.58	21100
48	0	6900																	54.93	378998
51	0	4400																	21.02	92483
58	0	11430																	17.62	201442
4	1	4900			0.34	1655													1.23	6030
5	1	2772																	1.84	5100
7	1	3268														21		4.50	18.67	61017
8	1	953					0.20	0.34	320	1.40	1.95	1858	3.40	4.56	4343			4.90	6.84	6521
9	1	5727																3.57	4.58	26248
10	1	8852											30.00	6.99	61877					
11	1	9350												0.98	9158					
12	1	6412											5.40	2.28	14590					
13	1	5303																23.18	15.62	82859
14	1	16552																8.10	4.80	79500
15	1	4858	11	6.19			0.60			7.00			13.00			21		17.00	4.11	19960
16	1	7153					0.58	0.73	1597	3.77	6.31	10192						11.20	4.08	29215
17	1	728																	4.02	2930
18	1	8272	7	0.9	1.10	9096	0.09	0.11	910	0.60	0.71	5846						1.42	1.64	13563
19	1	3359		14.8	2.28	7669														
22	1	8635		1.7	1.37	11838	0.05	0.04	349	2.40	1.91	16536						5.40	4.35	37601
25	1	3613		4.2	2.75	9945	0.08	0.06	220	0.34	0.24	854								
28	1	14251	4	0.	0.41	5805				0.80	0.38	5438				9		2.20	1.09	15541
29	1	3817					0.00			1.70			4.30					6.60	3.27	12494
32	1	5886		16.8	5.36	31530												18.90	6.03	35472
33	1	4610																	49.24	227000
34	1	10462			1.66	17371					2.60	27239	5.20							
35	1	3624		2.7	0.17	615													2.39	8660
36	1	5622	15	2.7																
37	1	7293																9.80	3.50	25508
39	1	10098	5	0.5	0.14	1400										8		1.60	0.45	4500
40	1	5668		2.5	0.58	3300												4.00	1.01	5700
41	1	3942			0.46	1800			400		1.24	4900							2.82	11100
42	1	10916	23	0.4	0.10	1037										43		19.50	5.04	55000
46	1	9712		4.2	1.25	12108														
47	1	11871														19		5.00	0.98	11596
49	1	15000					0.12	0.07	1060	0.49	0.16	2467	16.70	5.59	83823			18.32	5.47	82064
50	1	4620					2.24	3.13	4402	5.95	11.80	12261	5.21	2.25	10385			13.42	5.51	25452
52	1	4990	32	2.7														6.00	2.00	10000
53	1		2	0.04		50										40		15.00		18000
54	1	10794		7.5	2.87	30991												9.10	3.51	37851
56	1	6276																4.00	0.45	2837
57	1	5778			5.59	32318													5.88	33955
59	1	3513		4.58	0.75	2635	0.51	0.08	291.7	20.51	3.36	11789	8.12	1.33	4666			27.96	4.80	16856
60	1			1.45		2995	0.12		238.5	5.44		11275	2.98		6171			8.13		16944
61	1			8.95		94475	0.88		9277	1.00		10508	13.04		624.5			13.87		146349
No	51	48	8	22	19	22	13	8	11	15	13	15	13	8	10	8	31	38	41	
Average (³)		7579	12	4.71	1.64	14617	0.47	0.23	1733	4.60	2.37	17520	9.86	3.57	24281	23.5	12.84	8.19	56152	
5th perc. (³)		2499	2	0.36	0.13	587	0.03	0.05	229	0.43	0.20	1456	3.19	1.08	2112	8.24	1.75	0.69	3872	
50th perc. (³)		5753	9	2.70	1.10	6737	0.16	0.10	400	1.70	1.42	10192	5.40	2.28	9158	21.2	8.12	4.05	18000	
95th perc. (³)		14363	29	15.00	5.40	35426	1.49	0.74	6840	12.40	3.00	20817	20.35	6.57	75045	42.1	22.26	17.30	108255	

(¹): 0 = collective, 1 = dedicated (²): intermediate concentration (in mg/l) after API, CPI and SWS (³): only for dedicated WWTP
Source: [TWG data collection questionnaires]

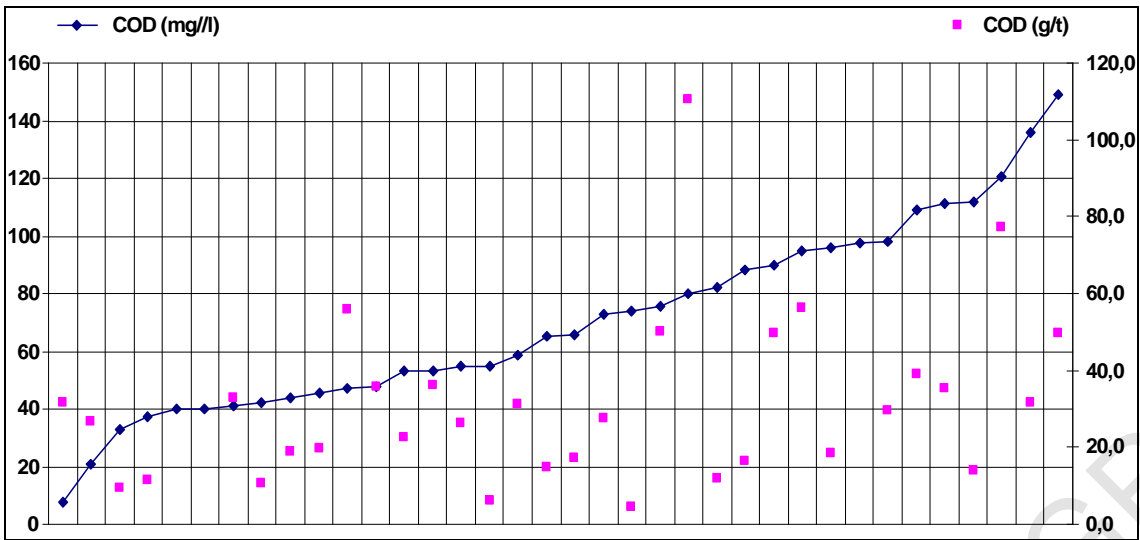


Figure 3.20: Distribution of COD emissions for a sample of 36 European refineries

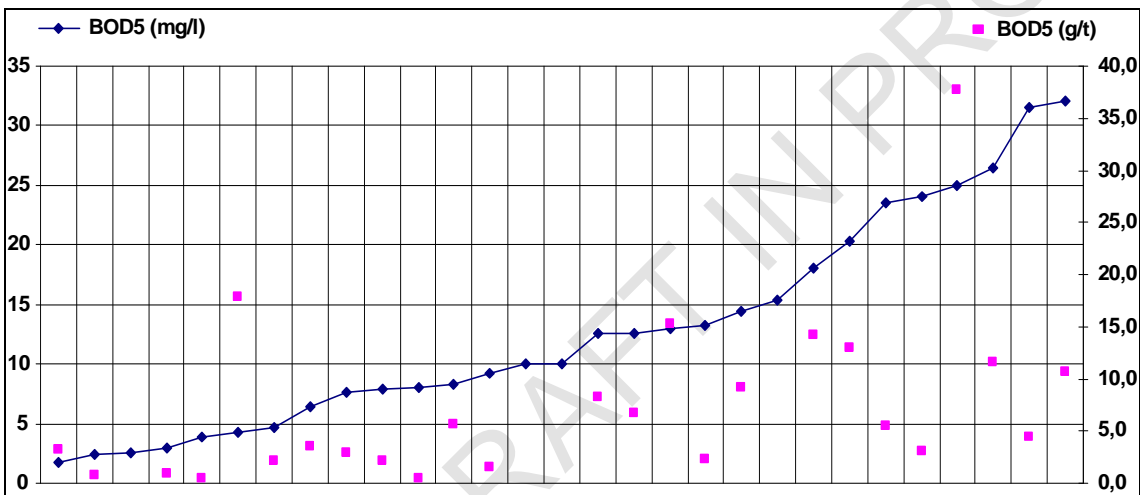


Figure 3.21: Distribution of BOD₅ emissions for a sample of 29 European refineries

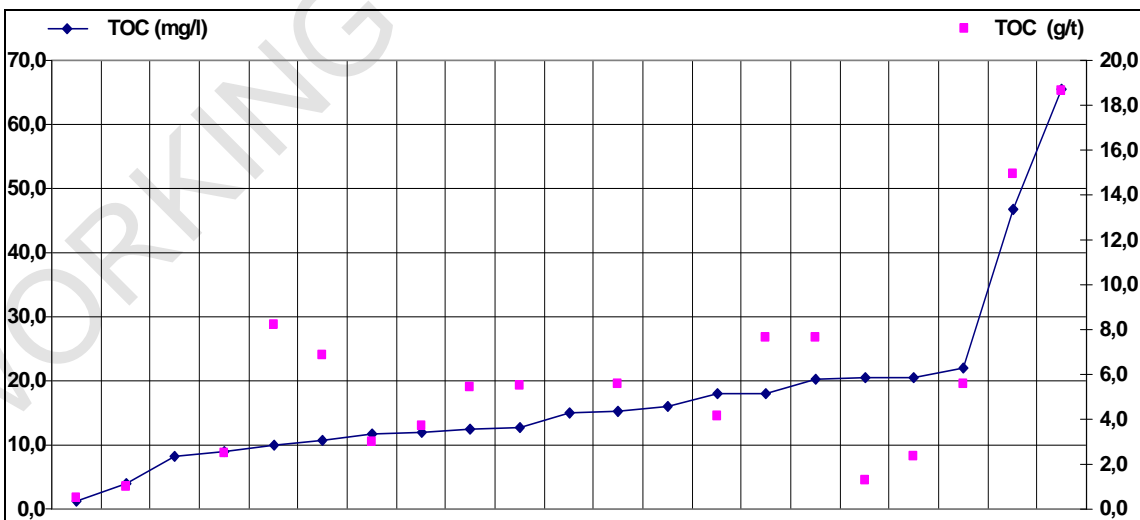


Figure 3.22: Distribution of TOC emissions for a sample of 21 European refineries

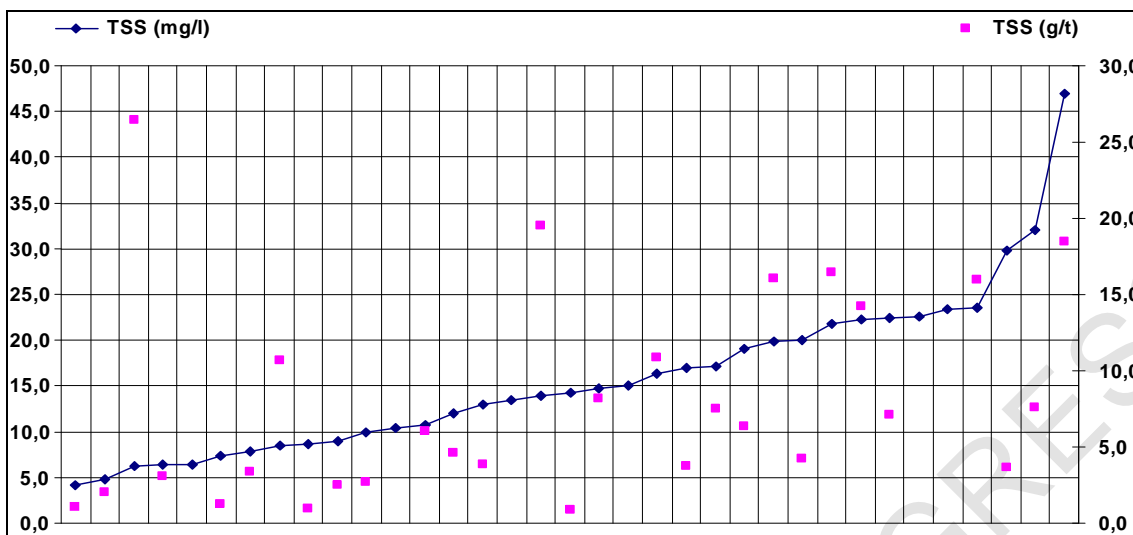


Figure 3.23: Distribution of suspended solid emissions for a sample of 34 European refineries

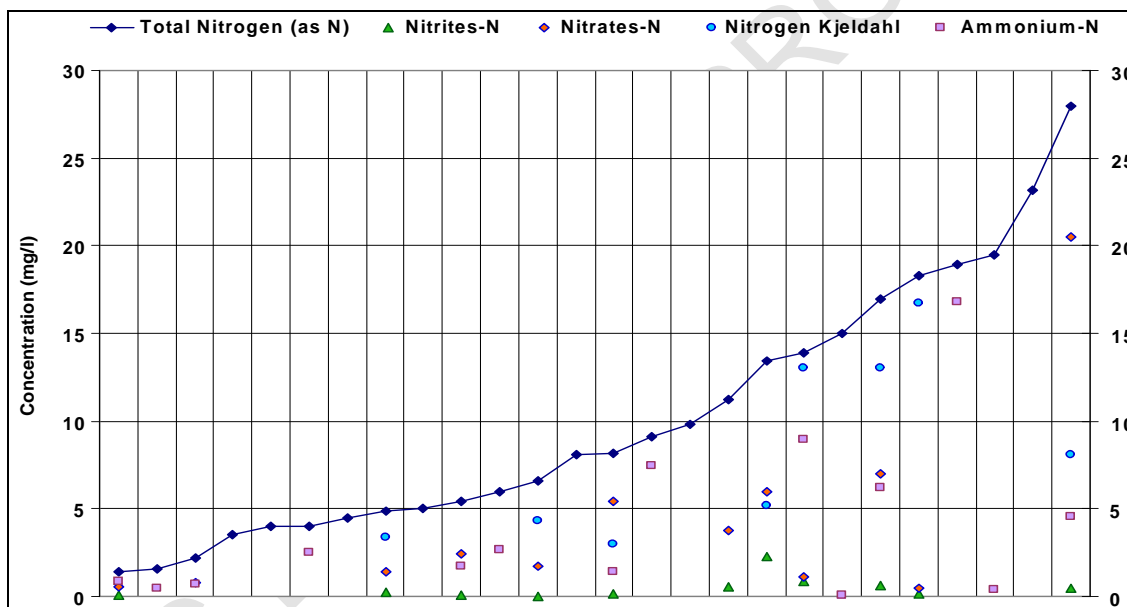


Figure 3.24: Distribution of annual average concentrations of nitrogen compound discharges for a sample of 26 European refineries

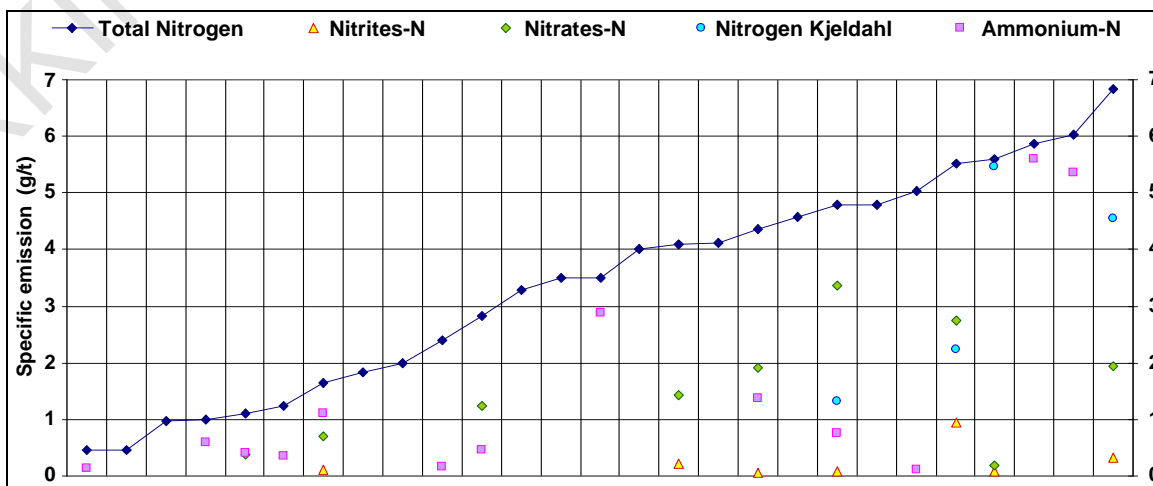


Figure 3.25: Distribution of specific emissions of nitrogen compounds for a sample of 27 European refineries

3.2 Alkylation

This section contains data on consumption and emissions generated by alkylation processes.

Consumptions

Table 3.19 gives a summary of the utility and chemical consumptions in the two techniques currently used in the alkylation processes, and for the new solid-acid process.

Table 3.19: Estimated utilities and chemical consumption for the various alkylation techniques

Values per tonne of alkylate produced	Sulphuric acid	Hydrofluoric	Solid Acid
Utilities			
Electricity (kWh)	80 – 130	20 – 65	134
Fuel (MJ)	Not required	1 000 – 3 000	Not required
Steam (kg)	815 – 1 200	100 – 1 000	1028
Cooling water (m ³) ($\Delta T = 11\text{ }^{\circ}\text{C}$)	40 – 83	62	0.78
Industrial water (m ³)	0.08		Not required
Chemicals			
Fresh acid (kg)	78 – 180	1.15	0.14
Caustic (as 100 % NaOH) (kg)	0.41	0.57	Not required
Lime	NA	NA	Not required
NB: AlCl ₃ and water-free CaCl ₂ consumption depend on operating conditions (water content of feed- and side-reactions).			
Sources: [175, Meyers 1997], [168, VROM 1999], [204, Canales 2000]			

Emissions

Emissions generated by the alkylation processes are summarised in Table 3.20 to Table 3.22. [161, USAEPA 1995], as reviewed by the the TWG.

Table 3.20: Air emissions generated by the alkylation processes

Air pollutant	Sulphuric acid	Hydrofluoric	Solid acid
CO ₂ , SO ₂ , NO _x and other pollutants from the furnaces(*)	No furnace	From column heating furnaces	No furnace
Hydrocarbons Hydrocarbons	May be released from pressure reliefs, storage, handling operations, spillages and fugitive emissions		No water discharge No waste discharge
	May be released from water and waste discharges		
Halogens	NA	Fluoride compounds may be released from pressure reliefs, vent gas and spillages	No halogens
Odours	NA	Acid-soluble oil may be released from process shutdown ponds during maintenance work, particularly the de-scaling of pipes conveying hydrogen fluoride. This may be odorous	No odour
(*) Emissions from these combustion processes are addressed in an integrated way in Section 3.10.3.1.			
Source: [161, USAEPA 1995]			

Table 3.21: Waste water generated by alkylation processes

Water parameter	Sulphuric	Hydrofluoric	Solid acid
Waste water	Waste water produced in the alkylation process may have a low pH if the neutralisation section operates in non-normal conditions, suspended solids, dissolved solids, COD, H ₂ S, and spent acid.		No liquid waste at all
Hydrocarbons	NA	HC from separator drains (surge drum, accumulator, dryer) and spillages, and of acidic effluent containing dissolved and suspended chlorides and fluorides from the settlement pit or the process shutdown ponds.	
Acid	Sulphuric acid	Effluents from HF scrubber are 2 – 8 m ³ /h with compositions min/max of 1 000 – 10 000 ppm F; after lime treatment 10 – 40 ppm F.	

Table 3.22: Solid waste generated by the alkylation techniques

Solid waste	Sulphuric	Hydrofluoric	Solid acid
Sludge	NA	The flow 7 – 70 kg sludge per kg used HF (dry solids content 3 – 30 %)	No sludge
Hydrocarbons	Sludge generated in the neutralisation process contains hydrocarbons. Dissolved polymerisation products are removed from the acid as a thick dark oil.	HC from spent molecular sieves, carbon packings and acid-soluble oil. Sludge generated in the neutralisation process contains hydrocarbons. Dissolved polymerisation products are removed from the acid as a thick dark oil.	No acid soluble oil - No salts
Acid/catalyst products in the sludge	Sludge generated in the neutralisation process contains sulphuric acid.	Inorganic fluorides (Na/KF) and chlorides from treatment stages. Sludge generated in the neutralisation process contains CaF ₂ .	Spent catalyst sent back to supplier for Pt recovery after years of operation
Halides	NA	Composition of sludge is 10 – 40 ppm F ⁻ after lime treatment	No halides
<i>Source:</i> [161, USAEPA 1995]			

3.3 Base oil production

This section gives the consumption and emission values that can be found in the base oil production process identified. It also provides additional information about the nature of substances used in base oil production, in order to highlight the more environmentally significant sub-processes.

Nature of substances used

It is reported that unrefined and mildly-refined distillate base oils contain the highest levels of undesirable components, have the largest variation of hydrocarbon molecules; and show the highest potential carcinogenic and mutagenic activities. Highly- and severely- refined distillate base oils are produced by removing or transforming undesirable components from the unrefined and mildly ones. In comparison, the highly- and severely- refined distillate base oils have a smaller range of hydrocarbon molecules and have demonstrated very low toxicity for mammalian species.

3.3.1 Deasphalting

Consumption

A conventional solvent-based base oil lube complex is energy intensive. The main reason is the high amount of heat required to evaporate the solvents and to separate them from the raffinate and extract streams. Solvent losses are usually in the order of 1 %, despite extensive solvent recovery. In the tower method, for example, four to eight volumes of propane are fed to the bottom of the tower for every volume of feed flowing down from the top of the tower. It is reported, taking into account the specific input of some crudes and the output of crucial specifications (e.g. CCR), that there is a need to use a higher propane ratio, of up to 9 or 11 to 1.

As an example, the figures below give the utility requirements of a solvent deasphalting absorption (SDA) unit.

Table 3.23: Consumption data of deasphalting units

Utility	Data corresponding to 1 000 tonnes of feedstock
Fuel	136 – 150 MWh
Power	12.2 – 21 MW
Steam	166 – 900 tonnes
Cooling water	Nil (maximum air cooling)
<i>Sources: [175, Meyers 1997], [204, Canales 2000]</i>	

Table 3.24: Emission data of deasphalting units

Emissions		
Air	Waste water	Solid waste
Air emissions may arise from fugitive solvent emissions and process vents. Heater stack gas	The solvent recovery stage results in solvent-contaminated water which is typically sent to the waste water treatment plant. Oil components	Little or no solid waste generated.

3.3.2 Aromatic extraction

Consumptions

As an example, the figures below in Table 3.25 and Table 3.26 give the utility requirements and the emissions data of an aromatic extraction unit.

Table 3.25: Consumption data of aromatic extraction units

Examples of utilities consumption per m ³ feedstock		
Fuel absorbed	862 – 1 300	MJ
Electricity	5	kWh
Steam	8	m ³
Water cooling ($\Delta T = 14\text{ }^{\circ}\text{C}$)	12.5	m ³
<i>Source: [183, HP 1998] reviewed by TWG</i>		

Table 3.26: Emission data of aromatic extraction units

Emissions		
Air	Waste water	Solid waste
Fugitive solvent VOC emissions can come from the furfural and NMP from its storage tanks.	The total amount of process water is around 2 – 4 m ³ per tonne of product, containing around 15 – 25 ppm furfural, 10 – 15 ppm NMP.	Little or no solid wastes generated.
Flue-gas from fired heater	The water stream leaving the fractionator is likely to contain some oil and solvents.	
<i>Source: [168, VROM 1999]</i>		

3.3.3 High pressure hydrogenation unit

As an example, the figures below in Table 3.27 provide the utility requirements data of an high pressure hydrogenation unit.

Table 3.27: Typical utility consumption of an high pressure hydrogenation unit

Utilities, typical per kt of feedstock		
Fuel	11.5	t
Electricity	26	kWh
Net steam consumption ⁽¹⁾	200	t
Water cooling ($\Delta T = 14\text{ }^{\circ}\text{C}$)	110	m ³
⁽¹⁾ 50 % is recovered as condensate		

3.3.4 Solvent dewaxing

Consumptions

The utility requirements in this process together with the aromatic extractions are:

Table 3.28: Typical combined utility consumption of solvent dewaxing and aromatic extraction units

Fuel (MJ/t)	Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m ³ /t, $\Delta T=10\text{ }^{\circ}\text{C}$)
1 000 – 1 300	60 – 160	300 – 800	10 – 20
<i>Source: [168, VROM 1999], [204, Canales 2000]</i>			

Table 3.29: Emission data of solvent dewaxing units

Emissions		
Air	Waste water	Solid waste
VOCs may arise from solvent vapour extraction from the wax filters as well as fugitive emissions. Fugitive solvent VOC emissions can come from the MEK/Toluene from storage tanks. Flue-gas from fired heater	The solvent recovery stage results in solvent-contaminated water which is typically sent to the waste water treatment plant. Potential releases into water are hydrocarbons, sulphur compounds and organic compounds from spillages and leaks, and organic compounds from process waters from solvent recovery operations. Waste water contains 1 – 3 ppm MEK/toluene	Little or no solid wastes generated

3.3.5 Hydrofinishing

Consumptions

The utility needs for a hydrofinishing unit are:

Table 3.30: Typical utility consumption of hydrofinishing units

Fuel (MJ/t)	Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m ³ /t, $\Delta T=10\text{ }^{\circ}\text{C}$)
300 – 550	25 – 40	100 – 150	5 – 15
<i>Source:</i> [168, VROM 1999]			

Table 3.31: Emission data of hydrofinishing units

Emissions		
Air	Waste water	Solid waste
Pressure relief valves of the hydrofiner, solvent recovery systems and refrigerant systems; Leakages from flanges, glands and seals on pumps, compressors and valves.	Leakages from flanges, glands and seals on pumps, compressors and valves.	NA

Reference literature

[76, Hydrocarbon processing 2011], [168, VROM 1999], [183, HP 1998], [204, Canales 2000], [272, US EPA 2003], [274, IARC 1983].

3.4 Bitumen production

Consumptions

Bitumen blowing is a very low energy process. Some electricity is required for the air blower, product run down pump, and the overhead condensing system. The electricity utilisation in this process is 15 – 35 kWh/tonne and the steam produced in the process is 100 – 200 kg/tonne. For cooling-water utilisation, it is assumed that an air cooler is used as a condenser. If a direct water quench is applied instead of scrubbing, more water is normally used.

Emissions

Available information has been gathered in Table 3.32.

Table 3.32: Emission data for bitumen production units

Air	<p>Flue-gas from fired heater</p> <p>Flue-gas from the overhead vapours incinerator. The overhead vapours from bitumen production, consisting mainly of light hydrocarbons, N₂, O₂, CO₂ and SO₂, are incinerated at high temperature (~800 °C) to ensure complete destruction of components such as H₂S, CO, complex aldehydes, organic acids, PAHs and phenolics, which have a highly unpleasant odour. The flow of the oxidiser overhead is around 0.07 – 0.30 Nm³ air/kg feed.</p> <p>The main problems with bitumen production relate to hydrogen sulphide releases from the distilled residues and sour condensates and gas produced in the blowing process. Hydrocarbons and sulphur compounds may emanate from leakages (particularly from overhead systems) and pressure relief valves and in the form of aerosol-containing liquid droplets from the venting of tanker top-loading operations.</p>
Process waste water	<p>Sour water is produced in the oxidiser overhead waste water. Its flow is up to 5 m³/tonne feed and it contains H₂S, oil, aromatics, PAHs, sulphuric acid, odorous oxidation products (ketones, aldehydes, fatty acids) and particulates.</p> <p>Other potential releases into water are of hydrocarbons and sulphur compounds from spillages and leakages.</p>
Solid waste	<p>Slop oil emulsions are formed in the oxidiser overhead slop oil. It consists of an emulsion of light oil, water and particulates.</p>

3.5 Catalytic cracking

3.5.1 Consumptions

The next table shows the energy and process materials usage in the catalytic crackers.

Table 3.33: Typical utility consumption of catalytic crackers

Utility	FCC	RCC
Fuel (MJ/t)	120 – 2 000	120 – 2 000
Electricity (kWh/t)	8 – 50	2 – 60
Steam consumed (kg/t)	30 – 90	50 – 300
Steam produced (kg/t)	40 – 60	100 – 170
Cooling water (m ³ /t, $\Delta T=17$ °C)	5 – 20	10 – 20
Catalyst make-up (kg/t)	0.4 – 2.5	2 – 4
<i>Sources:</i> [204, Canales 2000], [183, HP 1998], [168, VROM 1999], [175, Meyers 1997], [207, TWG 2001]		

Virtually all the heat required in a FCC or a RCC unit is generated in the regenerator.

The catalysts consumed and released to air as emissions depend on the type of product processed and can be silica-alumina substrate carrying rare earth and/or precious metals, or more typically consist of rare-earth exchanged zeolites on alumina matrices and clays.

3.5.2 Emissions

3.5.2.1 Air emissions

Within a refining complex, one of the sources with a major potential for atmospheric emissions is the catalytic cracking unit. Air emissions arise principally from the regenerator and are mainly CO, CO₂, NO_x, particulates (mainly catalyst fines including their constitutive heavy metals) and SO₂. The emissions from catalytic crackers are very variable reflecting the variation of the feedstocks used (nitrogen, sulphur, metal contents), and the regenerator and waste heat boiler operating conditions.

Emissions from a FCC unit can increase over time as the quality of air catalyst mixing in the regenerator deteriorates as a result of wear. For example, internal mechanical damage or equipment wear/erosion could occur towards the end of run of the unit and this could significantly increase all unit emissions CO, (NO_x, SO_x and PM).

As already shown in Section 3.1.2, emissions from an FCC unit can be 10 – 30 % of total refinery SO₂ emissions (see Figure 3.13), 15 – 25 % for NO_x (See Table 3.4) and 30 – 40 % for particulates. However, these figures can be subject to wider variation [163, FWE 1999]. The next table shows a summary of the emission factors and emissions from FCCs.

Table 3.34: Emission data and factors found in catalytic crackers (with and without abatement techniques)

Emissions	PM	SO _x (as SO ₂)	CO	HC	NO _x (as NO ₂)	Aldehydes	NH ₃
Emission factors (kg/m ³ of fresh feed)	0.009 – 0.976	0.19 – 1.50	0.08 – 39.2	0.630	0.107 – 0.416	0.054	0.155
Emission data (mg/Nm ³ at 3 % O ₂)	15 – 1 600	320 – 2 500	135 – 66 000	NA	180 – 700	NA	NA
NB: Values attainable in continuous operation. Emissions values as half hourly mean values Lower levels in the range are catalytic crackers with abatement techniques.							
Sources: [172, MRI 1997], [221, Italy 2000], [204, Canales 2000], [167, VDI 2000], [194, Winter 2000], [208, Confuorto 2000] Updated TWG 2010							

There is a growing trend in the EU towards processing more residual feedstock in FCC units in response to increasing demand for road transport fuels and a decreasing demand for residual fuels. Residual feedstock brings higher content of coke precursors, sulphur, nitrogen, Ni and V metals, and aromatics. The increased sulphur load has proportional and related effects on the S content in the coke and thus on SO₂ emissions, if abatement provisions as a consequence of the change are not made. The increased nitrogen load potentially leads to the increased production of NO_x precursor compounds NH₃ and HCN, which may or may not lead to increased actual NO_x emissions, depending on the FCC unit regenerator operations.

Potential consequences of the high metals content include:

- a substantial increase in catalyst consumption and potentially higher regenerator PM losses due to increased catalyst attrition;
- the formation of FeS (from the increased feed Fe content) over the equilibrium catalyst, which is then oxidised to SO₂ and SO₃ in the regenerator, thus increasing the flue-gas SO_x content;
- an increase of NO_x emissions, due to the required antimony additions used to passivate nickel to reduce the production of hydrogen.

Residue catalytic crackers (RCC) mainly use atmospheric residue as feedstock. Hence the Conradson carbon, sulphur content and nitrogen content are higher. Therefore, RCCs are potentially a stronger source of SO_x, NO_x, PM and contaminated catalyst than normal FCCs. However, as a consequence of the type of feedstock used in the RCC, the RCC produces more coke and hence more heat should be removed from the regenerators.

Because the catalytic cracker is a significant emitter of pollution in a refinery, there follows a more detailed analysis by type of pollutant.

Carbon dioxide

Carbon dioxide is generated in the catalyst regeneration train and its load depends on the size.

Table 3.35: Range and examples of emissions of CO₂ from catalytic crackers

Throughput (kt/yr)	% S in feed	Flue-gas flow (Nm ³ /h at 3 % O ₂)	CO ₂ emission load (t/yr)	Specific CO ₂ emission (kg/t)
1314	<0.5	110 000	272 243	207
2350	0.35	200 000	498 006	212
Range of emissions			130 000 – 600 000	160 – 220 ^(*)
(*) High Conradson carbon feed can lead to increasing CO ₂ emissions.				
Sources: [194, Winter 2000], [172, MRI 1997] reviewed by TWG				

Carbon monoxide

Relatively high concentrations of carbon monoxide (CO) can be produced during the regeneration of the catalyst. CO is typically converted to carbon dioxide either in the regenerator (full combustion mode) or further downstream in a carbon monoxide boiler (partial combustion mode).

In the full combustion mode, incomplete combustion can lead to releases of carbon monoxide. CO from units operating in full combustion mode ranges typically between 50 and 1200 mg/Nm³ (depending on temperature, CO promoter level, size of unit).

In the partial combustion mode, depending on the conditions under which the regenerator is operating, the levels of CO in the regenerator exhaust gases feeding the CO boiler may be in the region of 5 to 10 %, and levels of CO in the exhaust from the CO boiler can be maintained at less than 100 mg/Nm³, depending on the type of CO boiler used [156, MCG 1991].

Table 3.36: Examples of CO from catalytic crackers

Throughput (kt/yr)	%S In feed	Flue-gas flow (Nm ³ /h at 3 % O ₂)	CO concentration (mg/Nm ³)	CO emission load (t/yr)	Specific CO emission (kg/t)
1 314	0.5	110 000	215 – 814	558	0.43
2 350	0.5	200 000	125	194	0.08

NB: data are related to yearly average, 3 % O₂, dry conditions
 Source: [194, Winter 2000]

CO boilers are usually used only in connection with FCCs operating in partial combustion mode with CO concentrations in the flue-gas from 5 to 10 %. They are not used to further reduce CO emissions from units operating in full combustion mode.

Nitrogen oxides

The wide range in NO_x emissions (levels) from catalytic cracker regenerators (gases) reflects the main effects of different combustion conditions on FCC regenerators or FCC CO boilers, the spread in unit capacities and the coke (feed) nitrogen contents. These depend on crude type and upstream process configuration. NO_x are generated in different ways for the two combustion modes.

In the full combustion mode, key parameters potentially affecting the FCC unit NO_x emissions are:

- uneven regenerator catalyst bed temperature and oxygen profiles and distribution;
- use of a CO combustion promoter containing platinum (contributes to NO_x increase);
- antimony additions, often used for high-metal feed applications.

In the partial combustion mode, key parameters potentially affecting the FCC unit NO_x emissions are (Sources: [24, Bruhin et al. 2003]):

- The formation of NO_x precursor compounds (HCN and NH₃) from the coke nitrogen, depending upon the CO content. Operating conditions with higher excess CO usually favour the formation of these precursors which react to form NO_x and N₂ in the CO boiler downstream of the regenerator.
- Thermal NO_x generated in the CO boiler and fuel NO_x formed depending upon the nitrogen content of the supplemental fuel, the amount and type of fuel, the burners design and the operating conditions in the CO Boiler.

The final stack NO_x emissions for a partial-burn regenerator may be similar to, or even higher than an equivalent full combustion regenerator. It is typically higher than a full combustion unit operating at low excess O₂ (<2 %). Figure 3.26 displays NO_x yearly average concentrations

achieved in 2007-2008 for a sample of 21 European FCC units. When available, summary information is also given on NO_x-reducing techniques that were implemented on these plants (values are expressed in mg/Nm³ dry at 3 % O₂). Lower emission values can be found when highest NO_x reduction additives rates are applied, or when dedicated end-of-pipe treatment techniques are implemented.

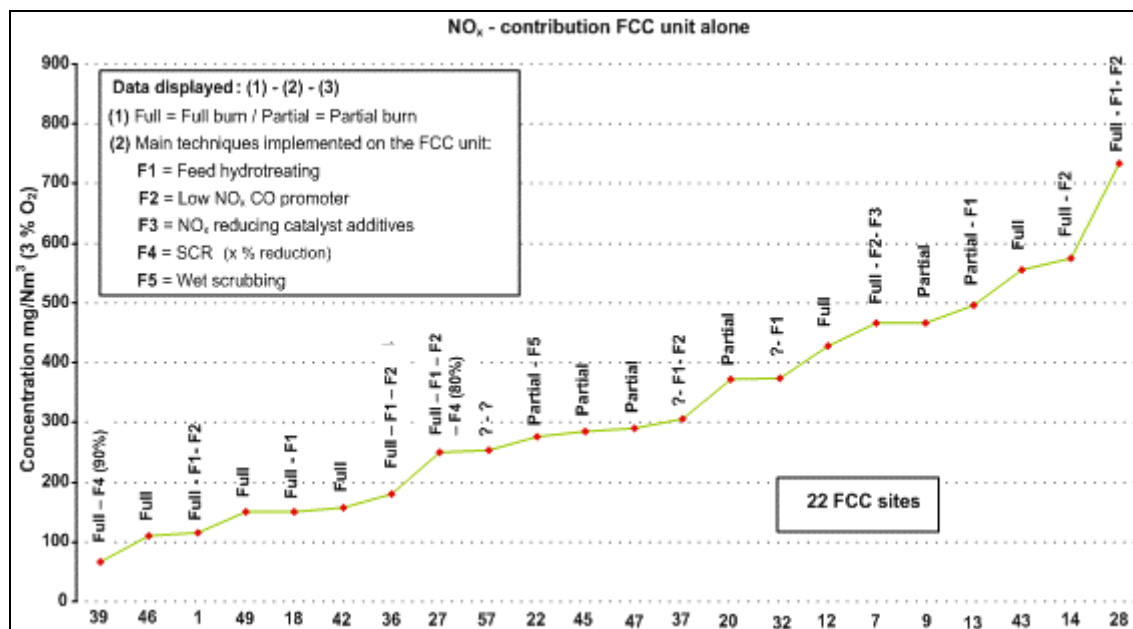


Figure 3.26: NO_x yearly average concentration from a sample of 21 European FCC units

Additional data received for 2009 for a feed hydrotreated (F1) FCC full combustion unit show a yearly average of 116 mg/Nm³ (Source TWG Austria: Emission declaration for 2009).

According to CONCAWE 4/09 report, from a nine FCC unit data-set, eight show NO_x emissions under 500 mg/Nm³ and one shows up to 800 mg/Nm³. In the latter case, the unit was using supplementary fuel and firing heavy residue in the CO boiler.

Particulates

Generally a FCC unit is the biggest single emitter of particulates, although the calciner in a coking unit is also a significant emitter. Particulate matter arises from catalyst fines from the catalyst regeneration exhaust gases and catalyst handling and disposal. The emitted catalyst is fine and is produced in a catalytic cracker as a result of the constant movement of the catalyst grains. In the absence of moisture or sulphuric acid condensation, the normal cause of stack plume opacity is the presence of the fine catalyst particles. In practice, operating conditions may have a large effect on particulate emissions. Table 3.37 gives three examples of particulate emissions from catalytic crackers. Lower values in the provided range correspond to FCC equipped with abatement techniques.

Table 3.37: Examples of particulate emissions from catalytic crackers

Throughput (kt/yr)	Flow (Nm ³ /h at 3 % O ₂)	% S in feed	Concentration (mg/Nm ³)	PM load (t/yr)	Specific emissions ^(*) (kg/t)
1 314	110 000	0.5	17	11.6	0.009
2 350	200 000	0.5	50	44.5	0.033
1 750	NA	NA	47	33.8	0.019
Ranges and averages in a sample of 20 European FCC			[25 – 189] Avg: 69	[13 – 340] Avg: 88	[0.015 – 0.100] Avg: 0.040
(*) Range and average estimated from FCC capacity.					
Sources [194, Winter 2000], [172, MRI 1997], [207, TWG 2001], [77, REF TWG 2010]					

Figure 3.27 displays the PM yearly average concentrations achieved in 2007-2008 for a sample of 20 European FCC units. Whereavailable, summary information is also given on PM-reducing techniques that were implemented on these plants. Values are expressed in mg/Nm^3 dry at 3 % O_2 . Lower emission values are not necessarily linked with the combustion mode, but are often related with the most advanced ESP or filtering techniques reported.

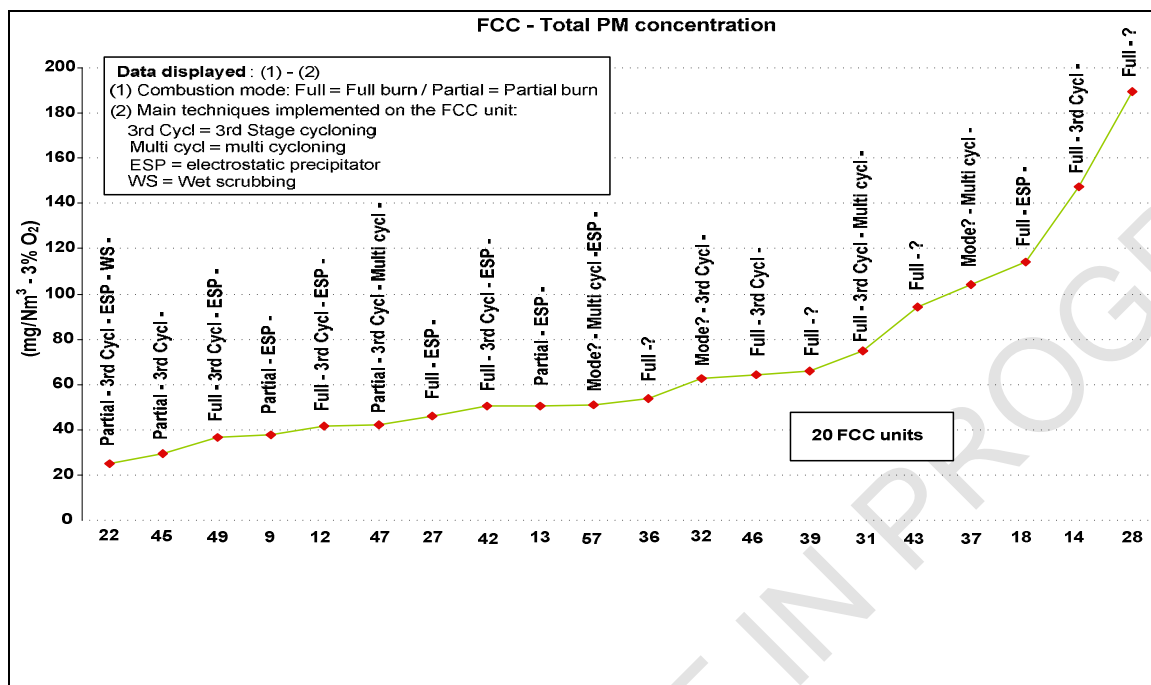


Figure 3.27: PM yearly average concentration from a sample of 20 European FCC units

Additional data received for 2009 for a hydrotreated feed (F1) FCC full combustion unit show a yearly average of $25 \text{ mg}/\text{Nm}^3$ (Source TWG Austria: Emission declaration for 2009).

Table 3.38: Example of composition of particulate matter generated by catalytic crackers when feedstock is hydrotreated

Parameter	Actual value	Dimension
Total particulate	23	mg/Nm^3
Mass flow	2.0	kg/h
Total metal content	<0.1	%
Nickel	0.05	% Ni/PM
	0.012	mg/Nm^3
Vanadium	0.02	% V/PM
	0.005	mg/Nm^3
Platinum	<0.004	% Pt/PM
	<0.001	mg/Nm^3

Source: [194, Winter 2000]

Particulates emitted by the catalytic cracker regenerator consist predominantly of catalyst particles with a typical size of $10 \mu\text{m}$ max. The particle size distribution shows that by weight, almost 90 % are smaller than $10 \mu\text{m}$. Much of this dust consists of silica/alumina, nickel and vanadium (as well as other metals) present in the feedstock. The deposited coke (including metals) on the catalyst ranges between approximately 4 and 5 % w/w. Metal compounds are enriched in the heavy residues during distillation, and are therefore present in the FCC

feedstock. If hydrotreated heavy residues are used as FCC feed, heavy metal concentrations will be smaller.

Sulphur oxides

The sulphur in the feed to the catalytic cracker is split between liquid product streams: H₂S in the gaseous products and SO₂ emissions from the regenerator, with the approximate ratio of 50/45/5. In the case of a RCC, the SO₂ emissions from the regenerator can reach 20 - 30 % of sulphur in the feed. The degree of sulphur dioxide leaving the exhaust gases from the catalytic cracker depends on the sulphur content of the feedstock used, as well as the technology used to control these emissions. SO₃ aerosols will also contribute to the catalytic cracker stack plume opacity.

Figure 3.28 displays SO₂ yearly average concentrations achieved in 2007-2008 for a sample of 24 European FCC units. When available, summary information is also given on SO₂-reducing techniques that were implemented at these plants (values are expressed in mg/Nm³ dry at 3 % O₂).

It can be noted that lower emission values are not particularly correlated with the sulphur input in the refinery overall feedstock, nor with the FCC combustion mode. However, best performances are linked to the highest hydrotreatment rates directly applied to the FCC feedstock, and dedicated end-of-pipe treatment techniques that are implemented.

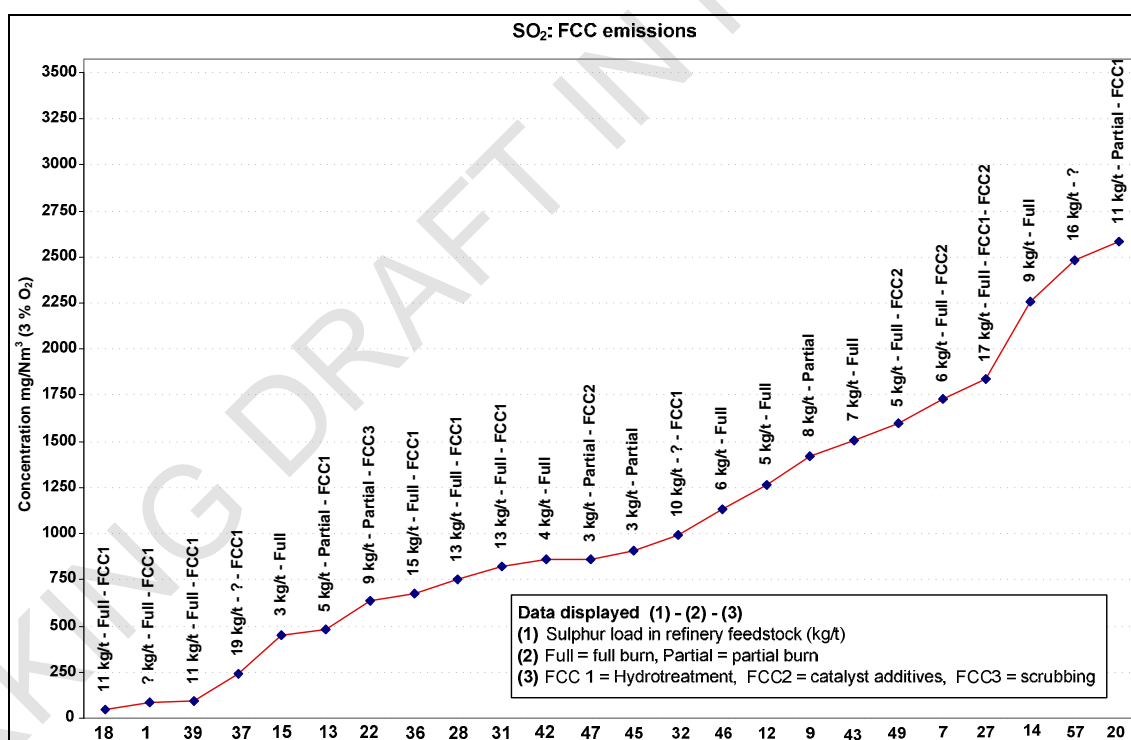


Figure 3.28: SO₂ yearly average concentrations from a sample of European FCC units

Additional data received for a feed hydrotreated (F1) FCC full combustion unit show a yearly average of 82 mg/Nm³ (Source TWG Austria: Emission declaration for 2009).

Other compounds

Hydrogen sulphide, mercaptans and ammonia may arise from sour waters from reflux condensers. Hydrocarbons (typically 80 % alkanes and typically 15 % olefins) may be released from pressure reliefs, storage and handling operations, spillages and water discharges. Measured dioxin and PAH emission values in two European FCCs are reported above.

Table 3.39: Examples of emission measurements in 2008 of other compounds from two catalytic crackers

Installation	Abatement techniques	Operational Conditions	Total dust mg/Nm ³	Dioxins ng TEQ/Nm ³	PAH (16 EPA) µg/Nm ³	Flue-gas flow/ measurement conditions
# 1	ESP, SCR and SO _x -reducing catalyst additive	full combustion without CO boiler	14 – 23	0.002	0.46 – 0.6	230000 Nm ³ /h 2.6 – 2.7 % O ₂
#2	ESP	full combustion without CO boiler	41 – 46	0.002 – 0.03	0.41 – 0.73	220000 Nm ³ /h 1.4 – 1.7 % O ₂

Average value of three spot measurements under normal operating conditions - Source: [77, REF TWG 2010]

3.5.2.2 Waste water emissions

The typical flow of waste water generated by a catalytic cracking process is around 60 – 90 litres of waste water per tonne of feedstock treated. Generated waste water is typically from sour water drains and spillages from the fractionator containing some hydrocarbons: high levels of oil, COD, suspended solids, sulphur compounds (H₂S), phenols, cyanides and ammonia. The next table shows an example of loads and composition of waste water generated in the catalytic crackers.

Table 3.40: Waste water emissions generated by catalytic crackers

Source of waste water	Parameter	Value	Units
Steam used to purge and regenerate catalysts	Metal impurities from the feed oil	NA	ppm
Fractionator overhead reflux drum	Percentage of feed intake	7 – 10	% v/v
	Flow	20 – 40	m ³ /h
	H ₂ S	10 – 200	ppm
	HCN	>1	ppm
	COD	500 – 2000	ppm
	N-Kj	15 – 50	ppm
	Phenols	5 – 30	ppm
Caustic washing of hydrocarbons	Free oil	50 – 100	ppm
	Flow	128	m ³ /h
	Phenolic caustic	NA	
	Cresylic acids	NA	

3.5.2.3 Solid wastes

There are potential releases into land from catalyst in the form of fines from particulate matter arrestment equipment and intermittent spent catalyst discharge. These solid residues are enriched in the heavy cycle oil and clarified oil (distillate of FCC unit) fractions. Catalyst addition rates for resid operation depend on feed metal levels. Addition rates shown are typical values covering a feed metal range of 10 – 20 ppm Ni+V+Na.

Table 3.41: Solid wastes generated in the catalytic cracking

	Source	Flow	Composition min/max
Replacement of old catalyst during turnaround maintenance	Regenerator	50 tonnes/4 yr	Spent Catalyst: Grey, solid powder consisting of Al ₂ O ₃ , SiO ₂ , carbon, refractory material and metals
Catalyst fines	Regenerator overhead cyclone/ESP		Dust containing high levels of V, Ni, Sb
Tank sludge slurry		Depends on slurry filtration system	10 - 30 % oil, depending on draining for cleaning, PAH

3.6 Catalytic reforming

Consumptions

Table 3.42 shows a summary of the utilities and catalyst requirements for the catalytic reforming.

Table 3.42: Examples of utilities requirements for catalytic reforming

Utilities	Reforming	Semi-regenerative process	Continuous regeneration process
Electricity, kWh	-	246(*)	6142(*)
Specific consumption (kWh/t)	25 – 50	55	-
Fuel fired, GJ	-	185(*)	232(*)
Specific fuel consumption (MJ/t)	1400 – 2900	71.5 t/kt	-
Cooling water, (m ³ /t, $\Delta T=10$ °C)	1 – 3	0.12 – 3	5.5
High-pressure steam generated, kg/t	50 – 90	64 – 90	97
Boiler feed water, kg/t		170	22
Condensate return, t/h		88	113
Specific value (t/kt)		20	-
Catalyst (containing Pt) t/(Mt/yr)	1.35		

(*) Values related to a capacity of 2351 t/d. Specific values related to capacity values
 NB: First column gives ranges for all types of reformers.
 Sources: [168, VROM 1999], [175, Meyers 1997], [204, Canales 2000]

Emissions

Emissions to air

Air emissions from catalytic reforming arise from the process heater gas, fugitive emissions (hydrocarbons from pressure relief valves and leakages) and regeneration. Hydrocarbons and dust releases may arise from venting during catalyst replacement procedures and during clean-out operations.

In the reforming process, very little of the naphtha feed is converted to coke requiring regeneration. In the regeneration process of the catalyst in a continuous catalyst regeneration (CCR) reforming unit, catalyst fines are withdrawn, the coke (0.05 – 0.5 kg coke/tonne feed) is burnt off with hot nitrogen diluted with air. Trace quantities of a promoter (chlorine precursor), normally an organic form of chlorine (such as tri- or per-chloroethylene) are added to retain the catalyst activity. Moisture is removed and the regenerated catalyst is returned to the reformer.

The off-gas from catalyst regeneration varies with the reforming technology employed and the routing of the off-gas. While the off-gas stream from a CCR is continuous, the regeneration emissions from cyclic or semi-regenerative reforming processes are discontinuous. The regeneration vent gas can contain air with diluted oxygen content, steam, CO₂, traces of HCl, Cl₂, CO (<10 mg/Nm³ [167, VDI 2000]), SO₂, hydrocarbons and low levels of dioxins and furans. Depending on the technology and the system design, the regeneration vent gas may be routed over an adsorption bed, through a caustic scrubber, or combined with a basic water wash system. Air emissions of trace components vary significantly depending on the unit configuration.

In addition, catalyst regeneration can be performed in a wet burning loop or in a dry burning loop. Applying the regenerator following wet burning loop leads to a high water content in the regeneration gas. In addition, this burning gas stays hot in the loop. The dry burning loop process is different as the regeneration gas is quenched and moisture is removed to get a dry gas. These difference of technology leads to different pollutants emissions (like dioxins and furans).

Table 3.43: Data reported on dioxins emission from catalytic reforming units

Sources	Abatement techniques	Operational conditions	Concentration ng TEQ/Nm ³	Specific dioxins emission ng TEQ/tonne
US EPA Study				0.196 ng/t (semi-regenerative) 1 172 ng/t (CCR)
Measurements in 4 Belgian refineries			<0.1-0.13 3.3-6.7 <0.01 <0.01	
Measurements in 2 Swedish refineries	a. CCR with regeneration gas recycling loop b. Discontinuous with wet scrubber	99 % abatement	a.NA b.NA	a. Total load: 0.045 g TEQ/yr b. NA
Source: [77, REF TWG 2010]				

The differences in unit configuration and regeneration vent gas routing have not always been taken into account. In some designs, the regenerator gas can be treated in a water or caustic scrubber to remove dust, chlorine compounds and SO₂ prior to release to the atmosphere. The storage and handling of organic chlorides used during the regeneration may also lead to releases. The organic chloride compounds used for catalyst regeneration are thermally and catalytically converted to HCl or Cl₂ in the regeneration process.

Waste water

In the reforming unit, with a design that generates waste water (water or caustic scrubbers), the amount of waste water generated is around 1 – 3 litres per tonne of feedstock. The waste water contains high-level oils, suspended solids, COD and relatively low-levels of H₂S (sulphides), chloride, ammonia and mercaptans. These compounds may also be found in the stabilising tower used to remove light ends from the reactor effluent. Hydrocarbons from spillages and leaks may occur. A study shows that, in the case of released water, the untreated waste water and spent caustics from the reformers can contain a wide range of PCDD/PCDF concentrations of 0.1 pg I-TEQ_{DF}/l to 57.2 ng I-TEQ_{DF}/l. [227, USAEPA 2000].

Solid wastes generated

Most reformers do not generate a continuous solid waste stream. CCR generate a small quantity of catalyst fines that are collected and sent for platinum reclamation. CCR unit catalyst fines are typically less than 1 tonne per year for a 1.7 million tonnes per year reformer. On average, catalyst life is around 10 years. Other potential discontinuous solid wastes might include spent promoted alumina adsorbents used as chloride guards and spent molecular sieve dryer adsorbents. Some solid wastes may also be generated during the equipment maintenance.

3.7 Coking processes

Consumptions

Delayed coking

Table 3.44 shows the energy and process materials usage in the delayed coking process. The amount of required make-up water for the coking process depends on the evaporation losses and the bleed to the desalter. Treated effluent can be used for this. The water used for coke cutting during decoking of the drums contains (un)saturated hydrocarbons and coke particles.

Table 3.44: Utility requirements of a delayed coking process

Fuel (MJ/t)	Electricity (kWh/t)	Steam consumed (kg/t) ⁽¹⁾	Steam produced (kg/t)	Cooling water (m ³ /t, $\Delta T=17\text{ }^{\circ}\text{C}$)
800 – 1 200	20 – 30	50 – 60	50 – 125	6 – 10
NB: Electricity including the electric motor drives for the hydraulic decoking pump. (¹) Taking into account the ensemble (including the gas concentration integrated unit) will lead to a steam consumption around three times the production.				

Flexicoking

Table 3.45 shows the energy and process materials usage in flexicoking.

Table 3.45: Utility requirements in the flexicoking process

Electricity (kWh/t)	Steam consumed (kg/t)	Steam produced (kg/t)	Cooling water (m ³ /t, $\Delta T=10\text{ }^{\circ}\text{C}$)
60 – 140	300 – 500 (MP)	500 – 600 (HP)	20 – 40

Calcliner

The calciner specific energy consumption and production figures are given per tonne of calcined coke produced in Table 3.46.

Table 3.46: Typical utility requirements in the calcinating unit (updated TWG 2010)

Electricity (kWh/t)	Refinery fuel gas (kg/t)	Steam produced	Steam consumed (kg/t)
13.2	0.03	2.2 t/h (115 barg)	2.4

Emissions

The most important emissions (and also health and safety aspect of these processes) is the handling of the coke fines.

Emissions to the air

Air emissions from coking operations include the process heater flue-gas emissions and fugitive emissions. In addition, the removal of coke from the drum (delayed coking) can release particulate and any remaining hydrocarbons to the atmosphere. The main pollutants generated as well as the sources, are described below.

- Hydrogen sulphide and sulphur compounds as mercaptans may be released from the sour water stream from reflux condensers.
- Hydrocarbons may be released from pressure reliefs on reflux drums and vessels, quench tower emissions, storage and handling operations, spillages and waste and water discharges.

- Particulate matter may be released from the kiln gas cleaning system, the rotary coker gas cleaning system, coke handling and storage, loading operations and from the calcinator process. The back pressures of the gas discharges from the kiln are critical to maintain the flame front in the kiln. This could mean the cyclone operating conditions are dictated by the requirement of the kiln rather than the optimum conditions for dust removal. Overall particulate emissions of 10 – 460 mg/Nm³ are achieved [156, MCG 1991], [195, Krause 2000]. Storage, crushing and handling of green coke takes place in the wet state with no releases to air. Typical size distribution profiles for particulate matter in calciner exhaust gases after passing through a cyclone system are given in Table 3.47.

Table 3.47: Typical size distribution profiles for PM emitted from calciner cyclone systems

99 % w/w below	100 microns
98 % w/w below	45 microns
90 % w/w below	8 microns
60 % w/w below	5 microns
20 % w/w below	2.5 microns
10 % w/w below	1.5 microns

Waste water

Waste water is generated from the coke removal, water bleed from coke handling, sour water from fractionator overhead, cooling operations and from the steam injection and should be treated. The amount of waste water generated in the coking processes is around 140 litres per tonne of feedstock. It contains H₂S, NH₃, suspended solids (coke fines with high metal contents), COD, high pH, particulate matter, hydrocarbons, sulphur compounds, cyanides and phenols. Detailed analysis of the contaminants of such waste waters is not available because they are transferred directly to the refinery main waste water system for treatment.

Solid wastes

Solid wastes generated in the coking processes are coke dust (carbon particles and hydrocarbons) and hot oil blowdown sludges containing hydrocarbons. Table 3.48 shows a typical analysis of these sludges.

Table 3.48: Typical chemical characterisation of the sludge generated in the coker

Species	Concentration (ppm)	Species	Concentration (ppm)
Solids	91.4 %	Selenium	53
Oil	8.6 %	Antimony	40
Carbon	28.5 %	Nitrate	35.8
Hydrogen	3.5 %	Naphthalene	32.4
Nitrogen	0.3 %	Vanadium	32
Iron	80537	Phenan	20.1
Sulphur	27462	Phenol	11.2
Calcium	8166	Arsenic	10.5
Aluminium	3098	Toluene	7.8
Magnesium	2237	Fluorine	6.7
Sulphide	613.0	Pyrene	6
Sodium	459	Benzo(A)Pyrene	5.6
Lead	272.9	Benzene	2.2
Nickel	230.4	Ethylbenzene	2.2
Chromium	166.7	Mercury	1.0
Xylene	145.4	Cyanide	1.0
Sulphate	115.0		

NB: Figures quoted on a moisture-free basis.
Source: [156, MCG 1991]

3.8 Cooling systems

The information given in this section should be read in conjunction with the ICS BREF, [84, COM 2001] the reference document on industrial cooling systems, particularly the extensive coverage it gives to the consumption of additives.

The need for cooling in a refinery depends on the processes used and on the degree to which they are integrated but, where water cooling systems are applied, it certainly accounts for the majority of water usage. In a refinery, it is important to maximise heat integration at a plant level and at a process/activity level to minimise cooling duty. Therefore, energy requirements for cooling will depend on the cooling system used, together with the cooling strategy applied.

Table 3.49 shows a typical split of the cooling needs in a refinery (Hydrocracking refinery with a throughput of 7 Mt/yr).

Table 3.50 gives a distribution of the cooling capacity according to temperature range within a typical refinery. (Hydrocracking refinery with a throughput of 7 Mt/yr).

Table 3.49: Cooling needs in a refinery

Application	Cooling capacity	
	MW	%
Process streams	400	94
Pumps, compressors	10	2
Vacuum systems	15	4
Total	425	100
<i>Source: [169, Bloemkolk et al. 1996]</i>		

Table 3.50: Typical cooling duty according to temperature range

End temperature (T) process fluid (°C)	Cooling duty	
	MW	%
T>43	380	95
43>T>38	15	4
38>T>30	0	0
30>T	5	1
Total	400	100
<i>Source: [169, Bloemkolk et al. 1996]</i>		

Consumptions

Power is consumed by pumps in a water cooling system and by fans in an air cooling system. The water cooling system uses water and requires chemicals as corrosion and bacterial growth inhibitors. For more detailed information and annual consumption figures, reference is made to the ICS BREF. Both recirculating and once-through cooling water systems require additives, to prevent fouling and/or corrosion. Because once-through systems generally use surface water (either fresh or salted), the chances of fouling are higher, compared to recirculating systems. Therefore, in these systems, more anti-fouling additives (i.e. chlorinated biocides) should be used. On the other hand, anti-corrosion additives are mainly applied in recirculating systems and not used in once-through systems.

Water utilisation in cooling systems is lower in a recirculating system, compared to a once-through system (up to only 3 %). In the recirculating system, a certain amount of water exits the system through evaporation, as mist droplets and as bleed or blowdown to the waste water treatment system. Therefore, make-up water in the range of about five % of the circulation rate

is required, a figure equivalent to the use of 0.23 m³ of cooling water per tonne of crude oil processed. However, to make a balanced comparison between the two kinds of cooling systems, it is necessary to take into account the quality of the water used (often once-through cooling systems are fed with low quality water, marine or brackish water).

Emissions

The main direct environmental impact of the cooling systems is the heat, increasing the temperature of the cooling fluid used. In refinery water cooling, the increase of the temperature (ΔT) is around 10 – 15 °C.

Water consumption (mentioned above), energy consumption (pumps, air-cooler fans) and water pollution are the main environmental issues of cooling systems. Other environment-related effects include noise production (cooling tower, pumps, air-cooler fans: 97 – 105 dB(A) at source) and plume formation (cooling tower).

The main pollutants to be considered in water cooling systems are the anti-fouling additives, and anti-corrosion additives containing zinc, molybdenum etc. Special attention should be paid to the use of dispersing additives in closed cooling water systems, particularly when the bleed is routed to an oil separating water treatment unit, where it can interfere with the oil-water separation process. A once-through system coupled with a low rate of leaks and a high volume of water mean that cooling water discharges contain between 0.1 and 1 mg/l oil. Hydrocarbon emissions to air from cooling towers (as a result of leakages and stripping) may occur. Emissions to the air were reported to vary between 0.5 and 85 g hydrocarbons per m³ cooling water recirculating over the cooling tower [169, Bloemkolk et al. 1996]. Cooling by quenching (only used in delayed cokers within refineries) results in high vapour emissions, significant energy losses, large water use and severe water pollution.

Table 3.51: Environmental impact of different cooling systems for a typical refinery

Emission or effect	Once-through	Once-through (closed-loop)	Cooling tower	Cooling tower (closed-loop)	Air coolers	Air-cooled (closed-loop)
Water						
Thermal heat (MW)	300	300	Negligible	Negligible		
Hydrocarbons (kg/h)	2.6 - 26					
Chemical conditioning ⁽¹⁾ (kg/h)	2.6	2.6	3 – 25	3 – 25		
Water blow-down discharge (m ³ /h)	26 000	26 000	156	156		
Air						
Visible plume			+(³)	+(³)		
Water vapour (kg/h)			468 000	468 000		
Hydrocarbons (kg/h)			13	(+)(⁵)		
Energy consumption ⁽⁴⁾ (kW)	3 500	5 500	5 600	7 000	2 000	8 700
Fresh water consumption (m ³ /h)		In closed circuit	624	624		
Other nuisances						
Noise ⁽²⁾	+	+	+	+	+	+
Other	Entrainment of fish in intake	Entrainment of fish in intake	Legionella risk in air releases			
⁽¹⁾ Hypochlorite in once-through cooling water; anti-corrosives, hypochlorite and anti-scalants in cooling tower make-up water. ⁽²⁾ See text ⁽³⁾ Suppression of plume possible at extra cost ⁽⁴⁾ Process energy losses not included ⁽⁵⁾ Possible effect: the leaking of air coolers is not a well-described phenomenon. The absence of water would suggest that corrosion is not an important factor compared to water-cooled systems. Further study would be needed for an accurate assessment. + Effect occurs Source: [169, Bloemkolk et al. 1996] Completed by TWG 2010						

3.9 Desalting

The quantity of inorganic impurities in the crude oil depends very much on both the crude origin and the crude handling during transport from the crude well to the refinery.

Consumptions

The water used in crude desalting is often untreated or partially treated water from other refining process water sources. Table 3.52 shows the typical operating conditions and water consumptions in the desalters, depending on the type of crude oil used.

Table 3.52: Typical operating conditions of the desalting process

Crude oil density kg/m ³ at 15 °C)	Water wash, % v/v	Temp (°C)
<825	3 – 4	115 – 125
825 – 875	4 – 7	125 – 140
>875	7 – 10	140 – 150

For desalting long or atmospheric residue, 10 % w/w water on feed is common. Once the water and the oily phase have been well mixed, the water should be separated from the oil feedstock in a separating vessel. This is done by adding demulsifier chemicals (5 – 10 ppm) to assist in breaking the emulsion and, in addition, by applying a high-potential electric field across the settling vessel to coalesce the polar salt water droplets. The electricity consumption used in the desalting processes varies typically from 0.075 to 0.15 kWh per tonne of crude oil.

Emissions

Air emissions

No major emissions to air are produced during the desalting processes. Air emissions from the heating process are expected, and fugitive emissions (hydrocarbons) may be expected.

Solid wastes generated

The quantities of desalter sludge generated depend on the solid content of the crude, the separation efficiency and the applied desludging mode and frequency. Normally a desalter clean-out is done twice a year, yielding from 60 – 1500 t/yr oily sludge, dependent on the throughput and efficiency of the process to capture solids. The sludge generated can contain iron rust, clay, sand, water (5 – 10 %), emulsified oil and wax (20 – 50 % w/w) and metals.

Waste water

The desalter contributes greatly to process waste water (30 – 100 litres/tonne feedstock desalted). The desalting process creates an oily desalter sludge and a high-temperature salt waste water stream (possibly the most polluted in the refinery), which is typically added to refinery waste water treatment facilities. The waste water generates a wide variety of pollutants and in considerable amounts that can never be discharged without proper treatment. Table 3.53 shows the ranges to be expected from waste waters from desalters.

Table 3.53: Composition of the waste water generated in the desalting process

Water pollutants	Typical concentration (mg/l)
Temperature (°C)	115 – 150
Suspended solids	50 – 100
Oil/oil emulsions	High
Dissolved hydrocarbons	50 – 300
Phenols	5 – 30
Benzene	30 – 100
BOD	High
COD	500 – 2000
Ammonia	50 – 100
Nitrogen compounds (N-Kj)	15 – 20
Sulphides (as H ₂ S)	10
<i>Source:</i> [181, HP, 1998], [159, WB 1998]	

3.10 Energy system

The energy system is an important, if not the most important activity from the environmental perspective. The energy (heat and power) necessary to transform the raw materials to products is provided by the combustion of hydrocarbon fractions that mainly generates emissions to air. As mentioned in Section 2.10, this section contains the emissions generated by the energy system as a whole. As a consequence of this, the emissions generated by furnaces or boilers of specific processes are integrated here and they are not considered in the other sections.

3.10.1 Energy management

Energy efficiency in refineries

There are currently three methodologies in use in refineries briefly described below:

- The first is *specific energy consumption (SEC)*. This is the most simple index. It is calculated as the ratio between the energy consumed by the refinery and the tonnes of feedstock processed. According to data gathered by the TWG from a sample of 50 European refineries, the specific energy consumption of European refineries (from 5th to 95th Percentiles) ranges from 1.6 to 3.7 GJ per tonne of throughput (crude and intermediates). Because it is a simple index, this ratio does not take account of the complexity of the refinery (more complex refineries tend to consume more energy).
- The second methodology is the *products method*. [230, G. J. M. Phylipsen, K. Blok, et al. 1998] This method considers the products and internal energy products produced in the refinery, giving a specific energy consumption benchmark per tonne of energy product produced. Multiplying these specific energy consumptions by the amount produced within the refinery and adding all the totals together gives an energy consumption benchmark for that refinery. Some calculations based on 2008 data indicate that the best specific energy consumption figures are between 2.4 and 2.9 GJ/tonnes, whereas actual values were from 1 to 4.8. That means that some European refineries are doing better than figures that are considered a good benchmark.
- The third methodology is the *energy intensity index (EII)*. It is a measure used to compare energy consumption in refineries. The standard energy use is based on the energy consumption at more than 500 refineries worldwide. Since the beginning of this benchmarking (property of Solomon Associates) in the 1980s, an EII of 100 corresponds, by design, to the current average calculated for all the participating US plants. The average EII obtained in a worldwide market survey (Solomon study, 1994) was 92, with a range from 62 to 165 [160, Janson 1999]. More energy efficient refineries correspond to the lower values of EII. Therefore, some refineries are almost three times as energy efficient as others. In 2005 the top 10 % of all best EII values reported worldwide were equal to or below 75. This index reflects the types of processes and throughput of each process in the refinery. This data is not available for all refineries and typically is considered confidential by refineries. As shown in Figure 3.29, a total of 41 European refineries have reported their EII (2006, 2007 or 2008) in TWG questionnaires, and the values have been plotted together with specific energy consumptions calculated for each of the concerned sites. A clear correlation is naturally observed. Within this European sample, EII ranges from 65 to 124, with an average of 93 very close to the world average, and five plants in the best 10 % in term of worldwide performance.

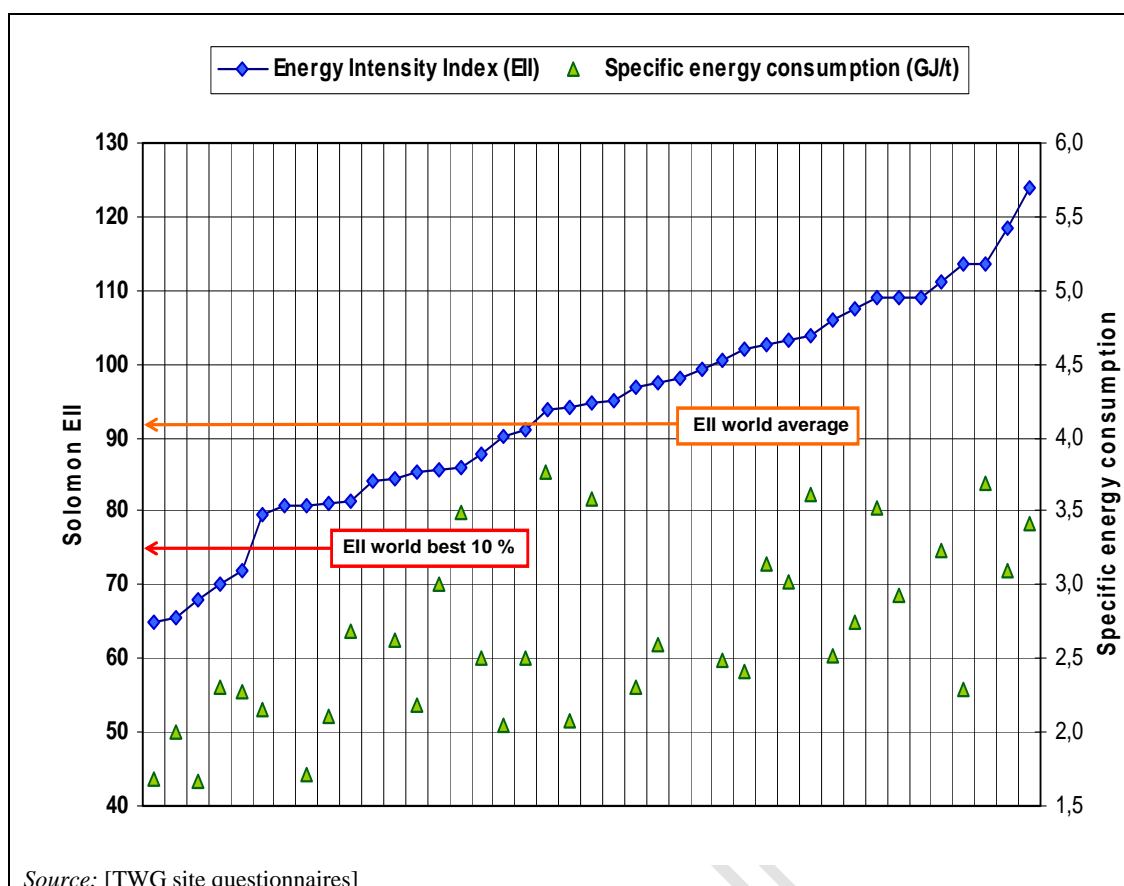


Figure 3.29: Energy Intensity Index and specific energy consumption for 41 EU refineries

3.10.2 Energy capacity and consumptions

Capacity of the refinery energy system

The capacity of the individual combustion plants in a refinery varies widely from less than 10 to 200 Megawatts thermal input (MW); and the total installed capacity ranges from several hundred to more than 1500 MW in the largest refineries. The energy consumed at the combustion plants of the refineries ranges from 200 to more than 17 000 TJ per year. Deep conversion refineries in general use more than three times as much energy (10 % of crude intake) as simple hydroskimming refineries (3 %) [159, WB 1998].

Gasification plant

An IGCC unit produces 130 t/h of syngas mainly composed of CO and H₂ in the ratio 1: 1 (calorific values of 9 600 – 10 000 kcal/kg) starting from 58 t/h of feedstock (calorific value of the heavy residue varies between 8800 and 9200 kcal/kg, sulphur content: 3.5 – 7 % and metal content: 300-800 ppm). A solid effluent in the form of a filter cake (about 160 – 400 kg/h dry) is discharged and sent to external plants for recovery of the metals. Two Claus units recover 4 t/h of elemental sulphur from the H₂S recovered in the acid gas removal section. A tail gas treatment section that permits an overall sulphur recovery of 99.9 %, follows the Claus units [221, Italy 2000].

Refinery fuels

The baseline ratio of gas to liquid refinery fuel used in a refinery is a function of a number of factors, important amongst which are the size, degree of complexity, LPG recovery efficiency and extent to which refinery fuel gas is processed into other products (e.g. olefins) or exported to adjacent chemicals plants (either directly or as energy from common facilities). It varies from 80/20 or 70/30 (gas/liquid) at a stand-alone, moderately complex refinery to 40/60 at a highly complex site which also services a chemicals complex. However these ratios can be increased when energy conservation measures are applied and the gas availability becomes sufficient for

the energy supply of the refinery. Table 3.54 illustrates the calorific value and the sulphur content of the different fuels.

Table 3.54: Properties of the fuels used within a refinery

Type of fuel	Calorific value (MJ/kg)	Sulphur content
Refinery fuel gas (RFG)	29 – 49	20 – 4000 mg H ₂ S/Nm ³
Hydrogen gas	55 – 70 (LHV)	20 – 1200 mg H ₂ S/Nm ³
Catalyst coke from FCC	38 – 40	0.11 – 0.3 % S
Liquid refinery fuel	40	<0.1 – 4 % S
<i>Source:</i> [updated TWG 2010]		

There are differences in the characteristics of the liquid refinery fuel used in European refineries. The data from a CONCAWE report show that in 2006 about 50 % of oil fired had a sulphur content of ~1 % or less, only 10 % of refineries used oil with more than 2 % sulphur in 2006, compared with 20 % in 2002 and 35 % in 1998. The average sulphur content was 1.7 % in 1998, 1.34 % in 2002 and 1.33 % in 2006 [63, CONCAWE 2010].

Table 3.55 shows the chemical characteristics of three different liquid fuels.

Table 3.55: Chemical properties of several typical heavy liquid oils

Property	High sulphur	Intermediate sulphur	Low sulphur
Sulphur % by weight	2.2	0.96	0.50
Carbon % by weight	86.25	87.11	87.94
Hydrogen % by weight	11.03	10.23	11.85
Nitrogen % by weight	0.41	0.26	0.16
Ash %	0.08	0.04	0.02
Vanadium (ppm)	350	155	70
Nickel (ppm)	41	20	10
Sodium (ppm)	25	10	<5
Iron (ppm)	13	9	<5
<i>Source:</i> [243, Blas 2000]			

The nitrogen and sulphur contents are two of the most important chemical parameters and are responsible among other factors for the emissions of NO_x and SO_x. Ash content combined with high sulphur can directly affect particulate matter emissions. Figure 3.30 shows the distribution of nitrogen and sulphur contents in various types of vacuum residues according to their geographical origin.

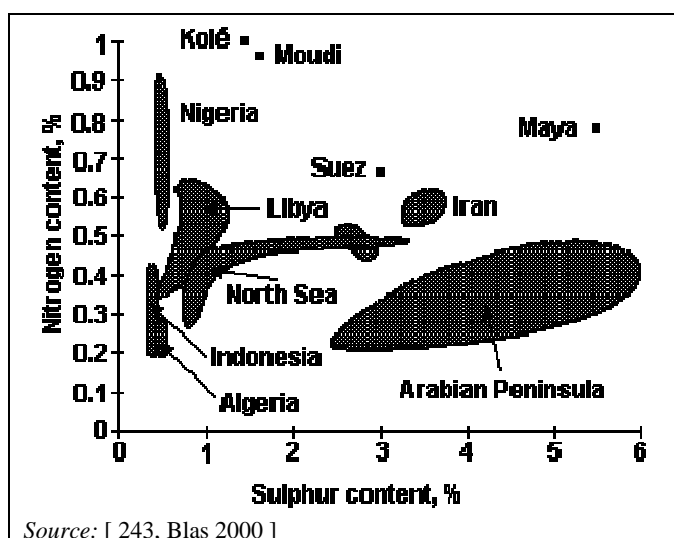


Figure 3.30: Sulphur and nitrogen contents in HFO (vacuum residues) according to their geographical origin

Steam generation

Steam generation requires an energy input of 2 700 – 3 200 MJ per tonne of steam produced. Conditioning chemicals are dosed to the BFW in low concentrations and comprise the following groups of chemicals: anti-scaling agents, corrosion inhibitors and anti-foaming agents. A 100 t/h steam generation system requires approximately 1.5 – 3 t/yr corrosion inhibitors and 2 – 4 t/yr anti-scaling agents. These conditioning chemicals included are:

- Corrosion inhibitors (mainly oxygen scavengers and alkaline compounds). Sulphite (<60 bar), oximes, hydroxyl amines, and hydrazine (declining use due to safety issues) etc. are commonly applied as oxygen scavengers for deaerated boiler feed water prior to pumping into the boiler. Commonly applied alkaline compounds are sodium phosphates (which are also hardness binders), caustic, ammonia and neutralising amines.
- Anti-scaling agents such as polyacrylates and phosphonates that are rest hardness binders and dispersing agents.
- Anti-foaming agents, in general intermittently dosed, to combat foaming in case the condensate contains oil or organics.

3.10.3 Emissions

3.10.3.1 Air emissions

General aspects

Since emissions to water are minimal and very little is generated in the way of solid waste, emissions to air are the primary emissions, both from the energy system and from the refinery as a whole. The sum of flue-gas flows generated from all combustion processes associated with the energy system (i.e. central power plant, process furnaces, stand-alone boilers and eventual gas turbines) in a refinery range from around 1 – 20 GNm³/yr (0.1 to more than 2 million Nm³/h at 3 % O₂), which corresponds to 0.2 – 2 million Nm³/t of feedstock processed.

The main releases to air from combustion processes are stack gases containing oxides of sulphur, oxides of nitrogen, oxides of carbon (carbon monoxide and carbon dioxide) and – particularly important when liquid refinery fuel or coke is combusted – particulate matter, including PM₁₀ and metals (e.g. V, Ni). When operating properly and when burning cleaner fuels such as refinery fuel gas, low-sulphur fuel oil or natural gas, these emissions are relatively low. If, however, combustion is not complete, or heaters are fired with refinery fuel pitch or residuals, emissions can be significantly higher. Incomplete combustion may lead to releases of

carbon monoxide, smoke and, if heavy fuel oils are used, particulate matter. As a result of that, combustion plants are major contributors to the release of air emissions from refineries. The level of pollutants emitted will depend on the quality of the fuels burnt, which can vary considerably. There are conflicting factors in a combustion process which contribute to emission levels. For example, combustion conditions which favour low particulate emissions for liquid refinery fuel, i.e. excess air, high temperature, good air/fuel mixing and good fuel-atomisation, are not favourable for low NO_x emissions.

Refinery fuel gas, if properly treated, is a low polluting fuel. Liquid refinery fuels generate more emissions to the air than refinery fuel gas. Gas-fired heaters and boilers generate little dust and lower SO₂ emissions, as the refinery fuel gases are usually cleaned in amine scrubbers. NO_x emissions are also much lower than those of liquid-fired boilers and heaters.

By way of example, Table 3.56, Table 3.57 and Table 3.58 show, respectively, the air emissions generated by gas and liquid refinery fuels in two power plants in European refineries.

Table 3.56: Air emissions from boilers and furnaces fired with refinery fuel gas

Fuel Consumption (GWh/yr)	Throughput (t/yr)	Units	CO ₂	CO	NO _x	Particulates	SO ₂
561.4	41 000	mg/m ³		<80	<100	1	1 – 20
		t/yr	108 917	23.6	75.7	0.6	74
		kg/t feed	2 657	0.58	1.85	0.014	1.81
NB: Data in table refer to daily average, 3 % O ₂ , dry. Source: [191, UBA Austria 1998] updated TWG AT 2010							

Table 3.57: Air emissions from a power plant fired with heavy fuel oil

Fuel consumption (GWh/yr)	Through put (t/yr)	Units	CO ₂	CO	NO _x	Particulates	SO ₂
4 821.5	NA	mg/m ³	-	18 – 79	60 – 98	2 – 3	55 – 159 ⁽¹⁾
NB: Data in table refer to monthly average, 3 % O ₂ , dry. Vacuum cracked flashed residue from the thermal gas oil unit is co-fired. ⁽¹⁾ The flue-gas is treated in a SNO _x plant - RFG and natural gas are co-fired with heavy fuel oil Source: [191, UBA Austria 1998] updated TWG AT 2010							

Figure 3.31 and Figure 3.32 show the 2009 emissions data for SO₂, NO_x and dust from large combustion plants in refineries reported by the Member States to the Commission.

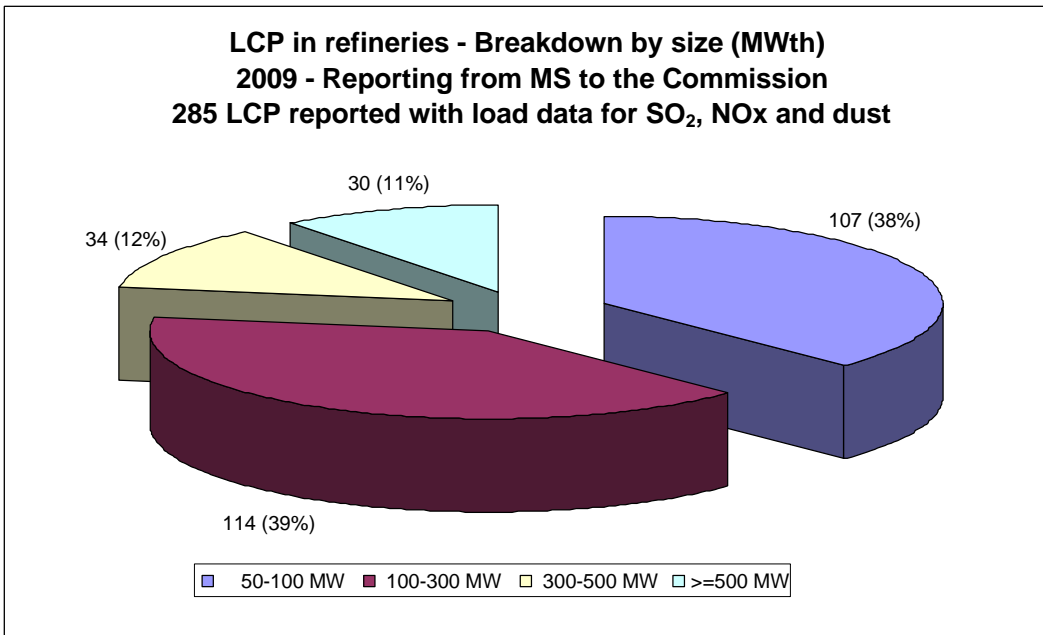


Figure 3.31: Large combustion plants in refineries 2009 reporting of Member States to the Commission

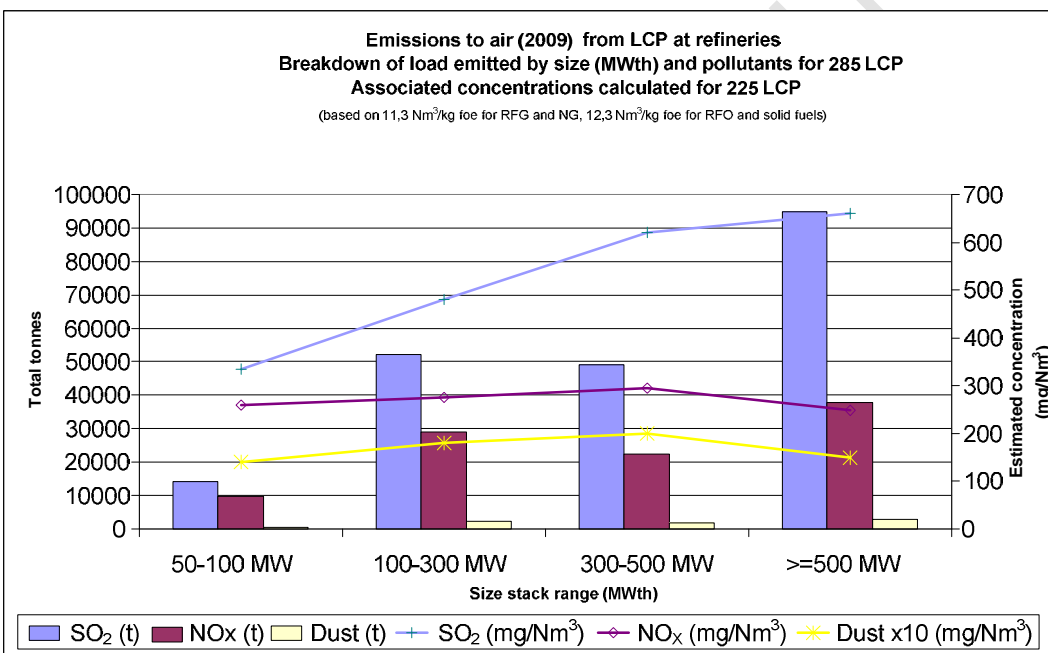


Figure 3.32 Emissions to air from LCP in refineries: loads and associated concentrations

Table 3.58: Air emissions from TOTAL Mitteldeutschland refinery power plant burning refinery liquid residue

Emissions parameters	Raw gas	Clean gas
Volume, wet (m ³ /h, 7 % O ₂)	171 690	188 249
Gas temperature (°C)	180 – 200	up to 72
Particulates (mg/m ³ , 3 % O ₂)	220	<10
NO ₂ (mg/m ³ , 3 % O ₂)	800	<150
SO ₂ (mg/m ³ , 3 % O ₂)	6 500	
SO ₃ (mg/m ³ , 3 % O ₂)	650	<10
SO _x as SO ₂ (mg/m ³ , 3 % O ₂)		<400
NB: It includes a FGD process. Liquid refinery fuel contains 7 % of sulphur. Source: [191, UBA Austria 1998]		

Carbon dioxide

Combustion processes of fossil fuels produce CO₂ as a result of the combustion of hydrocarbons. The amount of CO₂ emitted to the atmosphere by European refineries varies from 0.15 to 5.5 million t per year (range depending on the type of refinery and the energy integration). The specific CO₂ emissions (calculated from 5th to 95th percentiles within a sample of 58 European refineries) range from 0.1 to 0.4 tonnes of CO₂ per tonne of feedstock processed. CO₂ emissions from power plants in the refineries correspond to around 42 % of the CO₂ emitted by the refinery. The use of liquid fuels results in lower thermal efficiencies and higher CO₂ emissions than the use of gaseous fuels.

Table 3.59 shows the sources (type of fuels) of the CO₂ emissions of the refining industry. The table also includes the calculated emission factors for CO₂ for various refinery fuels.

Table 3.59: CO₂ emission factors for different types of fuels

Fuel type	Typical composition (% w/w)	kg CO ₂ /kg fuel	kg CO ₂ /GJ
Refinery fuel gas (RFG)	30 H ₂ /35 C ₁ /35 C ₂ % v/v	2.83	43
Natural gas (NG)	100 % methane	2.75	56
Liquified Petroleum Gas (LPG)	50 C ₃ /50 C ₄	3.02	64
Distillate Fuel oil	60 P/10 O/30 A	3.22	74
Residual Fuel	50 P/50 A	3.26	79
Coke	90 C/10 ash	3.30	117
NB: abbreviations: Carbon, Hydrogen, Paraffins, Olefins, Aromatics Sources: [166, CONCAWE 1999], [202, Dekkers 2000]			

Carbon monoxide

One of the products of partial combustion processes is carbon monoxide. The CO emissions, which range from 20 – 42 mg/Nm³ at 3 % O₂, are very dependent on the type of fuel used and the completeness of the combustion process. Specific emission values for CO are 0.58 kg CO per tonne of refinery fuel gas and 0.24 kg CO per tonne of liquid fuel.

Nitrogen oxides

NO_x emissions from a refinery energy system depend on the fuel type, fuel nitrogen or hydrogen content, combustor equipment design and operating conditions. The formation and release of NO_x from combustion processes arises from the oxidation of nitrogen present in the fuel source and/or the air used. Accordingly, large differences in the NO_x emission level can be expected between refineries and even between different combustion installations at the same refinery at different times. Differences in temperature, residence time and oxygen concentration result in

varying levels of thermally formed NO_x. The influence of temperature is most important, with NO_x emissions increasing exponentially with temperature.

Gaseous fuels typically release less NO_x per unit of energy compared with liquid fuels, especially liquid refinery fuels. Oil burning normally leads to higher levels of NO_x releases for several reasons: the problem of fuel NO_x arising from the nitrogen content (0.03 – 1 %), the way in which the plant is often operated so as to balance NO_x and particulate releases, and the frequent design requirement for firing in combination with gas. However, the latter statement is only true for non-abated emissions, since the inclusion of secondary measures can reduce both NO_x and particulate emissions. One refinery in 1996 found that fuel oil can generate about three times more NO_x than gas fuels. NO_x factors (NO_x produced per tonne of fuel combusted), used by some refineries to report NO_x emissions, indicate NO_x from oil firing to be two to three times that from gas firing.

Figure 3.33 gathers the NO_x equivalent concentrations (expressed as yearly average in mg/Nm³ dry at 3 % O₂) of all flue-gases emitted by the overall energy system of some European refineries. For each site, summary information is given on the existence of typical NO_x-related techniques implemented at various parts of the energy system, and on the portion of total gaseous fuels (refinery fuel gas + eventual external natural gas supply) in the site energy mix. Most sites emit in the range 100 – 500 mg/Nm³. As expected, a clear correlation is observed between the highest gaseous fuel ratios in the site energy breakdown and the lowest NO_x equivalent concentrations.

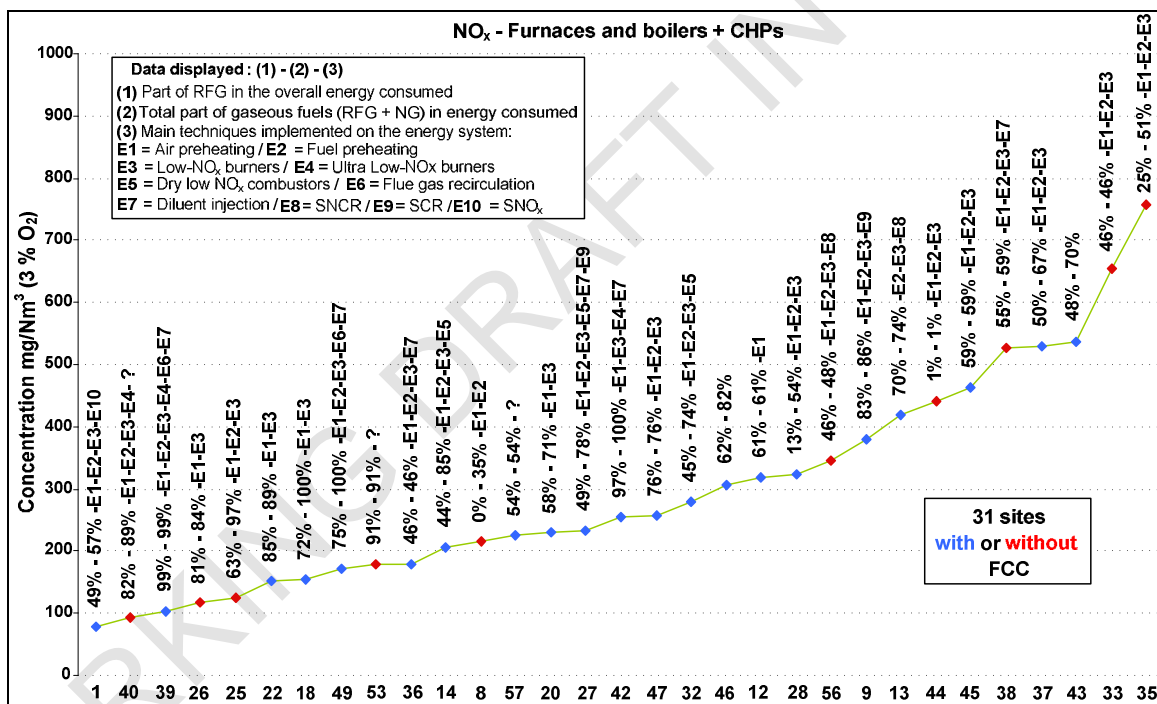


Figure 3.33: Distribution of NO_x yearly average equivalent concentrations from the energy system of a sample of European refineries

Additional data received for 2009 show, for the energy system, a yearly average of 71 mg/Nm³ of NO_x emissions (Source: Questionnaire 1 updated with emission declaration for 2009).

The fired heaters, boilers and gas turbines running on refinery blend gas generate lower NO_x emissions than FCCs. Specific NO_x emissions related to energy consumption range from 15 to 200 mg/MJ for furnaces with 100 % gas fuel. Specific NO_x emissions related to the throughput range from 84 to 700 tonnes of NO_x per million tonnes of crude oil processed. The NO_x load ranges from 20 to more than 2000 tonnes per year.

Particulates

Under normal operating conditions, the solids in the flue-gases of a furnace or boiler consist mainly of coke particles with some cenospheres, depending on firing conditions. The particulate emission of oil-fired equipment may vary considerably since they depend on a number of more or less independent parameters such as: fuel type, burner design, oxygen concentration at the outlet of the radiant section, the flue-gas outlet temperature of the radiant box, and the residence time of the fuel droplets. The particle size of the particulate matter (PM) from furnaces and boilers on HFO is in the order of 1 μm . The PM in flue-gases can take any of the following four forms:

- soot where the particle size is below 1 μm (the visible smoke from a stack is caused by all particles but mainly these with a particle size between 0.5 and 5 μm);
- cenospheres: they originate from the liquid phase wastes of combustion of heavy oil droplets at relatively low temperature (<700 °C), the size is equal to or larger than that of the original oil droplets;
- coke particles, formed through liquid phase cracking in combustion at high temperatures (>700 °C), the particle size is generally from 1 to 10 μm ;
- fine particles (<0.01 μm): their contribution to the total mass emission is negligible.

The PM in the flue-gas of furnaces and boilers fired with heavy fuel oil is a mix of metal compounds and soot/coke. Metals (mainly V and Ni) are a natural constituent (indigenous) of the crude. Soot and coke result from imperfections of the combustion process. Contaminants such as sand, rust and other metals, and coke particles of the fuel itself, may also contribute to the formation of particulates. The indigenous metal content of the heavy fuel oils (see Section 2.10), which can be calculated from the metal content of the crude oil from which the HFO is made) is the basis for calculating the minimum ash content of the HFO and therefore also the basis for the PM in the flue-gas. Ash contents are higher than the metal content itself (as the metal compounds are in the ash), and generally lie in the range 500 – 1 500 ppm (0.05 - 0.15 % w/w). In practice, the PM content is normally higher by a factor of 2 – 4, because unburnt fuel (soot) adheres to the metallic PM, and because aerosols of SO₃ are also monitored as PM.

The range of the unabated PM (150 – 500 mg/Nm³) is typical for the current burners application (steam atomisation and low- NO_x), assuming all measures are taken to achieve good combustion (optimum oxygen content and lowest practicable NO_x in the flue-gas) and is directly related to the ash content of the fuel. For older furnaces, liquid refinery fuel-fired flue-gas levels may range from 500 to 1 000 mg/Nm³. For boilers, all these figures are on average lower. For a new optimal burner design with steam atomisation this can be well below 200 mg/Nm³. The range of 150 – 500 mg/Nm³ represents the current typical range with liquid refinery fuels employed (ash contents) and burners installed (low-NO_x with steam atomisation). Table 3.60 shows the particulate emission range found in current European refineries.

Table 3.60: Particulate emissions ranges for existing installations

	Refinery fuel gas	Liquid refinery fuel
Process furnaces	0.4 – 2.4	5 – 1000
Boilers	<5	5 – 500
CHP	-	2 – 3 ⁽¹⁾
NB: All figures in mg/Nm ³ @ 3 % O ₂ (monthly average).		
⁽¹⁾ The flue-gas is treated in a SNO _x plant RFG and natural gas are co-fired with heavy fuel oil.		
Sources: [151, Sema,Sofres 1991], [191, UBA Austria 1998] updated TWG NL 2010		

Soot blowing is an operation that is carried out at regular intervals to remove soot from the furnace that is accumulating on the furnace equipment and hampers proper functioning. During this operation the PM content of the exhaust gas can reach values of 2000 mg/Nm³. Abatement

techniques installed for normal operating conditions will be effective to reduce the PM emissions from this operation.

Sulphur oxides

The release of sulphur dioxide is directly linked to the sulphur content of the refinery fuel gas and fuel oils used. Heavy fuel oil residues normally contain significant proportions of sulphur and nitrogen, depending mainly on their source and the crude origin. Data from the 2006 CONCAWE sulphur survey [63, CONCAWE 2010] show that the average SO₂ content in the flue-gas of refinery energy systems (from oil/gas firing) has been roughly reduced by a factor of almost two between 1998 and 2006. The weighted average concentration has been calculated to be 594 mg/Nm³.

Figure 3.34 gathers the SO₂ equivalent concentrations (expressed as yearly average in mg/Nm³ dry at 3 % O₂) of all flue-gases emitted by the overall energy system of some European refineries. For each site, a summary of information is given on factors likely to influence SO₂ emissions from the concerned refinery combustion plants: the sulphur input from the overall feedstock, and the portion of total gaseous fuels (refinery fuel gas + eventual external natural gas supply) in the site energy mix. Most sites emit in the range 50 – 1 500 mg/Nm³. As expected, a clear correlation is observed between the highest gaseous fuel ratios in the site energy breakdown and the lowest SO₂ equivalent concentrations reported here.

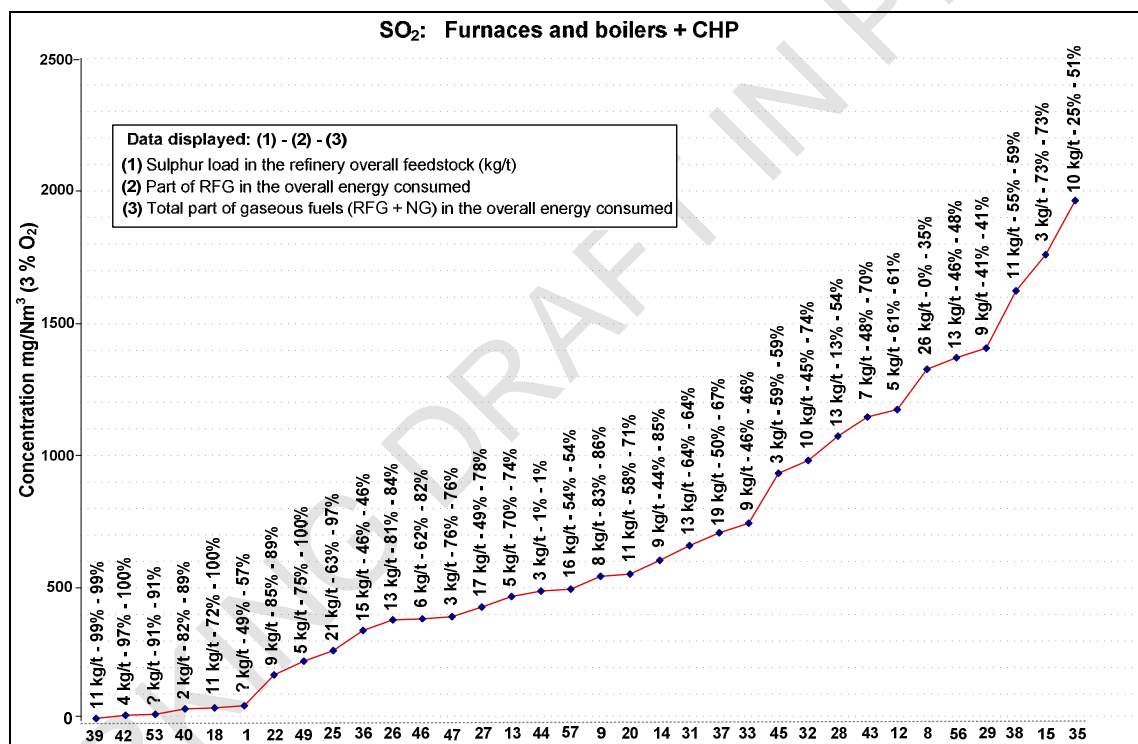


Figure 3.34: Distribution of SO₂ yearly average equivalent concentrations from the energy system of a sample of European refineries

In air-blown gasification of coke, the sulphur content will be about 4000 mg/Nm³ per % sulphur in the feed.

3.10.3.2 Waste water

Steam used for stripping, vacuum generation, atomisation and tracing is usually lost to waste water and to the atmosphere. The waste water generated in the energy processes comes mainly from the boiler feed water (BFW) system (i.e. demin water plant and condensate treatment

plant). The main streams are the boiler blowdown (1 to 2 % of the BFW intake) and the BFW preparation regeneration wash (2 – 6 % of the BFW produced). The main pollutants and composition of the first stream are COD: 100 mg/l; N-Kj: 0 – 30 mg/l; PO₄: 0 – 10 mg/l. The BFW preparation regeneration stream is combined with NaOH/HCl for pH neutralisation. Normally no biotreatment is required.

3.10.3.3 Solid wastes generated

Releases to land may result from the routine collection of grit and dust and arisings during cleaning procedures. The composition is 0.5 – 1 % w/w Ni and 2 – 3 % w/w V in furnaces and 1 – 3 % Ni/V for boilers. The amount depends on the furnace design and the liquid fuel quality, but in boilers varies from zero to 10 tonnes per year. Liquid refinery fuel tank bottom sludge may be generated in the storage tanks. Sludge may also be generated from the cleaning of fouled exchanger bundles. The flow depends on the liquid refinery fuel quality and the presence of fuel tank mixers. Depending on the mode of draining, 20 – 80 % is oil.

3.11 Etherification

Consumptions

The etherification reaction is exothermic, and so cooling to the proper reaction temperature is critical in obtaining optimal conversion efficiency. Methanol is needed for the production of these ethers. The utility consumptions in Table 3.61 are specified per tonne of MTBE processed in an oxygenate unit.

Table 3.61: Utility requirements in the etherification processes

Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m ³ /t, $\Delta T=10^{\circ}\text{C}$)
12 – 20	1 000 – 2 000	2 – 8

Emissions

Air emissions

Potential releases of hydrocarbons into air come from pressure reliefs on vessels, depentaniser column overheads drum and distillation column reflux drum, methanol plant, steaming vents on scavengers and reactor catalyst.

Waste water

Potential releases of hydrocarbons, methanol and ethers to water come from spillages and water bleed from methanol recovery. The water bleed is generated at a flow of 1 – 2 m³/t and with a composition of COD: 50 – 200 mg/l and a N-Kj: 5 – 20 mg/l. Some components that can be found in this waste water are methanol (ethanol), ethers and formic acid (acetic acid).

Solid wastes generated

Waste generated is the spent catalyst/resin with no possibility of regeneration. Every two years, it should be changed and steamed to flare before recycling. The catalyst is recycled for recovery of its palladium content. Some efforts in the recycling of the resin have not successful.

3.12 Gas separation processes

Consumptions

The electricity demand of a gas separation process varies between 15 and 20 kWh per tonne of feedstock processed. These processes also consume between 300 and 400 kg of steam per tonne of feedstock and between 1 and 2 m³/t of cooling water ($\Delta T=10^{\circ}\text{C}$).

Emissions

Air emissions

Potential releases into air include hydrocarbons from pressure reliefs on vessels, regeneration vent gas from molecular sieves, C₁/C₂ refinery fuel gas, refrigeration system leaks, storage and handling operations. Mercury if present in the feedstock of the refinery, will concentrate in overhead sections, particularly coolers. LPG, tops and naphtha coolers are most likely involved. Steaming that contaminated equipment may give mercury emissions to atmosphere. Mercury is sometimes found upon opening equipment for inspection and maintenance.

The final process in LPG production is the addition of some odorants. The odorants used are typically volatile organic sulphur compounds, i.e. mercaptans and sulphides. Potential releases into air include leaks or spillages of odorant and vapours displaced during tank filling or from thermal expansion of blanket gas. They also include the displaced vapours residue post incinerating or flaring if these techniques are used, including a small release of sulphur dioxide from combustion of the odorant.

Waste water

Potential releases into water include spillages of hydrocarbons, H₂S, NH₃ and amines.

Solid wastes generated

Potential releases into land include hydrocarbons from contaminated spent molecular sieves and from odorant addition including solid waste such as materials used to absorb odorant spillage.

3.13 Hydrogen-consuming processes

Consumptions

In this section, two groups of processes have been included: hydrocracking and hydrotreatments. Both types of processes are catalytic and consume hydrogen. Table 3.62 shows approximate hydrogen consumption for hydrotreatment and hydrocracking of various feedstocks.

Table 3.62: Hydrogen consumption data

Process (Chemical consumption data)	% S w/w in crude	% S w/w in feed	Nm ³ of H ₂ per tonne of feed
Deep atmospheric residue conversion	1 – 2	2 – 3.5	260 – 500
Hydrocracking vacuum gas oil	0.5 – 0.8	2 – 3	260 – 400
Cycle oil hydrogenation	0.3	3	370
Hydrotreating			
FCC naphtha/coker naphtha	0.05 – 0.01	1	110
Kerosene	0.1 – 0.02	0.1	11
Straight-run naphtha	0.01	0.05	4
Hydrodesulphurisation			
FCC gas oil/coker gas oil	0.1	1	130
High-sulphur gas oil to 0.05 % S	0.05	0.35	200
High-sulphur gas oil to 0.2 % S	0.04	0.3	44
Low-sulphur gas oil to 0.05 % S	0.04	0.15	17
Low-sulphur gas oil to 0.2 % S	0.03	0.1	13
Hydroconversion		Metal content <500 ppm	
<i>Source:</i> [175, Mevers 1997], [168, VROM 1999]			

3.13.1 Hydrotreatments

Hydrotreatment units consumptions

The H₂ consumption, and consequently the energy requirement, significantly increase in the order naphtha (0.05 % H₂), distillate (0.3 % H₂) and residue hydrotreating (1.8 % H₂). Table 3.63 shows the utility requirements for different hydrotreatments.

Table 3.63: Utility requirements for different hydrotreatments

	Fuel (MJ/t)	Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m ³ /t, ΔT=10°C)	Wash water (kg/t)	H ₂ (kg/t)
Naphtha processed	200 – 350	5 – 10	10 – 60	2 – 3	40 – 50	1 – 15
Distillate processed	300 – 500	10 – 20	60 – 150	2 – 3	30 – 40	1 – 15
Residue processed	300 – 800	10 – 30	60 – 150	2 – 3	30 – 40	10 – 100
<i>Sources:</i> [151, Sema,Sofres 1991], [168, VROM 1999]						

Table 3.64: Catalysts used in hydrotreatments

Process	Composition	Cycle lengths/average consumption (t/Mt feedstock)
Hydrodesulphurisation	CoO/MoO ₃ /Al ₂ O ₃	1 year/46
Denitrification	Ni/Mo catalyst	2 – 6 years/46
Demethalisation	NA	<1 year/NA
Saturation of olefins and aromatics	Ni/Mo catalyst	1 year/NA
Hydrogenation of light dienes	NA	2 years/NA

Emissions from hydrotreatment units

Emissions to air

Air emissions from hydrotreating may arise from process heater flue-gas (dealt with in Section 3.10), vents, fugitive emissions and catalyst regeneration (CO₂, CO, NO_x, SO_x). The off-gas stream may be very rich in hydrogen sulphide and light fuel gas. The fuel gas and hydrogen sulphide are typically sent to the sour gas treatment unit and sulphur recovery unit. Hydrocarbons and sulphur compounds may be emitted to air from pressure relief valves; leakages from flanges, glands and seals on pumps, compressors and valves, particularly on sour gas and sour water lines; venting during catalyst regeneration and replacement procedures or during cleaning operations. The following Table 3.65 shows two examples of emissions from hydrotreating processes. These air emissions include the emissions generated by the combustion of fuel required in these processes.

Table 3.65: Examples of air emissions generated by hydrotreatment units

Installation	Fuel consumption (GWh/yr)	Throughput (t/yr)	Units	SO ₂	NO _x	CO	CO ₂	Particulates
OMV Schwechat(*) (2007)	205.9	1 160 000	mg/m ³	700 (1)	74	10		20
		Naphtha	t/yr	142	15	2	40 152	4.1
			kg/t feed	0.13	0.013	0.002	36	0.004
Middle distillate	135.8	1 780 000	mg/m ³	59	242	5		1
		Kerosene. GO	t/yr	8.1	33	0.7	26 341	0.1
			kg/t feed	0.005	0.019	0	15	0
Vacuum distillate	72.4	1 820 000	mg/m ³	700 (1)	442	10		20
		VGO	t/yr	51.6	32.6	0.7	19 466	1.5
			kg/t feed	0.028	0.018	0	10.7	0.001

(1) Raw gas was treated in a flue-gas desulphurisation (Wellman Lord)
 Data are related to yearly average, 3 % O₂, dry conditions.
 (*) Since 2010, the Schwechat refinery (AT) uses only gas (except for the SNO_x power plant unit) with the following daily average emissions:
 SO₂: 1 – 20 mg/Nm³
 NO_x: <100 mg/Nm³
 CO: <80 mg/Nm³
 PM: 1 mg/Nm³
 Source: [194, Winter 2000] updated TWG-AT 2010

Installation TOTAL Mitteldeuts chland	Fuel consumption (GWh/yr)	Throughput (t/yr)	Units	SO ₂	NO _x	CO	CO ₂	Particulates
Naphtha hydrotreater		1 500 000	mg/m ³	35	100	100		5
	205.9	Naphtha	t/yr	7.1	20.3	20.3	39 937	1
			kg/t feed	0.005	0.014	0.014	27	0.001
Middle distillate		3 000 000	mg/m ³	35	100	100		5
	205.9	GO	t/yr	7.1	20.3	20.3	39937	1
			kg/t feed	0.002	0.007	0.007	13	0
Vacuum distillate		2 600 000	mg/m ³	35	100	100		5
	578.2	VGO	t/yr	18.6	53.2	53.2	164 776	2.7
			kg/t feed	0.007	0.02	0.02	63	0.001

NB: Emissions are only limit values. Loads and specific emissions were calculated.
Data are related to yearly average, 3 % O₂, dry conditions.

Waste water

Hydrotreating and hydroprocessing generate a flow of waste water of 30 – 55 l/tonne. The waste water contains H₂S, NH₃, high pH, phenols, hydrocarbons, suspended solids, BOD and COD, and should be sent to the sour water stripper/treatment. Potential releases into water include HC and sulphur compounds from spillages and leaks, particularly from sour water lines. In distillate hydrotreatments, solid deposits such as (NH₄)₂SO₄ and NH₄Cl are formed in the cooler parts of the unit and must be removed by water wash.

Solid wastes generated by hydrotreatments

These processes generate spent catalyst fines (aluminium silicate and metals Co/Mo and Ni/Mo 50 – 200 t/yr for 5 Mt/yr refinery). For process units using expensive catalysts, contracts with the supplier exist for taking the spent catalyst back for regeneration and/or recycling. This practice is also being adopted for other types of catalysts. The use of catalytic processes has increased considerably and hence also the regeneration and rework services, particularly for Ni/Mo and Co/Mo hydrotreating catalysts. Molecular sieve beds are sometimes used to capture the water content of some streams (e.g. distillate hydrodesulphurisation).

3.13.2 Hydrocracking

Consumptions of hydrocracking units

Hydrocracking is an exothermic process. The heat generated in the reactors is partially recovered in a feed/product heat exchanger. A significant amount of heat is required in the fractionation section. Catalysts used in this process are typically cobalt, molybdenum, nickel or tungsten oxides impregnated on alumina. Fluorided alumina, activated clay, silica-alumina or zeolites are also present. Average consumption of catalysts is 57.4 t/Mt of feedstock. A small amount of coke-like material is formed which accumulates over time on the catalyst. This deactivates the catalyst, requiring regeneration off-site every one to four years by burning off the coke. Water is removed by passing the feed stream through a silica gel or molecular sieve dryer. The utility requirements for hydrocracking are shown in Table 3.66:

Table 3.66: Utility consumption of hydrocracking units

	Fuel (MJ/t)	Electricity (kWh/t)	Steam produced (kg/t)	Cooling water (m ³ /t, ΔT=17°C (*ΔT=10°C))
Hydrocracking	400 – 1 200	20 – 150	30 – 300	10 – 300
Hydroconversion	600 – 1 000	50 – 110	200 – 300	2 – 10

Source: [151, Sema,Sofres 1991], [168, VROM 1999]

Emissions from hydrocracking units

Emissions to air

Heater stack gas contains CO, SO_x, NO_x, hydrocarbons and particulates that generate smoke, grit and dust in flue-gas (covered in Section 2.10), fugitive emissions (hydrocarbons) and catalyst regeneration (CO₂, CO, NO_x, SO_x, and catalyst dust). Fuel gas and bleed stream will contain H₂S and should be further treated. VOCs are generated by the non-condensable from vacuum ejectors.

Waste water

Hydrocracking generates a flow of waste water of 50 – 110 l per tonne processed. It contains high COD, suspended solids, H₂S, NH₃ and relatively low-levels of BOD. The sour water from the first stage HP separator, LP separator, and overhead accumulator should be sent to the sour water stripper/treatment. Effluents from hydroconversion processes may occasionally contain metals (Ni/V).

Solid wastes

Hydrocracking also generates spent catalysts fines (metals from crude oil, and hydrocarbons). Catalyst should be replaced once every one to three years generating an average of 50 – 200 t/yr for a refinery of 5 Mt/yr. Hydroconversion normally generates between 100 and 300 t/yr of spent catalysts which contain more heavy metals than hydrocracking catalysts.

3.14 Hydrogen production

Consumptions

Steam reforming

The steam reformer has to supply a large amount of heat at high temperature for the steam reforming reaction by burning fuel. Global fuel consumption of a unit includes the one for hydrogen production plus that associated with steam export to nearby installations.

Fuel requirement values indicated in Table 3.67, are those associated with hydrogen production strictly. They refer to large size equipment (50 000 Nm³/h of H₂ or more). Achieving such values requires both the use of the technique described further in Section 4.14.1 (preheating feed process, steam superheating, combustion air preheating) and the use of the PSA separation process in order to recover energy contained in by-products, mainly CO and CH₄, and feed back it to burners (up to 90 % recovery of the required energy for steam reforming).

As more and more steam is produced and exported, total energy requirements can be higher.

Values of the electricity requirement do not include product compression. Also the cooling for such compressors is not included in the values presented for the cooling water utility.

Table 3.67: Utility requirements for steam reforming (large sized recent equipment)

Fuel (MJ/t H ₂)	Electricity (kWh/t)	Steam produced (kg/t)	Cooling water (m ³ /t, ΔT=10 °C)
20 000 – 30 000	200 – 400	2 000 – 8 000	25 – 100
<i>Source: [151, Sema,Sofres 1991], TWG 2010 (EIGA)</i>			

On average, these processes produce 3 000 – 3 600 Nm³ of hydrogen (240 – 310 kg) per tonne of feedstock. The catalyst for reforming is 25 – 40 % nickel oxide deposited on a low-silica refractory base. The catalyst used in the reformer furnace is not regenerable and is replaced every four or five years. Longer lifetimes can be achieved when the feed is light, such as CH₄, of constant quality and the catalyst is well sulphur-protected. Lifetime doubling may be achieved, especially when desulphurised feed is first fed to a pre-reformer unit installed upstream of the reformer.

The composition of the product depends on the purification technique, as shown in Table 3.68.

Table 3.68: Composition of the hydrogen product in steam reforming

Parameter	Wet scrubbing technique	Pressure-swing adsorption
Hydrogen purity, % v/v	95 – 97	99 – 99.99
Methane, % v/v	2 – 4	100 ppm v/v
CO+CO ₂ , ppm v/v	10 – 50	10 – 50
Nitrogen, % v/v	0 – 2	0.1 – 1.0
<i>Source: [175, Meyers 1997]</i>		

Coke gasification

Coke gasification produces between 2 600 and 3 500 Nm³ of hydrogen (210 – 300 kg) per tonne of coke gasified. Figure 3.35 shows a scheme of the hydrogen production from a coke gasifier and the amount of hydrogen produced per tonne of petroleum coke.

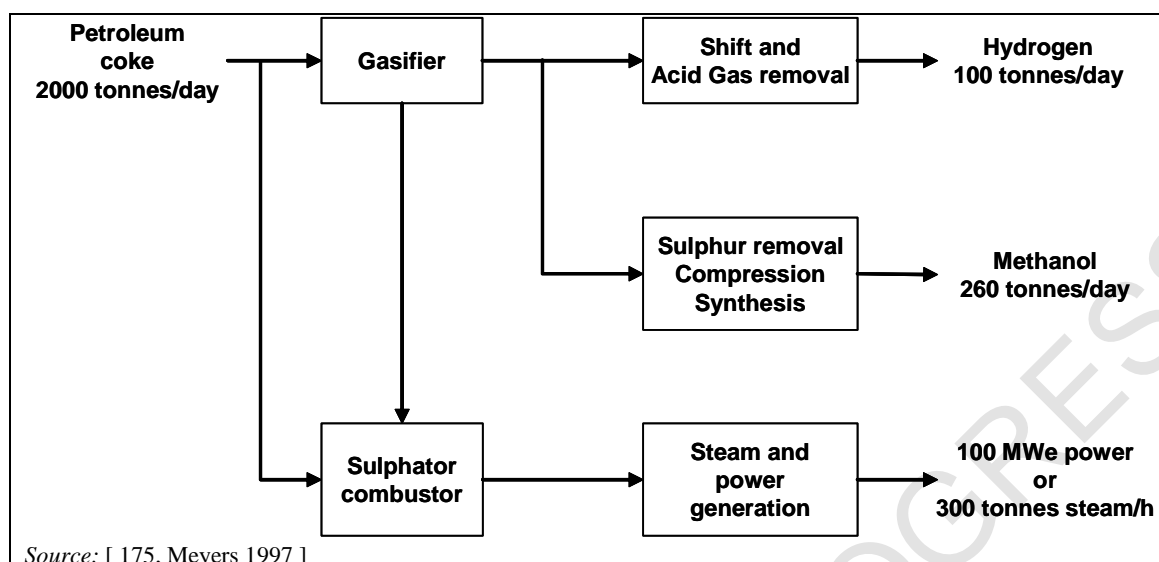


Figure 3.35: Petroleum coke commercial process

Heavy fuel gasification

Bitumen and heavy fuel can be gasified. The bitumen used in the gasification have the characteristics that are shown in Table 3.69.

Table 3.69: Characteristics of bitumen used as partial oxidation feedstock

Parameter	Typical value	Unit
Density at 15 °C	1.169	kg/l
Carbon	85.05	% w/w
Hydrogen	8.10	% w/w
Nitrogen	0.80	% w/w
Sulphur	6.00	% w/w
Ash	0.05	% w/w
Vanadium	600	ppm
Nickel	200	ppm

Source: [175, Meyers 1997]

Air emissions

Steam reforming

NO_x emissions are the most important to consider. Other emissions such as SO_x or water emissions are minimal, because low-sulphur fuel is typically used and there are few emissions other than flue-gas. The choice of heat recovery system can have a major effect on NO_x production, since both the amount of fuel fired and the flame temperature will be affected. NO_x emissions from a steam reforming unit using gas or light gasoline as fuels and with low-NO_x burners are 25 – 40 mg/MJ (100 – 140 mg/Nm³, 3 % O₂) [160, Janson 1999]. In case air is preheated, those values reach up to 200 mg/Nm³ (3 % O₂) [56, EIGA 2009]. Other emissions, such as CO₂, originate from carbon in the feed.

Coke gasification

Sulphur sorbents, such as limestone (CaCO₃) or dolomite (Mg, Ca carbonate), are normally used in the gasifier, drastically reducing the sulphur content. Sulphur composition in the exhaust gas ranges from 600 to 1 200 mg/Nm³ of H₂S and COS. If no sorbent is used, the sulphur content of

the gas will be in proportion to the sulphur in the feed. In oxygen-blown gasification, the sulphur content will be about 10 000 mg/Nm³ per % sulphur in the feed. Ammonia is formed in the gasifier from the fuel-bound nitrogen. Ammonia in the product gas typically contains less than 5 % of the fuel-bound nitrogen when limestone is present in the gasifier.

Heavy fuel gasification

For the TOTAL Mitteldeutschland Refinery, data are available concerning air emissions of the partial oxidation unit and are given in Table 3.70.

Table 3.70: Example of air emissions generated by heavy fuel gasification

Fuel consumption (GWh/yr)	Throughput (t/yr)	Units	SO ₂	NO _x	CO	CO ₂	Particulates
2452.8	670 000	mg/m ³	35	158	100		5
		t/yr	243.4	1 099	695.5	475 843	34.8
		kg/t feed	0.363	1.64	1.038	710	0.052
NB: For the emissions, only limit values are given. Loads and specific emissions were calculated. Data are related to yearly average, 3 % O ₂ , dry conditions Source: [191, UBA Austria 1998]							

Solid waste

Coke gasification

The solid waste from the process consists mainly of spent limestone and metals from the petcoke. The particulates in product gas are removed in the barrier filter to a level of less than 5 ppm. Volatile metals and alkalis tend to accumulate on the particulate as the gas is cooled. The particulates contain a high percentage of carbon and are usually sent with the ash to a combustor, where the remaining carbon is burnt and the calcium sulphide is oxidised to sulphate. In this hot-gas clean-up system, there is no aqueous condensate produced, although some may be produced in the subsequent processing of the gas. The solid waste from the process consists mainly of spent limestone and metals from the petcoke. After processing in the combustor/sulphator, this material is sent to disposal. Vanadium and nickel are found in most petroleum cokes in concentrations far greater than in coals or lignites. They remain in the ash product.

3.15 Integrated refinery management

Emissions in abnormal circumstances

Accidental discharges of large quantities of pollutants can occur as a result of abnormal operation in a refinery and potentially pose a major local environmental hazard. Emergency situations are normally regulated in the refinery permit. Quantification of these emissions is difficult.

Start-up and shutdown

Conditions such as start-up and shutdown operations occur fairly infrequently, and are normally of short duration. Modern designs include fully automated fail-safe start-up and shutdown systems with interlocks to maximise safety and to minimise risk and emissions. Start-up and shutdown of a full refinery or part of the installation may result in substantial emissions to atmosphere, mainly VOC, SO₂, CO₂ and particulates. Effluent drainage and treatment facilities could also be temporarily overloaded. Refinery design and operational constraints call for safe and environmentally acceptable management and disposal of emissions, discharges and waste in upset conditions. Start-up and shutdown procedures, and hence emissions and discharges, vary according to the type of unit and the purpose of the shutdown. If a particular unit is only to be depressurised and heavy components flushed out for a temporary stop, the emissions will be far less than if all equipment must be purged, steamed out and filled with air to allow workers to enter. Stringent safety and health care procedures are normal practice in present-day refineries. Not only personnel but also contractors have to adhere to these procedures. Nevertheless, occasional accidents take place and safety precautions should be practised regularly. Shutdown or blowdown can also have an impact on neighbouring dwellings (noise and light flaring).

Heat exchangers cleaning

The bundles of heat exchangers are cleaned periodically to remove accumulations of scale, sludge and any oily wastes. Because chromium has almost been eliminated as a cooling water additive, wastes generated from the cleaning of heat exchanger bundles no longer account for a significant portion of the hazardous wastes generated at refining facilities. The sludge generated (oil, metals and suspended solids) may contain lead or chromium, although some refineries which do not produce leaded gasoline and which use non-chrome corrosion inhibitors typically do not generate sludge that contains these constituents. Oily waste water is also generated during heat exchanger cleaning. VOC emissions may occur during these processes.

Utilities management

Water management

Surface water run-off is intermittent and will contain constituents from spills to the surface, leaks in equipment and any materials that may have collected in drains. Run-off surface water also includes water coming from crude and product storage tank roof drains.

The daily sanitary waste water production of an individual is about 120 litres, so the total sanitary effluent of the refinery can be easily calculated. Normally this domestic effluent is collected in a septic tank and then treated in the waste water treatment plant.

Ballast water is relevant to these refineries that have crude receipt facilities or handle large product tankers or inland barges. This ballast water can be high in volume and salt content (seawater), and heavily polluted with oil. It can easily lead to an upset of existing effluent treatment systems. The use of ballast water tanks is therefore an important equalisation tool for feeding the water in a controlled way to either the process water system or the continuously oil-contaminated system, if the COD is lower than 100 ppm. As more and more tankers are equipped with segregated ballast tanks, the ballast water problem is slowly phasing out.

Water used in processing operations also accounts for a significant portion of the total waste water. Process waste water arises from desalting crude oil, steam stripping operations, pump gland cooling, product fractionator reflux drum drains and boiler blowdown. Because process

water often comes into direct contact with oil, it is usually contaminated and requires adequate treatment before reuse or discharging.

The water usage depends both on purpose and complexity of the refinery. While there are usually opportunities to economise on water use, the scope for major reductions in existing refineries is sometimes limited. The CONCAWE 2010 survey (100 refineries) reports the following data on water usage (annual data).

Annual median total fresh water intake :	5.7	Mm ³ /yr
Range (5 – 95 percentile):	0.4 to 220	Mm ³ /yr
Annual median fresh water:	3.7	Mm ³ /yr
Range (5 – 95 percentile):	0.14 to 37.8	Mm ³ /yr
Annual median fresh water per tonne throughput:	0.70 m ³ /yr	
Range of fresh water per tonne throughput:	0.1 to 8.6 m ³ /yr	

The recorded fresh water consumption is that taken from:

- potable (mains) water;
- river water;
- privately extracted groundwater (including in some cases contaminated groundwater extracted for purposes of treatment).

It does not include:

- recycled final effluent;
- storm water;
- ballast water from ships;
- waste water from adjoining facilities;
- seawater.

Blowdown systems

The gaseous component of the blowdown system typically contains hydrocarbons, hydrogen sulphide, ammonia, mercaptans, solvents and other constituents, and is either discharged directly to the atmosphere or is combusted in a flare. The major air emissions from blowdown systems are hydrocarbons, in the case of direct discharge to the atmosphere, and sulphur oxides, when flared. The liquid is typically composed of mixtures of water and hydrocarbons containing sulphides, ammonia and other contaminants, which are sent to the waste water treatment plant.

A seal drum blowdown generates an effluent of 1 – 2 m³/h and 10 times as much in the case of emergency, with a composition of (analysis of water seal after e.g. visbreaker startup) :

- COD : 500 – 10 000 mg/l;
- H₂S : 10 – 1 000 mg/l;
- NH₃ : 10 – 1 000 mg/l.

3.16 Isomerisation

The main environmental problems for isomerisation, apart from the energy consumption, are the catalyst promotion and the possible side-effects.

Consumptions

The total energy requirement depends mainly on the isomerisation catalyst technology used, the configuration including for the hydrogen recycle, the hydrocarbon recycle operation (2 – 2.5 times higher than once-through), and the technology used to separate the n- from the iso-paraffins; absorption/desorption process or a deisohexaniser column. The isomerisation processes require an atmosphere of hydrogen to minimise coke deposits. The utility requirements for the isomerisation process vary widely depending on the design options. An example of the utility requirements for an isomerisation process is shown in Table 3.71:

Table 3.71: Utility requirements of the isomerisation processes

Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m ³ /t, T=10°C)
20 – 30	300 – 600	10 – 15

Catalyst life can range from two to more than ten years depending on unit operation. The chloride promoted catalyst (chlorinated alumina containing platinum) requires the addition of very small amounts of organic chlorides to maintain high catalyst activities, to avoid catalyst deactivation and potential corrosion problems. See Section 2.16 for further information about the type of catalysts used.

Table 3.72 shows the utility and chemical requirements for the adsorption process for a feed rate of 600 tonnes per day.

Table 3.72: Utilities and chemical requirements of an adsorption process

Utilities and chemical requirements of the adsorption process	
Fuel consumed (90 % furnace efficiency) MW	9
Water ($\Delta T = 17^\circ\text{C}$), m ³ /day	2 159
Power, kWh	1 455
Steam at 10.5 kg/cm ² , saturated, kg/h	2.8
Hydrogen consumption, Nm ³ /day	17.7
Soda consumption (kg)	8.4
Hydrogen chloride (kg)	6
Catalyst consumption (kg)	0.12
<i>Sources: [175, Meyers 1997], [241, O. G. Journal 2000]</i>	

Emissions

Air emissions

Air emissions may arise from the process heater (used in some designs), vents and fugitive emissions. Other emissions are HCl (potentially in light ends from organic chloride added to maintain the catalyst activity), from vents and fugitive emissions, pressure reliefs on surge drum, separators and column reflux drum, regeneration vent gas from dryers, storage and handling operations and spillage (hydrocarbons). Releases of hydrogen may occur from pressure relief on the hydrogen system. Product stabilisation, however, does result in small

amounts of LPG (C_3+C_4 , rich in $i-C_4$) and in stabiliser vent ($H_2+C_1+C_2$) products. The stabiliser vent products are usually used as refinery fuel. In the chlorided-alumina catalyst isomerisation design, fuel gas is normally caustic-treated to remove HCl.

Process waste water

Potential releases into water include hydrocarbons from the reflux drum boot drain and spillages. With the chlorided alumina isomerisation catalyst design, additional waste water is generated by spent sodium hydroxide from the scrubber system. In this design, the process waste water contains chloride salts, caustic wash, traces of H_2S and NH_3 and has high pH. Brine from the feed dryer (desiccant, water free $CaCl_2$) contains dissolved $CaCl_2$ and hydrocarbons. Its flow depends on moisture content and is usually drained to the effluent treatment plant.

Residual wastes generated

Potential releases to land include hydrocarbons from spillages/contaminated molecular sieves and catalyst. Calcium chloride sludge (or other desiccants) is the waste generated in this process. The catalyst used in these processes normally is regenerated by the catalyst manufacturers. Mainly platinum is then recovered from the used catalyst off-site. Molecular sieves can be used as feed drying agent. The flow and composition are plant-specific and the spent molecular sieves are disposed of as non-regenerable solid waste.

3.17 Natural gas plants

Consumptions

Water and energy consumption within a natural gas plant are shown in Table 3.73:

Table 3.73: Example of utility consumption in natural gas plants (Norway)

Water and Energy consumption	Existing plant (Kårstø Plant)	New Plant (Ormen Lange Plant at Nyhamna)(*)
Capacity	88 million Nm ³ /day of rich gas 840 t/h unstabilised condensate	70 million Nm ³ /day export gas 8 400 Nm ³ /day condensate
Fuel gas	60 tonnes/h at full capacity	8 tonnes/h
Power (gas power))	775 MW	2 x 42.1 MW installed
Water (steam production)	60 m ³ /h	NA
Seawater cooling	44 000 m ³ /h	14 400 Nm ³ /h (Energy flux ~160 MW for normal operations)
(*) Norske Shell operates the gas plant at Nyhamna for the processing of gas and condensate from the Ormen Lange gas field offshore Norway. Source: [217, Statoil 2000] Updated TWG NO 2010		

Emissions

Emissions to air

The major emission sources in the natural gas processing industry are compressors, boilers and furnaces, acid gas wastes, fugitive emissions from leaking process equipment and, if present, glycol dehydrator vent streams. Regeneration of the glycol solutions used for dehydrating natural gas can release significant quantities of benzene, toluene, ethylbenzene and xylene, as well as a wide range of less toxic organics.

Potential release routes for prescribed substances and other substances which may cause harm are shown in Table 3.74.

Emissions of SO₂ will result from gas sweetening plants only if the acid waste gas from the amine process is flared or incinerated. Most often, the acid waste gas is used as a feedstock in nearby sulphur recovery (see Section 4.23.5.2) or sulphuric acid plants. When flaring or incineration is practised, the major pollutant of concern is SO₂. Most plants employ elevated smokeless flares or tail gas incinerators for complete combustion of all waste gas constituents, including virtually 100 percent conversion of H₂S to SO₂. Little results from these devices in the way of particulates smoke or hydrocarbons and, because gas temperatures do not usually exceed 650 °C, no significant quantity of nitrogen oxides is formed. Emission factors for gas sweetening plants with smokeless flares or incinerators are presented in Table 3.75. Factors are expressed in units of kilograms per 1 000 cubic metres. Emission data for sweetening processes other than amine types are very meagre, but a sulphur mass balance will give accurate estimates for sulphur dioxide (SO₂).

Table 3.74: Releases to the environment commonly associated with the natural gas processes

Type of process	H ₂ S	SO ₂	NO _x	CO, CO ₂	Organic compounds	Oily waters	N ₂	Spent catalysts/ adsorbents	Sand/ corrosion products	Acids/ alkalis/ salts, etc.
On-shore reception	A(*)				AW	W			L	
Gas Treatment processes	A(*)		A	A	AW	W		L		L
Acid gas processes	A(*)	A(*)	A	A	AW	W		L		
Nitrogen removal	A(*)				A		A			
Hydrocarbon removal					AW	W				
Gas compression			A	A	A					
Condensate treatment			A	A	AW			L		W
Field water treatment					W	W				
Flares/vents	A(*)	A(*)	A	A	A					
Gas storage sites	A	A	A	A	AW	W		L		

(*) If sour gas is being processed
 NB: A: air, W: water, L: land
 Source: [173, HMIP UK 1997]

Table 3.75: Emission factors for gas sweetening plants

Amine process	kg/10 ³ Nm ³ gas processed	Comments
Particulate	Negligible	
SO _x (as SO ₂)	26.98	Assumes that 100 % of the H ₂ S in the acid gas stream is converted to SO ₂ during flaring or incineration and that the sweetening process removes 100 % of the H ₂ S in the feedstock.
	0.408(*)	For an emission ratio of 0.75 %
	0.272(*)	For an emission ratio of 0.50 %
CO	0.25(*)	
Hydrocarbons	-	Flares or incinerator stack gases are expected to have negligible hydrocarbon emissions.
NO _x	Negligible	

Sources: (*) [172, MRI 1997], [54, Gallauner et al. 2009]

Emissions to water

Routine process-derived liquid effluent produced by natural gas plants is normally derived mainly from water arising from the drying of the gas and associated condensate. The effluent principally occurs as condensed steam from the glycol or methanol regeneration plants and usually contains a number of organic contaminants, including glycol, methanol, aliphatic and aromatic hydrocarbons, amines and mercaptans. The presence of these contaminants typically causes the effluent to have a very high biochemical and chemical oxygen demand. The process of refining natural gas which contains mercury can generate waste water which contains that metal.

Solid waste

Natural gas refining gives rise to relatively small quantities of process wastes. These typically include occasional disposal of spent catalysts, activators, corrosion inhibitors, absorbents,

adsorbents, filter cartridges, separator dusts, etc and they may be contaminated with trace amounts of hydrocarbons. Some natural gas sources contain traces of Hg which should be collected (generating spent adsorbent) and safely disposed of. For every 1000 kg of sludge treated, 12 kg of metallic mercury is produced. Total sludge production within some Dutch natural gas plants is on average 250 tonnes/yr, with a maximum of 400 tonnes/yr. This corresponds to 3-5 tonnes of mercury annually.

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3.18 Polymerisation

Consumptions

The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst. Typically 0.2 grammes of phosphoric acid are consumed to produce 1 tonne of polymer or 1.18 kg of catalyst (phosphoric acid + support) per tonne of product. Catalyst life is normally limited from three to six months, depending on unit size and operating conditions. A typical unit, capable of producing 25 tonnes of polymerised gasoline per day, is customarily filled with 12 tonnes of catalyst.

Caustic solution is used to remove mercaptans from the propene/butene feed, followed amine solution to remove hydrogen sulphide, then, water to remove caustics and amines. It is finally dried by passing through a silica gel or molecular sieve dryer.

Table 3.76 shows the typical utility consumption of a polymerisation process.

Table 3.76: Utility consumption in polymerisation process

Utility	Consumption	Unit
Electric power	20 – 28	kW/t of product
Steam	0.7 – 1.1	t/t of product
Cooling water	4.4 – 6.0	t/t of product
<i>Source: [175, Meyers 1997]</i>		

Emissions

Emissions to air

Potential releases into air include hydrocarbons from pressure reliefs, storage and handling operations, spillages and water and waste discharges, and of particulate matter from catalyst fines, from handling and disposal of spent catalysts. Sulphur dioxide and H₂S may arise during the caustic washing operation.

Process waste water

Potential releases into water include hydrocarbons from sour water purge from the washtower, condenser drains and spillages, and of particulate matter from spillages of catalyst fines. Waste water streams will contain caustic wash and sour water with amines and mercaptans. Its more important parameters are H₂S, NH₃, caustic wash, mercaptans and ammonia, and low pH (2 – 3) due to the phosphoric acid.

Solid waste generated

Spent catalyst containing phosphoric acid, which typically is not regenerated, is occasionally disposed of as a solid waste. Potential releases into land include acids in solid form and hydrocarbons from spent catalyst. Typically, 0.4 grams of used silica is disposed of per tonne of polymer gasoline produced.

3.19 Primary distillation units

Consumptions

Despite the high level of heat integration and heat recovery that is normally applied, crude distillation units (CDU) are among the most intensive energy-consuming units in a refinery, because the total volume of crude oil being processed has to be heated to the elevated processing temperature of 350 °C. The overall energy consumption of a refinery is normally dominated by a few processes. Atmospheric and vacuum distillation accounts for 35 – 40 % of the total process energy consumption, followed by hydrotreating with approx. 18 – 20 % [177, WRA 1999]. The various processes downstream of the CDU make use of the elevated temperatures of the product streams leaving the CDU. The number of side-streams in a high vacuum unit is chosen to maximise heat integration of producing streams at different temperatures, rather than to match the number of products required. The utility requirements for the atmospheric and vacuum distillation units are shown in Table 3.77.

Table 3.77: Utility requirements for atmospheric and vacuum distillation units

Type of unit	Fuel (MJ/t)	Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m ³ /t, ΔT=17 °C)
Atmospheric	400 – 680	4 – 6	25 – 30	4.0
Vacuum	400 – 800	1.5 – 4.5	20 – 60	3 – 5

NB: Replacement of the steam ejectors by vacuum pumps will reduce steam consumption and waste water generation but increase the electricity consumption.
Sources: [168, VROM 1999], [204, Canales 2000], [207, TWG 2001]

Emissions

Air emissions

Potential releases into air are from:

- Flue-gases arising from the combustion of fuels in the furnaces to heat the crude oil.
- Pressure relief valves on column overheads; relief from overhead accumulators are piped to flare as well as the vent points.
- Poor containment in overhead systems, including barometric sumps and vents.
- Glands and seals on pumps, compressors and valves.
- De-coking vents from process heaters. During furnace decoking (once or twice a year), some emission of soot can occur if the operation is not properly controlled in terms of temperature or steam/air injection.
- Venting during clean-out procedures.
- Some light gases leaving the top of the condensers on the vacuum distillation column. A certain amount of non-condensable light hydrocarbons and hydrogen sulphide passes through the condenser to a hot well, and is then discharged to the refinery sour fuel system or vented to a process heater, flare or other control device to destroy hydrogen sulphide. The quantity of these emissions depends on the size of the unit, the type of feedstock and the cooling water temperature. If barometric condensers are used in vacuum distillation, significant amounts of oily waste water can be generated. Oily sour water is also generated in the fractionators. The emissions of non-condensables from vacuum ejector set condensorS are between 50 and 200 kg/h, depending on furnace design and type of crude and throughput. They include hydrocarbons and H₂S.
- Fugitive emissions from atmospheric and vacuum distillation units account for 5 – 190 t/yr for a refinery with a crude capacity of 8.7 Mt/yr [155, API 1993].

Table 3.78 gives some examples of the air emissions generated by the atmospheric and vacuum distillation units by two European refineries. This table includes the emissions from combustion of fuels in the furnaces.

Table 3.78: Examples of air emissions generated by crude oil and vacuum distillation units

Installation	Fuel consumption (GWh/yr)	Throughput (t/yr)	Units	SO ₂	NO _x	CO	CO ₂	Particulates
CDU TOTAL Mittel deutschland		8 500 000	mg/m ³	35	100	100		5
	1138.8	Crude oil	t/yr	35.2	100.4	100.4	220 927	5
			kg/t feed	0.004	0.012	0.012	26	0.001
Vacuum distillation TOTAL Mittel deutschland		4 500 000	mg/m ³	35	100	100		5
	639.5	Atm. Res.	t/yr	19.8	56.6	56.6	182 252	2.8
			kg/t feed	0.004	0.013	0.013	41	0.001
⁽¹⁾ Raw gas was treated in a flue-gas desulphurisation (Wellman Lord) NB: Data are related to yearly average, 3 % O ₂ , dry conditions For the emissions from the TOTAL Mitteldeutschland refinery, only limit values are given. Loads and specific emissions are calculated. Source: [194, Winter 2000]								

Process waste water

Process waste water generated in the atmospheric distillation units is 0.08 – 0.75 m³ per tonne of crude oil processed. It contains oil, H₂S, suspended solids, chlorides, mercaptans, phenol, an elevated pH, and ammonia and the caustic soda used in column overhead corrosion protection. It is generated in the overhead condensers, in the fractionators, and can also become contaminated from spillages and leaks. The overhead reflux drum (gas oil dryer condenser) generates 0.5 % water on crude + 1.5 % steam on feed, with a composition of H₂S 10 – 200 mg/l and NH₃ 10 – 300 mg/l. Sour water is normally sent to water stripper/treatment.

Waste water (sour water) is generated in the vacuum distillation units from process steam injection in the furnace and the vacuum tower. It contains H₂S, NH₃ and dissolved hydrocarbons. If steam ejectors and barometric condensers are used in vacuum distillation, significant amounts of oily waste water can be generated (± 10 m³/h) containing also H₂S, NH₃.

Residual wastes generated

Sludges can be generated from the cleaning-out of the columns. The amount depends on the mode of desludging and the base solid and water content of the crude processed. The range of solid waste generation from a crude unit of 8.7 Mt/yr ranges from 6.3 – 20 t/day.

3.20 Product treatments

Consumptions

Gasoline sweetening

Utility requirements in the gasoline sweetening process are:

Table 3.79: Typical utility consumption of a gasoline sweetening process

Electricity (kWh/t)	Steam consumed (kg/t)	Caustic (kg/t)
1 – 10	10 – 25	0.02 – 0.15
Sources: [204, Canales 2000], [168, VROM 1999], [175, Meyers 1997]		

Catalytic dewaxing

Catalytic dewaxing catalysts typically last 6 to 8 years. During that time, they are regenerated as needed. Typical cycles last 2 to 4 years between regenerations. Utilities needed in the catalytic dewaxing process are summarised in the following table.

Table 3.80: Typical utility consumption of catalytic dewaxing units

Utilities for a feed capacity of 3 500 tonnes per stream day	
Power, kW	5 100
Steam (tracing only)	Minimal
Cooling water, m ³ /h	80
Condensate, m ³ /h	4
Fuel absorbed, MW	23 084
Source: [175, Meyers 1997]	

Emissions

Air emissions

Potential releases into air from oxidation-extraction processes include hydrocarbons, sulphur compounds (e.g. disulphides); and nitrogen compounds from sour water drains, pressure relief valves, vents from feed vessels, spillages and leakages from flanges, glands and seals on pumps and valves – particularly from overhead systems and fugitive emissions. Emissions may occur from the spent air from the disulphide separator that contains less than 400 ppm of disulphides and is normally incinerated.

Process waste water

Product treating processes do not generate much waste water. The potential releases into water are from spillages and leakages (hydrocarbons), and the sulphur and nitrogen compounds arising from inadequate stripping performance.

Residual wastes generated

In the extraction process, an oily disulphide waste stream leaves the separator. Most refineries are able to regenerate their spent caustic, but sometimes they have to dispose of some excess quantities of spent caustic, mainly from caustic pre-wash activities. Usually these quantities are small and can be managed within their effluent treatment system or they are disposed of externally via contractors or may be reused elsewhere. From the extraction process, the disulphide recovered can be sold as product, or recycled to a hydrotreater or incinerator. The amount of spent caustic generated varies between 0.05 - 1.0 kg/tonne feed and contains

sulphides and phenols. The concentration of organic compounds in spent caustic solutions is typically higher than 50 g/l.

Table 3.81: Typical emissions from the catalytic dewaxing process

Catalytic dewaxing process		
Air	Waste water	Solid wastes
Flue-gas from fired heater VOCs may arise from venting during catalyst regeneration/replacement procedures and cleaning.	none	Potential releases into land are from disposal of spent catalytic dewaxing catalyst. (50 t/yr for a 50000 t/yr hydrofining process). Spent Ni-W catalysts containing sulphur and carbon sent to specialised off-site regeneration companies. After two - three regenerations catalyst is disposed of and subjected to metal reclaiming.

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3.21 Storage and handling of refinery materials

Consumptions

No energy or process material is required for balancing lines, double seals or floating roofs on tanks. However, some tanks need mixers (a heavy user of power) and some need heating too. Handling refinery materials also requires electricity for the pumps that move the materials through the pipes.

Emissions

Air Emissions

Air emissions, and more specifically VOC emissions, are the main emissions that occur during the storage and handling of refinery materials. Emissions from hydrocarbon liquids in storage occur because of evaporative loss of the liquid during storage and as a result of changes in the liquid level. Even if equipped with floating tops, storage tanks account for considerable VOC emissions at petroleum refineries. Moreover, fugitive emissions in storage systems are mainly from imperfect seals or tank fittings. The amount of emissions from a particular tank will directly depend on the vapour pressure of the product stored. A study of petroleum refinery emissions found that the majority of tank losses occurred through tank seals on gasoline storage tanks [161, USAEPA 1995]. Since that time, emissions from gasoline tanks in Europe have been significantly reduced by the installation of control measures mandated by Directive 94/63 on the control of VOC emissions resulting from the storage of petrol.

VOC emissions from storage can represent more than 40 % of the total VOC emissions in a refinery. The emissions from tanks have been estimated by using API estimations [100, API 2002] As an example, these emissions can lead to 320 tonnes per year from the storage systems. It is a much lower figure than the one calculated from the DIAL measurements: 1900 tonnes per year for a refinery processing 11 million tonnes per year [160, Janson 1999]. However, API methods have been updated and storage losses can be predicted with acceptable accuracy [202, Dekkers 2000]. A CONCAWE study [186, Smithers 1995] was the first trial of DIAL where measurements were conducted over a reasonably long period and showed that there was reasonable agreement between DIAL and the latest API estimation methods as to when the test times were long enough. In that case, the estimation method was acceptable to provide annual inventory values. It is important to take into account that the API emissions factor method assumes that no technical problems occur with the considered tank.

DIAL and SOF have now been used for over 20 years e.g. at Swedish refineries and in France, Belgium, Netherland and the US. These monitoring campaigns all give higher results for emissions than calculations. In the beginning, in Sweden, the difference was often close to a factor 10–15. Over the years, the factor has become smaller, but still a factor 2–5 is common (see also Section 3.26.1.3).

When transferring liquids to vessels at atmospheric pressure, the vapour phase in the receiving vessel, comprising both the vapours existing in the vessel prior to loading and those generated by evaporation of the loaded liquid, is often emitted to atmosphere. Such loading operations are recognised as having an impact on the environment due to the presence of VOCs. VOC emissions from blending come from blending tanks, valves, pumps and mixing operations. The amount depends on design and maintenance of the systems. Although barge loading is not a factor for all refineries, it is an important emissions source for many facilities. One of the largest sources of VOC emissions identified during the Amoco/USAEPA study was fugitive emissions from the loading of tanker barges. It has been estimated that during the loading of products with high partial pressure, 0.05 % of the throughput can be emitted to the air. As previously stated, through the impact of Directive 94/63, air emissions have been significantly reduced in Europe, including, these from the barge loading of gasoline.

VOC emissions to the air from cavern storage of hydrocarbon materials can be prevented by connecting the gas spaces of several caverns, so the breathing gases when filling one cavern are

led to the other caverns. In the case of only one cavern, the breathing gases must be sent to the air. For a given product, the VOC emissions from cavern storage are generally slightly lower than from a conventional aerial vessel (of group of vessels) of the same capacity, the yearly average temperature of storage is lower (5 – 10 °C).

Waste water

Leaking flanges and valves may contaminate rainwater. The amount depends on the maintenance service. Liquid tank bottoms (primarily water and oil emulsions) are periodically drawn off to prevent their continued build up. That waste water is contaminated with tank product. Oil levels up to 5 g/l in tank water bottoms can be found [159, WB 1998]. However, if the draw off rate of the water is too high, oil can be entrained with the water, thereby giving a false high reading of oil in the water.

Groundwater leaking into underground storage systems (caverns) should be pumped out and led to the waste water treatment system of the refinery. The amount of water depends on the solidity of the rock and how carefully the fractures in the rock are sealed by injection of concrete [199, Lameranta 2000]. The quality of waste water depends on the product (or crude) which is stored in the cavern. Typically the waste water contains hydrocarbons as emulsion and water soluble components of stored liquid. Some examples of waste water generated by cavern storage is given in Table 3.82.

Table 3.82: Examples of waste water generated by caverns

Cavern	Volume of the cavern (m ³)	Product	Seeping water removed (m ³ /yr)	Amount of hydrocarbons discharged after oil separation (kg/yr)
A	40 000	Light fuel oil	22 300	49
B	2x75 000	Heavy fuel oil	25 800	104
C	50 000	Light fuel oil	36 900	40
D	105 000	Light condensate	140	NA
E	52 000	Propane/butane	80	NA
F	150 000	Propane/butane	150	NA
G	430 000	Heavy fuel oil	50 000	76
H	100 000	Car fuel (diesel)	5 000	NA
I	100 000	Car fuel (petrol)	3 000	NA

Source: [199, Lameranta 2000]

Waste and soil contamination

The primary subsurface (soil and groundwater) contamination threats posed by above-ground storage tanks include the disposal of sludges from the bottoms of the tanks during periodic cleaning of tanks for inspections, loss of product from the tanks during operations such as tank water drainage, and product leakage to the ground caused by tank or piping failures or overfilling accidents. Spills may result in contamination of soil from handling processes, especially in loading, mainly due to human error. Storage tank bottom sludge contains iron rust, clay, sand, water, emulsified oil and wax, phenols and metals (lead for leaded gasoline storage tanks). Table 3.83 shows some analyses of sludges taken from the sewerage system around tank storage facilities. The analyses are unique to that site and are reproduced to show what may occur.

Table 3.83: Composition of the sludge taken from four different sewer systems close to the storage tanks

Species	Tank field sewers (two different sources)		Gasoline tank field sewers	Distillate tank field sewers
	Source 1	Source 2		
Solids	92.7 %	91.2 %	81 %	97.0 %
Oil	7.3 %	8.8 %	19 %	3.0 %
Carbon	26.9 %	27.1 %	44.9 %	58 %
Hydrogen	10.2 %	15.1 %	7.8 %	7.3 %
Nitrogen	1.2 %	<0.6 %(*)	0.4 %	0.6 %
Sulphur	64441	70034	58222	13514
Iron	25000.0	174024.0	62222.0	105326.0
Magnesium	9317.0	2695.0	4430.0	1331.0
Sulphide	8327.0	3624.8	4325.9	4238.9
Aluminium	4193.0	3969.0	8148.0	3180.0
Nitrate	2290.4	10.8	91.9	8.9
Sodium	1180.0	772.0	770.0	445.0
Sulphate	1037.3	165.5	19.3	39.7
Xylene	746.9	<4.2(*)	1121.5	4.0
Toluene	478.3	<4.2(*)	794.1	4.0
Ethylbenzene	158.4	<4.2(*)	106.8	4.0
Nepthalene	130.4	27.6	-	25.8
Benzene	80.7	<4.2(*)	35.6	4.0
Phenol	71.4	129.5	-	69.6
Nickel	68.3	106.1	500.7	190.8
Lead	55.9	492.4	308.1	234.5
Chromium	35.4	70.5	154.1	81.5
Pyrene	30.0	<105.0(*)	-	39.0
Carbonate	29	2.0	0.3	0.3
Vanadium	27.0	72.0	49.0	25.0
Antimony	19.0	42.0	15.0	20.0
Phenols	18.6	<105.1(*)	-	39.3
Fluorine	15.5	<105.1(*)	-	39.3
Benzo(a)pyrene	<7.8(**)	<105.1(*)	-	39.3
Selenium	7.0	<4.0(*)	4.3	5.0
Arsenic	5.0	16.1	14.5	15.9
Mercury	4.0	1.6	9.5	0.2
Cyanide	0.6	1.0	0.5	0.7
Calcium	<0.3(*)	39261.0	13185.0	11725.0
(*) Below Detection Limit Shown (**) Estimated Value Below Detection Limit NB: Figures quoted on a moisture free basis, all units mg/kg unless otherwise stated. Figures do not sum to 100 % because of double counting. Source: [156, MCG 1991]				

3.22 Visbreaking and other thermal conversions

3.22.1 Visbreaking

Consumptions

Table 3.84 represents typical utility consumptions for a visbreaker:

Table 3.84: Utility consumptions of a visbreaker

Utility (unit)	Consumption range
Fuel (MJ/t)	400 – 800
Electricity (kWh/t)	10 – 15
Steam consumed (kg/t)	5 – 30
Cooling water (m ³ /t, $\Delta T=10^{\circ}\text{C}$)	2 – 10
NB: The power consumption given is for furnace cracking. Sources: [168, VROM 1999], [204, Canales 2000]	

For visbreaking, fuel consumption accounts for about 80 % of the operating costs, with a net fuel consumption of 1 - 1.5 % w/w on feed. Fuel requirements for soaker visbreaking are about 30 - 35 % lower.

Emissions

Air Emissions

Air emissions from visbreaking include emissions from the combustion of fuels in the process heaters, vents and fugitive emissions. A sour water stream is generated in the fractionator. The gas produced contains H₂S and should be further treated. Hydrogen sulphide and mercaptans are released from the sour water stream from reflux condensers. Hydrocarbons are released from pressure reliefs on reflux drums and vessels, storage and handling operations, spillages and discharges of waste water. Particulate emissions occur during furnace decoking and cleaning operations about twice a year.

Table 3.85 shows the air emissions from visbreaking processes in two European refineries.

Table 3.85: Example of air emissions generated by visbreaking processes

Installation	Fuel Consumption (GWh/yr)	Throughput (Mt/yr)	Units	SO ₂	NO _x	CO	CO ₂	Particulates(*)
TOTAL Raffinerie Mitteldeutschland	306.6	1.20	mg/m ³	35	100	100		5
			t/yr	13	50.6	1.4	59 480	0.3
			kg/t feed	0.011	0.042	0.001	50	0
Emissions from TOTAL Mitteldeutschland refinery: only limit values are given, loads and specific emissions were calculated. NB: Data are related to yearly average, 3 % O ₂ , dry conditions. (*) No information available on PM size Source: [191, UBA Austria 1998]								

Process waste water

The fractionator overhead gas is partly condensed and accumulated in the overhead drum to separate into three phases: a hydrocarbon gas stream, a hydrocarbon liquid stream and a sour water stream. The sour water stream should be sent to the sour water stripper for purification.

The flow of waste water generated in the visbreaking process from the sour water drain is around 56 litres per tonne of feedstock. It represents between one and three % volume on feed intake.

Table 3.86 shows the range of composition of the visbreaker waste water.

Table 3.86: Typical composition of the waste water produced in visbreaking

Substance or parameter	Concentration (mg/l)
PH	High
Free oil	50 – 100
COD	500 – 2000
H ₂ S	10 – 200
NH ₃ (N-Kj)	15 – 50
Phenols	5 – 30
HCN	10 – 300

Solid wastes generated

The waste generated in visbreaking comes from the cleaning and turnaround of the process. It is generated discontinuously at a rate of 20 to 25 tonnes per year for a 5 million tonnes per year refinery. It contains between 0 and 30 % of oil/sludge.

The following sections cover the emissions arising from refinery processes that are used for the treatment of waste gas, waste water and solid waste. These techniques are described in Chapter 4 (Sections 4.23 to 4.25). The main objective of these processes is to reduce the concentration of pollutants in the effluents. Obviously the loads and concentrations of pollutants in these streams will be reduced by these processes, but some pollutants will remain in the streams and other may be generated. That is the purpose of the following next three sections. Emissions from the refinery as a whole are included in Section 3.1.

3.22.2 Thermal gas oil units (TGU)

Emissions

Table 3.87 shows the emissions to air from one European thermal gas oil unit in OMV Schwechat refinery (Austria).

Table 3.87: Example of emissions of a thermal gas oil unit in an European site

Installation	Fuel consumption (GWh/yr)	Annual capacity (tonnes/yr)	Units	SO ₂	NO _x	CO	PM
TGU OMV Schwechat	450.1	730 000	mg/m ³	0	27 – 38	2 – 16	1
			t/yr	<0.1	41.7	9.3	1.3
All data are monthly average from 2009 – 15 % O ₂ .							

3.23 Emissions from waste gas treatment techniques

This section includes end-of-pipe or abatement techniques of CO, CO₂, NO_x, particulates, sulphur compounds, VOC, combined techniques for the abatement of air pollutants, odour and noise.

3.23.1 Sour gas treatments

The sour gas is sent to the refinery sour gas treatment system which separates the fuel gas so that it can be used as fuel in the refinery heating furnaces. The area of the amine treating unit poses health risks because of the presence of H₂S, possibly by inadvertent leakages.

3.23.2 Sulphur recovery units (SRU)

In 1995, the average percentage of sulphur recovered in the SRU represented 42.6 % of the sulphur entering the refinery with the crude oil. From the data gathered for a sample of 50 European sites by the Technical Working Group (TWG) set up for the review of this document, this percentage can be estimated for the period 2007 - 2008 at 44.7 % (50th percentile). However, this median value hides a rather wide range of site performances from 10.7 to 79.9 % (5th to 95th percentile).

Sulphur is recovered in sulphur recovery units, extensively described in Section 4.23.5. As already shown on Figure 3.12 and Figure 3.13 in Section 3.1.2.4, they represent around 10 – 25 % of the SO₂ emissions from refineries, even if the fuel gas volume from SRU represent only around 1.5 % of the total flue-gas volume emitted by a refinery.

The sulphur recovery yield of SRUs operated in a sample of 47 European sites is displayed in Figure 3.36. Values reflect the overall SRU performance, including the utilisation factor achieved by the whole set of available treatment lines. The installed base of SRU has a recovery ranging from 93 to 99.99 %, with a median value (50th percentile) around 98.5 %.

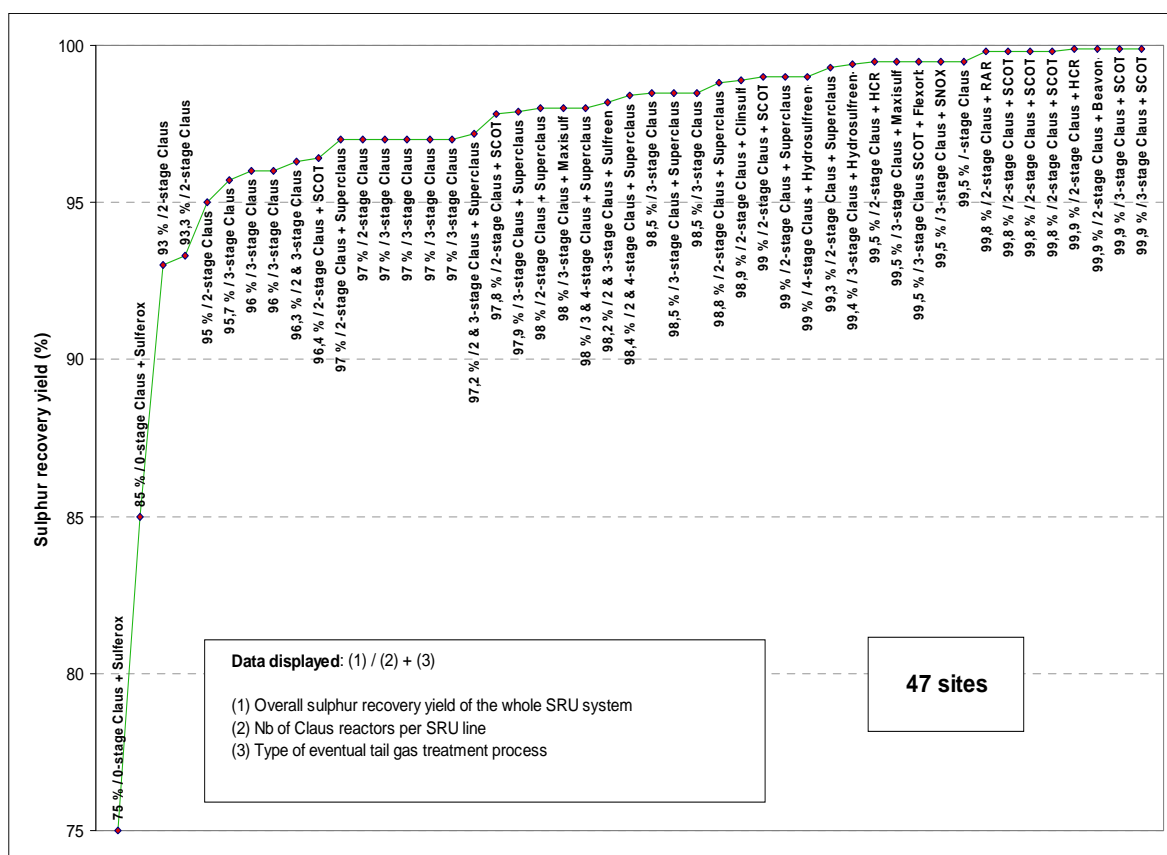


Figure 3.36: Sulphur recovery yield range of SRUs operated in a sample of 47 European sites

From the questionnaire data collection on SRU, SO_2 emissions range from 50 to 52 000 mg/Nm^3 . Emissions from these units typically contain some H_2S , SO_x and NO_x . They also generate process waste water that contains H_2S , NH_3 , amines and Stretford solution. Residual wastes are spent catalysts. The next table shows one example of emissions from European refineries.

Table 3.88: Examples of air emissions generated by sulphur recovery units

Installation	Fuel consumption (GWh/yr)	Throughput (t/yr)	Units	SO_2	NO_x	CO	CO_2	Particulates(*)
SRU	131.4	90 000 of sulphur	mg/m^3	4 322	200	100		50
TOTAL			t/yr	1 125.6	52.1	26.0	25 492	13
Mittel-deutschalnd			kg/t feed	12.5	0.58	0.29	283.2	0.15

NB: Data are related to yearly average, 3 % O_2 , dry conditions.
 For the Mitteldeutschalnd refinery, only limit values are given.
 Loads and specific emissions were calculated.
 (*) No information available on PM size

3.2.3.3 Flares

Flaring is both a source of air emissions and has the potential to burn valuable products. Therefore, for environmental and energy efficiency reasons, its use must be limited and the amount of flared gas reduced as much as possible. It is generally restricted to unplanned shutdowns or emergency cases. More information is available in the CWW BREF. [6, EC 2003]

Consumptions

The main utilities that flare systems will use are refinery fuel gas or nitrogen for purging the flare headers, fuel gas for the pilot burners and steam for heating purposes. However, the consumption of these utilities is very low under normal operating conditions.

Emissions

Flaring activity varies according to the real-time opportunity for refinery management optimisation. It may lead to extreme values during incidents, shutdowns or major maintenance periods. As an example, the following gives the evolution of the annual flare output for a German refinery which faced a major maintenance period for the installation of a new technique in 2007, as compared with the seven previous years.

Table 3.89: Evolution of the flaring activity according to annual maintenance programme

	2000	2001	2002	2003	2004	2005	2006	2007
Crude input (Mt/yr)	3.08	3.42	3.40	3.43	3.53	3.41	3.35	2.53
Flare output (t/yr)	704	201	560	1003	390	753	165	6155
Flaring ratio (‰)	0.23	0.06	0.16	0.29	0.11	0.22	0.05	2.43

Source: [28, Tebert et al. 2009]

Another example, from two refineries in Sweden, gives the following flaring ratios.

Table 3.90: Example of flaring ratio of two refineries in Sweden

	Flaring ratio (‰)	
	2008	2009
Preem Gothenburg refinery	0.6	0.6
Preem Lysekil refinery	0.8	1.0

Flares emit at least CO, CO₂, SO₂ and NO_x. Under specific conditions, flaring leads to soot formation and VOC emissions. Small amounts of complex hydrocarbons (e.g PAH), may also be released. Based on [86, SFT 2009] there is a clear link between soot formation and small emissions of PAH compared to other sources. Emissions of dioxins from flaring were considered as not existing, mainly due to the absence of necessary formation conditions. Conditions for emissions of PCB were regarded as highly unlikely.

The composition depends on a number of factors, including the composition of flare gas, flaring rate, flare system, wind and combustion efficiency at the flare tip. Flares are a very important point source of refinery emissions. Some plants still use older, less-efficient waste gas flares. Because these flares usually burn at temperatures lower than necessary for complete combustion (minimum 850°C), larger emissions of hydrocarbons and particulate, as well as H₂S, can occur. Noise from a flare has two components: flow noise and combustion noise. Flow noise occurs when the flare gas is flowing out of the flare tip with high speed. The greater the amount of flare gas, the more noise. Combustion noise is generated in the combustion zone. A short intense flame, where the energy turnover is fast and in low volume, generates more noise than if this occurs in a larger volume.

3.24 Emissions from waste water treatment techniques

Large volumes of waste water are released by the petroleum refining industry. Waste water treatment plants are advanced environmental protection systems for the control of surface water pollution. However, as this treatment is not complete the resulting discharges still contain pollutants that can contaminate the receiving environment. Moreover, during treatment a portion of the pollutants evaporate leading to aerial emissions that may be significant, depending on the type of treatment applied. The contributors to the influent of the treatment process are the desalters, storage tank drainage systems, slop system and other processes that have direct water-product contacts.

Process effluent volume can be compared to the volumes of process effluent discharged (excluding once-through cooling water). Although related, the values are not identical given that there are other sources of water to the effluent system including rainwater on plant surfaces, water separated from crude, ballast water, etc. Moreover, some water will be consumed by evaporation, be used in chemical reactions, etc. As a general trend, refineries are progressively treating less crude or throughput compared to their capacity because of more complex refining schemes, products specifications, and choices (e.g. more gas oil and less gasoline). Thus, the effluent volume per tonne of throughput also depends on the operations performed at the refinery.

Table 3.91 displays the data on water discharge volumes that has been made available to the TWG for 41 European refineries with dedicated waste water treatment plants. Data displayed here is drawn from released waste water while those in Table 3.3 are from consumption water.

Table 3.91: Summary data on the volume of waste water from 41 European refineries

Type of waste water	Volume discharged	Unit	Range (5th – 95th percentiles)	Median (50th percentile)
Waste water from process ^(*)	Annual	million m ³ /yr	0.55 – 10	2.58
	Specific	m ³ /t	0.11 – 1.57	0.38
Waste water from cooling	Annual	million m ³ /yr	0 – 212	0.9
	Specific	m ³ /t	0 – 58	0.08
Potentially contaminated rain water	Annual	million m ³ /yr	0.09 – 2.3	0.48
	Specific	m ³ /t	0.02 – 0.2	0.08
Total waste water	Annual	million m ³ /yr	0.54 – 65	2.9
	Specific	m ³ /t	0.15 – 11.68	0.44

(*) Waste water from process: Waste water annual release reported as from process.
Sources: [TWG site questionnaires]; annual averages reported for 2006, 2007 or 2008 - Dedicated WWTP

Emissions

Air emissions

The air emissions from waste water treatment plants stem from evaporation (hydrocarbons, benzene, H₂S, NH₃, mercaptans) from the numerous tanks, ponds and sewerage system drains that expose their surfaces to air. The sewage system and the waste water treatment in a refinery may be sources of odour nuisance, particularly from open drains and from oil separators. VOCs are also emitted during air stripping in flotation units and in the biotreater. The HC emissions from the waste water systems can be determined by calculation from the exposed surface area of the oil-contaminated untreated water tank (API separator) and an empirical oil evaporation factor of [167, VDI 2000]:

- 20 g/m² per hour for open oil separator;
- 2 g/m² per hour for covered oil separator;
- 2 g/m² per hour for flotation;
- 0.2 g/m² per hour for biological treatments.

Other methods to calculate emissions are available such as Litchfield correlation. [275, Litchfield 1971].

Emissions to water

Potential releases into water consist of the residual substances contained in the effluent after treatment. Depending on the nature of the refinery and the treatment efficiency, these may include carbon compounds (insoluble and soluble), nitrogen compounds (organic and inorganic; oxidised and reduced), sulphur compounds (oxidised and reduced), and metals and their compounds. More information on effluent composition downstream of a waste water treatment based on questionnaire data collection (2008) is included in Section 3.1.3.

Solid wastes generated

The limited information reported in the survey (for three units [166, CONCAWE 1999]) indicated an annual sludge production of about 2400 tonnes per year for a throughput of 600 m³/h. The induced air flotation generates 600 tonnes per year with a unit operating at 600 m³/h. Refinery waste water collection and pretreatment systems generate important amounts of solid wastes that have been in direct contact with hydrocarbons:

- Settleable solids (specific gravity greater than water) can separate from waste water in the collection and primary treatment systems. The collection system can include individual drain systems serving production areas as well as other areas affected by refinery activities and may include basins and/or tank systems to contain and manage peak flows of storm water.
- Suspended solids (specific gravity less than or equal to water) may be separated and extracted in gas flotation or sand filtration processes. Secondary biological treatment processes can generate important amounts of excess biosolid waste that must be continually removed from the process, as soluble substances are assimilated into new biomass in the bioreactors.

Table 3.92 shows the composition of the different sludges generated in the waste water treatment plants.

Table 3.92: Examples of analysis of refinery sludges

Species	API separator	Activated sludge	Settling basin plant
Solids	90.4 %	94.3 %	99.7 %
Oil	9.6 %	5.7 %	0.3 %
Carbon	25.8 %	13.1 %	1.7 %
Hydrogen	13.1 %	51.8 %	6.3 %
Nitrogen	0.6 % ^(*)	1.7 %	0.5 %
Sulphur	40 733	9 479.0	4 214.0
Carbonate	0.3 %	0.2 %	0.1 %
Iron	48 269.0	10 900.0	7 131.0
Aluminium	43 177.0	2 322.0	4 878.0
Calcium	11 609.0	4 692.0	8 104.0
Sulphide	6 180.2	2 165.9	103.7
Magnesium	4 878.0	1 351.0	1 767.0
Sodium	1 711.0	3 981.0	3 971.0
Xylene	469.5	9.5	3.2
Naphthalene	288.2	46.9	16.0
Lead	279.0	49.3	15.2
Phenol	265.0	46.9	16.0
Nickel	252.5	37.9	8.8
Nitrate	228.1	2 066.4	194.5
Toluene	138.5	9.5	32
Styrene	134.4	47	16.0
Vanadium	99.0	18.0	24.0
Ethylbenzene	82.5	9.5	3.2
Chromium	80.0	8.1	11.2
Fluorine	59.1	46.9	16.0
Antimony	49.0	14.0	5.0
Benzo(a)pyrene	42.6	46.9	16.0
Phenol	40.3	46.9	16.0
Selenium	35.4	26.0	9.0
Benzene	13.2	9.5	3.2
Sulphate	12.2	2 767.8	285.3
Arsenic	6.5	15.2	5.2
Mercury	3.0	1.0	0.0
Cyanide	1.0	7.0	0.7
^(*) Below detection limit shown NB: Figures do not sum to 100 % because of double counting. Figures quoted on a moisture-free basis, all units mg/kg unless otherwise stated. Source: [156, MCG 1991]			

3.25 Waste generation

An important issue when considering refinery waste is that there are still many differing definitions between countries, which makes comparisons of waste difficult.

Sludges

The amount of sludge generated depends on the types of processes and the availability of incineration. As a common figure, the generation rate of solid waste and sludges is normally less than 0.5 % of crude processed, but in some refineries it is less than 0.3 %. Annual sludge generation was 1250 kt per year (in 1993), some 0.2 % of refinery intake.

In 1993, CONCAWE carried out a survey of waste in Western European refineries [157, CONCAWE 1995]. In this survey 89 refineries reported their sludge production from all sources as one million tonnes. That means an average of 11 000 t per year per refinery. This figure represents a 0.20 % of the crude oil processed by these refineries. However, a variation range from 2.5 % to less than 0.02 % was found in European refineries, with the value being independent of the type of refinery. From that million tonnes of waste, 45 % was sludge, 20 % other refining wastes and the rest non-refining wastes. Sludges come from stabilisation processes (4.7 % of the total sludge generated after treatments), waste water sludges (39.8 %) and sludges with no treatment (55.5 %).

The total amount of identified other refining wastes which are specific to the refining process (e.g. spent catalysts, tank scales, contaminated soils, etc.) produced in 1993 by the 89 European refineries reporting was 201 983 tonnes (i.e. 0.04 % w/w of the total refinery throughput). Data provided by 16 EU+ refineries show that the specific production of waste ranges from 133 to 4 200 t/million t of crude. Table 3.93 shows the waste routes statistics for 2007 and 2009 in refineries.

Table 3.93: Waste routes and transfers in the refinery sector in 2007 and 2009

Type of waste and transfer	Routes	2007		2009	
		Tonnes	Number of sites	Tonnes	Number of sites
Hazardous waste in the country	Disposal	294 000	103	405 000	105
	Recovery	306 000	98	372 000	103
Hazardous waste outside the country	Disposal	3 000	5	4 000	3
	Recovery	34 000	30	19 000	23
Total hazardous waste		637 000	-	800 000	-
Non hazardous waste	Disposal	372 000	60	262 000	59
	Recovery	538 000	61	500 000	64
Total non-hazardous waste		900 000	-	762 000	-

Sources: E-PRTR and CONCAWE

Spent catalyst

Hydroprocessing requires the use of catalysts to remove impurities and to convert the oil into more useful products. The catalysts used consist mainly of oxides of nickel, cobalt and molybdenum on an alumina carrier. During hydroprocessing operations, the catalysts are loaded with sulphur, vanadium and coke. The porosity of the catalysts decreases and their activity is reduced, which eventually requires replacement of the catalyst in the reactors. Consequently, the catalysts become spent and must be replaced.

Co/Mo catalysts are used in hydrodesulphurisation, hydrocracking, hydrotreating. A 5 Mt/yr refinery, generates typically from 50 - 200 t/yr spent Co/Mo catalyst.

Ni/Mo catalysts are typically used in hydrotreaters and hydrocracking units. A 5 Mt/yr refinery generates typically 20 - 100 t/yr spent Ni/Mo catalyst.

Ni/W catalysts are used in lube oil hydrofinishing. There are limitations for disposal in view of the high tungsten content (24 % w/w). A 50 000 t/yr lube oil plant can generate 50 t/yr of this catalyst waste.

FCC spent catalysts, also including heavy oil and residue cracking spent catalysts (RCC), are the largest catalyst waste category in refineries (world production is about 0.5 Mt/yr). A 1 Mt/yr FCC unit generates 400 - 500 t/yr, predominantly as FCC fines if an ESP is installed. For a RCC, this amount can be a factor of 5 - 10 higher, depending on the type of feed as spent catalyst is withdrawn from the regenerator.

Reformer and isomerisation catalysts are exclusively reprocessed by the suppliers of the fresh catalysts. Replacement contracts have been concluded since the introduction of these processes due to the very expensive noble Pt metal involved. Typical average amounts involve 20 - 25 t/yr for a 5 Mt/yr refinery. If necessary, guard beds of HDS catalysts are used for protection and extension of the lifetime of the expensive catalysts.

Hydrodemetallisation catalysts typically have high vanadium contents (10 - 20 %) and are currently alumina based (used to be silica). The annual amount for regeneration is in the order of 500 - 1 000 t/yr for Hycon (Shell Pernis NL), dependent on the feed quality.

Zn containing beds from H₂ plants are typically recycled to the Zinc industry where ZnS ores are processed. Amounts are some 50 t/yr.

In hydrodesulphurisation, hydrotreating and hydrocracking, the world catalyst production (and thus also the generation of spent catalysts) grew considerably during the 1990s and was estimated at 100 kt/yr (1998). At the same time, regeneration capacity was estimated at 125 kt/yr. It was also estimated that 5 - 10 % of this category of spent catalysts was still being landfilled.

Table 3.94: Composition of spent catalysts from various sources in % w/w

Process	S	C	Mo	V	Ni	Co	Al	Other
FCC, RCC	<1	<1		4 - 8 000(*)	2 - 3 000(*)		30	
Reforming and isomerisation							30	0.5 Pt, Pa, Rh
Hydro processing	6 - 16	10 - 30	4 - 8	2 - 12	1 - 2	1 - 2	20 - 30	
Claus plant	5	5	4 - 8		2 - 3		20 - 30	
Hydrofinish	5	1 - 2			2 - 4		30	24 W
Hydrogenation	5 - 15						0	30 Zn
Hydro-demetallisation.	5 - 15	10 - 30		10 - 20	2 - 5		30	

(*) In ppm

3.26 Monitoring

There are a specific document [46, EC 2003] on monitoring (MON) and an expanding series of literature published by competent authorities at federal and national levels (e.g. HMIP Technical Guidance Notes in UK). These documents contain information on theory, methodology and related techniques. It should be considered that the requirements and frequency of sampling, analysis and type of monitoring requirements are site and/or process specific. They are influenced by consideration of the anticipated volume and composition of the waste streams and are included in the permits. The MON document also provides guidance to permit writers on compliance assessment and environmental reporting, and encourages the comparability and reliability of monitoring data across Europe.

This section aims to give recommendations on the scope and frequency (continuously or discontinuously) of monitoring streams in a refinery. Monitoring should be undertaken during commissioning, start-up, normal operation, and shutdown unless it is agreed that it would be inappropriate to do so.

The monitoring system should allow adequate processing and emission control. A monitoring system in a refinery generally includes:

- continuous monitoring of pollutants for high volume flows with high variability in pollutant concentrations;
- periodic monitoring or the use of emission relevant parameters for flows with a low variability and calculation based on high-quality emission factors;
- regular calibrating of measurement equipment;
- periodic verification of measurement by simultaneous comparative measurements.

In order to have a good idea of the emissions generated by an installation (e.g. a refinery), the emissions need to be quantified. This will give to the refinery and permit writer the ability to know where the actions to reduce a certain pollutant may be more economical. Typically abating higher emissions at high concentrations is more economical than lower emissions at low concentrations. As consequence, a quantification of the emissions for each single refinery is the first starting point in any environmental assessment. This quantification may contain a full mass balance also considering other outputs (e.g. products).

3.26.1 Monitoring of emissions to air

SO₂, NO_x, particulate matter, and CO are typically continuously monitored (on-line or predictive) in the refineries. Records of the volumes are also required for the calculation of the load (tonnes of pollutant per year) or for the application of the bubble concept. Table 3.95 shows the locations where the main air pollutants are typically monitored in a refinery.

Table 3.95: Examples of the most common air emission monitoring in oil refineries

Parameter	Example of monitoring	Location where normally is measured
Sulphur dioxide	Continuous if P>30 MW (except for natural gas) Continuous if P >20 MW and desulphurisation unit (elsewhere, daily estimation) or P >100 MW	FCC UNIT regenerators Sulphur recovery units (i.e. from tail gas incinerators) Incinerators or furnaces used to burn sour gas or liquid fuels Bitumen production units Gasification units Coking processes
Oxides of nitrogen	Continuous if >30 MW (except for natural gas) Continuous if P>20 MW and abatement unit or P >100 MW	Combustion processes FCC UNIT regenerators Gasification units Coking processes
Carbon monoxide	Continuous if P >10 MW Continuous if P >50 MW	FCC UNIT regenerators (for partial combustion type units if CO release is significant). Combustion processes
Particulate matter	Continuous for solid and liquid fuels if >10 MW Not relevant for natural gas or RFG (Examples from Austria) Continuous if P >50 MW (Examples from France – P expressed as MW th)	Combustion processes burning fuel oil FCC UNIT regenerators Coking processes and petroleum coke calciners and coolers Gasification units Catalyst regeneration (e.g. reforming)

Other common emission components to air commonly monitored are:

- carbon dioxide
- nitrous oxide
- volatile organic compounds (VOCs)
- heavy metals
- hydrogen fluoride
- halide compounds
- ammonia NH₃
- hydrocarbons (as unburnt hydrocarbons, UHC)
- dioxins and/or POPs.

The following sections include monitoring practices that have been found in European refineries.

3.26.1.1 Sulphur monitoring

It can be expected that the operators compute site sulphur balances over appropriate time periods as a part of monitoring their operations. The time period may vary according to the circumstances (e.g. how often feedstocks change) but could typically be quarterly. In the case of SO_x, the amount emitted by combustion processes may be calculated from the analysis of the fuel being burnt. In some countries (e.g. France), sulphur balance is established daily by the operator and sent monthly to the competent authorities.

3.26.1.2 Emissions from combustion processes

The monitoring of emissions is carried out to determine the concentration of regulated substances in the flue-gas under standard conditions so that they can be reported, or to control

the combustion process or abatement plant. Gaseous releases from gas turbines used for electrical generation or gas compression are typically also monitored.

In order to relate emission concentrations to mass releases, it will be necessary to determine the gas flow by direct measurement or other means. Additionally, in order to relate measurements to reference conditions, the temperature will need to be determined. The determination of oxygen and water vapour content may also be required. Monitoring and averaging periods required by the type of substances and the techniques used need to be reported.

3.26.1.3 Diffuse VOC monitoring

Diffuse VOC emissions are emissions arising from direct contact of gaseous or liquid volatile organic compounds with the environment (atmosphere, under normal operating circumstances). These can result from:

- inherent design of the equipment (e.g. uncovered oil/water separators);
- operating conditions (e.g. non collected vent of a fixed roof tank during loading);
- or fugitive emissions caused by an undesired gradual loss of tightness from a piece of equipment and a resulting leak. Fugitive emissions are a subset of diffuse emission.

VOC emissions by refineries come mainly from diffuse emissions. Four major diffuse emissions sources can be identified.

- Fugitive emissions by leaking equipment in the process area, such as valves, flanges, pumps, safety valves, etc. They usually account for 20 – 50 % of the total refinery VOC emission. Emissions may also be high after start-up operations due to a e.g. poorly undertaken tightning of equipment.
- Crude oil and products storage. External and internal floating roof tanks are emission sources because of evaporative losses that occur during standing storage and withdrawal of liquid from the tank. Emissions from fixed roof tanks are due to the venting during operations or to breathing due to variation of ambient temperature. Emissions from floating roof tanks occur from losses from seals and roof fittings They typically represent 20 – 40 % of the refinery emissions.
- Loading and unloading facilities, including road tankers, rail tank cars, barges and sea-going vessels. They account for 5 – 10 % of site emissions.
- Waste water treatment plants, where a gradual release of VOC may occur at all water/air interfaces. Depending on VOC reducing techniques applied, WWTPs usually generate 5 – 30 % of the total site emissions.

Overview of available methods for detection/quantification

The main available methods with their respective field and scale of application are displayed in Table 3.96. It can be remarked that all these methods are complementary and all potentially useful in order to build up an efficient monitoring programme. Some are appropriate for the detection and/or the quantification of spot sources, whereas others are devoted to area sources, and unit-scale or even site-scale global emissions. Moreover, each of these methods enables the monitoring of a different scope of VOC species, as seen in Table 3.97.

On one hand, it has to be emphasised that calculation methods based on emission factors and algorithms are reported to be unreliable and give significantly underestimated results, in particular for tank farms, cokers and flares [50, White, 2008], [51, Chambers et al. 2006].

On the other hand, a CONCAWE report [62, CONCAWE 2008] highlighted the potential errors introduced by using short-term values for extrapolation to annual ones due to the temporal variations in the emissions from diffuse sources. Some estimation algorithms (e.g. for storage) have been derived from extensive tests and are designed specifically to provide long-term estimates. However, these calculation methods represent an average situation and do not

take into account unexpected emissions causes (e.g. defective seals, contaminated cooling water). In addition, refineries need to perform measurements to obtain information on these unknown emission sources.

Table 3.96: Overview of main available methods for VOC detection and quantification

Type of diffuse VOC source	Calculations		Measurements				
	Emission factors and/or algorithms	Specific modelling (e.g. US TANKS, WATERS 9 codes, ToxChem+)	'Sniffing' and correlation curves (EN 15446: 2008)	Optical gas Imaging (OGI)	Solar occultation Flux (SOF)	Differential Absorption (LIDAR – DIAL)	Flux chamber
Small individual equipment (pumps, valves, flanges, etc)	Q		D/Q	D ⁽¹⁾			
Storage tanks	Q ⁽³⁾	Q		D ⁽¹⁾	D/Q ⁽²⁾	D/Q ⁽²⁾	
Loading/unloading facilities	Q			D ⁽¹⁾	D/Q	D/Q	
Water treatment plants	Q	Q			D/Q ⁽²⁾	D/Q ⁽²⁾	Q
Full scale unit/Whole site	Q ⁽⁴⁾				D/Q	D/Q	

NB: **D** = detection **Q** = quantification
⁽¹⁾ The detection exhaustivity regarding mass flowrate has to be confirmed.
⁽²⁾ Active area sources can be detected if they generate individual plumes that can be distinguished from the rest of the site, and if emissions occur during the measurement.
⁽³⁾ Algorithms designed for annual emission quantification.
⁽⁴⁾ Emission factors and algorithms cannot estimate the complete set of possible emissions sources and operating conditions (e.g. heat exchangers, defective floating roof seals, inaccessible leaking equipment).

Table 3.97: Overview of VOC species according to the measuring method applied

VOC species	Measurements				
	'Sniffing' and correlation curves (EN 15446: 2008)	Optical gas Imaging (OGI)	Solar Occultation Flux (SOF)	Differential Absorption (LIDAR – DIAL)	Flux chamber
Alkanes	Y	Y	Y	Y ⁽¹⁾	Y ⁽⁴⁾
Alkenes	Y	Y	Y	Y ⁽¹⁾	Y ⁽⁴⁾
Aromatics	Y	Poor ⁽³⁾	N	Y ⁽²⁾	Y ⁽⁴⁾
Cyclic hydrocarbons	Y	Y	Y	Y ⁽¹⁾	Y ⁽⁴⁾
Methane	Y	Y	N	Y ⁽¹⁾	Y ⁽⁴⁾
Total VOC	Y	Y	Y	Y	Y

⁽¹⁾ When based on IR light.
⁽²⁾ When based on UV light.
⁽³⁾ Poor for light aromatics when based on passive systems (2009 data).
⁽⁴⁾ With GC/MS used for speciating samples.

Description, main features and limitations of most used measuring techniques

This section gives a short description of the four monitoring techniques based on actual measuring which are most commonly used for the monitoring of diffuse VOC emissions. Respective costs, detection limits together with a comparison of their specific advantages and

drawbacks are summarised in Table 3.99. Calculation methods cannot be considered measurements and will not be described in this section.

Method EN 15446: 2008: conventional VOC ‘sniffing’

This method was originally developed as a support for the implementation of a LDAR programme (see Section 4.23.6.1) for the detection and ranking of leaking equipment pieces to be repaired. The first step is the detection (‘sniffing’) which is achieved using hand-held VOC analysers measuring the atmospheric VOC concentration adjacent to the equipment, as shown in Figure 3.37. The most frequently used measuring techniques are the flame ionisation (FID) and the photo-ionisation (PID), calibrated to operate in the range of 10 – 100 000 ppmv. The probe is characterised by a ‘response factor’ which takes into account the sensitivity to the actual VOC mixture measured compared to a reference gas, and a ‘response time’ defined as the time needed to register 90 % of a concentration step change. Both factors greatly influence the results and have to be optimised according to the EN 15446 standards



Figure 3.37: Leak concentration measurement



Figure 3.38: Bagging of a leaking valve

For mass flow quantification, the second step proposed by the standard method consists of bagging the source component as shown in Figure 3.38. This bagging is the only step of this method allowing for a direct measurement at the source of emission. However, as bagging is an extremely burdensome operation and is not always possible, mathematical correlation curves can be derived from statistical results obtained from a sufficiently large number of previous measurements of both leak concentration (Step 1) and mass flow (Step 2) made on similar components. Very few refineries have developed such correlation curves corresponding to their own set of components, related VOC leakage mixtures, and concentration measurement skills and real practices. Alternatively they use generic curves from the literature based on extensive measurement campaigns carried out on US facilities in the 1950-1980s and 1990s.

Optical gas imaging techniques (OGI)

Optical imaging uses small lightweight hand-held cameras which enable the visualisation of gas leaks in real time, so that they appear as ‘smoke’ on a video recorder together with the normal image of the component concerned. This technique is primarily used to easily and rapidly locate significant VOC leaks e.g. on process components, storage tanks fittings, pipeline flanges or vents. Most current commercial OGI cameras fall under one of these two categories.

- *Active systems* where the image is produced by a back-scattered IR laser light reflected on the component and its surroundings. The laser wavelength is optimised to be absorbed by the VOC concerned.
- *Passive systems* based on the natural IR radiation of the equipment and its surroundings. The contrast of the VOC image is based on the plume IR absorption and the heat radiance difference between the plume and its background. An optical filter selects the optimal IR wavelength according to the VOC nature.

Detection limits are related to the minimal thermal gradient for visualisation, and will depend on the gas temperature, the distance from the source, and the wind speed. Although these are higher than achieved by ‘sniffing’, OGI technology can more efficiently identify the main fugitive emission sources. The mass emission rate is still not directly quantified. Specific work is being done in order to propose and validate appropriate OGI emission factors based on comparison with EN 15446 quantification on the same set of components in an actual unit. In addition, the US API also developed OGI leak/no-leak factors.



Figure 3.39: An OGI videocamera



Figure 3.40: Typical visualisation of gas leak

Differential absorption lidar (DIAL)

DIAL is a laser-based technique using differential adsorption LIDAR (light detection and ranging) which is the optical analogue of radio wave based RADAR. As shown in Figure 3.41, the technique relies on the back-scattering of laser beam pulses by atmospheric aerosols, and the analysis of spectral properties of the returned light collected with a telescope. As each molecule present will absorb and re-emit a typical light, the returned beam acts as an optical signature of the concentration of most molecules present between the DIAL source and the reflecting particulate. By sampling the returned light pulse rapidly according to time, it is possible to distinguish how far each sample of the light pulse has travelled and, thus, locate it with the precision of a few meters in optimum conditions.

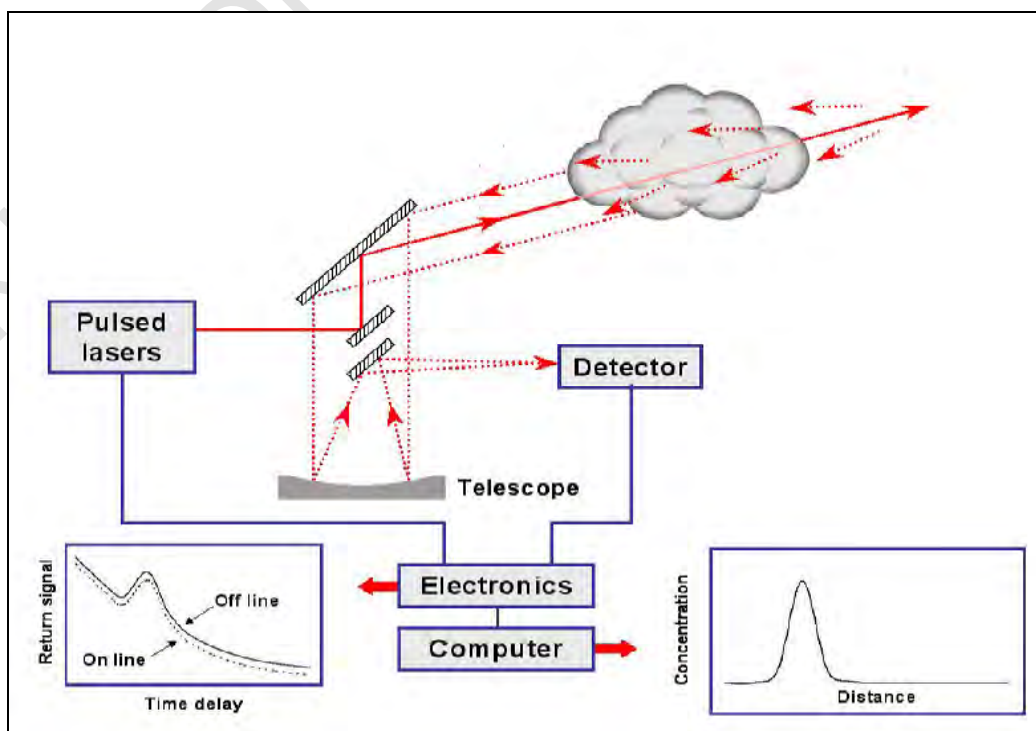
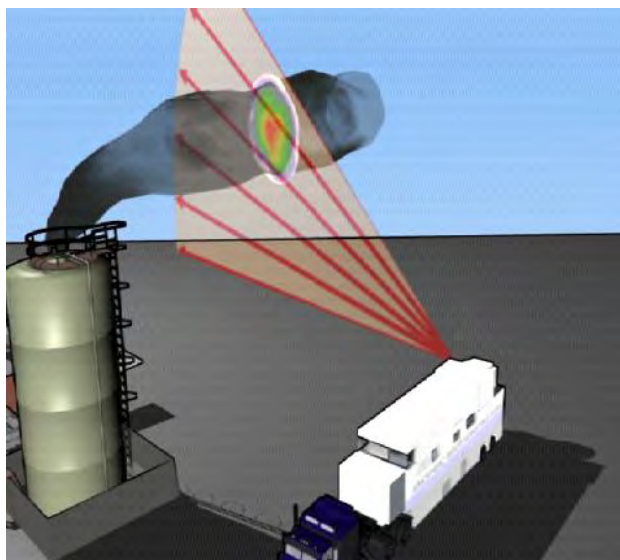


Figure 3.41: Scheme of the DIAL process



The laser beam and the optical reception system are rotated in order to cover a plane crossing the atmospheric VOC plume. The result of it is a 2-dimension map where the concentration can be integrated, as shown on Figure 3.42.

To obtain mass emission flux, the concentration data across the plume section should be multiplied by the wind velocity reported perpendicularly to the measurement plane.

Wind data availability, accuracy and representability are essential for reducing quantification uncertainties.

Typical sensitivities and maximum distance ranges are given in Table 3.98 for various emitted VOCs and other compounds of interest. Sensitivities apply at a range of 200 m for a 50 m width plume.

Table 3.98: DIAL Sensitivity and maximal distance range for various emitted compounds

Infrared DIAL system			UV/Visible DIAL system		
Species	Sensitivity (ppb)	Max. range	Species	Sensitivity (ppb)	Max. range
Methane	50	1 km	Benzene	10	800 m
Acetylene	40	800 m	Toluene	10	800 m
Ethylene	10	800 m	Xylenes	20	500 m
Ethane	20	800 m	NO	5	500 m
Higher alkanes	40	800 m	NO ₂	10	500 m
HCl	20	1 km	SO ₂	10	3 km
N ₂ O	100	800 m	Ozone	5	2 km
Methanol	200	500 m	Mercury	0.5	3 km

Various field validation measurements were performed and gave the following results:

- Repeated DIAL measurements downwind of a calibrated (10 kg/h) source of methane agreed to within +/- 10 % of emitted value;
- Comparison with a line of pumped absorption tube samplers inside a chemical plant agreed with DIAL measurements of aliphatic hydrocarbons to within +/- 12 %, and toluene to within +/- 15 %;
- VOC emission measurements from a petrochemical storage facility made by DIAL and standard point sampling methods agreed to within +/- 8 %;
- SO₂ plume from a tail gas incinerator (340 kg/h) agreed within -11 %;
- NO plume from a gas turbine power plant (66 kg/h) agreed within +1 %.

However, the overall uncertainty in industrial field conditions is evaluated at around 30 – 50 %, most of it from wind speed evaluation. A reduction of this uncertainty may be possible by making wind measurements at various heights in, or close by the DIAL scan plane. As with all short-term measurement techniques, the extrapolation to provide values of annual emissions for inventory purposes introduces further potential for error, particularly as the majority of refinery VOC sources have significant emission variations with time.

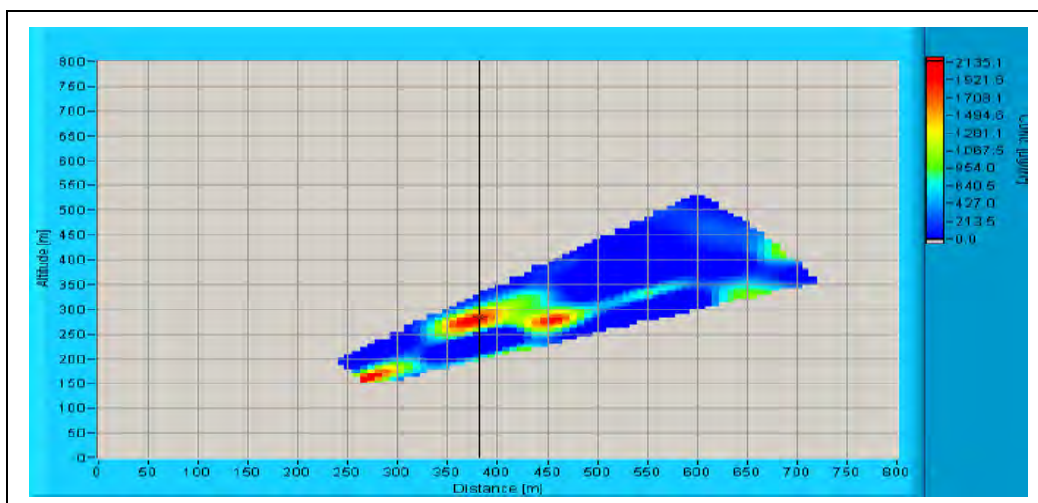
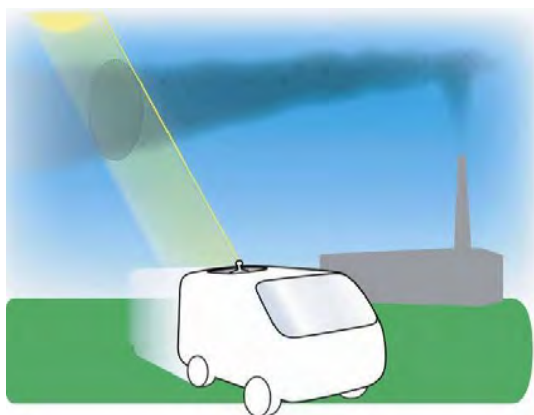


Figure 3.42: Typical DIAL concentration map obtained with DIAL measuring system

Solar Occultation Flux (SOF)

The technique is based on the recording and spectrometric Fourier Transform analysis of a broadband IR or UV/Visible sunlight spectra along a given geographical itinerary, crossing the wind direction and cutting through VOC plumes



The system is permanently guided to the sun by a solar tracker mirror, which reflects the sunlight into the spectrometer independent of its position. On short distance segments identified by GPS coordinates, path-integrated concentrations in mg/m^2 are calculated for various species present between the sun and the system. Results can be gathered on the same map for the whole measuring itinerary, giving an overall shape of main emitting areas and associated concentrations as shown in Figure 3.43

The spectral retrieval is based on a multivariable analysis in which lab-recorded calibration spectra from literature are fitted to the actual spectra measured, for all target species but also for other interfering species like H_2O and CO_2 . Alkanes, which correspond (in mass) to the main part of refinery VOCs, are summed but cannot easily be distinguished due to spectral overlap based on common C-H bond vibration. On the contrary, individual olefins can be measured with good specificity. Aromatics cannot be measured directly. In case of need, canister samples are taken at various positions downwind of the target source, and resulting mass distributions are used for the calculation of missing concentrations in the plume on a *pro rata* basis.

The overall uncertainty for quantification in industrial field conditions is evaluated [32, Mellqvist et al. 2008] around 35 – 40 %. Most of it originates from wind (speed and direction) evaluation uncertainty and retrieval uncertainty (combined effect of instrumentation and retrieval stability on the retrieved total columns during the course of a plume transect).



Figure 3.43: Overall shape of alkane emissions from an oil refinery as measured with SOF (the white arrow indicates the wind direction)

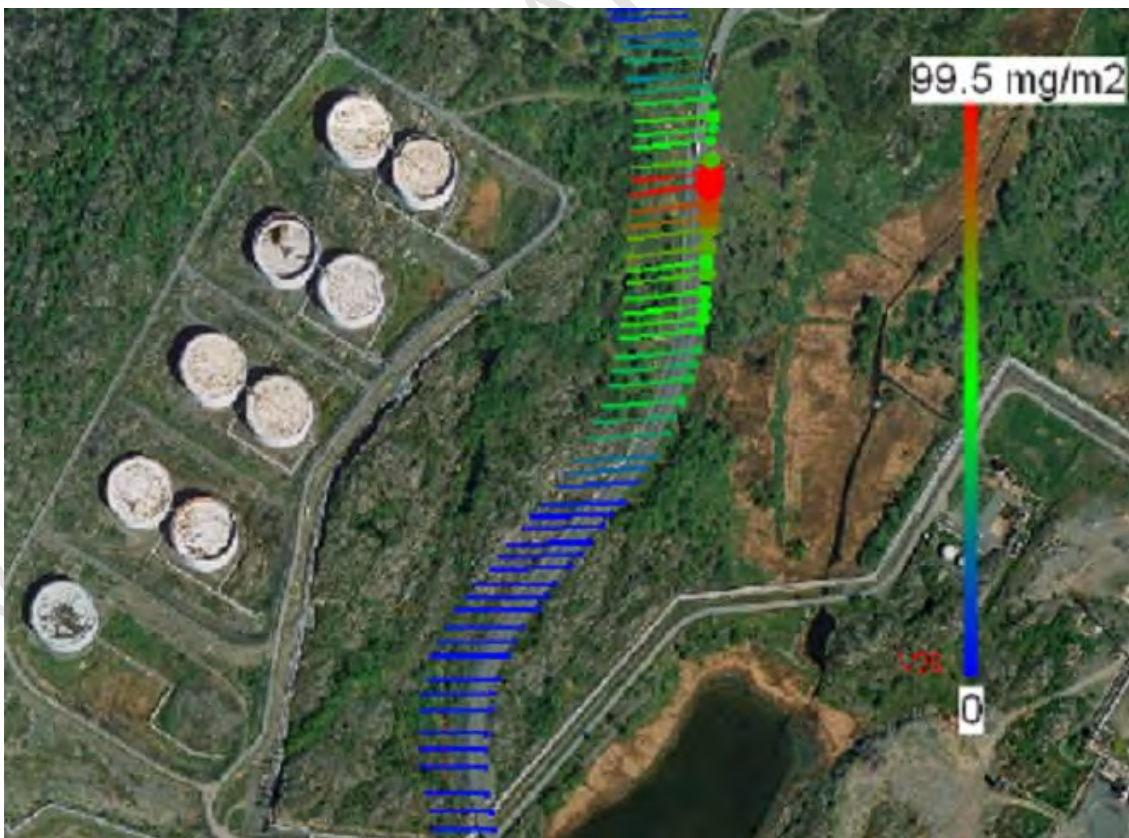


Figure 3.44: Detection of high leaking storages within a refinery tank farm using SOF

Table 3.99: Overview of performances, costs, advantages and drawbacks of diffuse VOC measuring techniques

	Detection limit	Indicative costs (EUR)	Advantages	Drawbacks
EN 15446	10 ppm at leak source <10 mg/h for correlated mass flow Increasing with wind	5 000 – 25 000 for one detector, depending on complexity 60 000 per campaign (2 000) for a 30 000 component site 600 000 for a mini 6-month campaign in a complex refinery	Low detection limit Low instrumentation cost Applicable in hazardous/congested areas	Not applicable to diffuse area sources Direct mass flow measurement not possible Low reproducibility (standard deviation 50 %) and repeatability (standard deviation 35 %) on measured concentration Low reproducibility (standard deviation 40 %) and repeatability (standard deviation 25 %) on indirect mass flow calculations High manpower requirement and operational costs (500 components per day per surveyor) Fully applicable to components only accessible by staircases or ladders (typically around 80 %).
OGI	0.4 – 60 g/h (<35mK @ 30 °C) depending on operational conditions 3 000 – 10 000 ppm	70 000 – 110 000 for one camera	High mobility Low manpower requirement (5 000 components per day per surveyor) Large monitoring scope, including remote or non accessible large leaks detection Limited training required for operators	Presence of a background surface imperative for the active system Sensitivity related to actual thermal gradients: OGI is less efficient with uniform temperature conditions Not applicable to explosive atmospheres, but can be used under permit to work scheme; Not applicable with rain or fog.
DIAL	10 – 50 ppbv at 200 m for a 50m-width plume Increasing through dust and water vapour plumes	A single 1 – 2 week campaign costs around 30 000 – 100 000 including data processing and report Device investment >0.2 million	Well established Open path 'single-ended' system independent from sun direction Day and night Significant area sources can be localised with horizontal plane scanning (e.g. tank farm) Possible 'free space' on-site calibration using calibrated gas mixtures	Limited commercial availability Logistics (12 m long – 7 to 12 t lorry) Heavy rain and fog not suitable No precise location of individual point sources Uncertainty of mass flow calculations (wind) 'Snap shot' measuring: must be repeated to take into account temporal variations (e.g. tank farms) Upwind sources cannot be simultaneously determined without upstream scan (time and logistics constraints)
SOF	0.5 – 1 mg/m ² 1 kg/h can be detected at 50 m distance	A single 2 week campaign costs around 60 000 including data processing and report Device investment >0.2 million	Recent but well established Well adapted to whole site estimates Significant area sources can be localised Comparatively simpler, quicker and cheaper than DIAL in favourable meteo conditions	Limited commercial availability Only daytime and sunny conditions No precise location of individual point sources No range resolved data for alkane species No direct measurement for aromatics Uncertainty of mass flow calculations (wind + unknown VOC plume height) As for DIAL 'snap shot' measuring and upwind sources.

Site-scale VOC monitoring and quantification using available measuring techniques

A number of investigations have been carried out in the US and Europe since the 1990s in order to compare the results given by conventional methods (e.g. TANKS emission factors for tank farms, EN 15446 point measuring with correlation curves for production units) with DIAL and more recently, with SOF long-range screenings. Generally, results obtained with the latter have been shown to be higher (usual factors 2 – 5, sometimes more). Reasons were often linked to:

- results obtained with DIAL and SOF were made from extrapolated short term measurements and have been compared to annual inventory emission estimates made by conventional methods;
- large missing sources, which were not taken into account in conventional methods (e.g. gasoline blenders in a tank farm, cooling towers, unknown leakage located in remote parts of pressurised process units, tank cleaning operations);
- underestimating assumptions about some key emission factors (e.g. flares, crude oil tanks, gas oil tanks, hot heavy fuel oil tanks) and the average massic composition of VOC mixtures (part of heavy alkanes evaporated from tanks).

However, one comprehensive study in which DIAL was used for a long, continuous period (four days), compared to a typical measurement period of a few hours, showed that there was agreement between the DIAL estimate and calculations using TANKS in the case of a new tank farm with well maintained tanks.

In Sweden, the results of measurements undertaken with SOF and DIAL during limited periods (weeks) have been very consistent through the years.

Modern fugitive VOC monitoring should be more and more based on exhaustive screening methods and real measurements. It also can benefit from recent improvements of component-scale conventional methods together with specific opportunities introduced by short and long range optical and airborne remote techniques.

Site level monitoring of the overall VOC diffuse emissions from refineries should be derived from a well balanced approach using all complementary techniques described below, and can be conducted mostly using the following steps.

- Fugitive emissions from leaking components can be evaluated within the implementation of a rigorous LDAR programme, using sniffing methods associated with correlation curves better established at the site level from the bagging of key equipment or, when not available, correlation curves developed for specific component types (e.g. by US EPA). Non-accessible sources are taken into account, as described in EN 15446, using these factors.
- OGI cameras should be introduced within ‘smart’ LDAR programmes for easier and faster identification of significant leaking components, in particular in remote areas, allowing for a better LDAR prioritisation and focus. This includes the identification of leaks from storage tank roof seals and fittings which can not be detected by LDAR or by DIAL/SOF technique.
- Permanent or chronic emissions from area sources (e.g. tank farms, WWTPs) still estimated from emission factors should be regularly validated by actual physical measurements, using point samplers (e.g. pumped sorbent tubes) or time correlation tracers (TCT).
- A regular full screening and quantification of site emissions undertaken with an appropriate combination of complementary methods, e.g. SOF and/or DIAL campaigns, using the results for trend evaluation in time, cross checking and updating/validation of the ongoing LDAR programme.

Sources: [32, Mellqvist et al. 2008], [50, White. 2008], [51, Chambers et al. 2006], [59, TOTAL - Béraud-Dufour, P 2009], [60, ENI - A. Selvaggi 2009], [61, INERIS 2009], [62, CONCAWE 2008]

3.26.1.4 Odour monitoring

Odour is potentially related to the emission of a large number of chemical substances and compounds. In oil and gas refining, these are most likely to be :

- **sulphur** compounds (e.g. hydrogen sulphide, mercaptans, sulphides, disulphides);
- **nitrogen** compounds (e.g. ammonia, amines);
- **hydrocarbons** (e.g. aromatics).

The perception of an odour in the surroundings of a refining plant and, eventually, the nuisance related to it, and the possibility to prevent or reduce this nuisance will depend on various parameters, highlighted below:

- The number of different sources and substances: the resulting odour from a combination of different substances can be perceived as more of a nuisance than the odour of substances emitted separately at the same concentration. Furthermore, in combination with other substances, the characteristic odour of a single substance can be modified so as to be unrecognisable.
- The olfactive thresholds of emitted substances: at the same concentration (or distance from the source), some substances will be strongly perceived as others will have disappeared. In case of a mixture, the combined odour will change as the mixture becomes diluted, until the concentration of each component falls below its own threshold.
- The individual olfactive ability and subjective reaction of exposed persons: odours can be judged as acceptable or unacceptable depending on the physical sensitivity to it, as well as on psycho-sociological factors which can influence personal preferences. For the same person, an odour can be pleasant when the substance is diluted and become offensive when concentrated.

In general, the human nose is very sensitive to certain substances or components that are typically emitted by oil and, into a lesser extent, by gas refining activities. Table 3.100 gives a selection of values according to different sources. It should be noted that most of these substances, and especially sulphur compounds, generate odours that are generally perceived as very unpleasant or aggressive.

Table 3.100: Odour thresholds of some substances and compounds typical of refining activities

Substances or compounds	Odour thresholds	
	Reported ranges ⁽¹⁾ (ppm weight)	Typical ⁽²⁾ (mg/m ³)
Methylmercaptan CH ₃ SH	0.00007 – 0.004	0.0021
Ethylmercaptan C ₂ H ₅ SH	0.0000087 – 0.002	0.00277
Hydrogene sulphide H ₂ S	0.00041 – 0.002	0.0253
Dimethylsulphide (CH ₃) ₂ S	0.0022 – 0.3	0.0058
Diethylsulphide (C ₂ H ₅) ₂ S	0.002 – 0.4	0.00146
Dimethylamine (CH ₃) ₂ NH	0.033	0.153
Diethylamine (C ₂ H ₅) ₂ NH	0.048	0.567
Benzene C ₆ H ₆	1.5 – 4.7	11.8
Ethylbenzene C ₆ H ₅ (C ₂ H ₅)	0.17 – 2.3	7.3
Toluene C ₆ H ₆ (CH ₃)	0.33 – 50	5.95
o -, m-, p-Xylene C ₆ H ₆ (CH ₃) ₂	0.08 – 3.7	1.43 – 3.77
Lighter alkanes (from C ₂ H ₆ to C ₄ H ₁₀)	>50	>500
Mid range alkanes (from C ₅ H ₁₂ to C ₈ H ₁₈)	>2	>30
Heavier alkanes (from C ₉ H ₂₀)	<2	<6
⁽¹⁾ [40, Nagata Y 1990], [42, Devos et al. 1990]		
⁽²⁾ [41, ADEME 2005]		

Refineries should have an odour management plan as a well identified part of their environmental management system (see Section 4.15.1.1). The odour management plan should include all of the following elements:

- an odour management strategy;
- protocols for conducting odour monitoring;
- a protocol for response to identified odour events;
- an ongoing odour prevention and elimination programme designed to identify the location, nature, emission and dispersion of on site odours, to characterise the odours, and to implement elimination and/or reduction measures in relation to these odours;
- an implementation timetable for all actions to be taken within this programme;
- reporting procedures to regularly advise management on the results of the plan;
- a review programme for regularly updating the plan.

Because odorous compounds are primarily VOCs and sulphur and nitrogen compounds, various prevention, reduction and abatement techniques already described in Section 4.23, in particular when applied to fugitive emissions, prevent and limit odour pollution. Furthermore, an overview of main odour management and treatment techniques is available in the CWW BREF [6, EC 2003].

The following sections focus on specific techniques that can be most appropriate to the oil refining sector.

3.26.1.4.1 Dynamic olfactometry with human assessors

Description

Odour concentration is determined by a panel of trained human assessors or panelists. Odour concentration is measured according to the European standard EN 13725-2003. The basis of this measurement method is that odour can be detected by a person if the individual odour threshold

is exceeded, independently from the preliminary knowledge on the odorous substance concerned.

The gaseous sample of odorants is collected on site using special bags to prevent the sample from being polluted by the pumping system used to collect it. The odour concentration is determined by olfactometry, that is by presenting a panel of selected and screened human subjects with that sample, varying the concentration by diluting the sample with odour-free gas in order to determine the dilution factor at the 50 % detection threshold (that is when the odour can just barely be perceived by 50 % of the test panel). The numerical value of the odour concentration is equal to the dilution factor that is necessary to reach the odour threshold. Its unit is the European Odour Unit (ou_E). Therefore, the odour concentration at the odour threshold is 1 ou_E by definition.

The persons that are members of the panel must fulfil certain requirements, for example regarding their sensitivity to odour perception. The main panel calibration gas used to verify this requirement is n-Butanol. To ensure the required level of accuracy, odour concentration is determined by a panel composed of 6 to 8 members. The laboratory must be ventilated to isolate the panelists from the odours in the ambient environment. Samples must be analysed within 24 hours after sampling.

Achieved environmental benefits

This method provides the necessary input for a well-established odour management plan (OMP).

Cross-media effects

None.

Operational data

No data submitted

Applicability

The technique is fully applicable to new and existing installations.

Economics

The cost reported for one analysis is in the range of EUR 300 – 400. The cost for a complete survey including panelist training is in the range of EUR 50 000 (refinery in Spain).

Driving force for implementation

This technique is used at installations when odour nuisance is an issue or when complaints occur in the vicinity of the industrial site.

Example plants

The technique is reported to have already been used successfully for various public or industrial activities (e.g. municipal waste water treatment plants, waste elimination, animal by-products manufacturing)

Reference literature

[41, ADEME 2005], [43, INERIS 2009].

3.26.1.4.2 Odour surveys by a committee of residents

Description

Odour nuisance is assessed by a committee of residents using different questionnaire techniques in order to evaluate the perceived nuisance. Questionnaires are filled in regularly, but always on a voluntary basis. The answers are correlated with meteorological conditions to get a link between actual emission sources and the described nuisance.

At a basic or preliminary step, the respondents are requested to rate the odour perception, the quality, and the level of nuisance on a multi-points scale. As an example, a conventional five-point scale can include the following ratings: 'definitely not annoying', 'slightly annoying', 'annoying', 'highly annoying' and 'extremely annoying'.

As a second step, after specific training, residents can also establish site olfactory imprints from a collection of odorous molecules organised in accordance with their dominance (e.g. amine, sulphurous, pyrazine) using recognised methodologies. One of these called 'Le Champ des Odeurs®' (developed by IAP Sentic) has been used since 1998 around industrial areas of the Seine estuary in France [47, AIR NORMAND 2006]. Site odour profiles are determined according to individual reference odourers distributed as follows in Figure 3.45.

Conducting a survey requires enough responses to carry out a statistical analysis. Representative sampling observations (in space and time) are obtained by considering, in particular, the population density, and the direction and the velocity of the prevailing winds. The theoretical impact distances (determined by odour dispersion modelling) can also be used for sampling validation.

Achieved environmental benefits

This technique allows for a better knowledge and understanding of the conditions under which odour nuisances occur. The results can be used for adjusting plant configuration and operations to reduce odour nuisance and the parameters which have to be assessed to limit olfactory impacts can be determined. Recommendations can be proposed and circulated back to the residents, e.g. specific practices to be avoided under characteristic meteorological conditions, and main sources identified as actually a nuisances and deserving newly adapted prevention measures or abatement techniques. This improves the preparedness, participation and response of the local community potentially exposed to odour.

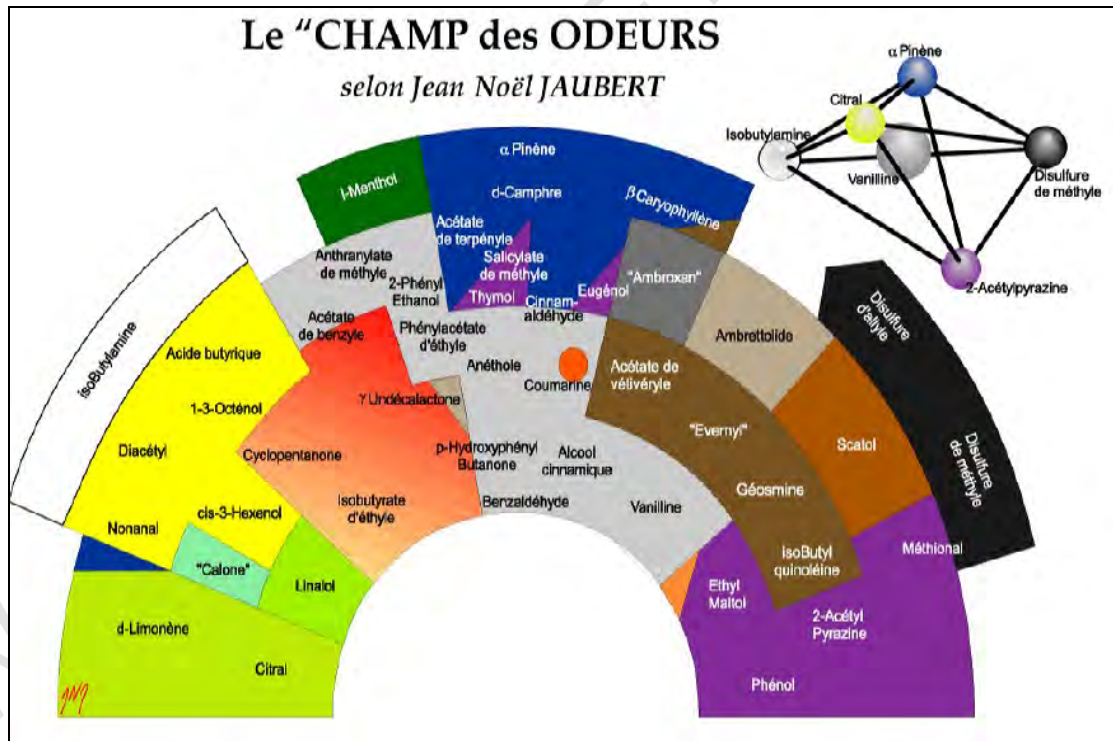


Figure 3.45: References used in a methodology for odour profile identification

Furthermore, the technique can also play a key role in the control of the effectiveness and efficiency of odour-reducing actions taken from previous monitoring campaigns. As an example, the latest olfactory profile carried out around the ExxonMobil refinery in Port-Jérôme

(2006) identified a 20 % odour reduction compared to initial campaigns (1998), enabling residents to perform by themselves a clear quantification of the results obtained from the odour-reducing action plans implemented by the refinery and neighbouring plants along this period.

Cross-media effects

There are no cross-media effects associated with the technique.

Operational data

Investigation campaigns can last quite some time (six months to one year) and require numerous observations and enough residents appropriately sampled on a spatial basis. As a consequence, steering resources should be put in order to ensure:

- having enough volunteers to perform relevant statistical analysis;
- motivating respondents during a minimal period lasting from a few month to one year, and ideally even longer in order to keep the same panel for several consecutive campaigns;
- the careful cross-analysis of all data.

In the case of the ExxonMobil refinery in Port-Jérôme (Rouen, France), typical training of residents for specific odour identification and site imprintings last 72 hours spread over 4 to 5 months. They involve 30 external voluntary ‘noses’ living in the vicinity, together with 12 internal ‘noses’ from the refinery staff. The odour profile of the refinery has been determined as shown in Figure 3.46.

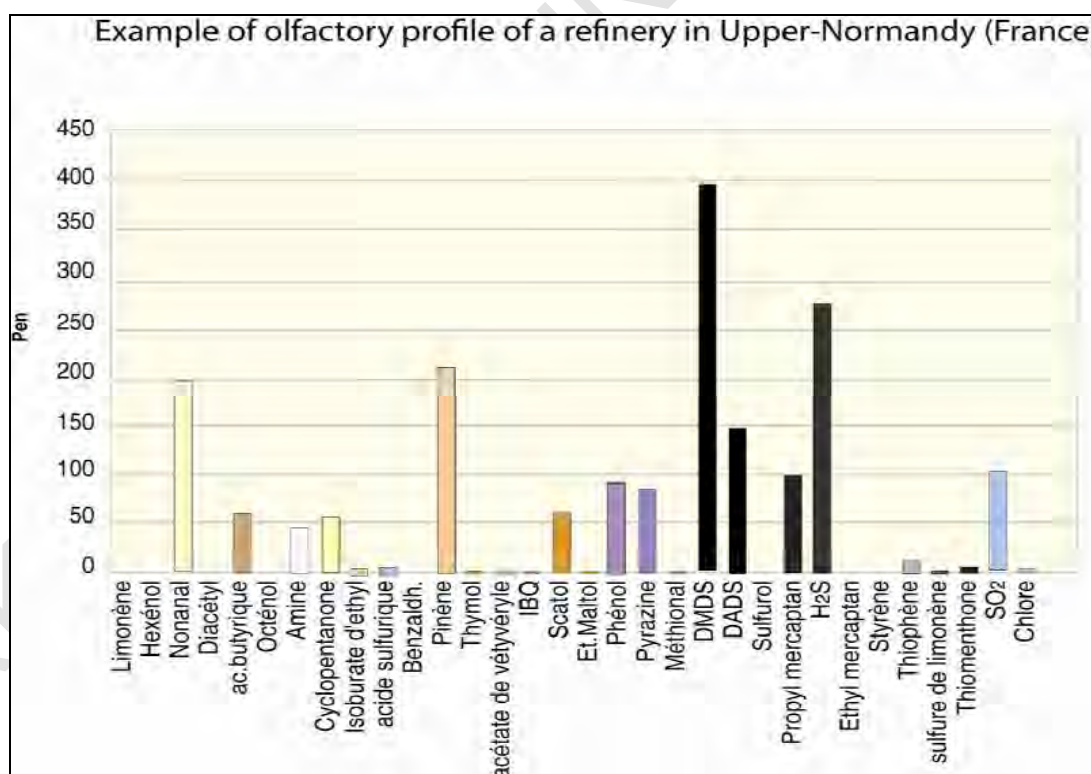


Figure 3.46: Olfactory profile of the ExxonMobil refinery in Port Jérôme (France)

Complementary methods (such as the dynamic olfactometry described in Section 3.26.1.4.1 in particular) can be used to qualify and describe the perceived odour in order to determine the odour sources responsible for the annoyance. Implementing this technique involves setting up a training programme for the volunteers and regular debriefings.

Applicability

The technique is fully applicable to new and existing installations. As an example, over 60 industrial companies are due to have their olfactory imprints defined so far, and have their odorous impact regularly tracked along the Seine estuary industrial area.

Economics

The technique costs for an odour survey are in the range of EUR 20 000 – 30 000 for a 6-month study including the recruitment of volunteers, management of questionnaires (by post, internet or by phone), analysis of the filled-in questionnaires, and meeting management for the presentation of the results to residents and other stakeholders (specific odour identification trainings excluded).

All of this can be managed by an external consulting firm. Equipment needed generally includes a PC, statistical software, and a weather station for a cost of about EUR 10 000.

Driving force for implementation

This technique is used at installations when odour nuisance is an acute issue, in order to provide the necessary input for a well-established odour management plan (OMP). It will help to solve complaints and to build up and maintain constructive relationships between the operator and the residents.

Example plants

The technique is reported to be used at several industrial areas in France, where in particular oil and petrochemical plants are in operation.

Reference literature

[44, INERIS 2009], [47, AIR NORMAND 2006], [49, ExxonMobil 2009]

3.26.2 Monitoring of releases to water

Continuous monitoring and flow proportional sampling for releases to water are always preferable but the use of a fixed interval or time proportional sampler for low flowrates (less than 1 litre per second) may be acceptable.

The monitoring of process effluents released to controlled waters and sewers will commonly be made for the following: flowrate, pH, temperature, and TOC (surrogate for COD/BOD). Samples are also being monitored for appropriate other parameters such as COD, BOD, Total Petroleum Hydrocarbons, suspended solids, nitrogen compounds, phenols, benzene, metals (typically Cd, Hg, Ni, and Pb). The periodicity can be typically daily, weekly or monthly, depending on the risk assessment and on local circumstances.

One problem with effluent discharge monitoring from refineries is related to the analytical method. For example for the analysis of petroleum hydrocarbons (oil) there are many different methods (e.g. GC-MS, IR one wavelength, IR two wavelengths, gravimetric) which give completely different results and that produce different results which prohibit a clear comparison. Unification of analytical methods or calibration against a standard preferred method can circumvent this issue.

3.26.3 Monitoring solid wastes

A recording of the quantity and composition (including prescribed substances) of residues generated is typically carried out. In addition, the operator typically has written procedures which ensure that releases are handled, treated and disposed of in an approved manner, and which specify how the accumulation and storage of waste are to be controlled. The frequency of analysis of the waste is site and/or process specific.

3.26.4 Soil and groundwater monitoring

Groundwater is an important resource and is protected from deterioration and pollution. In Europe, protecting groundwater is addressed through the Water Framework Directive (2000/60/CE establishing a framework for Community action in the field of water policy) and its daughter Directive (2006/118/CE on the protection of groundwater against pollution and deterioration).

As groundwater may be an important way of transfer for pollutants, the implementation of a groundwater monitoring network around industrial sites which could be at the origin of pollutions is essential. Therefore, the protection of this environmental compartment is integrated into the location's environmental management plan that includes the prevention of spills that could lead to groundwater contamination and a response plan to deal with unforeseen incidents.

Moreover, the collection of data on groundwater quality and quantity on a regular basis helps giving the alert in the case of an unnoticed accidental or chronic pollution, and will allow corrective control measures, if required. In addition, it is considered normal practise to install a groundwater monitoring system within the site's boundary to alert for groundwater contamination before these reach the site boundary or enter the site from neighbouring installations. An example of soil and groundwater monitoring is provided in Annex 9.5 below.

4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT

This chapter section describes techniques (or combinations thereof) considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this document. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers environmental management systems, process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimizing use and reuse are covered. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations).

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 4.1 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive

This chapter does not necessarily provide an exhaustive list of techniques which could be applied in the sector. Other techniques may exist, or may be developed, which could be considered for the determination of BAT for an individual installation.

Table 4.1: Information for each technique described in this chapter

Type of information considered	Type of information included
Description	Brief technical description using, as appropriate, pictures, diagrams and flow sheets.
Achieved environmental benefits	Main potential environmental benefits to be gained through implementing the technique (including energy, water, raw material savings, as well as production yield increases, energy efficiency, etc.).
Cross-media effects	<p>Potential environmental side effects and disadvantages to other media due to implementing the technique, including details of the environmental effects of the technique in comparison with others (advantages and disadvantages supported by data if available) in order to assess the impact of the technique on the environment as a whole. This may include issues such as:</p> <ul style="list-style-type: none"> consumption of raw materials and water energy consumption and contribution to climate change stratospheric ozone depletion potential photochemical ozone creation potential acidification resulting from emissions to air particulate matter in ambient air (including microparticles and metals) eutrophication of land and waters resulting from emissions to air or water oxygen depletion potential in water persistent/toxic/bioaccumulable components in water or to land (including metals) creation or reduction of (waste) residues ability to reuse or recycle (waste) residues noise and/or odour risk of accidents.
Operational data	Actual performance data (including reference conditions, monitoring periods and monitoring methods) on emission levels, consumption levels (raw materials, water, energy) and amounts of waste generated. Any other useful information on how to operate, maintain and control the technique.
Applicability	Indication of the type of plants or processes in which the technique may or cannot be applied as well as constraints to implementation in certain cases, considering, e.g. plant age (new or existing), factors involved in retrofitting (e.g. space availability), plant size (large or small), techniques already installed and type or quality of product.
Economics	Information on costs (investment and operating) and any possible savings (e.g. reduced raw material or energy consumption, waste charges) or revenues including details on how these have been calculated/estimated. Economic information relevant to new build and retrofit to existing installations will be included. This should allow for identifying, where possible, the overall economic impact of the technique.
Driving force for implementation	Specific local conditions, requirements (e.g. legislation, safety measures) or non-environmental triggers (e.g. increased yield, improved product quality) which have driven or stimulated the implementation of the technique to date.
Example plants	Reference to the plant(s) where the technique has been implemented and from which information has been collected and used in writing the section. Indication of the degree to which the technique is in use in Europe or worldwide.
Reference literature	Literature or other reference material (e.g. books, reports, studies, websites) that was used in writing the section and that contains more detailed information on the technique.

This chapter should be seen as the main background information for the determination of best available techniques in the refinery sector (Chapter 5). Techniques that are generally seen as obsolete are not included. Moreover, this chapter does not include all the techniques applied in

the refinery sector and described in Chapter 2. Only techniques with good environmental performance are included here.

Production, prevention, control, minimisation and recycling procedures/techniques are considered in this chapter. These techniques/procedures can be carried out in many ways, such as using production techniques that pollute less than others, changing the operating conditions, reducing material inputs, re-engineering processes to reuse by-products, improving management practices or employing substitution of toxic chemicals. This chapter provides information on some general and specific pollution prevention and control advances that have been implemented within industry in general and in the refinery industry in particular.

As in previous Chapters 2 and 3, each section of this chapter deals with a refinery process or activity and contains the process and abatement techniques worth being considered in the determination of BAT. If different techniques are applicable for one process/activity, they are discussed in the respective process activity section. Sections 4.2 to 4.22 in this chapter have been structured in the same way. Each of these sections contain first the pollution prevention primary techniques applicable in the process/activity section referred to, and second the end-of-pipe (EOP) techniques that may be applicable for reducing the emissions for the process/activity. The EOP techniques are grouped into media/pollutant categories to clarify the sequence of techniques applicable. In some cases, the number of EOP techniques that may be used is quite extensive.

At the end of this chapter, three sections appear containing the EOP techniques applied to waste gas, waste water and waste management. These sections contain the descriptions of the EOP techniques that may be applicable to more than one refinery process/activity, as well as some other EOP processes. Consequently, the descriptions of the EOP techniques that may appear in this chapter are included in Sections 4.23, 4.24 and 4.25 and not in the activities/process sections.

4.1 General overview

Table 4.2 gives the number of techniques considered in the document for each refining activity or process described. These techniques have been split into four categories. The numbers included in this table are only orientative and are not the simple recounting of the subsections. As it will be seen, some subsections include more than one technique. This table is only meant to give an overview of the number of techniques considered in each section of the document, as a first indicator of what activities/processes are more important from the environmental point of view (e.g. energy system, storage and handling, integrated management, catalytic cracking, coking).

Table 4.2: Number of techniques (or families of techniques) addressed in Chapter 4

Chapter section	Activity/process	Number of techniques applied to:		
		Production and prevention	End-of-pipe	Total
2	Alkylation	3	-	3
3	Base oil production	8	2	10
4	Bitumen production	2	5	7
5	Catalytic cracking	6	11	17
6	Catalytic reforming	1	3	4
7	Coking processes	21	12	33
8	Cooling	3	-	3
9	Desalting	13	4	17
10	Energy system	57	8	65
11	Etherification	3	-	3
12	Gas separation processes	2	-	2
13	Hydrogen-consuming processes	4	-	4
14	Hydrogen production	4	-	4
15	Integrated refinery management	13	-	13
16	Isomerisation	2	-	2
17	Natural gas plants	15	6	21
18	Polymerisation	3	-	3
19	Primary distillation units	21	2	23
20	Product treatments	4	-	4
21	Storage and handling of refinery materials	21	-	21
22	Visbreaking	3	1	4
23	Waste gas treatments	5	22	27
24	Waste water treatments	8	17	25
25	Waste management	12	2	14
	TOTAL	234	95	329

4.2 Alkylation

Three alkylation processes are considered in the determination of BAT the hydrofluoric acid (HF), the sulphuric acid (H₂SO₄) and the solid-acid process. As the third process is still considered an emerging technique, it has been described in Chapter 6.

4.2.1 Hydrofluoric acid alkylation process

Description

A brief description of this process can be found in Section 2.2.

Achieved environmental benefits

The main advantages of the HF-alkylation process in comparison with the sulphuric acid process are the regeneration of HF, which minimises waste formation and disposal, and the lower acid-catalyst consumption, as well as the minor consumption of energy and cooling.

Cross-media effects

Effluent gases

A scrubber using alkaline solution (NaOH or KOH) is necessary to remove HF from the incondensable gas stream. The acid relief neutraliser is operated so as to minimise the hydrogen fluoride content of the incondensable gas stream. Concentration of less than 1 mg HF/Nm³ can be achieved. The vent gas can then be passed to flare not to the refinery fuel gas system. A dedicated flare/stack is normally retained for this but, depending on the composition gases, it is reported that it may be vented to a non-dedicated flare/stack (e.g. operation at a Spanish refinery). Fugitive emissions are also generated by this process.

HF is a *very dangerous compound* because of its severe corrosive nature and the burning effects of both liquid and fumes to the skin, eyes and mucous membranes. Consequently, storage and handling should comply with all safety rules.

KF (or NaF) is formed during the neutralisation process. The spent solution is stored and then requires regeneration with lime. The regenerated KOH is recycled but typically NaOH is not. CaF₂ is regularly cleaned out and disposed of, usually to a landfill. Fumes can originate in the neutralising basin unit. To prevent the discharge of these odorous gases to the surroundings, the neutralising basins are tightly covered and equipped with a gas scrubber to remove any offensive agents.

Water

HF alkylation effluents are a potential cause of acid excursions in refinery effluents and a high standard of control should be exercised on the neutralisation treatment system, e.g. on-line pH monitoring. The effluent containing HF acid can be treated with lime (CaO-Ca(OH)₂), AlCl₃ or CaCl₂ or it can be neutralised indirectly in a KOH system to produce the desired CaF₂ or AlF₃ (insolubles) which is separated in a settlement basin. The supernatant liquor flows to the water treatment process. KOH may be regenerated for reuse. After this treatment, the supernatant still contains 10 – 40 ppm F and some hydrocarbons, and is directed to the WWTP. KOH may be regenerated from the aqueous solution for reuse.

Wastes

The HF process also yields tars (polymeric material) but these are essentially free from HF. HF-containing tars are neutralised and disposed of by incineration or blended as a fuel-oil component, usually in small amounts because of its pronounced odours. However, technology and special operating techniques such as internal acid regeneration have significantly reduced this liquid-waste stream.

Poor operation of the system (excessively cold acid, improper acid settler level, low reactor pressure, excessive acid recycling rate, low i-butane or acid concentration, high reactor temperature and improper mixing) increases the amount of waste generated.

Operational data

The potentially corrosive and toxic properties of HF require special engineering design and special construction materials, advanced process controls and stringent safety, personnel protection and maintenance requirements. These precautions include:

- special seals on acid-containing equipment such as pumps and valve stems;
- special safety clothing which must be worn by personnel entering an acid area;
- extensive operator training;
- special facilities (e.g. sprinkler systems, acid-inventory reduction, HF-detection systems, isolation valves, rapid acid transfer systems) should be included in the design of this kind of system to mitigate the effects of an accidental emission of HF vapour clouds. For leak detection, HF-sensitive colours on pipes and flanges are suitable as alternatives to continuous air analysers and video control. The potential reduction of aerosol formation of HF acid has also been demonstrated by using an additive based system. Special care should be taken during maintenance and cleaning of the plant, e.g. for major shutdowns, not to release odours from the drainage system and/or ponds.

The same developments (such as additives) have been already tested in order to lower the vapour pressure and to minimise the amount of HF released to the atmosphere in case of an accident. The downside of this is that handling and recycling the additive add to the complexity of the process.

Applicability

Fully applicable.

Economics

Table 4.3 shows the investment and production cost summary for HF alkylation. Disposal costs are not included.

Table 4.3: Examples of investment and operational costs for an HF-alkylation unit

Costs	Estimated erected cost (3 rd quarter 1995)	New HF plant (1999)
Investment cost		
Capacity (kt alkylate/yr)	348	160
Investment cost (EUR million)	25.6	35
Operating cost (EUR/tonne alkylate)		
Labour	0.016	
Utilities	0.066	
Chemical consumption, laboratory allowance, maintenance, taxes and insurance	0.056	
Total direct operating costs	0.138	

Driving force for implementation

Alkylation is a refinery process used to increase gasoline octane. Safety requirements due to HF are the main environmental driver for this process.

Example plants

HF-Alkylation is very widely used.

Reference literature

[175, Meyers 1997], [164, Noyes 1993], [204, Canales 2000], [240, Hommeltoft 2000], [207, TWG 2001].

4.2.2 Sulphuric acid alkylation process

Description

A brief description of the process can be found in Section 2.2.

Achieved environmental benefits

Sulphuric acid is an alternative process for alkylation, but has the drawback of more spent acid, which must be regenerated, typically outside the plant installation. Efficiency of the process is lower than with HF alkylation and more cooling is needed.

Cross-media effects

Technologies using sulphuric acid as a catalyst produce very large quantities of spent acid (sulphuric and sulphonc acids) that have to be regenerated. The transport of spent and fresh acid to and from the sulphuric acid regeneration has given rise to some concern and has increased pressure on refiners to establish sulphuric acid regeneration plants near alkylation units. In some cases, this transport to/from the regeneration facility is by pipeline. However, no major new improvements have been introduced in sulphuric acid alkylation technology dealing with the spent acid issue. Fugitive emissions from this process are similar to those from HF alkylation.

Acid-soluble oil is continuously generated as a by-product of sulphuric acid alkylation. This oil goes into the acid phase and dilutes the strength of the acid within the unit, unless a portion of the acid is continuously purged (spent acid) and replaced with fresh acid. The spent acid containing the acid soluble oil is sent to the regeneration process on site, through the acid regenerator unit, or off-site. Tars from the H₂SO₄ process contain sulphuric and miscellaneous sulphonc acids, which may cause disposal problems. In addition to spent acid, this process generates spent caustic and alkaline waste water streams, which must be sent to WWTP or to possible regeneration (in the case of the caustic). Depending on BOD and COD requirements at the WWTP, the waste water stream may require a nitrogen stripper to remove dissolved hydrocarbons.

Operational data

The product quality from butylenes (primary feedstock) is higher than in HF alkylation. To produce an equivalent product quality, HF alkylation would require similar energy consumption to sulphuric acid alkylation. As sulphuric acid is less toxic than HF and does not form a vapour cloud if released, this type of process is often considered to be safer. However, the actual determination of risk level is site-specific and has to be carried out within a specific risk assessment methodology.

Table 4.4: Example of utility and chemical consumption for H₂SO₄-alkylation

Utilities and chemical consumption (based on 716 m ³ /d alkylate plant)	
Power, kW	1 779
Compressor	1 235
Pumps	303
Mixers	240
Cooling Water, m ³ /h ⁽¹⁾	835
Industrial Water, t/d	39
Steam, kg/h	
3.45 barg	13
10.3 barg	3
Chemicals	
Fresh Acid, t/d ⁽²⁾	40
NaOH -15 Baume ⁽³⁾ , t/d	1.7
⁽¹⁾ Cooling water supply temperature is 26 °C and the average ΔT is 15 °C.	
⁽²⁾ Includes allowance for feed impurities.	
⁽³⁾ 15 'degrés Baumé' ≈10 % w/w	

The sulphuric acid removed needs to be regenerated in a sulphuric acid plant which is generally not a part of the alkylation unit and is normally located off-site.

Applicability

Fully applicable. On the economical point of view, this alkylation process is mostly driven by the proximity of a regeneration facility of sulphuric acid.

Economics

Some data are available in Table 4.4 and Table 4.5.

Table 4.5: Examples of investment and operational costs for H₂SO₄-alkylation

Capacity	Estimated costs	Units
290 kt/yr	Material USD12.0 million Labour USD1.7 million	US Gulf Coast, second quarter 1993. Operational data correspond to this plant.
28 300 m ³ /d	USD 14.49 million	
1 590 m ³ /d	USD 22 000 per m ³ /d	US Gulf Coast, 4th quarter, 1998

Driving force for implementation

Alkylation is a refinery process used to increase the gasoline octane.

Example plants

Sulphuric acid alkylation is widely used.

Reference literature

[175, Meyers 1997], [183, HP 1998], [240, Hommeltoft 2000], [207, TWG 2001].

4.2.3 Upgrade feedstock by selective hydrogenation or isomerisation

Description

More information about the processes can be found in Sections 2.13, 4.13.4, 2.16 and 4.16.

Achieved environmental benefits

The naphtha hydrotreatment or isomerisation (e.g. hydrogenation of butadiene, isomerisation of 1-butene to 2-butene) helps the alkylation units to reduce the acid losses and consequently the waste generation. As a consequence, the amount of caustic consumption is decreased. The reduction in acid and caustic consumption depends on the feed diene content, which varies widely at different refineries.

Cross-media effects

Drawbacks for the implementation of such a technique include the increased fuel/energy consumption, the increased fugitive emissions and the need for spent catalyst handling to be used in such a process. More information about these issues can be found in Sections 4.13 and 4.16.

Operational data

This technique requires hydrogen and consumes energy.

Applicability

There are no restrictions on the application of this technique.

Economics

See Sections 4.13 and 4.16.

Driving force for implementation

Because of the increased demands for higher octane gasoline and the increased conversion of heavier crudes to lighter products, there has been a relative decrease in the quality of alkylation feed throughout the industry.

Example plants

No information provided.

Reference literature

[164, Noyes 1993], [207, TWG 2001]

4.3 Base oil production

As described in Section 2.3, several types of processes can be found in the base oil production. They include the deasphalting unit, aromatic extraction, high pressure hydrogenation unit, dewaxing, hydrofinishing and wax processing. All of these processes are covered here and the good techniques from the environmental point of view are discussed in this section. Techniques applicable for the storage of the solvents used in base oil production (e.g. furfural, NMP, MEK, MIBK) and intermediates are also included here.

4.3.1 Multiple-effect extraction process

Description

Solvent-based processes used in the manufacture of base oils are energy intensive because large volumes of solvent must be recovered by flash distillation for recycling back to the process. The number of stages used for evaporation of the solvents has a significant effect on the energy cost for these processes and as many as five evaporation stages were used in some early liquid SO₂ extraction units in Europe.

Achieved environmental benefits

Heat efficiency can be improved (less water and steam usage) by applying 'double and triple effect configurations', especially in the deasphalting and aromatic extraction units. Energy saving for triple-effect evaporation is 30 – 33 % compared with double-effect evaporation.

Cross-media effects

None in particular.

Operational data

Utilities needed for this process are listed in the economic section below. The energy saving for the triple effect system is on the low-level heat side only (in most cases LP-steam) where refineries often already have a surplus. This means that the actual savings depends on the local circumstances and a retrofit/change should be evaluated for each individual location.

Applicability

Multiple effect evaporation requires both a pressure and a temperature driving force. In some instances, the increase in pressure and temperature required to go from the double to triple effect is not feasible and could result in higher emissions and energy consumption because of the larger residual amounts of solvent left in the oil leaving the evaporation section and entering the stripping section.

Triple effect systems are typically used for non-fouling feedstocks only (e.g. wax), as they are known to be more vulnerable in this respect, so their application is restricted.

Economics

An order of investment costs (based on a 318 – 6 360 m³/d capacity range) was around USD 5 000 –18 900 per m³/d (4th Q 1998, US Gulf). An example of comparative costs for single, double and triple-effect options is given in Table 4.6.

The number of stages used for evaporation of the solvents has a significant effect on the energy cost for these processes. As many as five evaporation stages have been used in some early liquid SO₂ extraction units in Europe. Double effect units are the most predominant type of evaporation process, but since around 1980 most new units have been designed for triple effect evaporation to reduce the cost of energy consumption. Some existing units have been converted. Heat efficiency can be improved (less water and steam usage) by applying double and triple effect configurations, especially in the deasphalting and aromatic extraction units.

The energy saving for the triple effect system is on the low-level heat side only (in most cases LP-steam) where refineries often have a surplus. This means that the actual savings depends on the local circumstances and a retrofit/change should be evaluated for each individual location.

Table 4.6: Economics related to energy savings for three multiple-effect deasphalting options

Type of cost	Single-effect	Double-effect	Triple-effect
Conversion investment USD ⁽¹⁾	0	1 300 000	1 900 000
Annual utility cost USD ⁽²⁾			
Medium-pressure steam, USD 8.1/t	91 100	91 100	91 100
Low-pressure steam, USD 6.8/t	931 600	465 200	377 500
Power, USD 0.04/kWh	218 400	218 400	218 400
Cooling water, USD 0.018/m ³	87 200	47 600	39 200
Fuel, USD 1.92/net GJ	44 100	44 100	44 100
Total annual utility costs	1 372 400	866 400	770 300
Annual utility reduction	0	506 000	602 100
⁽¹⁾ Estimated basis: United States Gulf Coast, third quarter 1995.			
⁽²⁾ Based on unit cost provided by SRI International, Menlo Park, CA (US). December 1994			
NB: Large savings are shown for low-pressure steam. In most refineries, low-pressure steam is considered 'free' since excess is vented to the atmosphere.			

Driving force for implementation

The conversion to a multiple-effect unit reduces the utility cost.

Example plants

Multiple-effect extraction is a common technology used in refineries with lubricant oil production. Double effect units are the most predominant type of extraction processes. Units built from 1950-1975 used double effect and a few used single. Because the cost of energy increased rapidly during the 1970s, most new units built since around 1980 have been designed, and older units have been converted, for triple effect evaporation, to reduce the cost of energy consumption.

Reference literature

[175, Meyers 1997], [183, HP 1998], [231, Sequeira 1998].

4.3.2 Conversion of a solvent extraction unit (from Furfural or Phenol to NMP)

Description

The selection of the type of solvent used in aromatic extraction has an impact on the energy consumption of the process. Moreover, a lower footprint solvent, like furfural or n-methyl pyrrolidone (NMP), can be used instead of a more hazardous selective solvent like phenol, cresol or sulphur dioxide. The relevant characteristics of the mainly used solvent are presented in Table 4.7.

Achieved environmental benefits

The use of a less polluting solvent (e.g. NMP or furfural) has a positive effect on the reduction of emissions of phenols and sulphur dioxide in the refinery effluents.

Compared to phenol, NMP has faster settling rates and a lower specific heat, requiring less energy for solvent recovery. Compared to furfural, NMP is more thermally and chemically stable, more selective, requires less energy for recovery, and avoids the need for a feed deaerator. [133, EXXON 2012]

Additional advantages of the use of furfural or NMP include a higher selectivity leading to a higher raffinate yield and a lower solvent ratio, which both result in a lower energy consumption by some 30 – 40 %.








Cross-media effects

Care should be taken to avoid solvent contamination of aqueous effluents by applying efficient solvent recovery techniques. Some contamination of aqueous effluents occurs, so care should be taken not to upset the downstream biological treatments. NMP is easier to degrade in the WWTP than furfural, however it is also more corrosive than clean furfural (NMP is corrosive when feed is not properly pretreated).

Operational data

The performance of NMP and furfural techniques are similar. Well maintained and operated furfural extraction units perform just as well as NMP plants. Similar quantities of furfural, as for NMP, are required when the plants are run in the correct manner

Table 4.7 Characteristics of some of the mainly used solvents for base oil production

	Aromatic extraction			Solvent Dewaxing			
Short Name	NMP	PHENOL	FURFURAL	Me	Di	MEK	MIBK
Composition	C ₅ H ₉ NO	C ₆ H ₆ O	C ₅ H ₄ O ₂	CH ₂ Cl ₂	C ₂ H ₄ Cl ₂	C ₄ H ₈ O	C ₆ H ₁₂ O
Name	N-Methyl-2-pyrrolidinone	Phenol	Furfural	Dichloromethane	1,2-Dichlorethane	Methyl ethyl keton	Methyl isobutyl keton
CAS number	108-88-3	108-95-2	98-01-1	75-09-2	107-06-2	78-93-3	108-10-1
Indication of danger	F,Xn 	T 	T 	Xn 	F,T 	F,Xn 	F,Xn 
Toxicity		R 32/24/25 Toxic by inhalation, in contact with skin and if swallowed	R23/25 Toxic by inhalation and if swallowed.				
Effects	R 38 Irritating to skin.	R 34 Causes burns.	R 36/37/38 Irritating to eyes, respiratory system and skin.		R36/37/38 Irritating to eyes, respiratory system and skin.	R 36 Irritating to eyes.	R36/37 Irritating to eyes and respiratory system.
Harmfulness	R48/20 Harmful: danger of serious damage to health by prolonged exposure through inhalation., R65, R67	R 48/20/21/22 Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.	R 21 Harmful in contact with skin.		R22 Harmful if swallowed.		R 20 Harmful by inhalation
Long term effects Mutagenic Carcinogenic	R63 Possible risk of harm to the unborn child.	R68: Possible risk of irreversible effects.	R40 Limited evidence of a carcinogenic effect.	R40 Limited evidence of a carcinogenic effect.	R45 May cause cancer.	R66, R67	R66

Source: European Commission [134, EC Esis 2012]

Applicability

Some technical restriction for applicability of change of solvent when switching to NMP from phenol is reported due to the following: NMP has a higher boiling point (by 22 °C), a lower melting point (by 64 °C) and no azeotrope. For these reasons, furfural is typically used when producing lower boiling point base oils (e.g. transformer oil distillates).

Major modifications would be required for existing units to change from furfural to NMP as the process conditions are different (for example a change from hot oil heat exchangers to a fired furnace to achieve the required temperatures in the solvent recovery section).

Nevertheless, the lower viscosity of NMP gives a higher throughput for a given size tower. This results in lower construction costs and reduced energy and operating costs. Raffinate oil yields average 3 to 5 % higher for the NMP extraction and with more stable and reliable plant operation, including at lower treat rates. It enables safer operations by using less toxic solvent and simplified solvent recovery. This conversion to NMP is applicable to the extraction of both paraffinic and naphthenic feed stocks and therefore makes it an attractive solution for the extraction of lubricating oil stocks

Economics

Costs for switching from one solvent to a more favourable one will have to be evaluated on a case-by-case basis. In some cases, the change of solvent used does not entail significant extra costs. On the other hand, the change from a SO₂ aromatic extraction to any other solvent requires a completely new unit.

The switch from a furfural to an NMP process requires economic calculations because major modifications may be required. As a consequence, the energy saving against the cost of the revamp has to be weighed individually. Changing from furfural to NMP requires significant investment, including, but not limited to, the extraction tower, furnaces, metallurgy, etc.

The cost for the conversion of a phenol unit to a NMP unit (100 m³ per operating day - feasibility study) is estimated at EUR 4.15 million (100 million CSZ). Other estimates show that the investment costs to switch from a phenol unit to an NMP unit is around 70 % the cost of a completely new unit.

A cost comparison for major base oil refining processes is given in Table 4.8.

Table 4.8: Basic cost comparison between three aromatic extraction processes

Costs	Furfural	NMP	Phenol
Solvent, relative	1.0	2.3	0.60
Investment	Medium	Low	High
Maintenance	Medium	Low	High
Energy	High	Low	Medium

Driving force for implementation

Reduction of energy consumption (25-50 % less loss of solvent due to easier solvent recovery) and of the emission of phenols and SO₂ in the refinery.

Example plants

Furfural and NMP solvent extraction processes are common technologies.

Reference literature

[162, HMIP UK 1993], [231, Sequeira 1998], [207, TWG 2001], [252, Ullmann's 2012], [135, Abdul-Halim A et al. 2009], [133, EXXON 2012], [134, EC Esis 2012].

4.3.3 Solvent recovery from dewaxing units

Description

Information about the process can be found in Section 2.3. The following prevention techniques may be applied to the solvent dewaxing process:

- Including vapours from the wax filters in the inert gas system by circulating the inert gas, and recovering solvent vapours by refrigeration as part of the process. Solvent incineration in furnaces should be minimised. An alternative to refrigeration is the pressure absorption of solvents in oil (e.g. fresh feed or finished).
- Using solvents for the process, including propane and mixtures of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK). Toluene (associated with a risk phrase R63: Possible risk of harm to the unborn child) or chlorinated hydrocarbons (this large family includes substances with a significant toxicity to humans and a high persistence in the environment) should be avoided. As described in Section 2.3 the chlorinated solvents used may be a mixture (DiMe) of 1,2-Dichloroethane (DCE) and Dichloromethane (DCM).
- Sending solvent-contaminated water resulting from the solvent recovery stage to the WWTP.
- Using inert gas, in place of steam, for stripping the last traces of solvent from the dewaxed oil and waxes. When chlorinated solvents are used this procedure is typically applied.

In wax-processing units, solvent recovery (e.g. for DCE) is carried out using two systems: one for the deoiled wax and another one for the soft wax. Both consist of heat integrated flashdrums and a vacuum stripper. Streams from the dewaxed oil and waxes product are stripped for removal of traces of solvents. This step of the process can be carried out by inert gas stripping or steam stripping.

In MEK and toluene solvent dewaxing units, inert gas is used for stripping. The solvent can be kept water-free and efficiently recovered from the contaminated inert gas flow arising.

In DiMe-units, steam stripping combined with a condensation stage is commonly used to remove the solvents from the products. The water can be treated efficiently within the process to separate the solvent. The solvent is then recovered and kept in the system.

Achieved environmental benefits

Maximising the recovery of the solvents used in the solvent dewaxing processes reduces the contamination of waste water by toluene or chlorinated hydrocarbons. The benefits of inert gas stripping in solvent dewaxing are the reduction of energy requirements in solvent refining units, the increase of dewaxed oil yields, reduction of the dilution ratios, reduction of solvent losses, decrease of the dewaxing differential, and maintenance cost reduction.

Cross-media effects

Large refrigeration systems are used and refrigerant losses from these should be minimised. Energy consumption is increased for refrigeration/pressure and heat. Care should be taken to avoid solvent contamination of aqueous effluents because most of the solvents used in solvent dewaxing are problematic for water microorganisms and waste water plants. VOC fugitive emissions may be generated during the processes.

Operational data

Table 4.9 gives some data on typical utility specific consumption for dewaxing solvent recovery units.

Table 4.9: Typical utility specific consumption for dewaxing solvent recovery units

Utilities, typical per m ³ feed		Units
Fuel	1 856	MJ
Electricity	290	kW
Steam	171	kg
Cooling water ($\Delta T = 25$ °C)	36	m ³
Solvent make-up	1.7	kg

Applicability

Generally applicable to new units. Existing units would require a feasibility study due to the specificity of the process used which are generally designed for a specific type of solvent

Economics

A new solvent recovery unit cost USD 66 000 per m³/day (based on 44 000 m³/day feed rate capacity, 1998 US Gulf Coast). Data on the implementation of inert gas stripping in refineries showed paybacks of 9 – 14 months.

Driving force for implementation

Solvent recovery from dewaxing can be used in refineries that have solvent dewaxing units in their lubricant oil production processes to promote the reduction of solvent losses.

Example plants

Many refineries with lubricant production have these types of processes.

In recent years, several furfural extraction plants have been converted into NMP plants.

Reference literature

[183, HP 1998], [148, Irish EPA 1993], [231, Sequeira 1998], [207, TWG 2001].

4.3.4 Wax reprocessing unit**Description**

Hydrofinishing or clay treating can be used in wax processing.

Achieved environmental benefits

Wax hydrofinishing offers several advantages over clay treating, including lower operating costs and the reduction of waste generation.

Cross-media effects

When hydroprocessing is used, hydrogen is necessary. Hydrotreatments consume energy, hydrogen and nickel, tungsten or even platinum catalysts. Spent clay needs to be appropriately disposed off.

Operational data

Hydrogen finishing yields are close to 100 %, whereas the clay treating product yield ranges from 75 to 90 % for the microcrystalline waxes, and as high as 97 % for light paraffin waxes. Hydrogen consumption is around 15 Nm³ per m³ of wax produced. Clay consumption runs from 2 to 45 kg/t of product.

Applicability

Hydrofinishing is fully applicable especially when hydrogen is available. However, in some cases, hydrofinishing processes cannot achieve certain special product quality specifications.

Economics

Investment costs for a wax hydrofinishing process are in the range of EUR 1.4- 2.3 million for a feed capacity of 20 000 t/yr (from an average USD 3 500 – 5 700/bpd depending on pressure level and size). [76, Hydrocarbon processing 2011]

Driving force for implementation

Hydrotreating offers a lower operating cost.

Example plants

Many examples exist.

Reference literature

[231, Sequeira 1998], [207, TWG 2001], [76, Hydrocarbon processing 2011].

4.3.5 Storage and benchmarking of solvents

Storage and benchmarking techniques are part of the VOC abatement programme (see Section 4.23.6.1).

4.3.6 Sulphur treatment from hydrogenation units

Description

Hydrogenation processes generate H₂S. As a consequence, off-gases containing H₂S are recovered in a sulphur recovery plant (See Section 4.23.5) or are incinerated. This will become more relevant over time since new lube oil units will be increasingly based on hydrogenation processes.

Achieved environmental benefits

Reduction of sulphur and H₂S emissions.

Cross-media effects

Amine recovery of H₂S consumes energy and chemicals. Sulphur recovery units consume energy (see Section 4.23.5). Incineration requires fuel.

Operational data

See Section 4.23.5.

Applicability

In stand-alone lube oil refineries, the small amounts of H₂S generated in this process are typically incinerated. Sulphur recovery is less commonly applied in these specialised refineries.

Economics

For more information on economics, see Section 4.23.5. Data from EU refineries have shown that the implementation of SRU in stand-alone lubricant refineries producing more than two tonnes of sulphur per day is cost-effective.

Driving force for implementation

Reduction of sulphur oxide and H₂S emissions.

Example plants

At least one specialised European refinery has an SRU which recovers 99.1 % of the sulphur in the acid gas.

Reference literature

[174, HMIP UK 1995], [207, TWG 2001].

4.3.7 Stripping of waste water from aromatic extraction

Stripping techniques applicable to aromatic extraction waste water are addressed in Section 4.24.

4.3.8 Energy use and integration

Description

A group of energy saving activities can be applied to the design, operation and maintenance of the base oil production units (see also Section 4.15 for the entire refinery integrated approach).

Design: Selecting hydrogenation based processes normally leads to lower energy usage than solvent based ones. A conventional solvent-based base oil lube complex is energy intensive. The main reasons are :

- the high amount of heat required to evaporate the solvents and to recover them from the raffinate and extract streams;
- the heat needed for keeping the product streams in the liquid state;
- the deep-freezing conditions for dewaxing/deoiling of base oil streams.

Combining aromatic extraction with hydrofinishing may lead to lower energy usage.

Operational: Use of advance process control or pinch analysis aims at achieving heat integration within the unit itself and with other units in the refinery (see Section 4.15).

Retrofitting existing process units that usually have individual energy sources (e.g. furnaces or boilers) with a common hot oil system coming from a single source may be used for heat transfer to all the solvent recovery units. When the base oil production units have a single energy system, the introduction of clean-up facilities in the flue-gases is more cost-effective. (See Section 4.23)

Achieved environmental benefits

The reduction of SO_x, NO_x and particulate emissions to air from a single, energy-wise, optimised system compared to several individual furnaces.

Cross-media effects

See different cross-media effects for the abatement of SO_x, NO_x and particulates in Section 4.23.

Operational data

See Section 4.23 for waste gas treatments. See section 3.3 on operational costs of various units

Applicability

Generally applicable to new units. This technique may nevertheless be difficult to apply to existing refineries.

Economics

See Section 4.23.

Driving force for implementation

Reduction of SO_x, NO_x, particulates emissions from the energy system. The main driving force is the energy efficiency. The heat integration within the process can be performed in a very energy and cost efficient way and provide stable process conditions.

Example plants

Some stand-alone lubricant refineries have already applied this concept and have switched to a common single heating source to reduce emissions coming from the burning of liquid fuels.

Reference literature

[207, TWG 2001].

4.3.9 Catalytic processes based on hydrogenation

Description

The hydrogen conversion technology converts undesired components directly to end products. The base oils are hydrofinished at higher pressure (>100 bars) than the around 30 bars pressure applied in conventional manufacturing. This technology has significantly lower operational cost but substantial initial investment. (see also Section 2.3)

Achieved environmental benefits

No use of toxic solvents and thus no emission to air or water of these substances.
Moderate energy usage and corresponding lower emissions to air. The undesired compounds are not separated with the need to treat or dispose off but are converted into useful species
The more recent processes normally allow a wider feedstock usages

Cross-media effects

Hydrogen streams may be generated and will need further treatment

Operational data

See Section 2.3.

Applicability

Applicable to new installations or major revamping of existing installations.
Installing hydrogenation based units upstream existing units is also possible to create an hybrid lube oil complex.

Economics

Lower investment and operating costs than for solvent-based processes. See Section 2.3.

Driving force for implementation

Less dependence on feedstock (more flexibility), lower investment cost, simpler process.
To produce non-carcinogenic naphthenic base oils.

Example plants

MOL refinery (HU)

Reference literature

[141, TWG FI 2012], [76, Hydrocarbon processing 2011], [137, Szeitl et al. 2008].

4.3.10 Improved solvent based plants with lower loss of containment

Description

Incorporating design and optimisation features reduces the emissions to air and water of pollutants such as toxic solvents. The solvents used in base-oil production are potentially harmful and need to be contained. In order to prevent and reduce the emissions to air or water from base oil production processes, the operator can use the following techniques:

- Closed process including a solvent recovery.
- Dedicated solvent sewage routed to recovery unit: depending on the plant configuration and process waste stream generated, a separate facility may be dedicated to treat streams containing solvents. A process concentrates solvents for further recovery or re-processing. The recovered water is routed to a central WWT or used elsewhere.
- All vents channelled to a header: Use of closed piping systems for draining and venting hydrocarbon containing equipment prior to maintenance, particularly when containing more than 1 % w/w solvent. Ideally, permanent piping can be used to minimise the risk of exposure during the breaking of containment.
- Closed loop sample systems routing the sampling flow back to the process.

- Canned pumps or magnetically driven pumps whenever feasible for services processing high solvent content streams. Otherwise use pumps fitted with double mechanical seals.
- Include the relevant units in a LDAR program to minimise fugitive emissions and ensure and repair of flanges/valves etc (see Section 4.23.6.1).
- Use high integrity packing materials in manual or control valves with rising stems.

Achieved environmental benefits

Lower emissions to water and to air of hazardous substances such as toxic solvents.

Cross-media effects

Higher energy consumption on some of the end-of-pipe abatement techniques applied.

Operational data

See chapter 2.3

Applicability

Applicable to new installations and existing installations that might undergo a major retrofit.

Economics

No data available.

Driving force for implementation

Economic benefits on reducing solvent usage by higher degree of containment and recovery.

Example plants

No information

Reference literature

[138, Hsu et al. 2006]

4.4 Bitumen production

4.4.1 Storage of bitumen products

Description

Bitumen should be stored in proper storage tanks normally under heating conditions and insulated. Bitumen is generally not handled as a solid. Loading and unloading of the tank is typically done as follows: when the tank is filled, nitrogen does not flow to the tank, and the pressure is lowered by letting part of the gas go to the atmosphere; when the tank is unloaded on a low speed, a small amount of nitrogen is led to the tank; however, when the speed of unload is higher, higher amounts of nitrogen must be used. If the tank is equipped with a cleaning system, it is mechanically very simple and easy to clean. More information on storage is available in Section 4.21.

Achieved environmental benefits

For preventing fire due to autoignition of condensed vapours, tanks containing oxidised bitumen are equipped with nitrogen blanketing and pressure/vacuum safety valves. These valves need maintenance due to the slime. In some cases, these valves may be removed and a gaseous overhead treatment scheme is used. As an example see new unit (2010) in CEPSA Huelva (Spain).

Cross-media effects

Hydrocarbons and sulphur compounds may emanate from leakages (particularly in overhead systems) and pressure relief valves and in the form of liquid droplet-containing aerosols from the venting of tanker top-loading operations.

Operational data

Electricity, hot oil and low pressure steam can be used for heating. The heat exchanger can be inside the tank or outside the tank, in which case bitumen is circulated through it. Differences in temperature should not be too high due to the surface temperature and coking.

Applicability

The storage of bitumen products is done in refineries that have bitumen production. Prevention techniques, as mentioned, are typically applied.

Economics

None available.

Driving force for implementation

For safety, i.e. to prevent accidents, bitumen tanks are equipped with nitrogen blanketing and a pressure/vacuum safety valve.

Example plants

Some refineries in Europe use the techniques mentioned here. There is a recent unit (2010) at Huelva (Spain).

Reference literature

[207, TWG 2001].

4.4.2 Techniques to control emissions to the air

4.4.2.1 Treatment of the gaseous overheads

Description

Oxidiser overheads can be routed to a scrubber rather than direct water quenching for contaminant removal prior to incineration. The off-gases are condensed in a scrubber, where most of the hydrocarbons are eliminated. The water vapour (sometimes after full condensation) is left in the air stream to incineration at a temperature of approximately 800°C.

Achieved environmental benefits

Reduction of H₂S, SO₂, SO₃, CO, VOC, particulates, smoke and odour emissions.

Cross-media effects

Additional contaminated water. Scrubber water is dirty and requires oil and solids separation prior to reuse as desalted wash water and/or biotreatment. The sour water from the scrubber is routed to a sour water stripper and stripped prior to reuse and/or purification.

Applicability

Typically applied to overheads from the bitumen blowing systems.

Example plants

Many plants in Europe, e.g. recent unit (Biturox design - 2010) in CEPSA Huelva (Spain), use a gaseous overhead treatment scheme.

Reference literature

[174, HMIP UK 1995].

4.4.2.2 Use the heat from incondensable products and condensates

Description

Both incondensable products and condensates from the separator, hydrocarbon and aqueous unit, can be burnt in a purpose-designed incinerator, using support fuel as necessary or in process heaters.

Oxidiser overhead slop oil can also be treated in the sludge processing or recycled in the refinery slop oil system.

Achieved environmental benefits

Reduction of emulsion of light oil, water and particulates. Another environmental benefit is the removal of odorous incondensables which are difficult to treat elsewhere.

Cross-media effects

On scrubbing, aerosols can give rise to plugging. Water streams can become contaminated. In a well-operated unit, SO₂ or odour from the incineration of bitumen-blowing incondensables do not pose any problem.

Operational data

The incinerator should operate at a temperature of at least 800 °C and the combustion chambers should have a residence time of at least 0.5 seconds. The oxygen concentration at the combustion chamber outlet should be greater than 3 % v/v. Low-NO_x burners can be fitted in these incinerators.

Applicability

Widely used to get rid of bitumen fumes. Incondensable and/or condensates can be burnt in process heaters. However, they should be treated or scrubbed to remove compounds of sulphur or combustion products that may cause odours or other environmental problems.

Driving force for implementation

Reduction of odours, sludge and oily waste.

Example plants

Many bitumen oxidisers have associated facilities to handle gas and liquid wastes.

Reference literature

[174, HMIP UK 1995]

4.4.2.3 Treatment of vents from the storage and handling of bitumen materials

Description

Techniques that may be applied to prevent VOC emissions and odours include:

- venting of odorous gases during the storage of bitumens and the venting of tank blending/filling operation to an incinerator;
- the use of compact wet-type electrostatic precipitators which have been proven capable of successfully removing the liquid element of the aerosol generated during the top-loading of tankers;
- adsorption on activated carbon.

Achieved environmental benefits

Reduction of emissions of sulphur compounds, VOC, particulates, smoke and odour emissions.

Cross-media effects

Energy consumption and, in the case of a wet ESP, waste generation.

Operational data

In the waste gas of a cleaning unit, a mass concentration of VOC of a total of 150 mg/Nm³ can be complied with. In the waste gas of an incineration plant, a mass concentration of VOC, given as total C, of a total of 20 mg/Nm³ can be complied with (half-hourly mean values attainable in operations).

Applicability

Fully applicable.

Driving force for implementation

Reduction of emissions and nuisances.

Reference literature

[174, HMIP UK 1995], [167, VDI 2000]

4.4.2.4 Sulphur dioxide abatement and sulphur recovery units

Description

SO_x abatement techniques and sulphur recovery units (SRU) are techniques to reduce sulphur emissions. They are extensively documented in Section 4.23

4.4.3 Waste water pretreatment techniques

Description

Oxidiser overhead waste water accumulated in the overhead condensate collection drum can be sent to a sour water stripper prior to sending it to the effluent water treatment facilities. In some particular schemes, water from the oxidiser is not suitable for the SWS and is directly sent to the WWTP. More information on waste water treatment is available in Section 4.24.

Achieved environmental benefits

The stripping reduces the H₂S, oil, aromatics, volatile PAHs, sulphuric acid and odorous oxidation products (ketones, aldehydes, fatty acids) in the sour waste water reducing the charge to the central waste water system of the refinery.

Cross-media effects

An increase in oil and particulates load to the sour water stripper.

Operational data

None available.

Applicability

Typically applied to waste water from bitumen blowing.

Economics

None available.

Driving force for implementation

Reduction of the pollutant charge to the refinery waste water.

Reference literature

[174, HMIP UK 1995], [207, TWG 2001].

4.4.4 Hot oil system

Description

When the bitumen production units have a single energy system, the introduction of clean-up facilities in the flue-gases is more cost-effective. More information is available in Section 4.23 and 4.3.8.

Hot oil systems using oil as a medium by heating coils are used for maintaining bitumen fluid during storage.

4.5 Catalytic cracking

4.5.1 Hydrotreatment of feed to the catalytic cracker

Description

Hydrotreatment of feed to the catalytic cracker operates at similar conditions as those for fuel oil and atmospheric residue hydrotreatment (see Sections 2.13 and 4.13). In a growing number of refineries in particular, an hydrotreating or hydrocracking unit is added upstream of the FCC unit, mainly for the purpose of producing low-sulphur gasoline and diesel (<10 ppm) and for optimising the process configuration towards the maximisation of heavy residue conversion and middle distillate production. Simultaneously, this additional treatment also benefits the reduction of FCC emissions, leading to a substantial abatement of SO₂. There are also effects on NO_x but they will be driven more by regenerator temperature and combustion dynamics.

Achieved environmental benefits

FCC feedstock hydrotreatment can reduce the sulphur content to <0.1 – 0.5 % w/w (depending on the feedstock). Given that around 9 % of this sulphur content is normally emitted in the regenerator flue-gas, emissions of SO₂ from the regenerator can be reduced by up to 90 % as a consequence of the hydrotreatment. The resulting flue-gas daily average concentration can remain in the range of 25 – 600 mg/Nm³ (3 % O₂) depending on the feedstock. One refinery reported values over 600 mg/Nm³ associated with fluctuations of sulphur content around 0.5 %. It is reported that the yearly average concentration can be decreased to as low as 89 mg/Nm³ (3 % O₂) [54, Gallauner et al. 2009].

Nitrogen compounds can also be reduced by up to 75 – 85 % (smaller percentage for the partial combustion mode), although a certain reduction of nitrogen compounds does not lead to an equivalent NO_x reduction (when it occurs, a maximum NO_x reduction of approximately 50 – 60 % is achieved from a 70 – 80 % nitrogen reduction in the feedstock). The resulting flue-gas daily average concentration can remain in the range 50 – 180 mg/Nm³ (3 % O₂) depending on the feedstock, with a yearly average concentration as low as 71 mg/Nm³ (3 % O₂) [54, Gallauner et al. 2009].

This process also reduces the metal emissions (e.g. Ni, V) to the air and prolongs the life of the catalytic cracker catalyst.

Another benefit of this technique is a lower concentration of mercaptans in the products. This may impact the next process stage which is the mercaptan removal. This reduces the amount of used caustic and emissions into water.

Cross-media effects

Cross-media effects include the increase of energy consumption and the consequent increase in CO₂ emissions, due mainly to the hydrogen, as discussed in Section 3.14. As an illustrating example, the overall energy consumption of a refinery increased from approximately 2 to 2.5 GJ/tonne refined after the addition of an hydrocracker (3 Mt/yr) and a complementary steam methane reforming H₂ production plant (220 000 t/yr).

Nevertheless, as hydrotreatment is generally required for products specification compliance, assessing the corresponding cross-media effects requires taking into account the already existing ones.

As discussed in Section 4.13, hydrotreatment processes generate catalysts for disposal and increase the H₂S production, with direct consequences for the sour water stripper and sulphur recovery units (which may need to be enlarged or replaced). In addition, heavy metals in FCC feedstock will be shifted from the FCC to the hydrotreater catalyst. Deep hydrotreatment, by reducing the metal content, may also lead to a reduced performance of the ESP (see section 4.5.5.2).

Operational data

The sulphur removal efficiency achieved by hydrotreatment depends on the boiling range of the catalytic cracker feed. The heavier the feed, the more energy is required for the same sulphur removal efficiency. The water used for the different catalytic sections yields 20 - 40 m³/h of sour water.

The proportion of catalytic cracker feed that is hydrotreated varies by quite a lot depending on the refinery configuration and strategy. The several sources of feed include:

- vacuum gas oil fraction 375-560 °C (main source)
- atmospheric distillation fraction (> 375 °C)
- other streams including imported.

Data on the effect of the feedstock hydrotreatment on the cracker's PM emissions have also been provided in Table 3.38.

The following graphs (Figure 4.1 and Figure 4.2 below) show the performance obtained after the commissioning, in mid-2005, of a new 1 Mt/yr hydrocracking unit upstream to a 1.5 Mt/yr FCC unit in a European refinery. The average emission from the FCC unit fell from a yearly average of 1 650 to 670 t/yr (- 60 %) while the corresponding average sulphur content in its feedstock decreased from 1.5 – 1.7 % to 0.25 – 0.35 %. For this particular application, the related specific consumption of hydrogen is in the range 8 – 9 kg H₂ per tonne of hydrotreated feedstock.

Applicability

Fully applicable. This process is more cost-effective when sufficient hydrogen, SWS and SRU capacities are already available in the refinery. The main driving force for the application of this technique is nevertheless the optimisation of the refinery configuration.

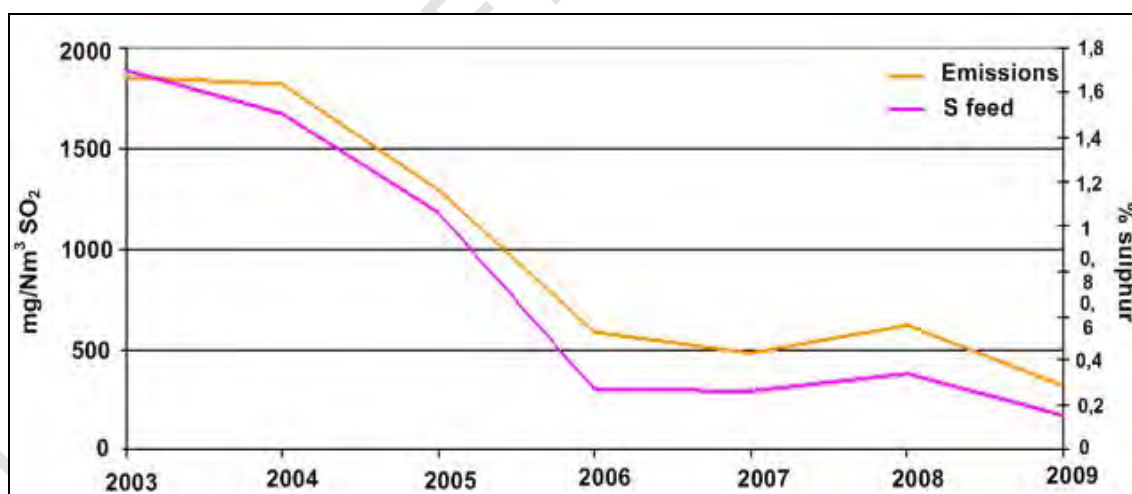


Figure 4.1: Evolution of the feed S content and SO₂ emissions after FCC feed hydrotreatment

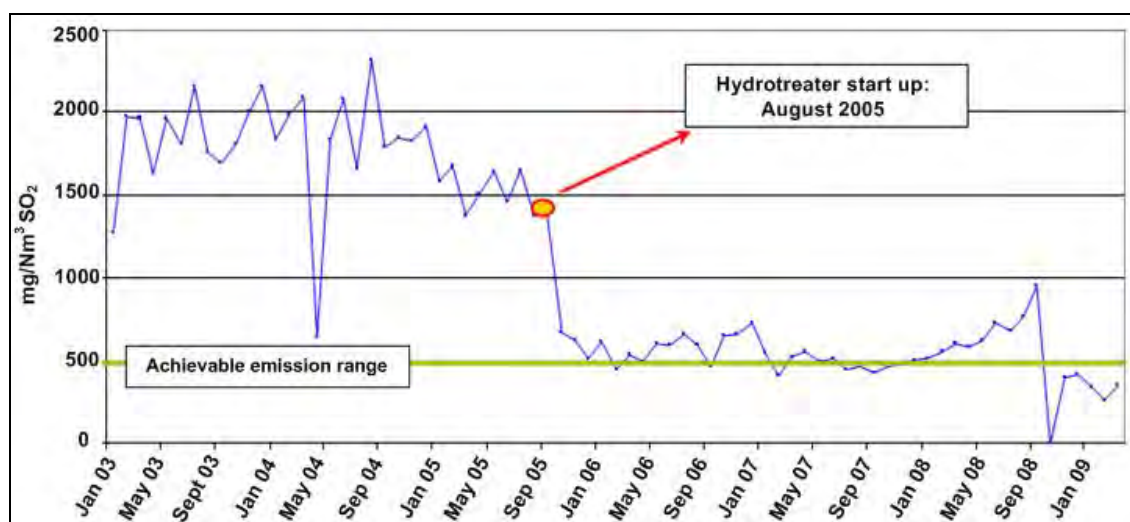


Figure 4.2: Monthly average SO₂ emissions after FCC feed hydrotreatment

Economics

Table 4.10 and Table 4.11 give examples of costs associated with FCC feedstock hydrotreatment.

Table 4.10: Catalytic feed hydrotreatment (typical feeds being atmospheric residue and vacuum gas oil) - Costs updated by CONCAWE, 2010

Size/capacity (ktonnes/yr)	Typical capital/installed cost (EUR million) costs include necessary interconnections to existing plant for integration purposes.	Operating cost (EUR million/yr)
1 250	198	9
2 500	303	17
3 750	394	26

NB: The cost assumes that there is adequate space and an existing SRU (sulphur recovery unit) and sour water stripping capacity. If further hydrogen production is needed, a new hydrogen plant for a 2 500 kt/yr FCC UNIT feed hydrotreater or hydrocracker would typically cost in the range of EUR 60 - 75 million

Sources: [163, FWE 1999], CONCAWE 2010

Table 4.11: Cost ranges associated with the hydrotreatment of a 1.5 Mt/yr FCC unit according to some typical configurations

Cost parameters	Distillate feed desulphurisation	Residue feed desulphurisation	Feedstock hydrotreating to reduce NO _x
Capacity of process	1.5 Mt/yr	1.5 Mt/yr	1.5 Mt/yr FCC UNIT with CO Boiler
Investment expenses (EUR million)	80 – 100 ⁽¹⁾ 45 – 50 ^(1,2)	200 – 300 ^(2,3)	80 – 100
Operating expenses (EUR million/yr)	4 – 9	15 – 25 ⁽³⁾ 30 – 50 ²	4 – 9

(¹) Excluding H₂ production and H₂S handling facilities
(²) [151, Sema,Sofres 1991]
(³) [166, CONCAWE 1999].

A recent example (questionnaire 36) of the hydrotreating of 56 % of a 1.5 Mt/yr FCC unit feedstock gives the following costs:

- Total investment (2005): EUR 230 million, including the three treatment units (cumulated capacity of 1.05 Mt/yr), the necessary adaptation of the FCC, and the related SRU unit and acid water treatment plant;
- Energy costs: EUR 7.15/t of treated feedstock (2009);
- Approximate hydrogen costs (annual): EUR 0.5 million (fixed term) + EUR 1 420/t of hydrogen supplied (2009), with a specific consumption of 8 – 9 kg H₂/t of treated feedstock;
- The total operating cost (including H₂ fixed term) is EUR 7.75/t of treated feedstock, and the corresponding specific cost is 6 640 EUR/t of SO₂ avoided.

In another example (questionnaire 32), the following data is provided for the hydrotreatment of a 3Mt FCC feedstock:

- SO₂ emissions reduced by 3.7 kg/t of treated feedstock;
- Related consumptions are 9.6 kg of H₂, 30.8 kWh of electricity, and 556 MJ of fuels per tonne of treated feedstock;
- The total operating cost is estimated to EUR 19.3 per tonne of treated feedstock, and the corresponding specific cost is 5200 EUR/t of SO₂ avoided.

Note: the operating costs of hydrotreatment should also partly be affected by the improvement of the product characteristics as ultimately this is its main objective.

Driving force for implementation

The implementation of this technique is typically product-specification driven because higher conversions are achieved with hydrotreated feedstocks. The majority of the products produced by the catalytic cracker without previous hydrotreatment need further treatment to comply with product specifications. Moreover, the flue-gas from the regenerator contributes significantly to the overall refinery SO_x/NO_x emissions. Desulphurisation or mild hydrocracking of the feed is an option to reduce these emissions.

Example plants

Many examples: 16 out of the 56 European sites reported by TWG members were said to use this technique.

Reference literature

[220, IFP 2000], [166, CONCAWE 1999], [163, FWE 1999], [151, Sema,Sofres 1991], [191, UBA Austria 1998], [221, Italy 2000], [207, TWG 2001], [Specific attachments to Questionnaires n° 31, 32, 36, 39], [270, CONCAWE 2012].

4.5.2 Waste heat boiler and expander applied to the flue-gas from the FCC regenerator

Description

Heat recovery from the regenerator flue-gas is conducted in a waste heat boiler or in a CO-boiler. Heat recovery from the reactor vapour is conducted in the main fractionator by heat integration with the unsaturated gas plant, as well as by feed preheating and by the generation of steam with the residual heat from product run down streams and pump-around streams. The steam produced in the CO boiler normally balances the steam consumed in the FCC. Installing an expander in the flue-gas stream from the regenerator can further increase energy efficiency. Figure 4.3 gives a simplified scheme of application of a waste heat boiler.

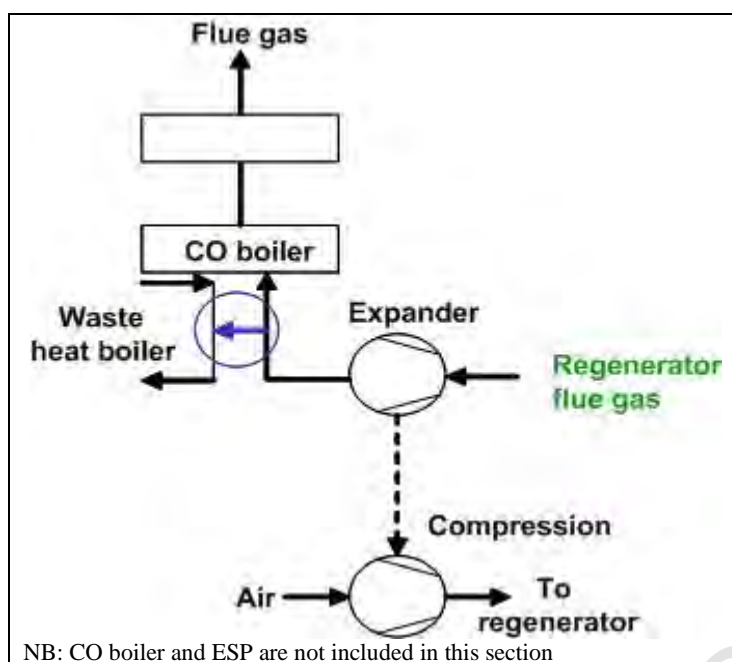


Figure 4.3: Waste heat boiler and expander applied to the regenerator flue-gas of a catalytic cracker

Achieved environmental benefits

The waste heat boiler recovers the heat from the flue-gas and the expander recovers part of the pressure for use in the compression of the air needed in the regenerator. An example of the application of an expander saved 15 MW_e from the flue-gas generated by a FCC of a capacity of 5 Mt/yr.

Cross-media effects

Significant quantities of catalyst fines are collected in the waste heat boiler (WHB). The newer WHBs avoid catalyst arrival by using configuration which include e.g. cyclones or have facilities which permanently remove the collected fines (e.g. sonic soot cleaners), but older WHBs are normally soot-blown once per shift. During heating surface cleaning (or soot blowing) in CO boilers, emissions of PM and metal can increase by about 50 %.

Examples of three German refineries where ESPs are installed downstream of the FCC are shown in Table 4.12.

Table 4.12: Examples of soot blowing effects for 3 German refineries

Reference	Capacity	Feed	Mode	PM		Metals ⁽²⁾ ⁽³⁾	
				Conc ⁽¹⁾ (mg/Nm ³)	Flux (kg/h)	Conc ⁽¹⁾ (mg/Nm ³)	Flux (g/h)
Refinery 1	82 %	Atmospheric residue, unconverted gas oil	Normal	11.7	1.07	0.091	8.4
			<i>Soot blowing</i>	<i>18.7</i>	<i>1.71</i>	<i>0.140</i>	<i>12.9</i>
Refinery 2	79 %	Atmospheric residue, heavy and light waxes	Normal	6.70	0.53	0.076	6.1
			<i>Soot blowing</i>	<i>10.2</i>	<i>0.80</i>	<i>0.115</i>	<i>9.0</i>
Refinery 3	79 %	NA	Normal	6.70	0.95	0.033	3.5
			<i>Soot blowing</i>	<i>9.70</i>	<i>1.43</i>	<i>0.052</i>	<i>7.7</i>

⁽¹⁾ Concentrations are mean values (3*30 minutes) in mg/Nm³ at 3 % O₂ (dry gas), based on the continuous emission monitoring system.

⁽²⁾ Metals include Ni except for Refinery 1 where it includes Ni, Cu, V.

⁽³⁾ Metals determined from PM constituents deposited on quartz filters according to national requirements.

Source: TWG 2010

Operational data

Energy recovery from the regeneration gas reduces the CO boiler duty, but contributes to an overall higher energy recovery from the FCC.

Applicability

Retrofitting of this equipment can be very difficult because of space limitations in the refinery. For small or low pressure units, expanders are not justified economically.

Economics

Applying an expander on the regenerator gas could be costly because of the additional high temperature particulate systems required. Turbo expanders are costly items and so are waste heat recovery units.

Driving force for implementation

Recovery of energy.

Example plant(s)

Energy recovery by utilising an expander in the regenerator flue-gas is only applied in the larger, more recently built units.

Reference literature

[172, MRI 1997], [207, TWG 2001], [263, TWG 2010].

4.5.3 Catalyst selection**Description**

Techniques to consider include:

- Use of a higher quality FCC catalyst. Process efficiency and metal tolerance (to V and Ni in particular) can be increased, while catalyst waste can be reduced and the rate of replacement reduced.
- Use of an attrition-resistant catalyst to reduce the amount of catalyst added on a daily basis and the reduce emission of particulates from the regenerator. Emissions reductions result from both a decrease in the small particulate emissions from the fresh catalyst, as well as from the catalyst resisting attrition during unit operations. These catalysts are typically alumina-based (Al-sol binder technology) and particulates arising from their use are much harder than from the silica-based former catalyst generation.

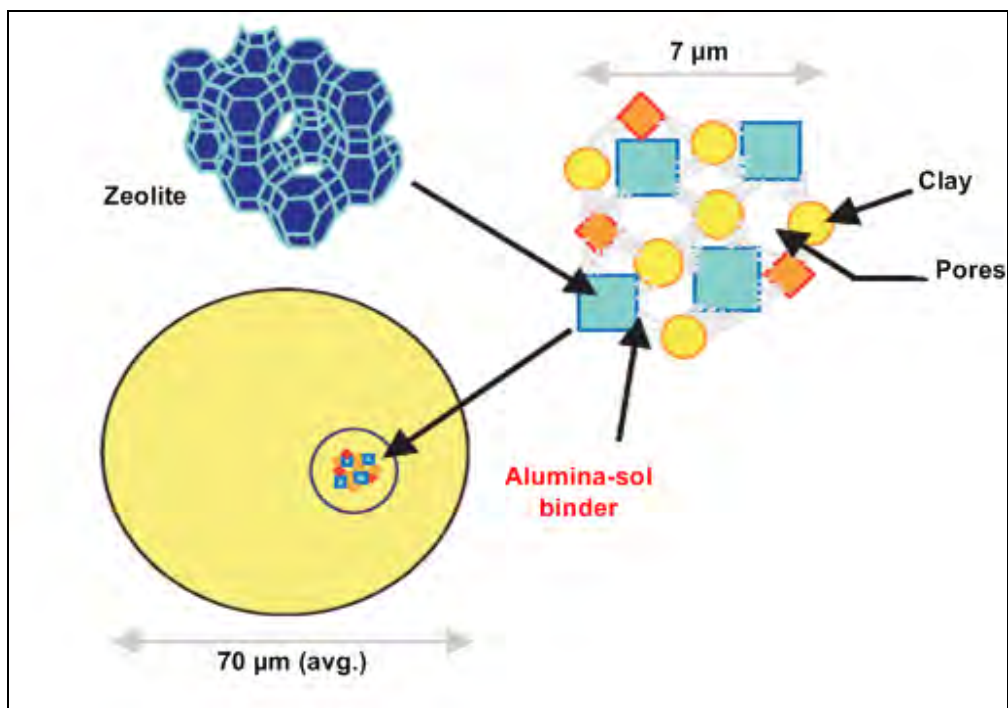


Figure 4.4: Typical structure of a low attrition catalyst for FCC process

Achieved environmental benefits

A good selection of the catalyst used in the FCC process can:

- increase the FCC efficiency by up to 20 %, coke production can be decreased and catalyst waste can be reduced;
- increase the recyclability of the catalyst;
- reduce the particulate content of flue-gas before treatment to 300 mg/Nm³.

Cross-media effects

None in particular.

Operational data

Based on data available from a 100-day trial [24, Bruhin et al. 2003], switching from a Si-sol catalyst to an Al-sol catalyst can reduce PM emissions (considered at constant % O₂) by up to 50 % after a transitory period of 50 – 100 days.

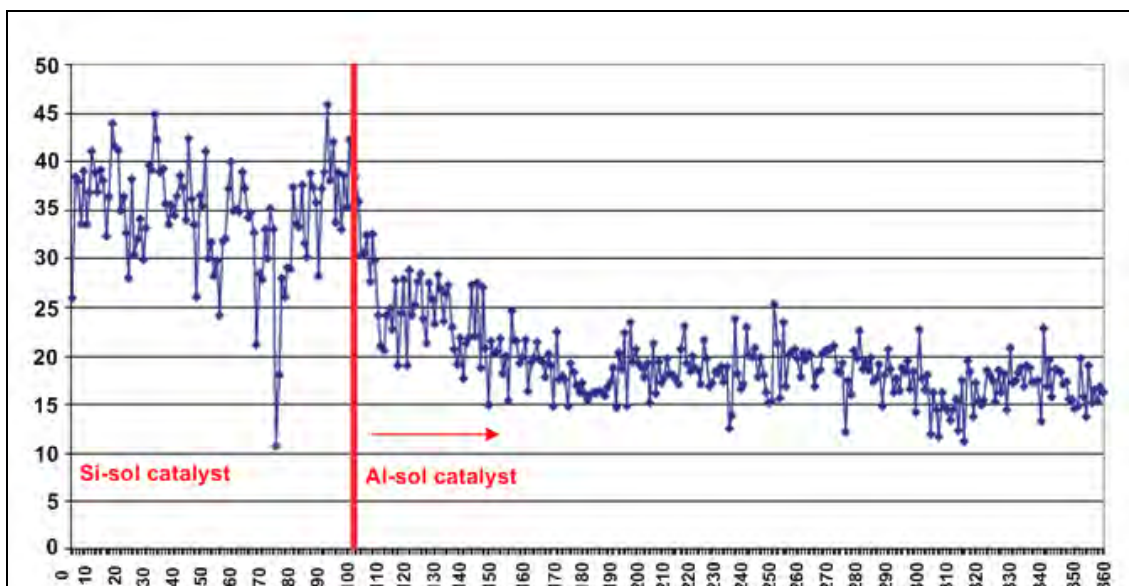


Figure 4.5: Effect of a low attrition catalyst on PM emissions (mg/Nm^3) after 100 days

Applicability

If not yet optimised, a change in the catalyst is usually favoured. In exceptional cases, however, it may have an adverse effect on the performance on the FCC.

Economics

Investment expenses: none.

Operating expenses: negligible.

Driving force for implementation

Process requirements and reduction of finest size PM emissions.

Example plants

Most FCC units in Europe have already optimised catalyst selection.

Reference literature

[156, MCG 1991], [166, CONCAWE 1999], [24, Bruhin et al. 2003].

4.5.4 Nitrogen oxides abatement techniques

This section includes NO_x abatement techniques that may be applied to FCCs. Among these are process-related techniques, which are very specific and mostly involve the reduction of NO_x by using or improving various catalysts and additives and by acting on the three major sources of nitrogen in the FCC regenerator: nitrogen compounds in the coke resulting from the feed, nitrogen from air admitted in the regenerator, and nitrogen from the combustion air to CO boilers in the case of partial-burn units. A strong relationship is observed between NO_x and excess O₂ in the flue-gas, and a poor distribution of O₂ in the regenerator bed can result in large variations of local scale NO_x formation.

4.5.4.1 Selective catalytic reduction (SCR)

Description

See Section 4.23.3.3.

Achieved environmental benefits

For FCC application, inlet NO_x concentrations to the SCR may vary from 200 – 2 000 mg/Nm³ at 3 % O₂, depending on the type of FCC used (total or partial combustion in combination with a CO boiler) and the type of feed used (heavier feed tends to produce higher NO_x emissions). A reduction of up to 80 – 90 % of NO_x emissions with the outlet concentration of NO_x reduced to 20 – 250 mg/Nm³ at 3 % O₂ can be achieved, depending on the inlet concentration. As an example, such reduction efficiencies may correspond to saving approximately 300 tonnes of NO_x per year from a catalytic cracker with a capacity of 1.65 Mt/yr (calculation based on an average of 450 mg/Nm³ inlet and 50 mg/Nm³ outlet, with a 0.7 10⁹ Nm³/yr waste gas flow).

Most SCR systems include an upstream section with a CO oxidation catalyst that shares SCR installation and achieves up to 95 % CO conversion to CO₂. In SCR systems not equipped with a CO oxidation catalyst, small conversions to CO₂ occur when CO reacts with NO and generates molecular nitrogen.

Cross-media effects

See Section 4.23.3.3. Concerning, more specifically, FCC units, the application of an SCR may reduce the potential for energy recovery using expander turbines, as it increases the pressure drop over the regenerator overhead circuit and is also prone to a build-up of pressure drop over time, thereby limiting the available operating window for a turbine expander, particularly in existing facilities with fixed pressure profiles. This may lead to a lower thermal efficiency.

Operational data

Catalyst performance and the pressure drop of SCR operated on FCC units are expected to deteriorate over time, mainly due to fouling by PM catalyst fines and SO_x salts. The theoretical expected catalyst lifetime is about four years but could be much different, depending on the PM filtering efficiency upstream of the SCR and the operating conditions. The two following examples are very illustrative on this respect.

- Intensive fouling has been experienced and deeply analysed in one European site: as seen in Figure 4.6, this is was mainly due to an excessive inlet gas temperature (most of time above 362 °C and part of time above 370 °C), which drove the operator to increase the NH₃ injection rate up to 120 % of the theoretical stoichiometry, in order to compensate the poor conversion.
- On the other hand, current examples in Europe have shown lifetimes well over the expected ones, reaching six to seven years and even much longer. In one particular case, the first three SCR catalyst layers installed at Preem Lysekil refinery (SE) in 1994 (and also the 4th one installed in 2003) were still in operation in 2010. Based on the latest tests, a lifetime of 140 000 to 150 000 hours is expected.

SCR applied below design loads and careful de-dusting of the inlet gas upstream of the SCR help to increase catalyst lifetimes. Particle size distribution and particulate load of the flue-gas entering the SCR should be evaluated to determine whether there is a potential for fouling (high particulate) and/or thermophoretic fouling (small particulates). If necessary, particulate mitigation equipment, such as sootblowers, may need to be installed. More general operational data for SCRs can be found in Section 4.23.3.3.

Table 4.13 illustrates the results obtained for some FCC units equipped with SCR treatment.

Table 4.13: Performances reported as obtained with SCR for six FCC units

Data-set reference [Questionnaire]	Type	Inlet	Outlet	% NO _x abatement	Ammonia slip	SCR shutdown frequency/Other information
CONCAWE 1 ⁽¹⁾ (²)	Full combustion with auxiliary fired boiler	36 – 244	2 – 26	88 %	–	4 years
CONCAWE 2 ⁽¹⁾ (²)	Full combustion unit	25 – 211	3 – 13	91 %	–	7 – 17 months
CONCAWE 3 ⁽¹⁾ (²)	Partial-burn with CO boiler	318	99	85 % (<70 % at end of run)	–	4 years
[n° 27] ⁽³⁾	Full combustion unit	–	249.6	79.1 %	–	– 1 351 t avoided (2006)
US refinery CITGO Lemont (IL)	NA	200 ppmv	< 20 ppmv (⁴)	90 %	–	Commissioned 2008 Wet-gas scrubber is in place downstream the SCR
US refinery SHELL Deer Park (TX)	NA	200 ppmv	< 20 ppmv (⁴)	90 %	Not measurable	Commissioned 2004 Flue-gas desulphurisation is in place downstream the SCR

⁽¹⁾ Daily average in mg/Nm³ at 3 % O₂ (dry gas), based on the continuous emission monitoring system.

⁽²⁾ Averages are calculated from the 5th – 95th percentile range of the complete available data-set.

⁽³⁾ Yearly averages in mg/Nm³ at 3 % O₂ (dry gas), based on the continuous emission monitoring system.

⁽⁴⁾ 365-day average based on the continuous emission monitoring system expressed as ppmv at 0 % O₂ 20 ppmv NO_x is around 32 mg/Nm³ at 3 % O₂

Sources: 1 – 3 : CONCAWE; 27: TWG 2010 data collection; US refineries: [140, Jensen-Holm et al. 2010.]

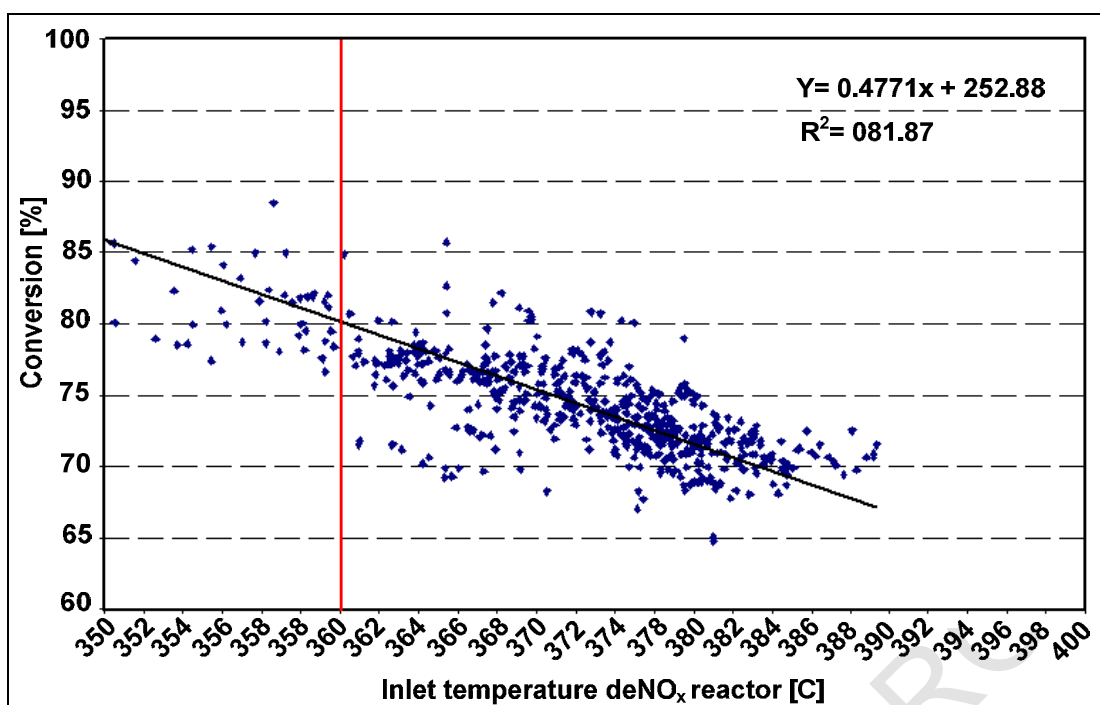


Figure 4.6: SCR conversion yield as a function of inlet temperature for a European FCC unit

Applicability

Because the temperature window is wide (300 – 400 °C), an SCR is relatively flexible for FCC retrofit applications. However, existing auxiliary fired boilers, CO boilers and waste heat boilers may have to be modified for temperature adjustment.

Considerable space is needed for the installation. SCR applications often require a new waste heat boiler (full burn) or a CO boiler (partial burn) if they are not present. Preferably the NO_x reduction unit is integrated into the waste heat boiler. Because an SCR operates at oxidising conditions, it cannot be installed upstream of a CO boiler (partial burn).

As the SCR catalyst could potentially be fouled by the particulates present in the flue-gas stream, additional filtering might be required upstream of the new SCR unit.

As for an SNCR, the ammonia dosing rate is limited by the potential risk of corrosion downstream of the unit.

Economics

Table 4.14 shows some examples of the economics of the application of SCR to FCCs.

Table 4.14: Economics of SCR applied to FCC units

Size of the FCC (Mt/yr)	Efficiency (%)	Outlet NO _x concentration (mg/Nm ³)	Installation cost (EUR million)	Operating and maintenance cost (EUR million/yr)	Specific removal cost ⁽⁴⁾ (EUR/t of NO _x removed)
1.65	90	40	3.8 (SEK 33 million) ⁽¹⁾ ⁽²⁾	0.24 (SEK 2 million) ⁽³⁾	2103
1.5	85	120	6.3 - 13	0.4 – 0.8	2023
1.5	85	37.5	1.2 – 3.6 ⁽⁵⁾	0.12 – 0.48	2042

⁽¹⁾ Cost in original currency – Built 1994.

⁽²⁾ Including an SCR reactor, ammonia storage and injection facilities and initial fill of catalyst.

⁽³⁾ Operation and maintenance cost including ammonia, steam and replacement of catalyst.

⁽⁴⁾ Including a CO boiler.

⁽⁵⁾ Using the same economic analysis presented in Table 4.15.

NB: All costs for a new SCR installation.

In addition, recent cost data for using SCR and SNCR are shown in Table 4.17. A more detailed economic assessment of a SCR in a FCC unit (year 2000) is shown in Table 4.15.

Table 4.15: Main cost factors for a selective catalytic reduction (SCR) installation (raw gas) after the FCC plant

Cost parameters	Quantity	EUR/unit	EUR/yr
Operating hours (h/yr)	8 000		
Investment costs (EUR million)	1.45		
Input factors for annual expenditure:			
Number of years	15		
Rate of interest (%)	6		
Annual repayment incl. interest (EUR/yr)	150 000		
Proportional investment costs incl. interest			150 000
Volume of catalyst (m ³)	20		
Duration (years)	8		
Renewal of catalyst (m ³ /yr)	2.5	EUR 15 000/m ³	
Average renewal of catalyst (EUR/yr)	36 300		
Catalysts			36 300
Maintenance + wear and tear (% of investment costs)	2		
Maintenance + wear and tear (EUR/yr)	29 000		
Maintenance + wear and tear			29 000
Pressure drop (mbar)	8		
Energy for reheating (MJ/h)	0	EUR 3.6/GJ	0
Electrical energy (kWh/h)	88	EUR 0.065/kWh	46 000
NH ₃ liquid (kg/h)	36.96	EUR 0.25/kg	75 200
Total costs			336 269
NB: In a refinery with a volume of exhaust gas of 100 000 Nm ³ /h achieving a NO _x emission reduction of 1 000 mg/Nm ³ in relation to actual oxygen content and for a clean gas concentration of <200 mg NO _x /Nm ³ . The inlet concentration may vary between 200 – 2 000 mg/Nm ³ at 3 % O ₂ . The outlet concentration of NO _x is reduced to 80 – 120 mg/Nm ³ by SCR.			

See also Table 4.18 for a cost comparison of various techniques.

Based on the CONCAWE 6/11 report, the costs (2011) for a 2Mt/yr unit are estimated as follows (see Annex 9.3):

- Capital costs: EUR 50 – 75 millions
- Annual cost : EUR 6 – 14 millions
- Cost per avoided ton of pollutant: EUR 25 000 – 60 000/t NO_x

A preliminary evaluation for the retrofitting of a 57 500 bpd (3Mt/yr) FCC with an SCR gives the following costs (2007):

- Capital cost: GBP 15 million (EUR 22.2 million on 2/07/2007)
- Operating cost: GBP 0.54 million per year (EUR 0.80 million per year)
- Estimated quantity of NO_x abated: 80 t/yr (assumed reduction yield of 50 %)
- Equivalent annual cost: GBP 34 079, (EUR 50 442) per t/yr of NO_x abated (15-year lifetime assumed).

Driving force for implementation

Reduction of NO_x emissions.

Examples plants

At least six SCR's are in operation in FCC's worldwide and two in Europe: Preemraff Lysekil (Sweden) and Shell in Pernis (Netherlands).

Reference literature

[160, Janson 1999], [151, Sema,Sofres 1991], [198, UKPIA 2000],[191, UBA Austria 1998], [166, CONCAWE 1999], [228, TWG 2000], [172, MRI 1997], [246, AL Group 2001], [17, Jeavons and Francis 2008], [Site questionnaires n°27, 39, 42], [139, CONCAWE 6/11 2011], [36, CONCAWE n°4/09 2009].

4.5.4.2 Selective non-catalytic reduction (SNCR)**Description**

See Section 4.23.3.2 for a general description of the SNCR technique.

Achieved environmental benefits

On FCC units, this technique achieves NO_x reduction levels from 30 % to 50 % and has shown to be able to achieve NO_x reductions of up to 70 % (on a daily basis). The outlet concentrations can be as low as < 100 – 200 mg/Nm³ at 3 % O₂ depending on the nitrogen content of the feedstock.

Cross-media effects

See Section 4.23.3.2 for a description of the general cross-media effects of SNCR.

One issue of particular concern with SNCR applications to FCC units is the potential increase in CO emissions. At the lower end of the SNCR operating temperature range, ammonia can inhibit CO oxidation and increase CO emissions from low temperature CO boilers.

Operational data

Table 4.16 illustrates the results obtained for three FCC units equipped with a SNCR treatment.

Table 4.16: Performances reported as obtained with SNCR for three FCC units

Data-set reference	Type	Inlet	Outlet	% NO _x abatement	Ammonia slip	Comments
CONCAWE 4	Full combustion with auxiliary-fired boiler	123 – 410	NA	23	<15	–
CONCAWE 5	Full combustion with auxiliary-fired boiler	90 – 530	50 – 180	50	8	95th Perc. abatement: 81 % (hourly)
CONCAWE 6	Partial combustion with CO boiler	318	99	67	10	95th Perc. abatement: 78 % (hourly)

NB: Daily average emissions in mg/Nm³ at 3 % O₂ (dry gas)
 Data based on continuous emission monitoring system.
 It is reported that % NO_x abatement is not unique and is dependent on the inlet concentration
 Source: CONCAWE 4/09

In a German refinery, the following data on a long time span are reported about an SNCR installed on a FCC unit:

- outlet NO_x concentration <100 mg/Nm³ (online measurements);
- outlet CO concentration <90 mg/Nm³;
- FCC unit with CO boiler in partial combustion;

- total nitrogen content of the FCC feed is about 1 200 ppm (determined by periodic feed analyses);
- ammonium flow 300 l/h (8 – 10 % concentration).

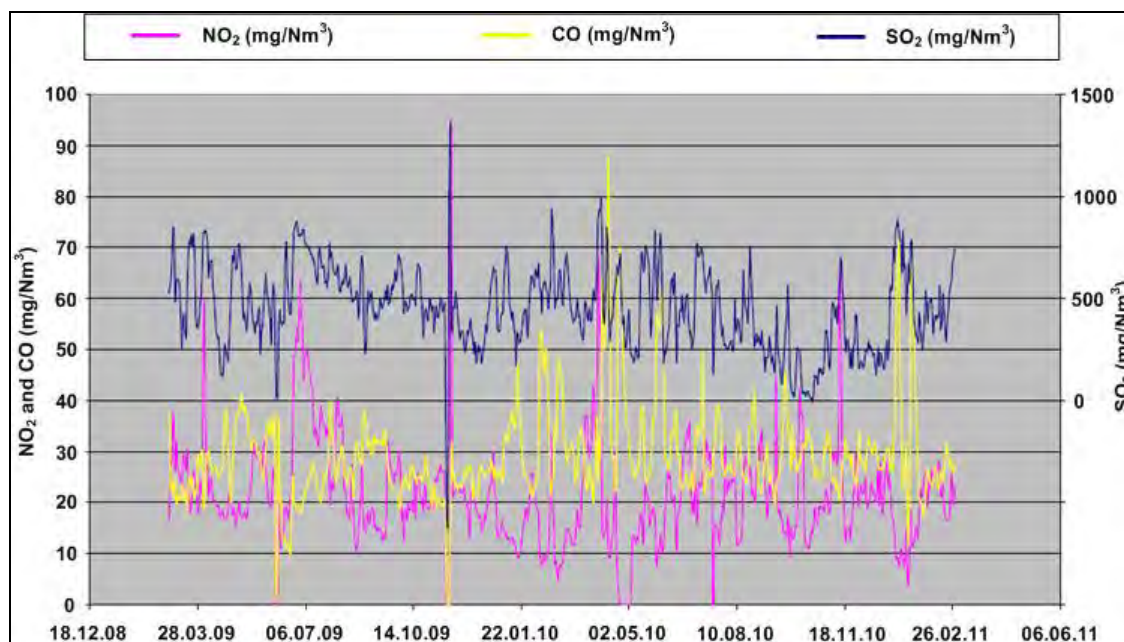


Figure 4.7: Emissions to air from an FCC unit with SNCR at a German refinery

Applicability

SNCR is applicable in partial combustion FCCs with CO boilers, and full combustion FCCs with auxiliary fired boilers, dependent on sufficient residence time in the boiler at the required temperature range. SNCR units cannot work properly during boiler shutdowns.

SNCR is also applicable to full combustion FCCs without auxiliary boilers, using hydrogen addition for injection into the regenerator overhead line. In this case, the application should take into account the unit specificity, including the starting process conditions.

Economics

An cost data for SCR and SNCR are presented in Table 4.17

Table 4.17: Economics of SCR and SNCR at FCC units – Cost effectiveness data from a sample of 6 FCC units

					Selective Non-Catalytic Reduction (SNCR)					Selective Catalytic Reduction (SCR)					
					Efficiency	ACC	Fixed OP	Variable OP		Efficiency	ACC	Fixed OP	Variable OP		
					45 %	7.4 %	4 % TEC/yr	0.37 €/tFF		85 %	7.4 %	4 % TEC/yr	0.18 €/tFF		
Base case in 2006 at 500 mg/Nm ³ NO _x					Outlet NO _x	NO _x Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to SNCR	Cost Effectiveness: Base to SNCR	Outlet NO _x	NO _x Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to SCR	Cost Effectiveness: Base to SCR	Incremental Cost Effectiveness: SNCR to SCR
Unit	Design Feed	Utilisation	Actual Feed	Outlet NO _x	mg/Nm ³	t/y	M€	k€/yr	€/tNO _x	mg/Nm ³	t/yr	M€	k€/yr	€/tNO _x	€/tNO _x
1	5 480	97 %	5 319	500	275	299	22.9	4 577	15 297	75	565	114.4	13 986	24 745	35 374
2	4 081	91 %	3 693	500	275	208	19.2	3 553	17 100	75	392	95.9	11 584	29 520	43 491
3	2 857	88 %	2 506	500	275	141	15.5	2 692	19 100	75	266	77.4	9 268	34 813	52 490
4	1 388	82 %	1 131	500	275	64	10.0	1 563	24 565	75	120	50.2	5 923	49 278	77 081
5	1 648	99 %	1 625	500	275	91	11.1	1 870	20 459	75	173	55.6	6 631	38 411	58 607
6	1 927	97 %	1 877	500	275	106	12.2	2 088	19 777	75	199	61.1	7 301	36 604	55 534
Base case in 2006 at 400 mg/Nm ³ NO _x					Selective Non-Catalytic Reduction (SNCR)					Selective Catalytic Reduction (SCR)					
Unit	Design Feed	Utilisation	Actual Feed	Outlet NO _x	Outlet NO _x	NO _x Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to SNCR	Cost Effectiveness: Base to SNCR	Outlet NO _x	NO _x Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to SCR	Cost Effectiveness: Base to SCR	Incremental Cost Effectiveness: SNCR to SCR
	kt/yr	%	kt/yr	mg/Nm ³	mg/Nm ³	t/y	M€	k€/yr	€/tNO _x	mg/Nm ³	t/yr	M€	k€/yr	€/tNO _x	€/tNO _x
1	5 480	97 %	5 319	400	220	239	22.9	4 577	19 121	60	452	114.4	13 986	30 931	44 218
2	4 081	91 %	3 693	400	220	166	19.2	3 553	21 375	60	314	95.9	11 584	36 900	54 364
3	2 857	88 %	2 506	400	220	113	15.5	2 692	23 875	60	213	77.4	9 268	43 516	65 612
4	1 388	82 %	1 131	400	220	51	10.0	1 563	30 706	60	96	50.2	5 923	61 598	96 351
5	1 648	99 %	1 625	400	220	73	11.1	1 870	25 574	60	138	55.6	6 631	48 014	73 259
6	1 927	97 %	1 877	400	220	84	12.2	2 088	24 721	60	160	61.1	7 301	45 755	69 418

Source: [139, CONCAWE 6/11 2011]

See also Table 4.18 for a cost comparison with other NO_x reducing techniques.

Driving force for implementation

Reduction of NO_x emissions with limited space requirements.

Example plants

Several applications are known, e.g. in Japan.

Reference literature

[166, CONCAWE 1999], [151, Sema,Sofres 1991], [228, TWG 2000],
[17, Jeavons and Francis 2008], [36, CONCAWE n°4/09 2009], [105, EPA 2002].

4.5.4.3 Low-NO_x CO oxidation promoters**Description**

There is little, if any contribution to NO_x from the thermal oxidation of N₂ in the catalytic cracking process itself, as the combustion in the regenerator takes place at reduced temperatures of less than 750 °C. In fact, NO_x released into the regenerator flue-gas is directly linked to the nitrogen contained in the feedstock. In the absence of feed nitrogen, no NO_x is formed and Pt-based CO promoters do not increase the overall emission from the FCC. Nearly half of the nitrogen in the catalytic cracker feed leaves the reactor as part of the coke laid down on the catalyst. Of the nitrogen in coke, about 80 % to 90 % is converted directly or indirectly to N₂ during regeneration, while the remaining nitrogen ultimately forms NO_x. Therefore, nitrogen oxides account for 5 – 10 % of the nitrogen introduced in the feedstock.

As shown in Figure 4.8, NO_x formation chemistry in the FCC regenerator is complex: the nitrogen in coke is pyrolysed and first appears in the regenerator as HCN or NH₃. These products are then oxidised in N₂, NO and NO₂, while a simultaneous reduction also takes place between NO and the available CO in order to regenerate gaseous N₂.

This technique only concerns the full combustion mode, where the aim is to burn the coke as fully and as efficiently as possible, and where conventional platinum-based CO combustion promoters are usually added which lower the CO concentration and enhance the oxidation of HCN, NH₃ and other reduced nitrogen intermediates to NO₂.

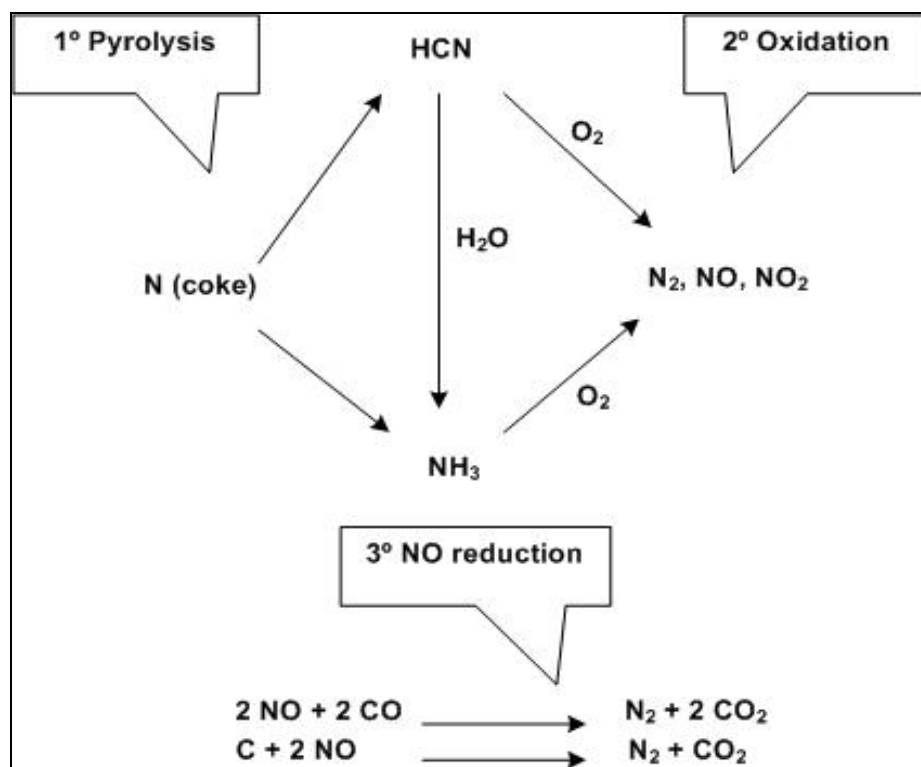


Figure 4.8: Simplified chemistry of the NO_x generation in FCC units

A first control option is to reduce the platinum load in the catalytic bed, either through minimising the addition rate or reducing the platinum content of the Pt-based CO promoter. However, as afterburning needs to be kept under control, this option can be limited.

Another alternative is to use low-NO_x non-platinum CO oxidation promoters. The non-platinum promoter selectively promotes the combustion of CO only and prevents the oxidation of the nitrogen which contains intermediates to NO_x. The addition rate of the non-platinum promoter is equal to two times that of the traditional platinum-containing promoter, depending on the regenerator operating conditions and excess oxygen level. The amount of non-platinum promoter is hence around 0.3wt % of the fresh FCC additive rate.

Achieved environmental benefits

Typical downstream effluent NO_x concentrations of 40 to 140 mg/Nm³ (daily average) at 3 % O₂ are reported for a feedstock nitrogen content of approximately 0.20 %. The amount of NO_x avoided depends on the amount of additive in the unit, but the removal efficiency is typically between 30 and 50 %.

When combining both low-NO_x non-platinum CO oxidation promoters and NO_x removal additives (see Section 4.5.8.4), or when using specific products which combine the two functions, structurally NO_x reduction of more than 80 % is achievable, depending on the added quantity.

Cross-media effects

None in particular.

Operational data

See Section 4.5.4.4.

Applicability

A low-NO_x non-Pt CO promoter is an option for NO_x reduction in full combustion FCC units already using a Pt-based CO promoter. It is not applicable at all for partial-burn FCC units. The

application of the additives is not specifically dependent on the FCC unit design. However, proper distribution of air in the regenerator is required to obtain the maximum benefit. No significant deterioration in unit performance is reported, nor any increase or decrease of the catalyst replacement rate. In addition, care must be taken to optimise the dosage of both Pt-based and non-Pt promoters to assure that the unit is not generating more NO_x.

Economics

Table 4.18 gives rough cost estimates reported for various control approaches for a typical 28 000 bpd (1.6 Mt/yr) FCC unit.

Table 4.18: Cost comparison of catalytic additives with other NO_x control techniques for FCC units

Technique	Expected efficiency (%)	Installation cost 2008 (USD million)	Operational cost 2008 (USD million/yr)	Specific removal cost (USD/tonne NO _x)
SCR	85	2.1 – 6.3	0.21 – 0.84	3 600
SNCR	60 – 80	0.6 – 2.6	0.09 – 0.70	3 000
Low-NO _x promoter ⁽¹⁾	40 – 70	–	0.32–1.76 (1)	1 200 – 3 600
Specific NO _x reduction additive	30 – 80	–	0.11 – 0.22	2 400 – 3 600

⁽¹⁾ Incremental cost compared with a Pt-based promoter.

In addition, cost data for using SCR and SNCR are detailed in Table 4.17.

The cost for removing NO_x with such a low-NO_x CO promoter will depend on the regenerator operating conditions and the actual mechanical design of the promoter. It is estimated that on average the cost will vary between EUR 1 to 5 per kg NO_x removed.

Driving force for implementation

A noticeable reduction of NO_x is achieved while no capital expenditure is required.

Example plants

Many refineries (around 40 units alone in the USA) have applied non-Pt CO combustion promoters to the catalyst. The method is well established commercially.

Reference literature

[27, Vierheilig et al. 2003], [23, Yaluris et al. 2006], [26, Kramer et al. 2009], [36, CONCAWE n°4/09 2009], [89, Galp 2011].

4.5.4.4 Specific additives for NO_x reduction

Description

As a complementary or substitutional approach to non-Pt low-NO_x CO promoters, this technique consists of using specific catalytic additives for enhancing the further reduction of NO by CO. These additives capitalise on the inherent concentration gradients of gases maintained in the regenerator, and catalyse those chemical reactions which belong to the third group as displayed in Figure 4.8. So far, they have proven to be efficient only for the full combustion mode. The additives can be used alone, in combination with conventional Pt-based promoters, or together with low-NO_x CO promoters, depending of the operational conditions of the unit.

Achieved environmental benefits

Results are highly variable and depend on the unit design (regenerator), feed quality (normal operations fluctuations), catalyst selection, and the achievable oxygen excess. Reductions of

NO_x emissions up to 80 % are reported when used in favourable conditions, either alone or in combination with a Pt-based conventional CO promoter. However, such reduction levels remain exceptional and typical reductions are more often observed range from around 40 to >60 %. [141, TWG FI 2012]. Figure 4.9, from around 30 applications (data from a DeNO_x additives supplier), illustrates the typical achieved reduction range with the use of additives.

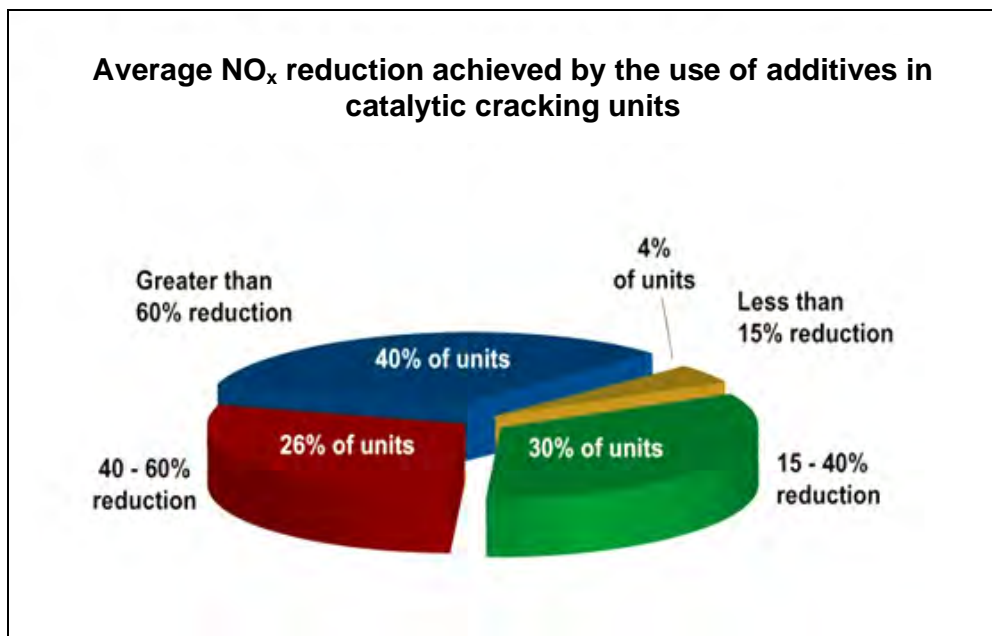


Figure 4.9: Achieved DeNO_x reduction from the use of additives in catalytic cracking units

As shown in Table 4.19, results also depend on the initial NO_x concentration to be abated in the FCC regenerator.

Table 4.19: Various NO_x additive performances reported in full combustion FCC units operated in the US

Type of additive ⁽¹⁾	NG-A	NG-A	NG-B	NG-B	NG-B	NG-B	NG-B
FCC design	Model IV	Ortho-flow	UOP stack	UOP stack	HOC	Model III	UOP HE
Regenerator bed temperature (°C)	710	706	721	718	721	740	740
Initial NO _x concentration (ppm)	125	160	65	69	67	137	90
Final NO _x concentration (ppm)	30	63	47	45	44	57	45
NO _x reduction	76 %	61 %	28 %	35 %	34 %	58 %	50 %
Additive concentration ⁽²⁾ (%)	5	5	1	1	1	0.5	1

⁽¹⁾ These types correspond to two different technologies based on different chemical actions for affecting NO_x reduction. They are developed by the same supplier and can be selected after a minimum 8-day real-run trial.
⁽²⁾ Expressed in % of the total catalyst addition.

Figure 4.10 gives more details on the NO_x reduction that was obtained for a high capacity (110 000 barrels/day – 6 Mt/yr) full combustion FCC unit operated in the US, with a NO_x reducing additive incorporated intermittently during two years of trials, at concentrations never exceeding 1 % of the catalyst inventory. In this specific case, it was observed that when such an

additive was used in conjunction with a conventional Pt-based CO promoter, the NO_x reduction was even greater than when used alone [27, Vierheilig et al. 2003].

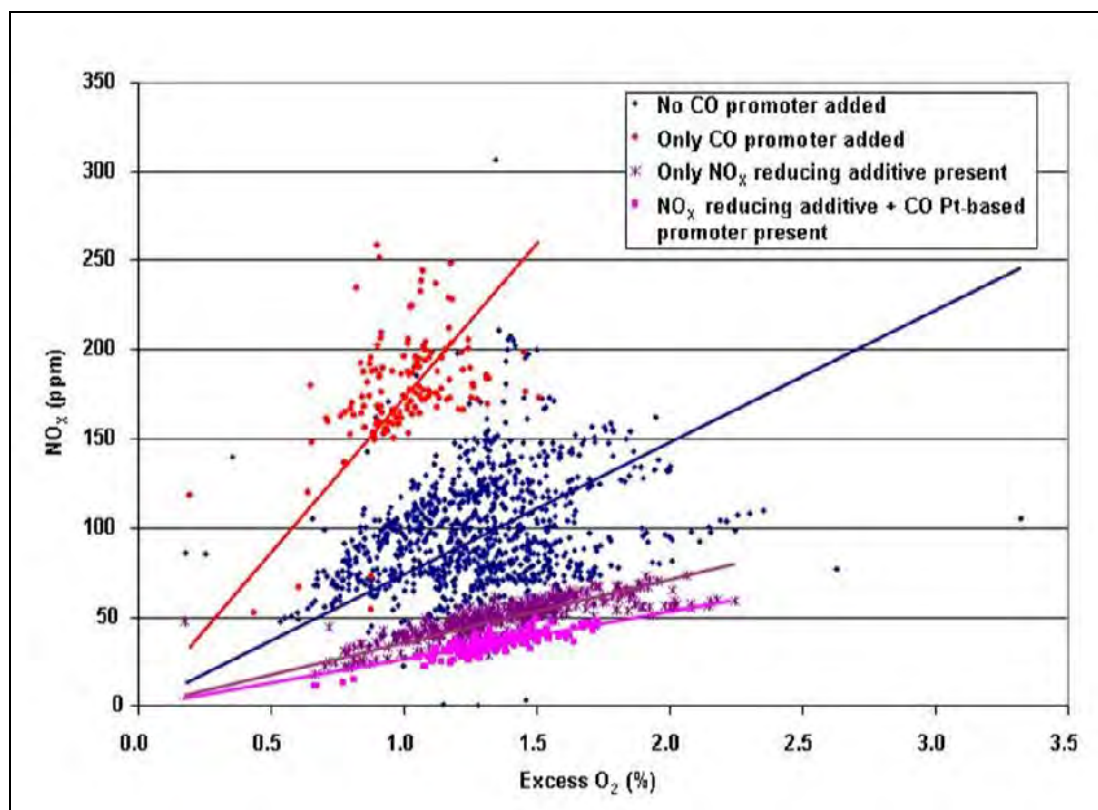


Figure 4.10: Full combustion FCC NO_x emissions as a function of excess O_2 in various catalyst additive configurations

When used in combination with a low- NO_x CO promoter as shown in Figure 4.11, a further reduction of up to 40 % can be obtained on the residual NO_x level, depending on the mutual additive rates chosen for the given unit. However, the adjustment of such a catalyst mixture CO promoter/additive for a given installation must be carefully evaluated and tested on a case-by-case basis.

Cross-media effects

Copper-based NO_x -reducing additives can also promote the production of hydrogen and create difficulties for FCC units operated at their gas compression capacity limits.

Operational data

Figure 4.11 gives an overview of the results obtained on a large 4.5 million t/yr FCC unit, operated in a full combustion mode, after pretreatment with a low- NO_x non-Pt CO promoter. As shown, the NO_x -reducing additive is incorporated both by using one-shot monthly doses, together with continuous addition at an increasing rate into the fresh catalyst renewal stream. After a three-month trial, NO_x emissions tended to stabilise at around 40 % below the original average.

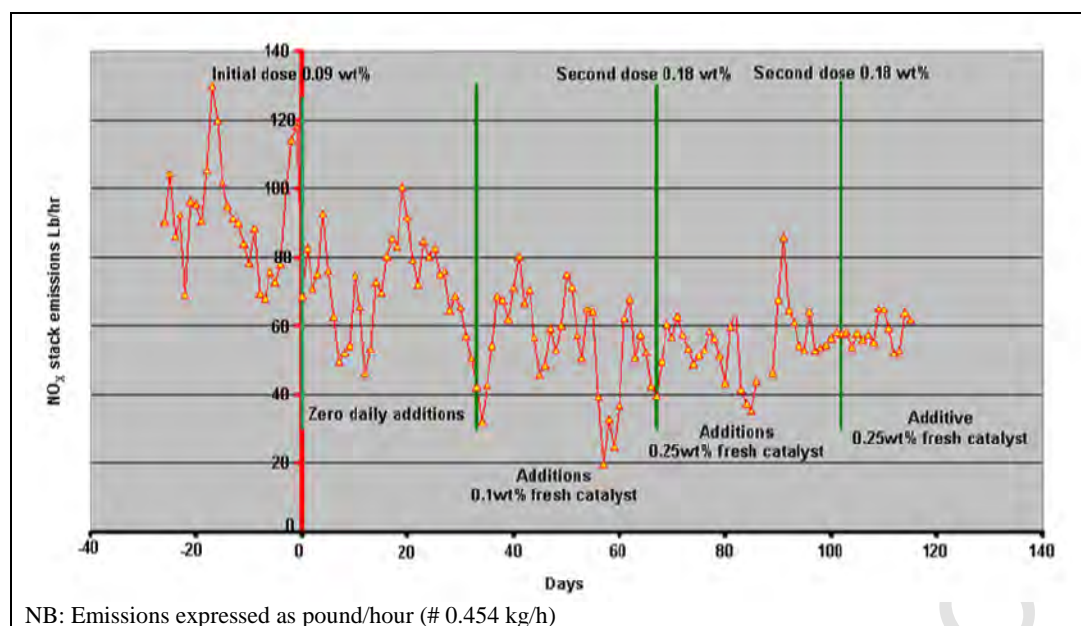


Figure 4.11: Performance obtained with a NO_x-reducing additive in a full combustion FCC unit

The use of a non Pt low-NO_x-Co promotor was experimented at a refinery in Portugal, at the beginning of 2010. At the end of the test period, it is reported that the replacement of the previous combustion promotor led to an 80 % reduction of NO_x emissions in the flue-gas with 80 ppm (about 130 mg/Nm³) NO_x concentration. In addition, the emissions are reported to be stable, and no longer depend on the nitrogen level in FCC feed [89, Galp 2011].

Applicability

This technique is proven to be efficient only in the full combustion mode.

The performances of such additives are naturally sensitive to the available concentration of CO as one of the reactants. Thus, low excess oxygen conditions favour their efficiency.

Even if good results are obtained with a combination of Pt-based conventional promotors, the logical approach is to first reduce the generation of NO_x at source as much as possible by using low-NO_x CO promotors, and then use the additives as complementary.

By 2008, there were four commercially available NO_x reduction additives, among which three were copper-based.

Applicability may be limited, for FCC units operated at their gas compression capacity limits, by the increased production of hydrogen caused by the copper, if present, in the additive. More generally, the technique is sensitive to numerous parameters and therefore, retrofitting requires preliminary tests to determine NO_x reduction.

Economics

See Table 4.18 in Section 4.5.4.3. The option of using such additives in combination with a low-NO_x non-Pt CO promotor compared with using them alone is very often the most economically-sound solution, as NO_x-reducing additives are added at rates of 0.5 – 2 % of fresh catalyst renewal, while CO promotors are added at much lower rates of 5 – 10 kg/day.

Driving force for implementation

To achieve a further reduction of NO_x emissions with little or no additional capital costs.

Example plants

According to equipment suppliers, this technique is said to be currently used by around 20 refineries in the US. In Europe, this technique is also used, e.g. at one refinery in Portugal.

Reference literature

[27, Vierheilig et al. 2003], [24, Bruhin et al. 2003], [26, Kramer et al. 2009],
[30, Sawyer et al. 2009], [36, CONCAWE n°4/09 2009], [141, TWG FI 2012].

4.5.4.5 Low-temperature oxidation (SNERT process/LoTO_x technology)

Description

See Section 4.23.3.1.

Achieved environmental benefits

The reduction of NO_x emission from an FCC unit by 85 – 95 %, with an outlet concentration reduced to 10 ppm (14 mg/Nm³ NO_x under EU reference conditions (0 °C -3 % O₂) 95 % NO-5 % NO₂).

Cross-media effects

The SNERT/LoTO_x process operates optimally above 150 °C and does not require heat input to maintain operational efficiency, enabling maximum heat recovery from the flue-gas.

Nevertheless, SNERT/LoTO_x is associated with a new or existing scrubbing unit, which generates waste water to be treated properly. An increase in nitrate load to the existing WWTP may have to be considered, together with the associated cost to control nitrates.

Nitric acid is produced and needs to be neutralised with an alkali used in the scrubbing section. In order to oxidise the NO_x to soluble higher oxides, ozone is required and should be generated on-site using an ozone generator, which consumes oxygen and electrical energy.

Operational data

NO_x-removal performance is directly linked to the ozone injection rate and its real-time regulation in relation to the NO_x outlet concentration target. The outlet NO_x can be adjusted by varying the set point on the system controller. In Figure 4.12, the set point was set in order to respect the permit conditions of 20 ppm (27 mg/Nm³ NO_x).

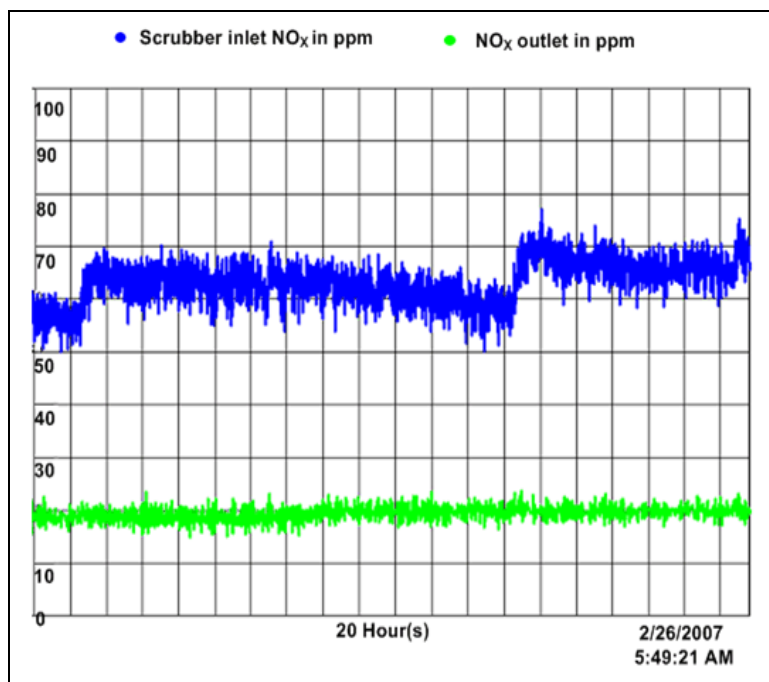


Figure 4.12: Initial results of commercial operation at a US (Texas) refinery FCC unit - 2007

Applicability

The first demonstration tests on the FCC unit were conducted in 2002. Between 2007 and 2009, low temperature oxidation units have been implemented in seven FCC units, among which six are operated in the US and one in Brasil. Four of them have been retrofitted on existing scrubbers, one of them was not originally installed by the LoTO_x patenting equipment supplier. In the case of retrofitting, a separate tower may have to be built in order to provide the required additional ozone injection and reaction stage. Ozone slip out of the stack will be associated with this technology. Appropriate design for additional processes related to ozone generation and personnel safety have to be taken into account.

The applicability may be limited by the need for additional waste water treatment. It should also be taken into consideration that an appropriate supply of liquid oxygen for ozone generation is needed. The applicability of the technique may also require significant space availability.

Economics

In 2005, potential investment and operational costs for implementing this technology on two FCC units in Colorado refineries (US) were estimated as a range of USD 1 900 – 2 100 per year and tonne of NO_x avoided, assuming a related NO_x emission decrease of 85 – 90 %. Additional cost associated to nitrates control in the waste water may also need to be considered.

Driving force for implementation

The main advantages of the LoTO_x process are: NO_x selectivity, adjustability of NO_x-removal performances, absence of interference with the FCC unit chemical process and operating conditions (including O₂ concentration in the flue-gas), compatibility with flue-gas energy recovery, and relative ability to handle unit upsets without impacting overall reliability and mechanical availability.

Example plants

US Refineries: BP (Texas City), Flint Hills (Corpus Christi), Lion Oil (El Dorado), Marathon (Texas City), Valero (Houston and Texas City), Western Gaint (Gallup).

Reference literature

[17, Jeavons and Francis 2008], [18, Confuorto 2007].

4.5.4.6 Process optimisation

Description

The FCC operating conditions and practices can be adjusted in order to reduce the NO_x formation. These ensemble of process optimisation techniques include but are not limited to:

- Reducing excess oxygen in the flue-gas
- Lowering the regenerator bed temperature
- Operating air staging in the CO boiler where present (in partial combustion mode).

Achieved environmental benefits

Dependent on design and operating conditions of the CO boiler (see below).

Environmental performance and operational data

A number of trials has been carried out at a German refinery site in order to determine the maximum NO_x reduction achievable by operating air staging in a CO boiler (FCC in partial combustion mode). By varying the airflow on the 3 air feed points 'burners 1-3', '1 stage' and '2 stage' (post-combustion), the NO_x content in the FCC flue-gas can be reduced by up to 100 mg/Nm³. This has been achieved by shifting the combustion air from the burners to the second stage.

Starting from an initial value of approximately 375 mg/Nm³ (without air to the 2nd stage), the NO_x in the flue-gas could be reduced at the end of the test to about 270-290 mg/Nm³ (at around 14 000 Nm³/h air to the 2nd stage), without negatively affecting the CO combustion or the combustion chamber temperatures of the boiler.

The results suggest that, in this particular configuration and operating conditions (7.5 % CO by volume in the regenerator flue-gas, feed nitrogen content 300 – 400 mg/kg.), an average emission limit of 350 mg NO_x/Nm³ can be achieved without the use of secondary measures.

Cross-media effects

To achieve a maximum CO burn, an O₂ excess of at least 2.0 – 2.2 % by volume is required. Below this value, the CO conversion is incomplete and it may lead to high CO releases.

A positive side effect of using air staging can be that furnace temperatures tend to rise through the reduction of air to the burners and, therefore, the additional firing needed to maintain the firebox temperature can be reduced slightly.

Technical considerations relevant to applicability

It is reported from some trials that the achieved results are strongly dependent on the design of the CO boiler and the current plant configuration. The maximum possible reduction would need to be determined on a case-by-case basis.

Economics

Very limited costs as no investment is required and only process fine tuning is used.

Driving force for implementation

CO and NO_x emissions control.

Example plants

Some trials have been performed at a German refinery site (see previous paragraph on Environmental performance and operational data). These trials consist of air staging carried out in order to determine the maximum possible NO_x reduction in the FCC flue-gas through optimal distribution of the CO boiler combustion air supplied at a constant CO content in the regenerator.

Reference literature

[130, Reza Sadeghbeigi 2012], [142, TWG DE 2012].

4.5.5 Particulate abatement techniques

The selection of the catalyst has an impact on particulate emissions, but will not be considered in the present section. That technique has been included in Section 4.5.3, together with other possible aspects of catalyst replacement.

4.5.5.1 Third-stage cyclone separators

Description

Third-stage separators (TSS) is a cyclonic collection device or system installed following the two stages of cyclones within the FCC unit. The most common configuration of a TSS consists of a single vessel containing many conventional cyclones, or may be new, improved swirl-tube technology (e.g. Shell Global Solutions, or CycloFines™). TSS is a common choice as a clean-up devices for particulates and as an aid to energy efficiency. The first attempts at power recovery from FCC unit regenerator flue-gas were unsuccessful because the expander blade lifetimes were limited to a few weeks. It was found that particles sizes of 10 micron and larger were particularly harmful to the blades. TSS were introduced to protect power recovery expander turbines from particulate damage. Recent advances in this technology, as shown in Figure 4.13, favour in particular, the use of a large number of axial flow swirl tubes of relatively small diameter, in order to induce a fast rotating motion and handle the large volume of flue-gas in more compact vessels. They are high-velocity devices and the recovered catalyst is returned to a dust hopper. In some cases, a new stage of filtration is used and they are then named 4th stage.

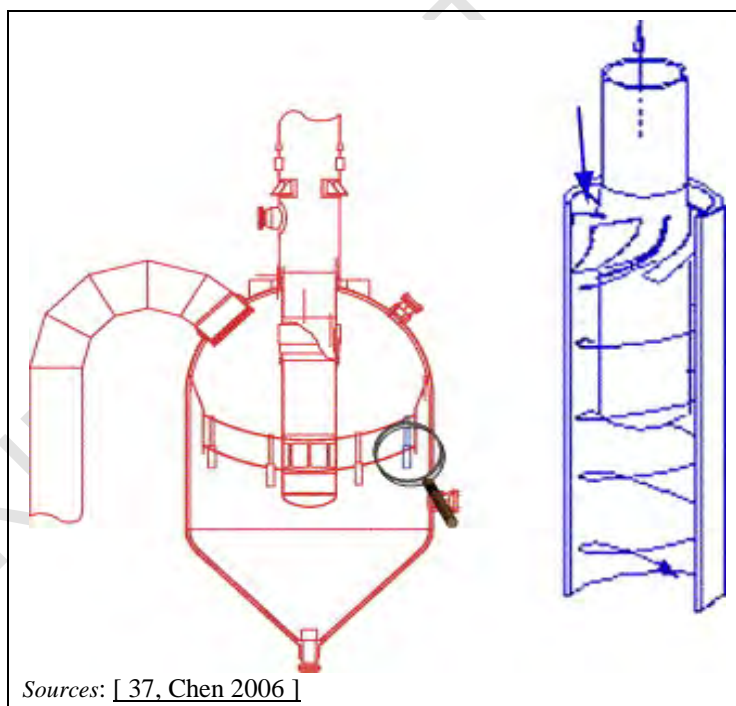


Figure 4.13: Scheme of a TSS using multiple-axial swirl-tube technology

Achieved environmental benefits

The average performance outlet concentration for an advanced TSS is $<50 - 100 \text{ mg/Nm}^3$, depending on the inlet particulate concentration and size distribution. Lower concentrations are not achievable because inlet velocities to the cyclones are in the region that causes additional attrition, which produces additional fines that pass through the cyclone.

Depending on the above factors and on the type of technology used, cyclones are generally efficient at removing particles larger than 10 to 40 microns. Recent swirl-tube devices allow a 50 % cut point of about 2.5 microns. Efficiencies can range from 30 to >90 %. For inlet concentrations below 400 mg/Nm³, the efficiency can only exceed 75 % for a particulate size distribution with a median (by mass) of >5 microns.

By reducing the particulate content in the air, the metal emissions are also reduced.

Cross-media effects

Catalyst fines recovered containing some hazardous metals are classified as hazardous industrial waste and have to be properly handled and eliminated in order to avoid any pollution transfer from air to water and soil.

Operational data

Catalyst fines removal is typically 300 – 400 tonnes/yr per unit. A TSS generates a pressure drop in the flue-gas. Good performance and reliability in many FCCs have been demonstrated. Table 4.31 shows emissions data from continuous monitoring, including dust, of a sample of European FCC units (See Section 4.5.7). The FCC units equipped with third-stage separators (TSS) only (no additional device) report dust emissions in the range 80 – 150 mg/Nm³, on a monthly average.

Applicability

TSSs are applicable to any FCC, but their performance will vary considerably, mainly depending on the particle concentration and size distribution of the catalyst fines downstream of the regenerator internal cyclones. These abatement devices are very often used in combination with other abatement technique such as ESPs.

Economics

Table 4.20 shows economic data for third stage cyclones used in FCC

Table 4.20: Economic data for third-stage-cyclones applied to FCCs

Size of the FCC (Mt/yr)	Efficiency (%)	Downstream particulate concentration (mg/Nm ³)	Investment (EUR million)	Operating cost (EUR million/yr)
1.5	30 – 40	40 – 250	1 – 2.5	0.7
1.5	30 – 90	60 – 150 ⁽¹⁾	0.5 – 1.5	0.1
1.2	75	50 – 100 ⁽²⁾	1.5 – 2.5	

⁽¹⁾ Initial concentration: 450 mg/Nm³ (300 – 600 mg/Nm³ range).
⁽²⁾ Initial concentration: 200 – 1000 mg/Nm³
 NB: Operating costs include only direct cash operating expenses, i.e. they do not include the depreciation of investment, nor financial charges. Investment costs refer to new plant installation. Economics do not include the cost of disposal of the waste generated.

The cost of disposal for the fine catalyst is around EUR 120 – 300 per tonne, including transportation.

Driving force for implementation

TSSs control particulate emissions and protect downstream equipment such as heat or power recovery units (e.g. expander blades).

Example plants

Many FCC units are operating with these systems.

Reference literature

[151, Sema,Sofres 1991], [156, MCG 1991], [221, Italy 2000], [166, CONCAWE 1999], [36, CONCAWE n°4/09 2009].

4.5.5.2 Electrostatic precipitators (ESPs)

Description

A short description of the basic principles of an electrostatic precipitator can be found in Section 4.23.4.

Particle resistivity is a key factor for the efficiency of the ESP. The following parameters are generally reported to lower the resistivity of the particles in order to improve the collection efficiency of the electrostatic precipitator used in a catalytic cracking unit flue-gas:

- higher inlet temperature;
- higher concentration of metals, rare earth or carbon in the catalyst;
- moisture content;
- ammonia injection.

Achieved environmental benefits

Typical concentrations achieved with electrostatic precipitators are usually $<20 - 50 \text{ mg/Nm}^3$ as a daily average based on continuous monitoring under normal operating conditions (e.g. excluding soot blowing in the CO or auxiliary boilers end of run conditions).

When available for shorter averaging periods, values of total particulate matter in the flue-gas of the FCC regenerator $<50 \text{ mg/Nm}^3$ as an hourly average are reported or included in permit (e.g. in Germany see under Operational data). As a consequence of the particulate reduction, metals (Ni, Sb, V and their components) can be reduced to less than 1 mg/Nm^3 (given as Ni, Sb and V total) and, within that, Ni by itself and its components can be reduced to less than 0.3 mg/Nm^3 (given as Ni), all concentrations being expressed as half-hourly mean values attainable in continuous operation and with soot blowing in the CO boiler.

Cross-media effects

The refinery may need extra facilities to manage the fine particulates (catalyst) recovered that require disposal. The high voltage in an ESP introduces a new safety risk in refineries and leads to increased operating costs for electricity and maintenance. For some installations, ammonia may be injected to improve the ESP performance (as a resistivity attenuation agent). For these installations, ammonia emissions result from ammonia slip through the ESP. Safety concerns are also expressed about the use of ESPs during the FCC start-up process. Special care must be taken to ensure that uncombusted hydrocarbons are never allowed to enter the ESP itself, as the sparking environment may result in an explosion. [31, BARPI 2009], [36, CONCAWE n°4/09 2009].

Operational data

The particulate abatement efficiency with an ESP in FCC is usually much greater than 90 %. The actual concentration range achieved at the ESP outlet will depend on the residence time (i.e. the ESP size), the properties of the particulate (i.e. catalysts), the mode of FCC operations, the flue-gas temperature, and whether other particulate removal devices are installed upstream of the ESP. In usual conditions, a residence time greater than 30 seconds would be necessary to achieve very low concentrations ($<10 \text{ mg/Nm}^3$). Particle size can also affect the ESP efficiency, since very fine particulate ($<2 \mu\text{m}$) is more readily re-entrained during the cleaning cycle (rapping) of the ESP electrodes.

Electrostatic precipitators add a small pressure drop to the system; higher pressure drops may result from the inlet and outlet ducting to the ESP. In some cases, a forced draft or induced draft fan may need to be added. The extra energy consumption (electricity) is typically low, but can be significant for ESPs with large residence times. ESPs also require regular maintenance to ensure high capture efficiency. Information from some EU refineries shows that the use of deep desulphurisation of the feedstock can have a great impact on ESP performance (because the content of sulphur and metals is lower), reducing the ESP efficiency. In these cases, achievable particulate emissions have been reported to be $30 - 35 \text{ mg/Nm}^3$.

Figure 4.14 and Figure 4.15 show a one year profile of the daily average concentration achieved by two ESPs operated in two German FCC units.

- Results for the first FCC displayed in Figure 4.14 are achieved under normal operating conditions, using a filtering configuration consisting of a conventional set of internal cyclones, an additional external cyclone and a 4-field ESP. The yearly average concentration is 10.94 mg/Nm^3 , with a standard deviation of 9.62, and the maximum recorded daily average is nearly 37 mg/Nm^3 . The typical daily average concentration is rather variable, mostly within the range $5 - 25 \text{ mg/Nm}^3$.
- In comparison, the second FCC (Figure 4.15) has a simpler configuration, with only a combination of an internal cyclone and a 2-field ESP. Moreover, this 1-year period includes a shutdown/start-up step (identified on the graph) during which emissions have been significantly higher than for stable conditions. The yearly average is 10.16 mg/Nm^3 (calculated from daily values different from zero) with a standard deviation of 5.2. Even though the maximum recorded daily average value of 38 mg/Nm^3 is comparable to the first ESP (Figure 4.14), the typical daily average concentration during stable operating conditions is much more constant, staying mostly within the range $5 - 15 \text{ mg/Nm}^3$.

Particulate emissions can increase after an FCC turnaround due to higher solids loading to the ESP. This can be attributed to higher attrition of new catalyst that may be loaded after a turnaround.

The following data for a German FCC plant are reported, after the ESP (no cyclone) in the waste gas of the CO boiler (normal operation):

- emission limits values in the permit:
 - total particulate matter, daily average value: 30 mg/m^3 ;
 - 30 minutes average value: 60 mg/m^3 ;
- monitoring data: total PM: $13 - 23 \text{ mg/m}^3$ (30 minutes, $\text{O}_2 = 3.1 \%$, 100 % capacity utilisation, feed 80 % atmospheric residues, 20 % heavy wax distillates).

Another similar FCC with a cyclone and ESP abatement techniques is reported to achieve $\text{PM } 9 - 21 \text{ mg/m}^3$ (100 % capacity with feed: 50 % vacuum gas oil, 40 % atmospheric residue, 10 % others). *Source: TWG 2010-DE*

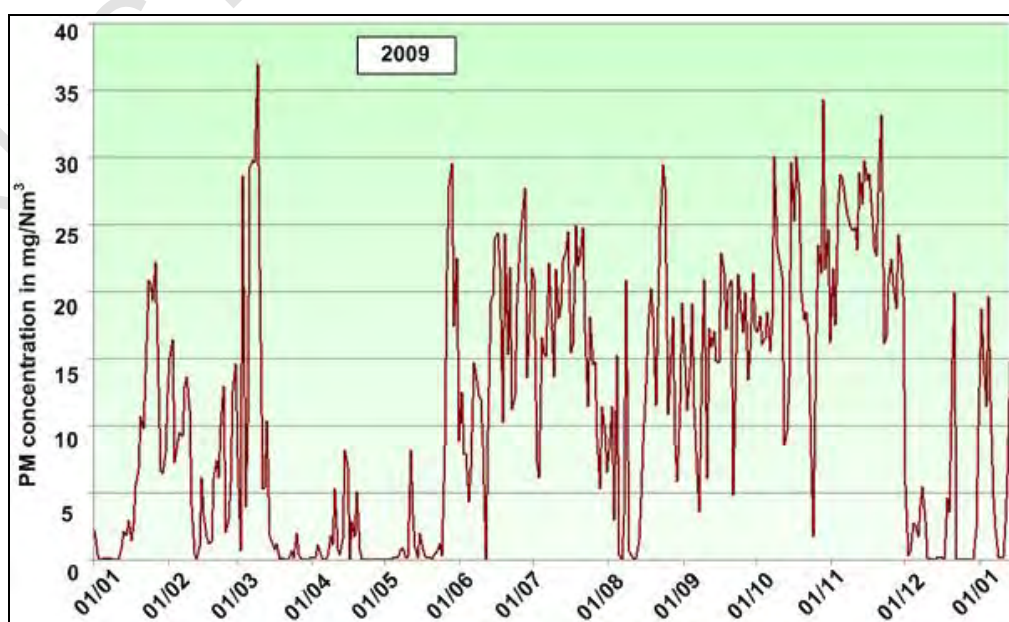


Figure 4.14: Daily average PM concentrations achieved by an ESP on a German FCC unit

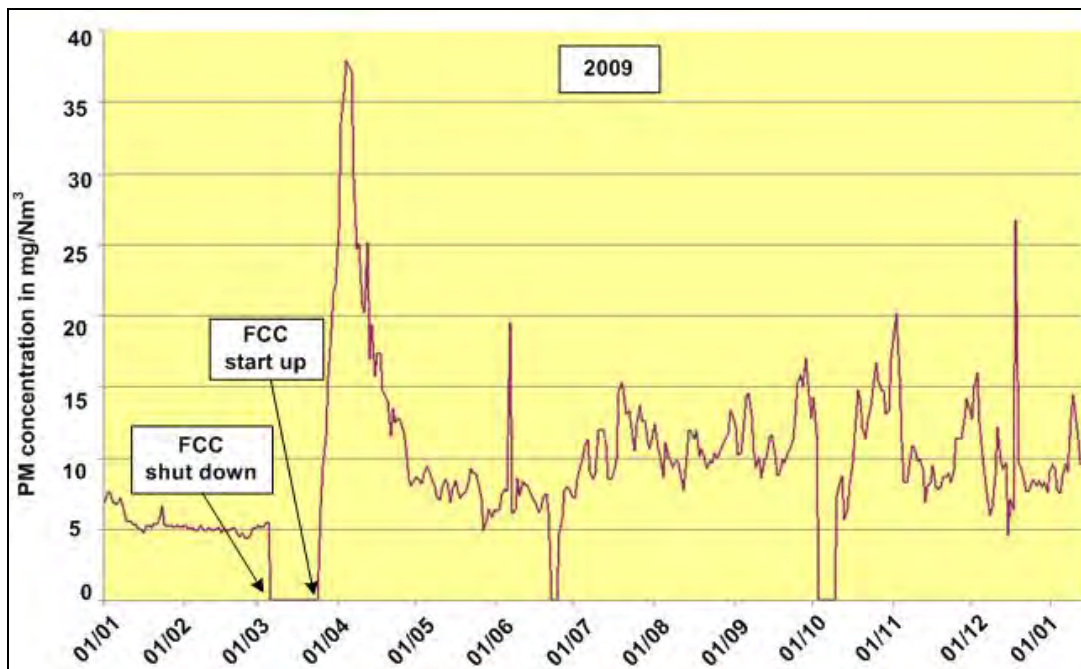


Figure 4.15: Daily average PM concentrations achieved by an ESP on a German FCC unit

Additional data linked to the TWG data collection questionnaire number 18 show dust emissions from a recent (2008 built) ESP on a full combustion mode FCC: (see Figure 4.16).

After a period of process development, isokinetic measurements (60 minutes sampling – year 2011) show the following values:

- 20 – 25 mg/Nm³ in normal operating conditions;
- 30 – 40 mg/Nm³ during soot blowing.

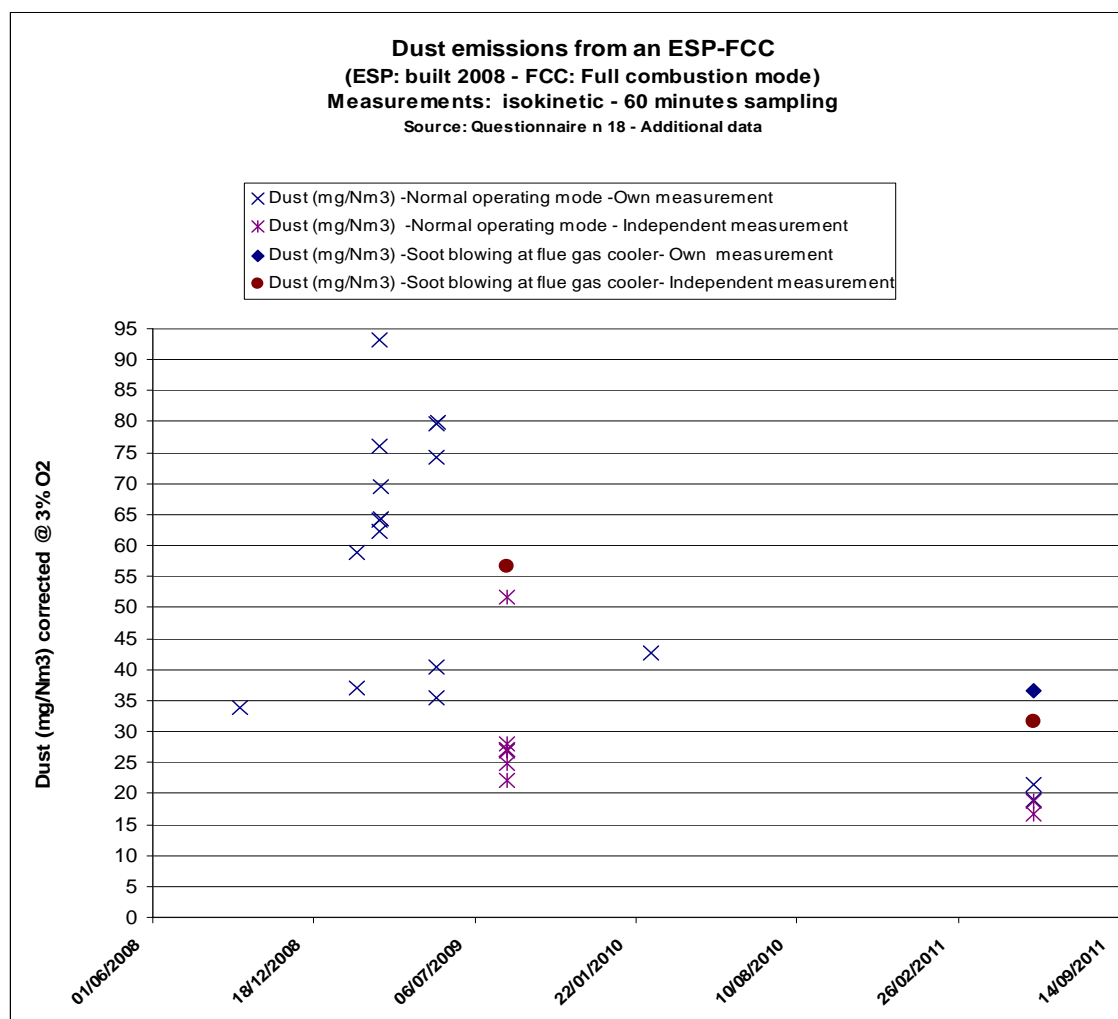


Figure 4.16: Reported dust emissions (isokinetics measurements) from a FCC unit equipped with ESP (TWG Questionnaire number 18)

Figure 4.17 shows the distribution of daily values of dust emissions (2011) from a German FCC processing desulphurised vacuum diesel and equipped with an ESP, installed in 2007 in addition to an existing third stage cyclone.

A compilation of the emissions data from continuous monitoring, including dust, of a sample of European FCC units is shown in Table 4.31 (See Section 4.5.7). The FCC units equipped with ESP report dust emissions in the range 10 – 50 mg/Nm³ on a monthly average. Among these, the ones equipped with a combination of tertiary cyclones and a 4-fields ESP perform better and in the range 10 – 25 mg/Nm³.

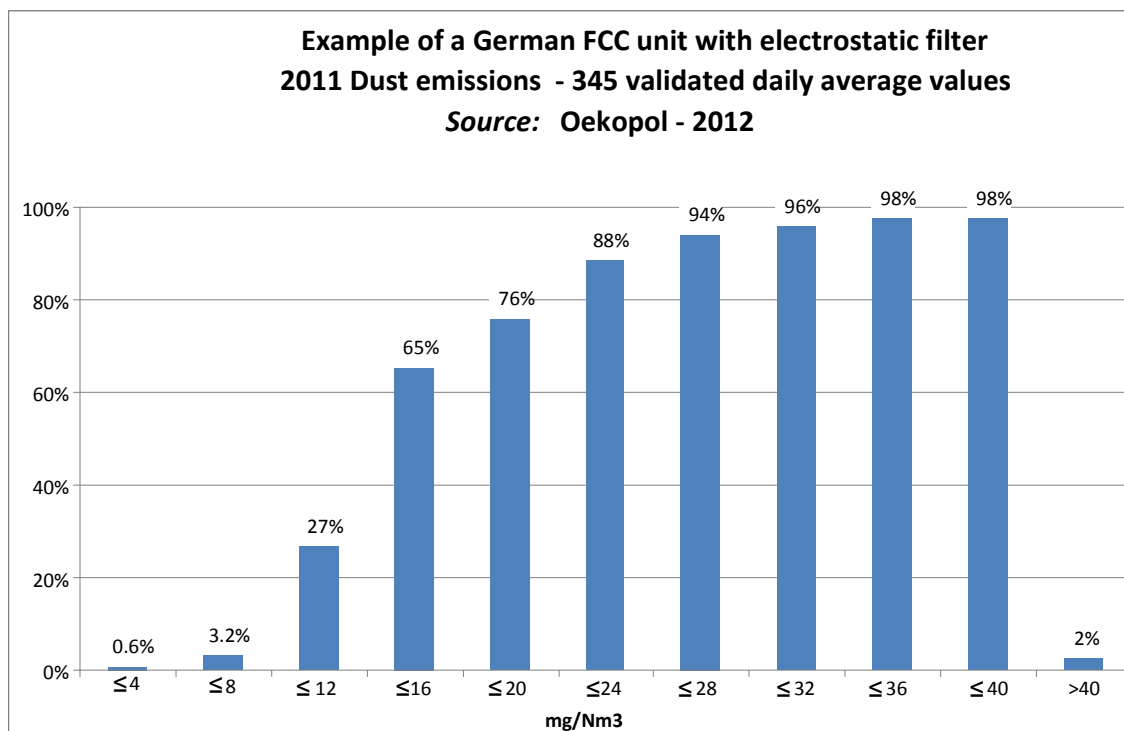


Figure 4.17: Reported distribution of dust emissions daily values from the continuous monitoring of a German FCC equipped with ESP

Applicability

ESPs require significant plot space, especially when they are sized to achieve very low particulate emissions levels. A large plot space is required because FCC outflows are typically large (a 1.5 Mt/yr FCC generates 2.8 million Nm³/day of flue-gas). ESP requires low internal velocity and therefore large volumes at typical design residence times to achieve the required performance levels. In order to not exceed gasflow speed specifications, the ESP performance may be adversely affected if the particulate has a high electrical resistivity. In addition deep hydrotreatment of the FCC feedstock will lower the catalyst metal content, reduce conditioning agents (SO₃) in the flue-gas and therefore reduce the collection efficiency. Also worth mentioning is that the performance of ESPs is likely to degrade from the start to the end of the FCC run. This may be due to either ESP maintenance issues, which require a shutdown, and/or the potential for increased attrition/loss of catalyst particles at the end of run. Finally, ESPs may not cover start-up and shutdown periods and will have to be electrically isolated due to safety reasons already described.

Economics

Available data has been gathered in Table 4.21 and additional information on costs for comparison of various filtration devices (tertiary cyclones, 3-field ESP and 4-field ESP) is presented in Table 4.22.

Table 4.21: Economic data of ESPs applied to FCCs

Size of the FCC (Mt/yr)	Efficiency (%)	Downstream PM concentration (mg/Nm ³)	Investment (EUR million)	Operating cost (EUR million/yr)(*)
2.4	>50 ⁽¹⁾	<50 ⁽¹⁾	15 – 30	0.15 ⁽²⁾
1.5	–	<30	2.05 ⁽³⁾	-

⁽¹⁾ Unabated concentration >100 mg/Nm³ → Abatement target <50 mg/Nm³.
⁽²⁾ 2009 USD respectively 20 – 40 million (installed capital cost) and 0.2 million [30, Sawyer et al. 2009].
⁽³⁾ 2008 HUF 1.3 billion for the whole ESP project.

Table 4.22: Cost data of various FCC filtration devices

Assuming Base Case Dust at 100mg/Nm ³																						
Base Case in 2006					Electrostatic Precipitator 3-Fields (ESP-3)					Electrostatic Precipitator 4-Fields (ESP-4)												
					%TEC/yr	%TEC/yr	mgDust/ Nm ³		Outlet dust mg/Nm ³	Efficiency %	ACC %	Fixed OP %TEC/yr	Variable OP %TEC/yr	Outlet dust mgDust/Nm ³								
					90 %	7.4 %	4 %	1 %	30	90 %	7.4 %	4 %	1 %	30								
	Design Feed	Utilisation	Outlet Dust	Dust Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to ESP-4	Cost Effectiveness: Base to ESP-4	Incremental Cost Effectiveness: ESP-3 to ESP-4	Cost Effectiveness: Base to ESP-3	Outlet Dust	Dust Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to ESP-4	Cost Effectiveness: Base to ESP-4	Incremental Cost Effectiveness: ESP-3 to ESP-4							
	kt/yr	%	mg/N _{m³}	t/yr	M€	k€yr	€tDust	€tDust	mg/Nm ³	t/yr	M€	k€yr	€tDust	€tDust								
Unit 1	5 480	97 %	30	93	32.5	4 029	43 286	49 077	40 969	30	93	32.5	4 029	43 286	49 077							
Unit 2	3 911	99 %	30	67	26.5	3 291	48 773	55 299	46 163	30	67	26.5	3 291	48 773	55 299							
Unit 3	2 857	88 %	30	44	22.0	2 726	62 168	70 487	58 841	30	44	22.0	2 726	62 168	70 487							
Unit 4	1 927	97 %	30	33	17.4	2 153	65 527	74 295	62 020	30	33	17.4	2 153	65 527	74 295							
Unit 5	1 646	99 %	30	28	15.8	1 958	68 876	78 091	65 189	30	28	15.8	1 958	68 876	78 091							
Unit 6	1 388	82 %	30	20	14.3	1 768	89 299	101 247	84 519	30	20	14.3	1 768	89 299	101 247							
Assuming Base Case Dust at 200mg/Nm ³																						
Base Case in 2006					Advanced Tertiary Secondary Cyclones (ATSC)					Electrostatic Precipitator 3-Fields (ESP-3)					Electrostatic Precipitator 4-Fields (ESP-4)							
					Efficiency	ACC	Fixed OP	Variable OP	Outlet dust	Efficiency	ACC	Fixed OP	Variable OP	Outlet dust								
					%	%	%TEC/yr	%TEC/yr	mg/Nm ³	%	%	%TEC/yr	%TEC/yr	mg/Nm ³								
					70 %	7.4 %	4 %	1 %	100	85 %	7.4 %	4 %	1 %	50								
	Design Feed	Utilisation	Actual Feed	Outlet Dust	Outlet Dust	Dust Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to ATSC	Cost Effectiveness: Base to ATSC	Outlet Dust	Dust Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to ESP-3	Cost Effectiveness: Base to ESP-3	Incremental Cost Effectiveness: ATSC to ESP-3	Outlet Dust	Dust Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to ESP-4	Cost Effectiveness: Base to ESP-4	Incremental Cost Effectiveness: ESP-3 to ESP-4	
	kt/y	%	kt/y	mg/Nm ³	mg/Nm ³	t/y	M€	k€y	€tDust	mg/Nm ³	t/y	M€	k€y	€tDust	€tDust	mg/Nm ³	t/y	M€	k€y	€tDust	€tDust	
Unit 1	5 480	97 %	5 319	200	100	133	8.8	1 094	8 228	50	199	22.0	2 724	13 656	24 513	30	226	32.5	4 029	17 824	49 077	
Unit 2	3 911	99 %	3 856	200	100	96	7.2	894	9 271	50	145	17.9	2 225	15 388	27 621	30	164	26.5	3 291	20 083	55 299	
Unit 3	2 857	88 %	2 506	200	100	63	6.0	740	11 817	50	94	14.9	1 843	19 614	35 207	30	106	22.0	2 726	25 599	70 487	
Unit 4	1 927	97 %	1 877	200	100	47	4.7	585	12 456	50	70	11.7	1 455	20 673	37 109	30	80	17.4	2 153	26 982	74 295	
Unit 5	1 646	99 %	1 625	200	100	41	4.3	532	13 092	50	61	10.7	1 324	21 730	39 005	30	69	15.8	1 958	28 361	78 091	
Unit 6	1 388	82 %	1 131	200	100	28	3.9	480	16 974	50	42	9.6	1 195	28 173	50 571	30	48	14.3	1 768	36 770	101 247	
Assuming Base Case Dust at 250mg/Nm ³																						
Base Case in 2006					Advanced Tertiary Secondary Cyclones (ATSC)					Electrostatic Precipitator 3-Fields (ESP-3)					Electrostatic Precipitator 4-Fields (ESP-4)							
					Efficiency	ACC	Fixed OP	Variable OP	Outlet dust	Efficiency	ACC	Fixed OP	Variable OP	Outlet dust								
					%	%	%TEC/yr	%TEC/yr	mg/Nm ³	%	%	%TEC/yr	%TEC/yr	mg/Nm ³								
					70 %	7.4 %	4 %	1 %	100	85 %	7.4 %	4 %	1 %	50								
	Design Feed	Utilisation	Actual Feed	Outlet Dust	Outlet Dust	Dust Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to ATSC	Cost Effectiveness: Base to ATSC	Outlet Dust	Dust Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to ESP-3	Cost Effectiveness: Base to ESP-3	Incremental Cost Effectiveness: ATSC to ESP-3	Outlet Dust	Dust Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to ESP-4	Cost Effectiveness: Base to ESP-4	Incremental Cost Effectiveness: ESP-3 to ESP-4	
	kt/y	%	kt/y	mg/Nm ³	mg/Nm ³	t/yr	M€	k€yr	€tDust	mg/Nm ³	t/yr	M€	k€yr	€tDust	€tDust	mg/Nm ³	t/yr	M€	k€yr	€tDust	€tDust	
Unit 1	5 480	97 %	5 319	250	100	199	8.8	1 094	5 485	50	266	22.0	2 724	10 242	24 513	30	293	32.5	4 029	13 773	49 077	
Unit 2	3 911	99 %	3 856	250	100	145	7.2	894	6 181	50	193	17.9	2 225	11 541	27 621	30	212	26.5	3 291	15 519	55 299	
Unit 3	2 857	88 %	2 506	250	100	94	6.0	740	7 878	50	125	14.9	1 843	14 710	35 207	30	138	22.0	2 726	19 781	70 487	
Unit 4	1 927	97 %	1 877	250	100	70	4.7	585	8 304	50	94	11.7	1 455	15 505	37 109	30	103	17.4	2 153	20 850	74 295	
Unit 5	1 646	99 %	1 625	250	100	61	4.3	532	8 728	50	81	10.7	1 324	16 297	39 005	30	89	15.8	1 958	21 915	78 091	
Unit 6	1 388	82 %	1 131	250	100	42	3.9	480	11 316	50	57	9.6	1 195	21 130	50 571	30	62	14.3	1 768	28 413	101 247	

Source: CONCAWE 6/11

Driving force for implementation

Reduction of particulate emissions.

Example plants

17 of 22 FCC European refineries within the 61 sites of the TWG sample use ESPs in their FCC unit. They are also used in many refineries in the US and Japan. As an example, TOTAL in Spargau has an ESP operated on a FCC unit receiving deeply-hydrotreated feedstocks.

Reference literature

[151, Sema,Sofres 1991], [221, Italy 2000], [167, VDI 2000], [191, UBA Austria 1998], [185, Pernis 1999], [166, CONCAWE 1999], [207, TWG 2001], [28, Tebert et al. 2009], [130, Reza Sadeghbeigi 2012], [139, CONCAWE 6/11 2011], [143, Oekopol 2012], [Questionnaire 18]

4.5.5.3 Other filters

Description

A further option for regenerator exhaust gases are bag or fabric filters, and ceramic or stainless steel filters (for bag filters, see additional information in Section 4.23.4.3).

Reverse flow (blowback) ceramic or sintered metal filters are devices where after retaining the solids elements at the surface as a cake, it is dislodged by initiating a reverse flow. The dislodged solids are then purged from the filter system.

Achieved environmental benefits

Reverse flow (blowback) and fabric filters are both able to achieve higher performance figures (1 – 10 mg/Nm³) than cyclones and electrostatic precipitators. Furthermore, in the case of ceramic filters, they prove to be particularly efficient for retaining the finest particulates, and to cope with start-up or upset conditions.

Cross-media effects

None identified so far, except for the need for elimination or valorisation of the collected dust, which is an issue for all dry filters.

Operational data

Bag or fabric filters are temperature sensitive (<200 – 240 °C) and hence their use is limited. They can also cause a significant pressure drop, which has to be taken into account in order to fit the overall process.

On the other hand, reverse flow (blowback) ceramic filters are more sophisticated systems which have proven to be appropriate for this application. One of them, installed since mid-2004 as a full 3rd stage filter on a 2100 t/day RCC unit, has operated without incident since its start-up. Blowback sequences are triggered in function of the progressive build-up of the pressure drop generated by the filter, which is an important parameter to monitor. The filter system achieved a steady-state recovery pressure differential after approximately 100 blowback cycles (i.e. nearly one month) and the operating pressure drop due to the filter has been low enough to avoid any adverse impacts on the RCC operation. The related environmental performance is much better than any other filtration processes applied to FCC. As shown on Figure 4.18, the PM concentration measured by opacity analysis has always been below 5 mg/Nm³ since the filter commissioning, and the typical filter performance is 1 – 2 mg/Nm³.

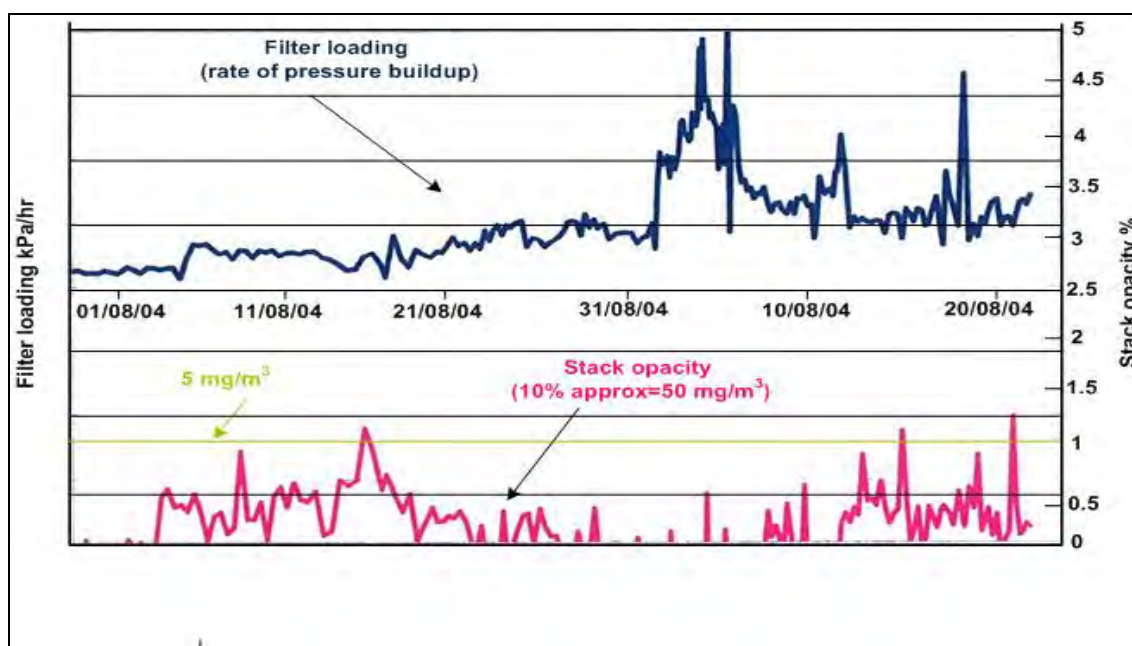


Figure 4.18: Performance of a FCC sinter alloy 3rd stage blowback filter

However, besides the filter pressure drop, other variables have to be monitored in order to ensure a stable filter functioning, such as valve operating and closing times, flue-gas temperatures, blowback accumulation pressure and blowback gas temperature.

Recent data provided for a full stream 3rd stage blowback filter (stainless steel made) operated at an FCC unit (1.1 Mt/y) at BAZAN (ORL) refinery in Haifa (Israel) show that PM emissions comply with the 20 mg/Nm³ emission standard and usually allow concentrations well below 15 mg/Nm³ [144, EIPPCB 2012].

Applicability

Bag or fabric filters can be retrofitted to the underflow of three-stage cyclones. However, they are not favoured for use in the FCC because of the pressure drop, the potential for ‘blinding’ of the bags, the large space required and their inability to cope with upset conditions.

On the other hand, 3rd-stage ceramic filters have proven to be applicable to catalytic cracking flue-gas cleaning since 2004. They are even successful in their ability to cope with various FCC upset conditions. Two specific cases have been reported in the available literature so far. The first one is the handling of upstream concentrations up to 20 000 mg/Nm³ during a two week catalyst attrition problem, with a solid load increase from 250 to 1 000 – 2 000 kg/day, allowing the RCC unit to keep complying with applicable emission standards and avoid shutdown. The second one is a safe operation of such a filter during a torch oil firing in the regenerator, in order to maintain its temperature during emptying and urgent repairing. Therefore, it is possible to benefit from the ceramic filter system also during start-up and shutdown, which corresponds to a major improvement compared with ESPs. Scale up to full regenerator flow from more commonly sized European FCC units needs to be clearly demonstrated.

Economics

The specific investment cost for blowback ceramic filters will depend on the temperature and the stream capacity. The cost for a 3rd stage (full stream) filter is estimated at USD 80/m³/h for temperatures below 450 °C, and USD 210/m³/h for higher temperatures up to 750 °C. For smaller hot filters concerned in four stage application, this cost is about USD 260/m³/h (all costs expressed for the year 2009 and for actual flue-gas volumes). For a generic 2.4 Mt/yr FCC unit, the installed capital cost in 2009 was estimated to be EUR 15 – 20 million (USD 22 – 30 million).

Driving force for implementation

Recent reverse flow (blowback) ceramic filters are of the highest interest for FCC applications, where PM emission magnitude, considered together with their associated granulometry and chemical content, are likely to raise health and environmental issues. This technique allows a high-performance filtration of catalyst PM emissions, including finest particulates and heavy metals. It has a very low sensitivity to start-up and upsets and prevents related adverse effects on dust loads, particle size, or flowrates. Its compactness is also favourable for retrofitting situations.

Example plants

Full-stream 3rd-stage ceramic or stainless steel filters are operated in three refineries: the BP refinery in Kwinana (Australia, 2004), the BAZAN (ORL) refinery in Haifa (Israel, 2009), and another in the US (to be commissioned). Around 15 partial-stream (4th-stage) ceramic separators and hopper filters are also operated in Western Europe, North America and the Middle East.

Reference literature

[156, MCG 1991], [22, Glenney et al. 2008], [30, Sawyer et al. 2009], [144, EIPPCB 2012].

4.5.6 Sulphur oxides abatement techniques**4.5.6.1 SO_x-reducing catalyst additives****Description**

Sulphur dioxide in the regenerator off-gas of an FCC unit can be reduced by using a metallic oxide catalyst (e.g. Al/Mg, Ce) which transfers a significant portion of the sulphur associated with the coke on the catalyst back to the reactor, where it is liberated as hydrogen sulphide. This leaves the reactor with the cracked vapour product for capture in the amine scrubbing system of the refinery and hence conversion of sulphur in the SRU.

SO_x reduction is a three-step process:

- (1) catalytic oxidation of SO₂ to SO₃ in the regenerator;
- (2) adsorption on the additive of SO₃ produced in the regenerator to give a sulphate which, on return to the reactor;
- (3) reverts to the oxide and releases hydrogen sulphide into the product gas stream for recovery.

Developed in the late 1970s, SO_x-reducing catalysts were initially alumina-based and very much subject to deactivation. Progressively, the potential for SO₃ picking-up in the regenerator was substantially increased by replacing pure alumina-based binders with magnesium-aluminate binders (1980s: 1 Al mole for 2 Mg mole) and later with hydrotalcite binders (1990s: 1 Al mole for 3 – 4 Mg mole). State-of-the-art catalysts developed since 2000 show performances improved by 35 – 80 % compared with the first hydrotalcite binder compounds. Pick-up factors (PUF – kg SO₂ removed per kg additive introduced) up to 20 can now be theoretically reached.

Achieved environmental benefits

The amount of SO_x removed is strongly dependent on the SO_x raw concentration in the regenerator, the amount of SO_x-reducing additive added to the unit, and on the type and efficiency of the SO_x-reducing additive itself. Some available test data also show that the removal performance is highly influenced by the current oxygen concentration and by the additive's own resistance to attrition in the operating conditions prevailing in the particular plant concerned.

In the full combustion mode, removal efficiencies achieved with state-of-the-art additives are typically >60 % Even higher removal rates (of up to 95 – 99 %) have been reported in commercial operation. Best performances are associated to the most favourable operating

conditions, in particular lowest raw sulphur concentrations in the regenerator and optimisation of the regenerator and other process variables.

In the partial combustion mode, the typical reduction might be lower than in full combustion mode, and in most cases, more additive is required. Specific partial-burn additives have been recently developed, and have shown to be twice as active as the older additives. State-of-the-art additives are now typically able to remove >50 % of emitted SO_x, and even higher reductions (up to 90 – 95 %) have been reported in commercial operation. Here again, best performances are associated with the most favourable operating conditions, as above, in particular the lowest raw sulphur concentrations, lowest proportions of pre-existing reduced species (COS, H₂S) in the regenerator before the CO boiler, and the longest regenerator residence times as shown graphically in Figure 4.19. Nevertheless, in some units with specific unfavourable conditions, the maximum SO_x removal may still be 30 – 35 %.

However, the higher the removal rate, the lower the pick-up factor observed.

- In one example, the literature [25, Pham et al. 2009] reports a case where a 85 % reduction in SO_x, resulting in a 50 ppmv residual emission (0 % O₂) could be achieved with a PUF of 18 kg SO_x removed per kg of additive incorporated. A further reduction of emissions to below 25 ppmv (0 % O₂) decreased the PUF to 14 kg SO_x removed per kg of additive. The concentration required to reduce emissions below 25 ppmv was in the order of 5 % by weight of the total catalyst inventory. The relative cost increase from 50 to 25 ppm was 31 %.
- A second example is described in detail as the case study n°1 for a short trial performed on a 'deep' partial-burn FCC with 7 – 8 mol % CO in the regenerator [57, Roberts et al. 2009]. It shows a relatively acceptable efficiency for achieving up to 30 – 35 % SO_x removal with a PUF >10. However, it confirms that an attempt to reach 50 % SO_x removal in such unfavourable conditions was technically and economically almost impossible, as the PUF fell below five and the additional energy consumption at constant steam production was increasing by >8 %, leading to specific costs above kEUR 10/tonne SO₂ saved.

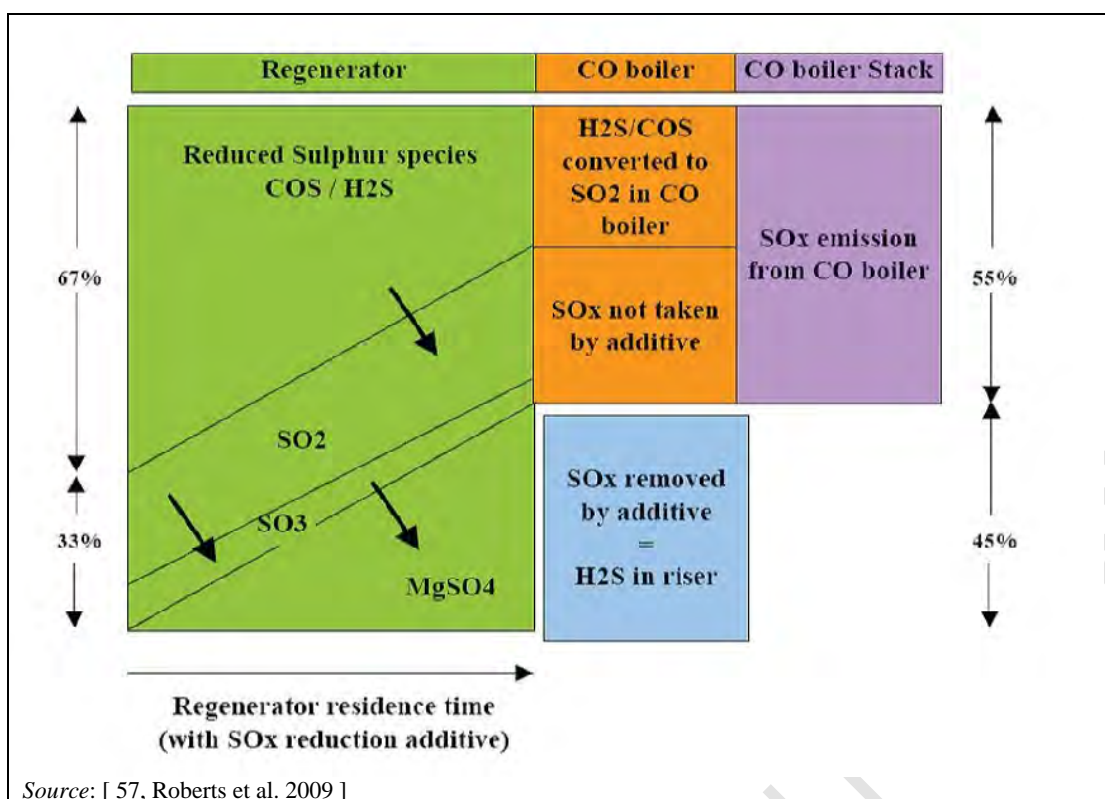


Figure 4.19: Graphical representation of the influence of SO_x-reducing additives in a partial-burn FCC unit for a given initial concentration profile

Cross-media effects

Disadvantages of this technique include the following:

- SO_x-reducing additive is not really a polyvalent technique implementable to all units as, despite recent progress made, it remains actually more efficient and economically more attractive in the full combustion mode.
- There is a possibility of poorer yield of products from FCC units and reduced FCC unit operating flexibility, especially when additives are applied at very high rates (>10 – 15 % of fresh catalyst addition).
- SO_x-reducing additives might have a detrimental effect on PM by increasing catalyst losses due to attrition, and on NO_x generation by participating in the CO promotion activity. When used in partial-burn mode, this can lead to significant increases in the supporting fuel consumption in the CO boiler for an equivalent steam production.
- Other impacts are additional waste generation, and the possibility of bottlenecks in the H₂S amine treating facilities.

Operational data

For an initial concentration of up to 4 000 – 4 500 mg/Nm³ (corresponding to a feedstock sulphur content of around 2 – 2.5 %), a typical downstream effluent of an FCC unit using this technique has a SO₂ concentration of 1000 – 3000 mg/Nm³ at 3 % O₂, depending on the additive usage rate and the unit combustion mode.

Figure 4.20 and Figure 4.21 below relate to a full-combustion FCC unit, operated under rather unfavourable conditions due to a very low inventory replacement rate (daily additions of only 0.5 % of the unit inventory), together with respective average rises and regenerator temperatures of 508 °C and 673 °C. The two given sets of data illustrate the results achieved in the case of a high average sulphur content (1.6 %) and a low one (0.5 %), for which the removal yield is higher.

These two graphs show the profile of the additives performance over time (expressed as days on X-axis) for two different types of feedstock (high and low sulphur).

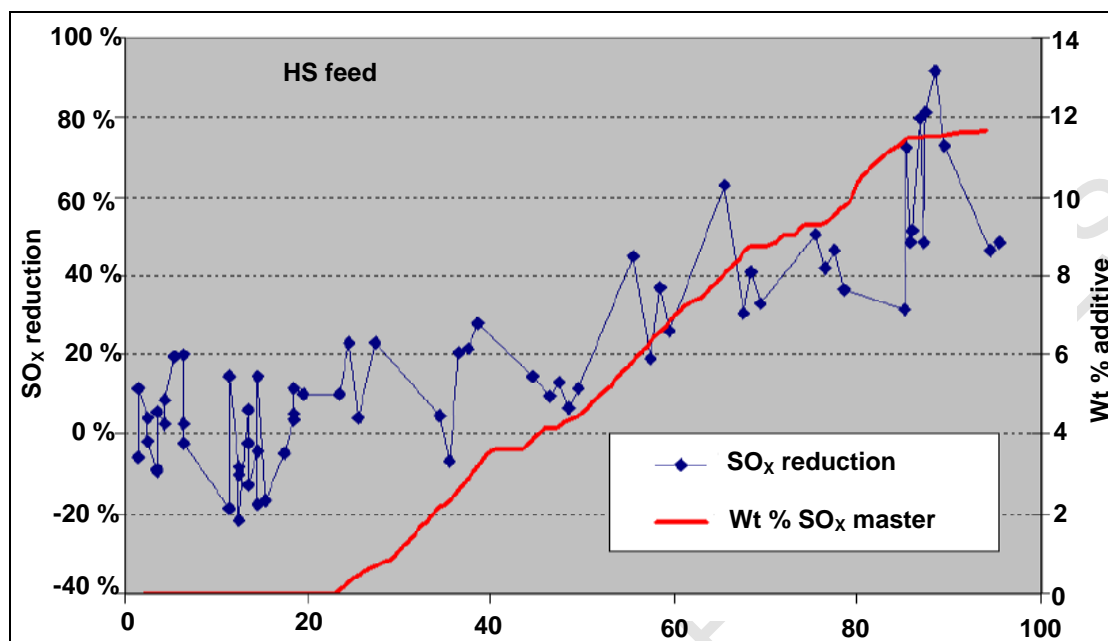


Figure 4.20: SO_x reducing additive performance with a 1.6 % sulphur FCC unit feedstock

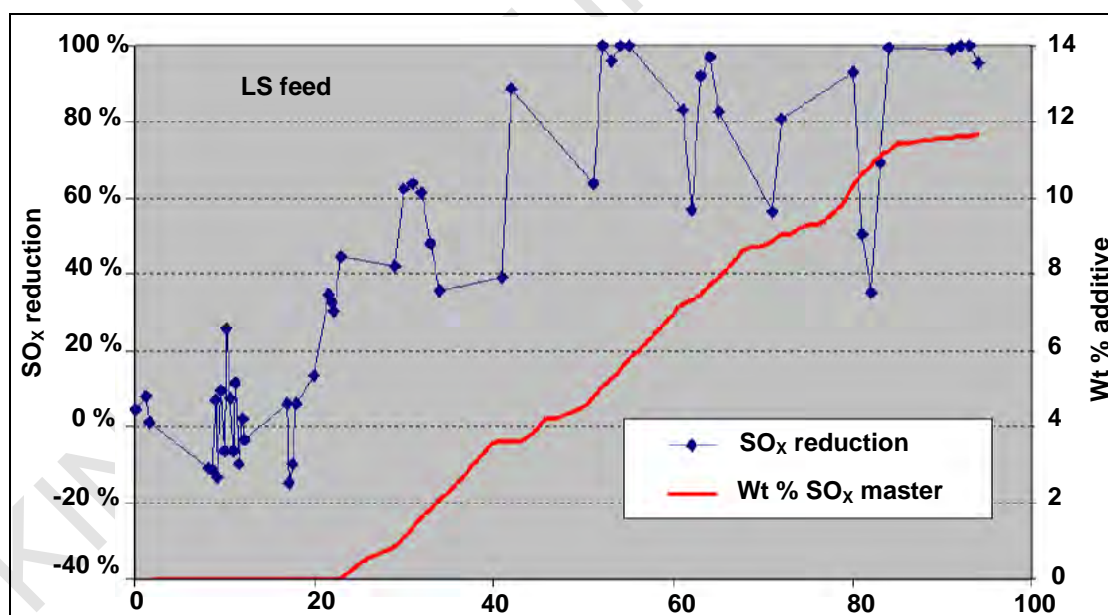


Figure 4.21: SO_x reducing additive performance with a 0.5 % sulphur FCC unit feedstock

These results are consistent with those reported by an European site, as illustrated on Figure 4.22, where a 50 % abatement (average concentration from 980 to 450 mg/Nm³ at 3 % O₂) has been currently achieved since 2009 on a 1.5 Mt/yr FCC with a 0.32 – 0.45 % S feedstock [Questionnaire N°15].

For an additive content of only 3 % in the catalyst inventory, a 25 % reduction of SO₂ emissions is reported even with a typical feed sulphur content of 0.6 – 1.8 % [Questionnaire N°50]. The SO_x removal ability of state-of-the-art SO_x reducing additives is determined by the amount in the catalyst inventory rather by the daily addition rate, showing an increased stability.

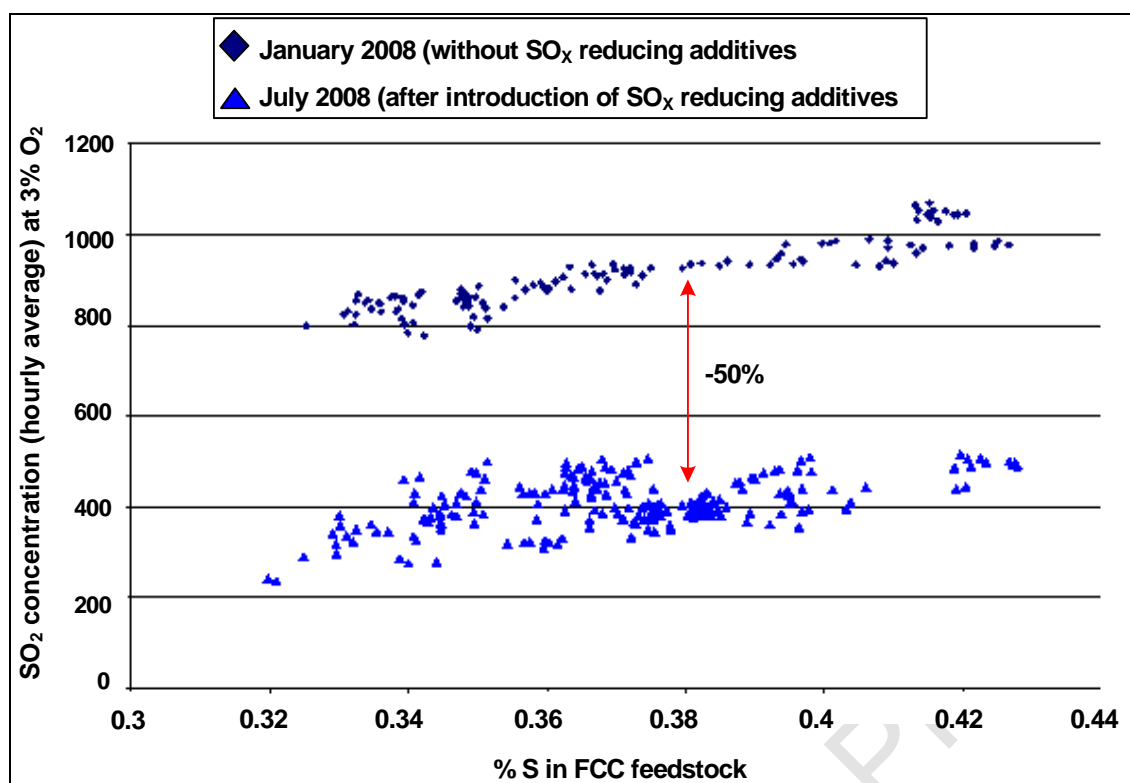


Figure 4.22: SO₂ emissions decrease from a French FCC unit using SO_x reducing additives
Applicability

The outlet SO_x concentration achievable with this technique is highly dependent on the SO_x inlet concentration, the amount of additive that can be used, and the unit operation mode.

This technique is sensitive to unit design, especially regenerator conditions. It operates most effectively under full combustion mode conditions, where virtually all the sulphur in the flue-gases can be removed when the technique can be retrofitted in the most favourable conditions.

FCC unit performance may, however, be affected and the transfer catalyst replacement rate may be significant. A fine retuning of the catalyst system might be required in the case of large quantities of additives being incorporated.

Thanks to its high adjustability, this technique can also be combined together with other process-related or end-of-pipe abatement techniques.

- In association with wet scrubbing, as has been the case since 2006 for a BP refinery in Texas City, where additives help to reduce the operating chemical consumption (e.g. caustic) and energy (e.g. pumping). Another example of this is reported for a Middle East refinery which processes 30 000 barrels per day (around 2 million t/yr) of a 100 %-atmospheric residue feedstock with a high-sulphur content of 2.7 % operated in full combustion, where it has been decided to use such an additive in order to master corrosion problems due to high inlet SO_x concentrations in an existing scrubber. In this refinery a 15 % reduction of the scrubber operating cost has been observed, exceeding the cost for the SO_x reducing additive, which was fully covered [26, Kramer et al. 2009].
- In association with high efficiency filters, the two techniques could lead to very cost effective conditions [30, Sawyer et al. 2009]
- In order to increase flexibility in the choice of the feed quality (e.g. external inputs), or for decreasing the severity of the upstream feed hydrotreatment.

On the other hand, this technique proves to be less efficient for FCC units operated in deep partial combustion modes, at high regenerator temperatures, with low daily replacement rates, or for which very low SO_x outlet concentrations are required. In North America, SO_x -reducing catalysts are being used preferably with wet scrubbing for FCC units in refineries with capacities lower than 150 000 barrels/day (8 Mt/yr).

Economics

There is no major investment cost required: only minor capital expenses are needed for the dosing equipment for introducing the additive to the catalyst system. As an example, the cost reported for a European site is EUR 300 000 including foundation, construction, piping, downstream capacity improvement, and the permit.

Operating expenses are dependent on the unit, the initial SO_2 emissions and the SO_2 target. The cost reported by a European site, for a 264 kg/day injection rate and a 94 t/yr additional waste elimination of spent catalyst is EUR 1.3 million/yr.

Potential investment and operational costs for implementing this technology on two FCC units in the Colorado refineries (US) were estimated in 2005. Data extrapolated to 2007 give USD 500 per tonne year of SO_2 saved, assuming a resulting SO_2 emission decrease of only

35 – 50 %. [17, Jeavons and Francis 2008]. This data is rather consistent with costs reported more recently by other US sources, also for 2007, according to which the cost for obtaining 25 ppmv at 0 % O_2 (yearly average) and 50 ppmv at 0 % O_2 (7-day rolling average) is in the range of USD 500 – 880 per tonne of SO_2 removed.

Another cost estimation is given in Figure 4.23, based on a major catalyst manufacturer's field experience within US refineries. The graph is provided for a reference unit of 50 000 barrels/day (around 3 million t/yr) capacity, with a 150 tonne catalyst inventory. The range reflects a wide variety of FCC unit configurations, with different untreated off-gas SO_x levels, feed types and regenerator operational conditions (including full and partial combustion). [25, Pham et al. 2009]

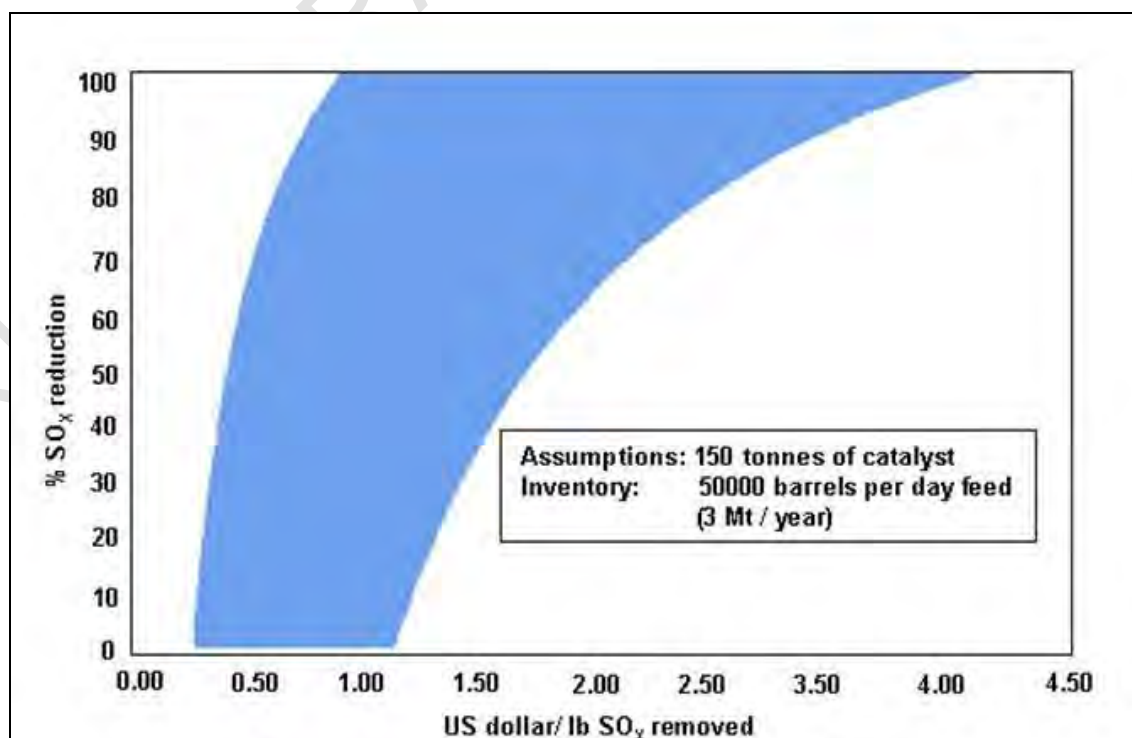


Figure 4.23: FCC SO_x reduction additives specific cost versus SO_x overall reduction target

A similar approach has been followed which proposes a cost estimation for full-and partial-combustion mode, as drawn from the European catalytic market. [280, ABERMALE 2008]

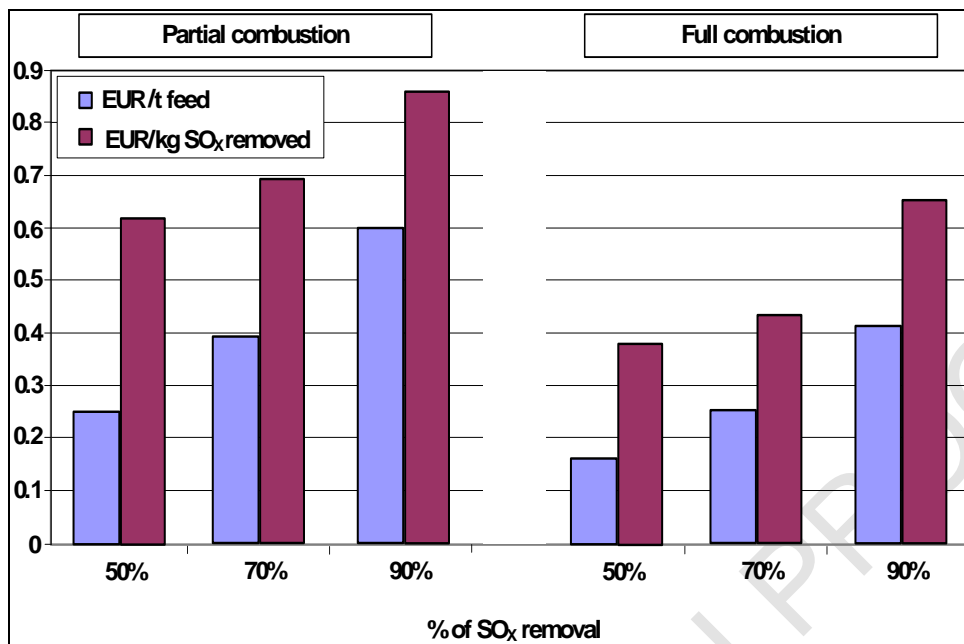


Figure 4.24: Economics of SO_x reduction additives for FCC units-general cost overview

Finally, the available literature also reports the following removal costs reached during particular trials aiming at ultra-low SO₂ emissions, as shown in Table 4.23 below [30, Sawyer et al. 2009].

Table 4.23: Performances and specific removal costs with SO_x reducing additives at a high injection rate

	Refinery A	Refinery B
Fresh feed rate (t/day)	2876	6847
Fresh feed (API)	24.9	28.5
Uncontrolled SO ₂ (vppm)	178	326
Controlled SO ₂ (vppm)	10	7
SO ₂ reduction	95 %	98 %
Removal cost ⁽¹⁾ (EUR/t SO ₂)	780	940
⁽¹⁾ Respectively USD 0.51 and 0.61 per lb of SO ₂ (2009 value)		

Table 4.24: Economics of two sulphur abatement techniques: additives and wet gas scrubber – Cost effectiveness data from a sample of 6 FCC units

					Sulphur reduction additives (SRA)					Wet gas scrubber (WGS)					
					Efficiency	ACC	Fixed OP		Variable OP	Efficiency	ACC	Fixed OP		Variable OP	
					40 %	7.4 %	4 % TEC/yr		1 000 €/t SO ₂	90 %	7.4 %	4 % TEC/yr		0.93 €/tFF	
Base case in 2006															
Unit	Design Feed	Utilisation	Actual Feed	Outlet SO ₂	Outlet SO ₂	SO ₂ Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to SRA	Cost Effectiveness: Base to SRA	Outlet SO ₂	SO ₂ Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to WGS	Cost Effectiveness: Base to WGS	Incremental Cost Effectiveness: SRA to WGS
	kt/yr	%	kt/yr	mg/Nm ³	mg/Nm ³	t/yr	M€	k€/yr	€/t SO ₂	mg/Nm ³	t/yr	M€	k€/yr	€/t SO ₂	€/t SO ₂
1	5 480	97 %	5 319	3 134	1 880	3 334	0.9	3 439	1 031	313	7 502	49.4	10 582	1 410	1 714
2	1 591	85 %	1 351	3 012	1 807	814	0.4	863	1 061	301	1 831	23.5	3 940	2 152	3 024
3	2 857	88 %	2 506	1 504	902	754	0.6	824	1 094	150	1 695	33.4	6 143	3 623	5 647
4	1 999	79 %	1 577	1 486	892	469	0.5	526	1 122	149	1 055	27.0	4 543	4 307	6 856
5	1 648	99 %	1 625	860	516	279	0.4	330	1 181	86	629	24.0	4 250	6 758	11 220
6	1 927	97 %	1 877	362	217	136	0.5	192	1 410	36	306	26.4	4 756	15 543	26 850

Source: [CONCAWE 6/11]

Driving force for implementation

Reduction of sulphur oxide emissions from the FCC.

Example plant(s)

More than 60 refineries worldwide are applying DeSO_x additives to the catalyst, including several partial-combustion units in Germany, Japan, and Republic of South Africa. The method is well established commercially.

Reference literature

[166, CONCAWE 1999], [151, Sema,Sofres 1991], [163, FWE 1999],[221, Italy 2000], [228, TWG 2000], [25, Pham et al. 2008], [26, Kramer et al. 2009],[30, Sawyer et al. 2009] [Questionnaires n° 15, 27, 49, 50], [36, CONCAWE n°4/09 2009], [57, Roberts et al. 2009], [139, CONCAWE 6/11 2011],[280, ABERMALE 2008].

4.5.6.2 Wet scrubbing

Description

There are several wet scrubbing processes. A brief description of them is included in Section 4.23.5.4. The types of wet scrubbing that are typically used for FCC units are:

- sodium or magnesium-based non-regenerative wet scrubbing, using packed towers, plate towers, spray chambers, or Venturi systems;
- these combining conventional scrubbing techniques with the use of a regenerative process (e.g. the LABSORB™ produced by BELCO using a patented solution containing soda and phosphoric acid or CANSOLV process with an amine solution– see Section 4.23.5.2.3).

Two Venturi systems have been developed successfully by ExxonMobil specifically for FCC application:

- The Jet Ejector Venturi (JEV) scrubber, for lower pressure streams, where the absorbing liquid is sprayed into the flue-gas stream at the inlet of the venturi above the ‘throat’. Gas and liquid then pass through the throat under conditions of high turbulence.
- The High Energy Venturi (HEV) scrubber, for higher pressure streams, which use the kinetic energy of the flue-gas to break the absorption liquid into droplets. This technique requires a greater drop in gas pressure but it has higher efficiencies for small particulates compared to Jet Ejector Venturi Scrubbers, in particular for PM_{10} and $\text{PM}_{2.5}$, and is typically being able to remove PM_2 .

Another successful system worth mentioning is the Electro-dynamic Venturi (EDV®) developed by BELCO, which combines the techniques used in Venturi scrubbers with electrostatic dust separation. The system houses a spray tower along with forced condensation and water spraying filtering modules and droplet separators. It can be associated, like in the ENI Sannazzaro refinery, with the LABSORB™ regenerative process (see Section 4.23.4.4), or also with the LOTOX™ de- NO_x SNERT process using ozone injection (see Sections 4.5.4.5 and 4.23.3.1).

Achieved environmental benefits

Even if SO_2 removal is the first objective, a suitably designed wet scrubbing process will normally provide a very high removal efficiency of both SO_2 and particulates, taking into account that SO_3 abatement is typically not as high as SO_2 . With the inclusion of an extra treatment tower to oxidise the NO to NO_2 , NO_x can also be removed efficiently. Table 4.25 shows the achievable emission levels that can be expected with a wet scrubber.

Table 4.25: Generic achievable efficiency and emission levels for wet scrubbers

Parameter	Efficiency (%) ⁽¹⁾	Inlet (mg/Nm ³) at 3 % O ₂	Outlet (mg/Nm ³) at 3 % O ₂
SO ₂	95 – 99.9	600 – 10 000	< 60 – 160 ⁽²⁾
Particulates	85 – 95	350 – 800	< 30 – 60 ⁽²⁾
NO _x	70	600	180

NB: Particulates removal is very much design related and system pressure drop is highly variable. Scrubbers are less effective on reducing submicron particles.
⁽¹⁾ Source: [45]
⁽²⁾ Based on sample data of non regenerative scrubbers as shown in Table 4.26

In the case of regenerative scrubbing, the main additional benefit is obviously the possibility to regenerate the SO_x absorbing reagent and to recover concentrated SO₂ streams which can be converted and sold/recycled as liquid SO₂, sulphuric acid or elemental sulphur. In correlation to this, a much lower amount of solid residue must be recovered and eliminated. Compared to a non-regenerative process, the energy consumption is also reported to be lower (see under Operational data and Economics paragraphs).

Cross-media effects:

Non-regenerative wet scrubbing systems create secondary problems of aqueous slurry waste disposal and increase the refinery energy consumption. The effluent water purge contains sulphates (e.g. Na₂SO₄). Another drawback is the consumption of a significant quantity of expensive raw material (e.g. caustic soda) which is roughly proportional to inlet sulphur loadings. Flue-gas reheat may be needed to prevent plume mist.

Typical impacts of regenerative systems are the possible debottlenecking of H₂S-handling facilities (e.g. SRU, amine scrubbers), the production of other eventual by-products, as well as the need for raw material supply and handling.

Operational data

Non-regenerative scrubbing

Table 4.26 provides data observed for seven FCC units operated in the US. All of them are Venturi-type [36, CONCAWE n°4/09 2009].

Table 4.26: Wet venturi scrubbing performances for some US FCC units

Type	Outlet PM	Outlet PM average	% PM abatement	Inlet SO ₂	Outlet SO ₂	% SO ₂ abatement
Partial combustion with CO boiler ⁽¹⁾	35 – 60	47	NA	NA	NA	NA
Partial combustion with CO boiler ⁽¹⁾	39 – 50	46	NA	NA	NA	NA
Full combustion unit ⁽¹⁾	48 – 109	74	NA	NA	NA	NA
Full combustion unit ⁽¹⁾	NA	56	NA	NA	NA	NA
Partial combustion with CO boiler ⁽¹⁾	43 – 61	56	NA	NA	NA	NA
Partial combustion with CO boiler ⁽²⁾	NA	NA	NA	425	61	90 %
Partial combustion with CO boiler ⁽²⁾	NA	NA	93 %	>1 800	125 – 160 ⁽³⁾	93 %

⁽¹⁾ Average in mg/Nm³ @ 3 % O₂ (dry gas), based on spot measurements.
⁽²⁾ Daily average in mg/Nm³ @ 3 % O₂ (dry gas), based on continuous emission monitoring Jet Ejector Venturi (JEV) system.
⁽³⁾ Daily average calculated from the 95th percentile range of the complete available data-set.
 NA Not available

Regenerative scrubbing

A LABSORB™ regenerative scrubbing system has operated since 2004 at the ENI refinery in Sannazzaro (Pavia, Italy). It treats all the flue-gas (0.18 million Nm³/h – 300 °C) from the 5 500 t/day FCC unit at an inlet concentration of >1 700 mg/Nm³ (3 % O₂). Outlet gas (208 000 Nm³/h – 67°C) is released at a concentration of 50 – 250 mg/Nm³ (3 % O₂) with a SO₂ removal efficiency >85 %, as a daily average. An extra 250 kg/h concentrated SO₂ stream is sent to the SRU. Liquid waste production is 1t/hr and solid waste production is 19 kg/h (compared to 9 t/h and 1 000 kg/h in the case of NaOH conventional absorption for the same capacity).

Another regenerative scrubbing system has been in operation since 2006 at VALERO refinery in Delaware City (Delaware, US). It includes a prescrubber, an amine-based regenerative packed-bed absorber, and a caustic polisher. It is designed to treat an inlet flow of 0.75 million Nm³/h with a SO₂ removal rate of >97 %. Since its installation, it has continuously achieved 1 – 2 ppmv SO₂ at 0 % O₂ (i.e. 3 – 6 mg/Nm³ at 3 % O₂) [25, Pham et al. 2009].

Table 4.27 gives the typical performance achieved with a Wellmann-Lord regenerative scrubber.

Table 4.27: Typical performance achievable with a Wellmann-Lord regenerative scrubber

Technique	SO ₂ Reduction efficiency (%)	Inlet SO ₂ concentration (mg/Nm ³) @ 3 % O ₂ 160 – 180 °C	Outlet SO ₂ concentration (mg/Nm ³) @ 3 % O ₂ 120 °C
Wellmann Lord	98	2 000 – 7 000	100 – 700

More information and comparison with other techniques can be found in Section 4.23.5.4

Applicability

Wet gas scrubbers are generally recognised as flexible and reliable. Day-to-day operating changes can be readily handled. They generate a low-pressure drop and operate at low temperatures. Their performance can be affected by deposition problems occurring in the course of a typical five-year run: the amount of deposition depends on the inlet catalyst and SO₂ load to the scrubber, the quality of the make-up water, the operating pH of the scrubber, and the level of purge applied to the scrubbing slurry. The deposits are formed by catalyst dust that settles at low points and by mist eliminators and hard deposits (e.g. salts of calcium) that precipitate as the operating pH is increased to achieve high SO₂-removal efficiency. Some CO₂ can be removed as well by wet scrubbers, however, in that case, it reduces the capability of the media to dissolve SO₂. These systems, in particular when using Venturi scrubbers, are also rather compact: the necessary plot spaces ranges from 93 to 465 m² for FCC capacities from 1.5 to 7.5 Mt/yr. More information can be found in Section 4.23.5.4.

The applicability may be limited in arid areas and in the case where the by-products from treatment cannot be reused or appropriately disposed of. The applicability of the technique may require significant space availability.

Economics

Table 4.28 provides an indicative order of retrofitting costs for various FCC wet gas scrubber applications.

Table 4.28: Retrofitting costs for FCC wet gas scrubber applications

Objective of the process	FCC capacity (Mt/yr)	Investment expenses (EUR million)	Operating expenses (EUR million/yr)
SO ₂ and particulate reduction	2.4	17 – 40 ⁽¹⁾	3.5 – 4.2 ⁽¹⁾
⁽¹⁾ Respectively, USD million 25 – 60 and 5 – 6 in 2009. Capital costs will vary considerably from location to location depending on the scrubber type and the need to upgrade infrastructure and WWTP facilities.			

Additional information for the comparison of cost data for the use of sulphur reduction additives and wet gas scrubber are available in Table 4.24 in the previous section.

Non-regenerative scrubbers

The 2003 estimated costs for the installation of non-regenerative wet scrubbers in six different refineries were quoted in a 2009 prospective report from the South Coast Air Quality Management District (California, US). Investment costs cover all production and installation expenses within the scrubber battery area. It does not include foundations, external main ductworks to the scrubber inlet, nor external piping and electrical supply equipment which may add 30 – 50 % to the above costs. Results of this estimation are displayed in Table 4.29.

Table 4.29: FCC UNIT - Cost estimates for various off-gas non-regenerative wet scrubbers

Refinery	Off-gas flowrate (million Nm ³ /h)	Capital investment ^(*) (million USD)	Operating expenses (million USD/yr)
# 1	0.04 – 0.16	10	0.37
# 2	0.34 – 0.36	13.8	0.56
# 3	0.16	10	0.36
# 4	0.37 – 0.47	15	0.57
# 5	0.20 – 0.23	12.23	0.39
# 6	0.15	9.5	0.32
^(*) Investment expenses cover the costs for all design, fabrication, supply, installation of the complete system, including its new stack, associated purge treatment unit, and internal piping and electrical supply equipment within the scrubber battery area - All costs in 2003 value			

With regard to the assumption of a 25-year life for the scrubber, and considering a 4 % annual increase rate, this report gives an overall cost effectiveness average for these six plants at 24600 USD/tonne of SO₂ removed, in order to achieve at least 5 ppmv outlet concentration and 90 % abatement.

Regenerative scrubbers

A regenerative wet gas scrubber typically costs more than a non-regenerative unit to install, due to additional complexity. One equipment supplier mentions an indicative factor of 2.4. However, the regenerative system has a significant advantage in annual operative costs because of the alkaline absorbing reagent saving and, eventually, the cost return related to by products (e.g. elemental sulphur) sales. The annual operating costs of a regenerative system are estimated to be no more than 35 % of those of a non regenerative system. A more detailed comparison is provided in Table 4.30.

Table 4.30: Cost comparison between regenerative and non-regenerative wet scrubbers for FCC application

Wet scrubbing cost breakdown	Cost of a regenerative system compared with a non-regenerative system (%)	
Capital costs	240 %	
Operating costs:		
- Electrical power	35 %	
- Steam	10 %	
- Caustic	18 %	
- Phosphoric acid	5 %	
- Make-up water	<5 %	<35 %
- Cooling water	<5 %	
- Water discharge and treatment	<5 %	
- Solid waste disposal	<5 %	
- Operating and maintenance staff	20 %	

Even more favourable costs have been reported in the case of the ENI Sannazzaro LABSORB unit, with a 40 % savings in total operating costs compared with a wet conventional process using caustic soda. This includes 95 % savings in absorbing solution make-up and 25 % savings in power consumption.

Driving force for implementation

Abatement of sulphur oxides and particulates from the flue-gas.

Example plants

This technique is widely used on FCC unit plants in the US. The Wellman- Lord system has been successfully applied to power plants. More information can be found in Section 4.23.5.4.

Reference literature

[181, HP, 1998], [208, Confuorto 2000], [151, Sema, Sofres 1991], [191, UBA Austria 1998], [45, Sabo et al. 2007], [25, Pham et al. 2009], [30, Sawyer et al. 2009], [36, CONCAWE n°4/09 2009].

4.5.6.3 Dry and semi-dry scrubbers

Description

Two types of scrubbing techniques exist: dry and semi-dry. The key component of the semi-dry process is a spray dryer in which the hot flue-gas comes into contact with a spray of fine droplets of lime slurry. The SO₂ is absorbed into the droplets, forming reaction products which are dried to a fine powder by the hot flue-gas. Both dry and semi-dry processes require downstream dust arrestment systems, such as an electrostatic precipitator or bag filtration. More information can be found in Section 4.23.5.4.

Achieved environmental benefits

Reduction of the SO₂ in the flue-gas. Efficiency of each process is a 90 % sulphur removal with semi-dry, and about 50 % removal with dry process. Dry process efficiency of 50 % is achieved with lime at relatively high temperatures (about 400 °C) when Ca/S=1, or at 130 - 140 °C when Ca/S=2. The Ca/S ratio has a major influence. With a reactant such as NaHCO₃, the abatement rate would be much higher. With lime, it is also possible to have a treatment at 900 °C in a reactor large enough to have a reasonable residence time. The abatement in this case is 80 % with CaS= 2.1 and 90 % with Ca/S=3.

Cross-media effects

Deposition of solid waste results in cases where the reaction products cannot fulfil the quality needed by consumers. Other drawbacks are:

- high-pressure drops across the bag filters if used;
- increased dust load in the gas stream; need for dust capture;
- operational difficulties in water/heat balance (spray dryers only);
- possibly significant pressure drops across bag filter dust arrestment plants, e.g. bag filters;
- generation of solid waste: one tonne of SO₂ reduction entails about 2.5 tonnes of solid wastes being generated;
- with the dry and semi-dry scrubbers a mixture of CaSO₃, CaSO₄, fly-ash and lime is produced.

Operational data

These systems are generally sensitive to other contaminants such as particulates, salts, sulphur trioxide, etc.

Applicability

Operates at low-temperature. Waste generated can be difficult to reuse (no market for gypsum), and difficult to landfill.

Economics

The dry process is a relatively low-cost solution. Raw materials for these processes are cheap. Capital cost and operating costs are typically less than for wet scrubbing. Investment costs are around EUR 15 - 20 million, and operating costs are around EUR 2 - 3 million/yr (lime cost + landfill waste disposal).

Reference literature

[163, FWE 1999], [200, Gilbert 2000], [151, Sema,Sofres 1991], [221, Italy 2000].

4.5.6.4 Seawater scrubbing**Description**

Seawater scrubbing uses the natural alkalinity of the seawater to remove SO₂. More information can be found in Section 4.23.5.4.

Achieved environmental benefits

SO₂ recovery can be as high as 99 %. In order to reduce the particulate emissions to the seawater, a particulate abatement technique should be included before the flue-gas is treated in the seawater scrubber. Seawater scrubbing transfers sulphur emissions from air as SO₂ to the sea as SO₄, with a significant reduction in the overall environmental impact.

Cross-media effects

Particulates containing metals (e.g. V, Ni, Sb) and other pollutants from the flue-gas are transferred to the seawater. The sulphur content of the effluent seawater from the process itself is increased by only approximately 3 %. Seawater pumping and compression facilities increase the electricity consumption of the plant.

Operational data

The system needs electrical power (seawater pumps, aeration fans and flue-gas fans) and seawater. The seawater flow required for treating the 497 t/h mixed flue-gas stream received from a RCC unit (with CO boiler) and a SRU is 5 000 m³/h in the Statoil refinery of Mongstad (Norway). The seawater scrubber outlet temperature must be 25°C. The seawater is further mixed with cooling water and the mixed temperature is around 15°C.

In the Mongstad refinery, SO_x emissions from the RCC unit (310 kg/h) and the SRU tail gas (521 kg/h) were abated to 31 kg/h (>96 % reduction), as a yearly efficiency average in 2008.

It is feasible to use spent cooling water, for example, when seawater is used as cooling water. The need for seawater is around 30 m³/h for treating flue-gas 1 000 Nm³/h with a SO_x concentration from 3 000 to 4 000 mg/Nm³. Special attention should be paid to minimise corrosion and the maintenance costs derived from it.

Applicability

The feasibility of applying seawater scrubbing depends on site-specific factors. The process requires access to large amounts of seawater at a competitive cost and high seawater circulation in the areas of the inlet and the outlet. It is fully applied for fuels with up to 1.5 % sulphur content. This system should be applied after a high particulate abatement removal technique to minimise as much as possible the contamination of the sea environment by particulates (containing metals).

Economics

Seawater scrubbers annual costs depend on size and SO_x input/output. The cost is comparable to wet scrubbers. Typical investment costs are in the order of EUR 60/net kW output of the power plant. The main operating cost is the electrical power for operation of the technique.

Driving force for implementation

Reduction of SO₂ emissions.

Example plants

This system has been applied to some power plants around the world (e.g. Norway) and one proven commercial application for the RFCC flue-gas (after an ESP filtration) operated by Statoil in Mongstad (Norway).

Reference literature

[212, Power 2000]

4.5.7 FCCU abatement techniques performances and emissions variability

The following Table 4.31 shows the achieved emissions values expressed as minimum and maximum monthly concentrations (at 3 % O₂ level) observed from continuous monitoring for a number of FCC units in Europe for dust, SO₂ and NO_x and the determining conditions of operation or the currently applied techniques at these units. [145, TWG CONCAWE 2012]

Examples of daily variability of dust, SO₂ and NO_x emissions to air are shown in Figure 4.25, Figure 4.26, Figure 4.27 and Figure 4.28.

According to a survey carried out in 2012 on 12 out of 14 sites currently operating in Italy, the trends of the emissions change from site to site and from plant to plant. According information provided in this survey, emissions to air from FCCUs are depending on technical and construction features, mainly linked to a process configuration designed to crack heavy products, characterized by different qualities of feed and its origin (coming from other refinery units or imported to the site). Thus, a broad daily variability of the emissions of SO₂ and NO_x occurs. [278, TWG-IT 2012]

Table 4.31: Abatement techniques and reported performance data for a sample of European FCC units

Refinery	Dust			SO ₂			NO _x		
	monthly min mg/Nm ³ @ 3 %O ₂	monthly max mg/Nm ³ @ 3 %O ₂	Technique	monthly min mg/Nm ³ @ 3 %O ₂	monthly max mg/Nm ³ @ 3 %O ₂	Technique	monthly min mg/Nm ³ @ 3 %O ₂	monthly max mg/Nm ³ @ 3 %O ₂	Technique
J	27	47	Secondary Cyclones, 4 stage ESP and ammonia injection						
E	11	21	TSS + 4-fields ESP. Ammonia injected when needed no continuous use.						
G	15	27	TSS + 4-fields ESP	450	900	HT (80 %) of feed + to give average S content 0.3 %	120	175	HT (80 %), low NO _x CO promotor. Effect of HT on NO _x unquantified
XY	18	38	3 -fields ESP with ammonia injection	600	650	Complex feed with average 26 % HT residue	80	395	Complex feed with average 26 % HT residue
L	26	40	3-field ESP with ammonia injection (30 mg/Nm ³ of NH ₃)						
S	38	55	TSS + 3-fields ESP No ammonia injection						
ZA	65	81	TSS						
H	62	85	Sec. cyclones, regular (4 hourly) soot blowing. Spot sample gives 66 mg/Nm ³ of 85 for opacity meter.				650	830	
U	60	90	Three stage separators	380	700	Partial hydrotreatment of feed	220	590	DeNox Additive
V	65	103	TSS	692	2 485	Partial hydrotreatment of feed	176	522	DeNox Additive. NO _x higher at 490 for month following start-up.
X	110	130	TSS	350	750	Feed is hydrotreated	180	300	Feed is hydrotreated
Z	120	130	TSS (limited data-set)						
N	60	155	TSS	750	1400	Hydrofined Feed	280	700	Antimony additive used to control adverse effects of Ni deposition on catalyst
YZ			TSS + ESP - 3 stage (no data)	650	1 200		60	130	Not known
1				410	590	Low S feed and Sulphur Reducing Additive (before additive was 900)			
2				800	1200	Feed S content below 1 %			
3	-	-	-	2 000	2 100	Feed S content above 1 % (3-month only)	-	-	-
Ø	-	-	-	2 500	4 500	No abatement measures, oil fired in auxiliary boiler	350	700	-
D				6	23	Fully Hydrotreated Feed to 0.03 % S.	100	150	Fully Hydrotreated Feed 0.03 % S. One month NO _x is at 40 mg/Nm ³ but this appears atypical

Source: [TWG CONCAWE 2012]

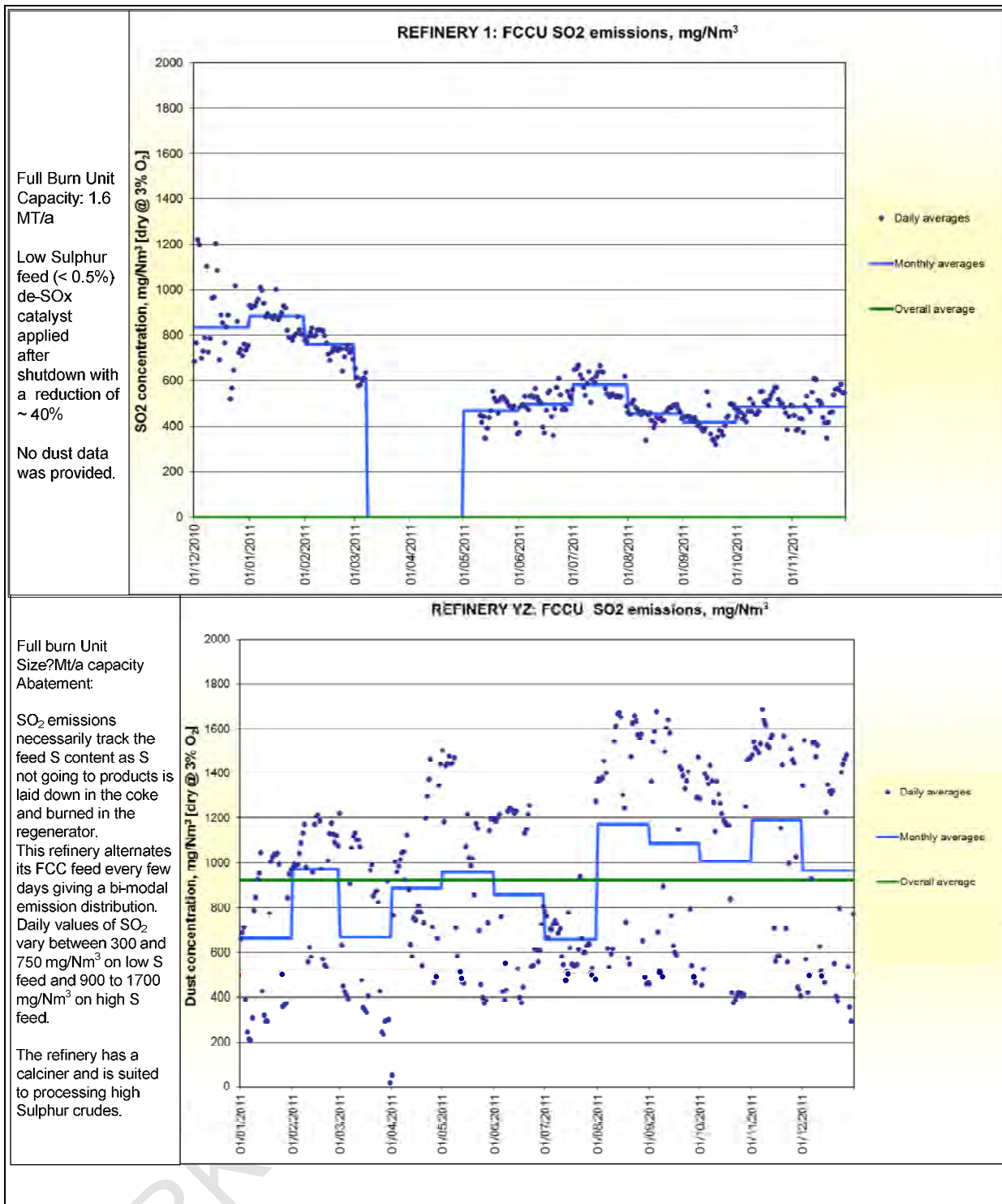


Figure 4.25: Daily variations of SO₂ emissions from FCC units: Example of sites 1 and YZ

The graphs presented in Figure 4.25 and Figure 4.26 illustrate some examples of the daily variations of SO₂ emissions reported for a number of European FCC units and the available contextual information.

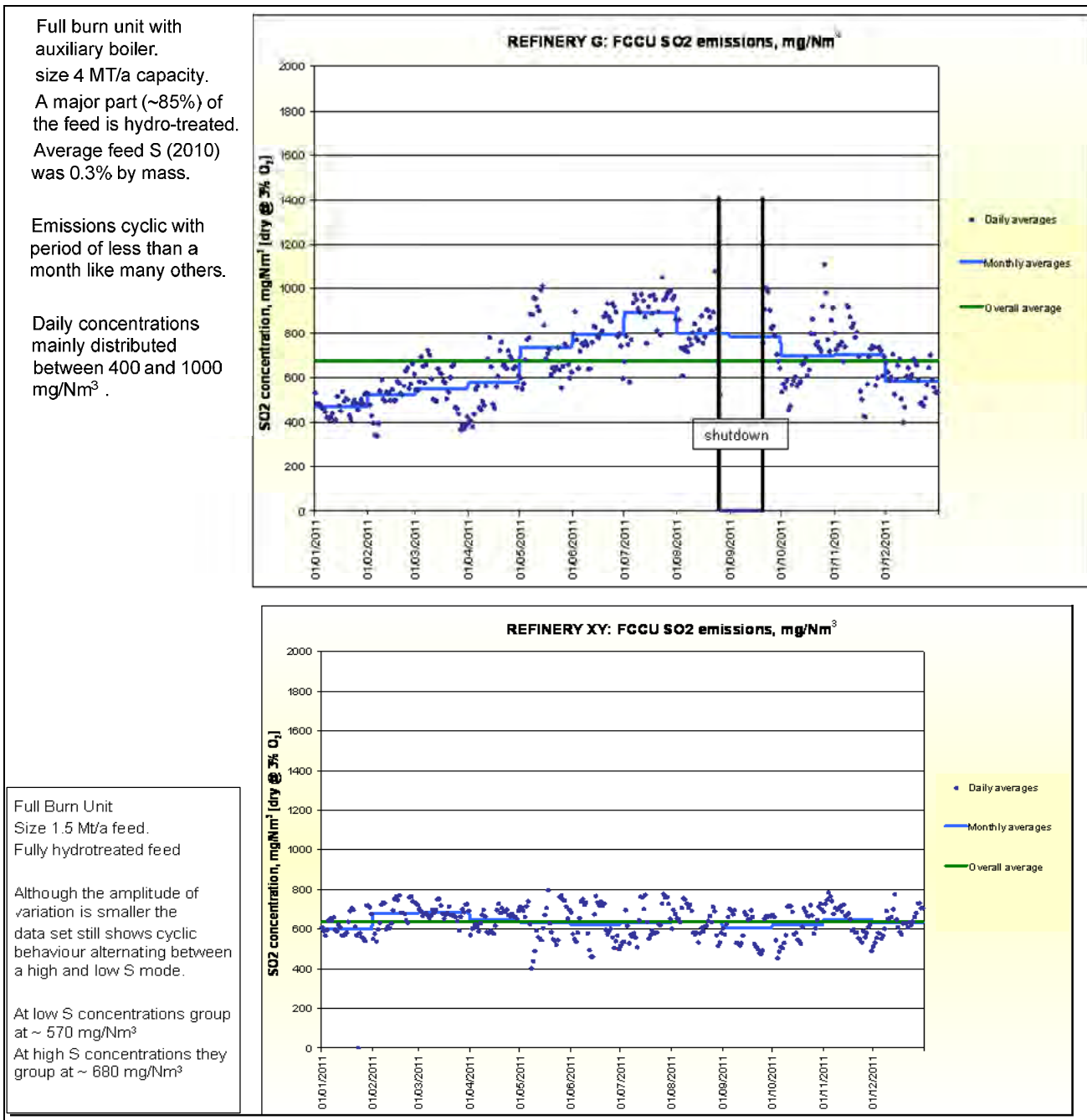


Figure 4.26: Daily variations of SO₂ emissions from FCC units: Example of sites G and XY

WORKING

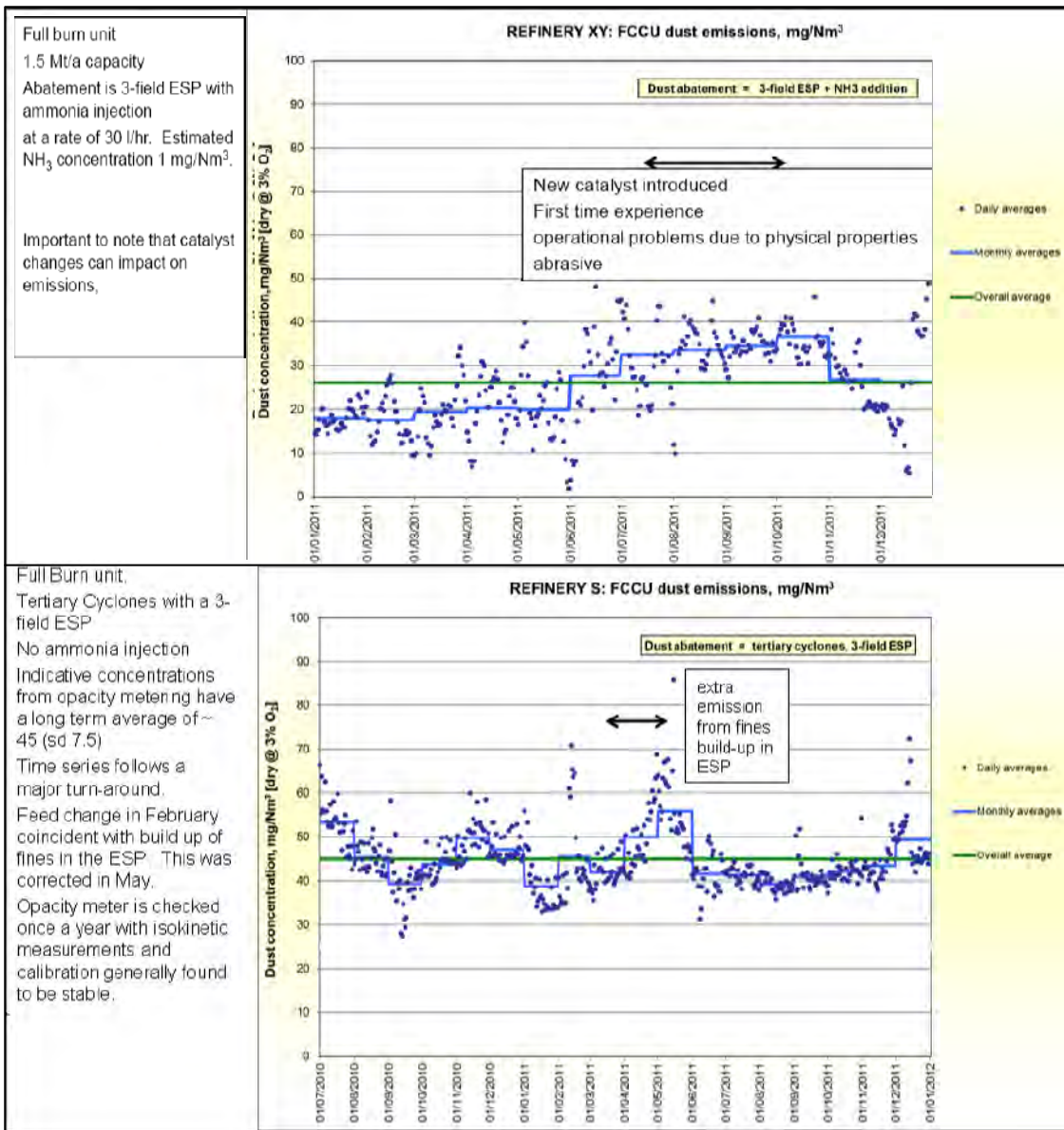


Figure 4.27: Daily variations of dust emissions from FCC units: Example of sites XY and S

The graphs presented in Figure 4.27 illustrate some examples of the daily variations of dust emissions reported from the continuous monitoring of two European FCC units.

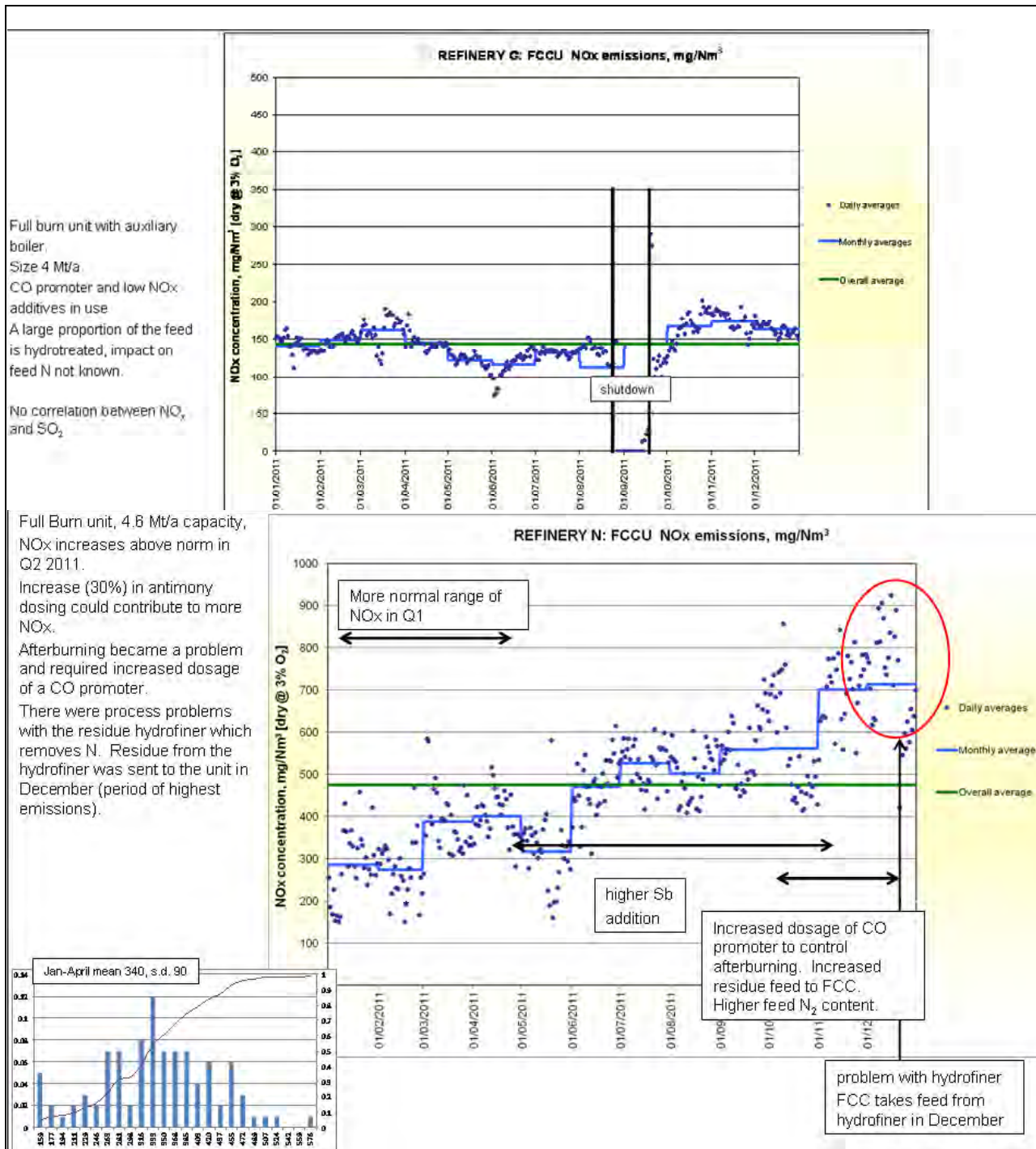


Figure 4.28: Daily variations of NO_x emissions from FCC units: Example of sites G and N

The graphs presented in Figure 4.28 illustrate some examples of the daily variations of NO_x emissions reported from the continuous monitoring of two European FCC units.

4.5.8 Waste management techniques

See previous sections for selection of catalyst, control of the emissions of particulates and proper management of product and slurry tank bottoms that can reduce the generation of waste.

4.6 Catalytic reforming

The first two techniques considered are process-integrated techniques and the rest are techniques for the prevention or control of emissions from the catalytic reforming processes.

4.6.1 Reduction and/or substitution of catalyst promoter (chlorine precursor)

Description

During the regeneration of the catalyst, organic chloride is needed for effective reforming catalyst performance: a chloride injection is needed to re-establish the proper chloride balance in the catalyst and to assure the correct dispersion of the metals. Ozone-depleting substances (e.g. carbon tetrachloride) were initially used during the regeneration. According to Regulation (EC) No 2037/2000 of the European Parliament and of the Council of 29 June 2000 on substances that deplete the ozone layer, the placing on the market and use of such substances, particularly carbon tetrachloride, are now prohibited.

Achieved environmental benefits

Optimisation and reduction of the use of catalyst promoters. Use of substitutes for ozone-depleting substances, such as perchloroethylene.

Cross-media effects

Due to the use of chlorinated compounds, the possibility of emissions of dioxins and furans during regeneration has been detected.

Operational data

Promoters should be handled in enclosed systems.

Example plants

Most refiners have switched to less ozone-depleting substances, such as perchloroethylene, during the regeneration of the reforming catalyst.

Reference literature

[156, MCG 1991].

4.6.2 Cleaning of the regeneration flue-gas

Description

The regeneration vent gas can contain traces of HCl, Cl₂, CO, SO₂, hydrocarbons, dioxins and furans. The storage and handling of organic chlorides used during the regeneration may also lead to releases. In some designs, the regeneration vent gas may be routed over an adsorption bed, through a scrubber, or combined with a basic water wash system.

Achieved environmental benefits

Adsorption beds, water or caustic scrubbers, and basic water wash systems lead to a reduction of the emissions of trace components in the regeneration vent gas and removal of the majority of the dioxins and furans from air emissions. However due to the hydrophobic characteristic of dioxins and furans, a part may pass through such cleaning system.

Cross-media effects

When the design includes a scrubber, the recirculated and bleed streams from the regeneration flue-gas wash should be sent to the waste water treatment plant. Due to the low pH of this waste water stream, neutralisation prior to biological treatment may be necessary. The use of scrubbers can move some dioxins from air to water emissions.

Applicability

Fully applicable to new units and with general provisions about retrofitting existing units, taking into account the current design (impact on pressure and temperature balances, existing structures, plot space availability, etc).

Economics

No data available for this particular application.

Driving force for implementation

Reduction of air pollutants.

Reference literature

[163, FWE 1999], [207, TWG 2001].

4.6.3 Electrostatic precipitator in the regeneration flue-gas

Description

Regenerator flue-gas containing HCl, H₂S, small quantities of catalyst fines, traces of Cl₂, SO₂ and dioxins can be sent to an electrostatic precipitator prior to release to the atmosphere. Emissions generated by other activities, such as venting during catalyst regeneration or replacement and plant cleaning, may be sent to the ESP.

Achieved environmental benefits

Reduction of particulate content in the flue-gas coming from the regenerator.

Cross-media effects

See Section 4.23.4.2.

Operational data

None available for this particular application. For general data see Section 4.23.4.2.

Applicability

Emissions from continuous regeneration sections require particular attention. No example of ESP used for continuous catalyst regeneration has been reported.

Economics

None available for this particular application. For general data see Section 4.23.4.2.

Driving force for implementation

Reduction of particulate emissions during the catalyst regeneration.

Reference literature

[163, FWE 1999], [207, TWG 2001]

4.6.4 Reduction of PCDD/F emissions from catalytic reforming

Description

Referring to Sections 3.6 and Sections in 4.6 on catalytic reforming, dioxins are typically formed in the three types (continuous, cyclic and semi-regenerative) of catalytic reforming during the regeneration of the catalyst.

De Novo reaction is the chemical reaction that produces dioxins and furans. This reaction is favored between 200-450°C and in presence of iron oxide particles produced from corrosion which act as a catalyst.

If the regenerator flue-gas is treated in a water scrubber (e.g. Section 4.6.4), the dioxins appear detectable in waste water from the scrubber, but they are not detected after the WWTP, possibly due to dilution effects.

In some other cases, because the use of other techniques such as fixed-bed filters. There is a combine reduction of chlorine and dioxins. In some cases, activated carbon has been used to remove dioxins. Another technique that has been used includes the recirculation of vent gases, however, it is not clear how it can reduce the emission of dioxins.

The study of dioxins emissions from reformers and how the regeneration conditions may affect these emission can be a good way to start to understand and solve the problem.

Achieved environmental benefits

Knowledge of origin and control of the dioxin emissions.

Cross-media effects

Some dioxins from the regenerator gases may be transferred to water via scrubbing.

Operational data

Preem refinery Lysekil (SE) installed a continuous regeneration gas recycling loop in 2001. The waste gas from the regeneration is recycled to the catalyst where chlorides, chlorinated hydrocarbons and dioxins are re-adsorbed. Emissions of dioxins from the reformer was 0.323 g TCDD-eq/yr before installation. Emission after the abatement technique installation was 0.0045 g TCDD-eq/yr (average). The following reductions for dioxins and other parameters were achieved:

- dioxins 99 % reduction;
- chlorobenzene 94 %;
- PCB 93 %;
- chlorides 83 %.

A similar technique is applied with a discontinuous regeneration at Preem refinery Gothenburg. In that case the gases are treated in a scrubber and after that the scrubberwater is filtered through active carbon.

Applicability

No data received

Economics

No data received

Driving force for implementation

Knowledge of the formation of dioxins in the regeneration of the catalysts.

Example plants

Some EU refineries have already applied and monitored dioxin emissions from catalytic reformers. Techniques such as chlorine traps and the recirculation of vents have not been reported to be applied to semi-regenerative reformers due to the use of basic water wash systems in these designs. Efficient abatement techniques are used at two Swedish refineries (see Operational data paragraph).

Reference literature

[207, TWG 2001], [77, REF TWG 2010], [268, CieGötaverken Miljö Cie 2012],
[269, Axens IFP 2012]

4.7 Coking processes

The first four techniques considered in this section are coking processes. The information given is intended to help in assessing how well coking processes can perform from the environmental point of view. The rest of the techniques are related to the cleaning of the coke gas, the use of the coking process to destroy solid residues/sludges and, finally, to these techniques related to the abatement of pollution generated by the coking processes.

4.7.1 Techniques to prevent emissions from delayed coking

Description

A description of this process can be found in Section 2.7. Following is a list of the techniques that may be applied to the delayed coker to prevent emissions.

- Preventing uncondensable vapours generated in the coking processes from passing to the flare system by sending them to a gas separator unit for passing to the refinery FG network.
- Passing pressure reliefs from the coke drums to a closed blowdown system, e.g. the quench tower.
- Techniques for coke drum pollution control including carrying the final venting to gas flare gas compressor to recover as refinery fuel gas, rather than flaring, and sending condensed water to WWTP.
- Using water in the delayed coker as described in Section 4.7.6.
- Using the steam generated in this process to heat up other refinery processes.
- Improving heat integration: the delayed coking process itself has a low-level of heat integration. The heat to maintain the coke drums at the coking temperature is supplied by heating the feed and the recycle stream in a furnace. However, the atmospheric residue and/or vacuum residue can be fed straight into the delayed coking unit without intermediate cooling, which results in a high heat-integration level between the different units and saves a considerable amount of capital on heat exchangers.
- Using coking gas. The energy efficiency of the coker can be further increased if the coke gas is combusted in a gas turbine of a combined cycle unit. Extra information on the application of refinery fuel gas in combined cycle units appears in Section 4.10.

Achieved environmental benefits

Reductions of VOC emissions, recovery of products and a reduction of H₂S emissions are achieved when applying some of the above-mentioned techniques. Water reuse is also promoted by the application of these techniques.

Cross-media effects

No data received.

Operational data

Some operational data of delayed cokers can be found in Section 3.7.

Applicability

No data available.

Economics

The typical investment of a full delayed coker (based on 1 Mt/yr straight run vacuum residue feed, US Gulf Coast, fuel grade coke, including vapour recovery) was estimated at USD 136 250 – 218 000 per t/yr in 1998.

Driving force for implementation

Production process.

Example plants

Many delayed processes exist in Europe, even though, coking process in general are more commonly used in the US. In 2011, 67 delayed coking units were installed worldwide.

Reference literature

[163, FWE 1999], [148, Irish EPA 1993], [168, VROM 1999]. [76, Hydrocarbon processing 2011].

4.7.2 Techniques to prevent emissions from fluid coking**Description**

A description of this process can be found in Section 2.7. General abatement techniques, such as ESP, (see Section 4.23) are applicable to fluid coking units. Another technique that can be used to prevent emissions or increase energy integration in fluid coking is to use the coking gas in a gas turbine of a combined cycle unit. Extra information on the application of refinery fuel gas in combined-cycle units appears in Section 4.10.

Achieved environmental benefits

Emission factors for fluid coking (units in kg/1000 litres of fresh feed) are given in Table 4.32.

Table 4.32: Emission factors for fluid coking

Process	PM	SO _x (as SO ₂)	CO	HC	NO _x (as NO ₂)	Aldehydes	NH ₃
Fluid coking units <i>uncontrolled</i>	1.5	NA	NA	NA	NA	NA	NA
Fluid coking with <i>ESP and CO boiler</i>	0.0196	NA	Neg	Neg	NA	Neg	Neg
Neg: negligible NA: not available							

Cross-media effects

No data.

Operational data

This system operates under fluidised-bed conditions.

Applicability**Economics**

Investment (US Gulf Coast 1996): USD 10 000 – 13 200 per m³/d.

Driving force for implementation

Production process.

Example plants

A number of fluid coking units exist around the world.

Reference literature

[172, MRI 1997].

4.7.3 Techniques to prevent emissions from the calcination process

Description

A brief description of this process can be found in Section 2.7. Certain techniques can be applied to the calcination process to prevent emissions, and some of those considered to be beneficial are included in the following list.

- The kilns can be directly fuelled by coke gas or coke fines, driving off volatile matter and burning it within the kiln.
- The hot stream of waste gas from the calcination of petroleum coke in rotary kilns contains considerable quantities of particulate matter, which, possibly after heat recovery from the waste gas, is separated with suitable filter devices, e.g. high efficiency multi-cyclones, bag filters and electrostatic precipitators (see also Section 4.7.7). During calcination in multiple-hearth furnaces, particulate abatement techniques are not usually used because of the comparatively low emissions in the waste gases.
- The unburnt gases from the calcinator are burnt in an incinerator, then passed through a waste heat boiler before being released to the atmosphere via a dust collection system.
- The SCR technique (as described in Section 4.10.4.6) and the SNCR technique (as described in Section 4.10.4.7) may be applicable to these calcination off-gases for efficient NO_x reduction.
- The calcined coke discharges to the rotary cooler where it is cooled by direct water injection. Off-gases from the cooler pass to gas cleaning by multi-cyclones and a wet scrubber.
- Collected fines from the dust abatement techniques should be conveyed to a silo with exhaust air filters. Collected cyclone fines may be recycled to product, used within the refinery, or may be sold as product.

Achieved environmental benefits

Some of the techniques mentioned above increase the heat integration of the calciner, reducing the consumption of fuel in the refinery. Others decrease the amount of particulates emitted to the atmosphere, re-using the coke fines generated during the calcination process. The emission values for petroleum coke production plants attainable in continuous operation are presented in

Table 4.33. These values can be achieved by applying the techniques mentioned above.

Table 4.33: Emission values for petroleum coke production (calcination of green coke)

Emission component	Values attainable in continuous operation (Emissions values as half-hourly mean values in mg/Nm ³ at 3 % O ₂ except stated otherwise)
Particulate (dust) emissions	20 – 60 (at boiler stack - daily - no O ₂ correction) 40 – 150 (at cooler or combined boiler/cooler stack daily - no O ₂ correction)
Particulate (dust) components: Ni, V and their components (given as Ni and V total)	3 - 15
NO _x (as NO ₂)	450 – 875 (No NO _x abatement technique included)
SO _x (as SO ₂)	(No SO ₂ abatement technique included) 1 100 – 2 300 ⁽¹⁾ 300 – 700 ⁽²⁾
CO	100
HC (given as total carbon)	20
⁽¹⁾ As daily average.	
⁽²⁾ As daily average for low sulphur coke.	

Taking into account the energy-saving additional devices and relevant temperature window availability, a further significant reduction of NO_x may be achieved using SCR or SNCR.

No examples of the use of SCR techniques have currently been reported in calciner service in the EU.

Operational data

Some operational data of petroleum coke calciners can be found in Sections 2.7 and 3.7.

Flue-gas flowrates from the calciner (3 % O₂ dry gas) are typically between 1.8 and 3 Nm³ per tonne of coke feed (wet feedrate into the calciner). Variation can be connected to the type of coke, and the type of flue-gas (e.g. possible combination of cooler and boiler stacks).

Additional data of emissions to air of NO_x, SO_x, and dust at the calciner stack from some European sites (reported monitoring) are provided together with the associated information on techniques and operational conditions in the following Table 4.34.

Table 4.34 Emissions to air from a sample of calciners operated at European refineries

Refinery calciner stack code	Type of calciner	Type of green coke	Techniques in place	SO ₂		NO _x		Dust	
				Min Monthly	Max Monthly	Min Monthly	Max Monthly	Min Monthly	Max Monthly
SA1 Shared by 2 calciners	Rotary kiln	Two different grades: anode and graphite	Cyclones	600	1 200	500	750	28 ⁽¹⁾	62 ⁽¹⁾
SB1	Rotary kiln	Single grade	Cyclones	1 500	2 200	280	380	55 ⁽¹⁾	152 ⁽¹⁾
G	Rotary hearth (disk)	Sulphur content: 1.6 %	Cyclones + ESP	2 100	2 500	280	380		<20
K	Rotary kiln	NA	Cyclones + ESP	2 000 ⁽²⁾	2 300 ⁽²⁾	370 ⁽²⁾	430 ⁽²⁾		<10

All concentration values expressed as mg/Nm³ @ 3 % O₂ content
⁽¹⁾ For S refinery, dust emissions converted from actual 8 % O₂ content provided data
⁽²⁾ For K refinery: all values converted from actual 7 % O₂ content provided data
Source: CONCAWE 2012

The following Figure 4.29 shows the variability of emissions to air, over a long time span, of SO₂, NO_x and dust from two calciners connected to a unique stack (named SA1 in the previous Table 4.34) and operating on two grades of coke (with different sulphur contents). The SO₂ and NO_x emissions appear to be mainly influenced by the type of coke, whereas the dust emissions are less influenced (abatement technique in place for dust only).

For secondary techniques NO_x abatement, it is reported that one site operating a calciner equipped with SNCR reports a daily value of less than 350 mg/Nm³. [146, TWG DE 2012]

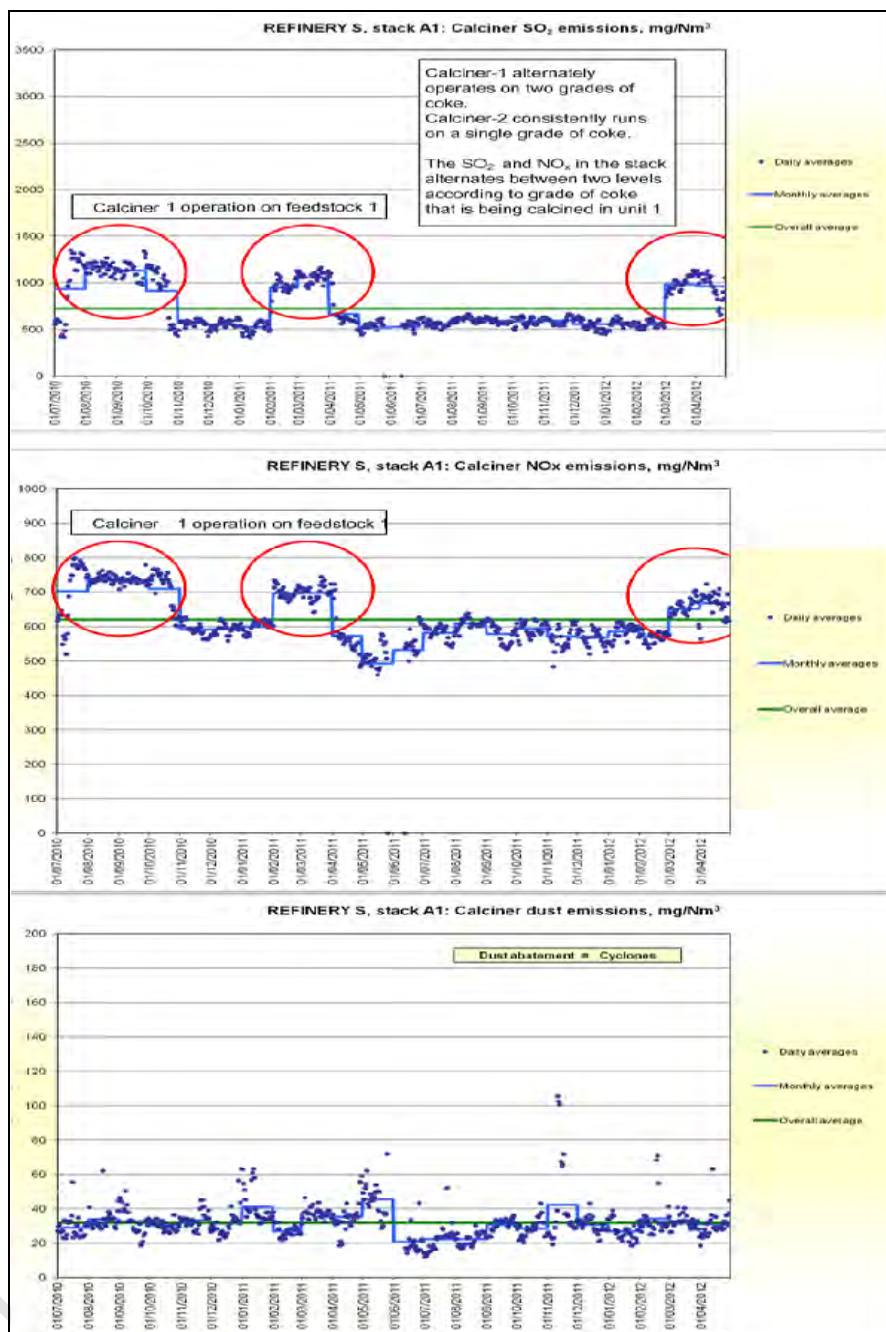


Figure 4.29: Variability of emissions to air– Example of two calciners (rotary kilns) with a common stack

Applicability

Applied to coke produced by delayed cokers and fluid cokers.

The applicability of the techniques for dust abatement is linked to the type of calciner in use: rotary kiln or rotary hearth (disk). Table 4.34 shows that multi-stage cyclones are commonly used and that on ESP may be installed at both rotary kiln or rotary hearth calciner process.

No examples of abatement techniques for SO_x abatement at the calciner have been reported in the EU.

No primary techniques have been reported to be applicable for NO_x abatement at the calciner.

For secondary techniques NO_x abatement, one site equipped with SNCR reports a daily value of < 350 mg/Nm³. [146, TWG DE 2012]

Economics

A preliminary very brief evaluation for the retrofitting of an SCR on two calcination kilns gives the following costs that should be taken only as first estimations of the order of magnitude:

- Design N°1: capital costs EUR 24.24 million, operating costs EUR 0.920 million per year (2007); estimated quantity of NO_x abated 601 t/yr (EUR 7 450/t for 15-year lifetime, 12 % rate assumed) for a 85 % reduction yield;
- Design N°2: capital costs EUR 20.8 million, operating costs EURO 0.71 million per year (2007); estimated quantity of NO_x abated 563 t/yr (EUR 6 672/t for a 15-year lifetime, 12 % rate assumed) for a 85 % reduction yield.

Driving force for implementation

Production process. For certain applications, green coke produced by the delayed coker should be calcinated before being used or sold.

Example plants

Many examples exist in Europe and around the world. Multiple-hearth furnaces have been extensively applied to waste incineration. The majority of facilities that calcine coke utilise a rotary kiln. The last two calcining facilities built were rotary kilns.

Reference literature

[167, VDI 2000], [174, HMIP UK 1995], [207, TWG 2001], [245, M. H. F. Services 2001], [Site questionnaire n°42], [90, EIPPCB 2011].

4.7.4 Flexicoking

Description

A brief description of this production process can be found in Section 2.7. Some techniques that may be applied to prevent emission from the flexicoker are the following.

- The flexicoking process has a high level of heat integration. The only source of heat in the flexicoker process is the gasifier, where the coke is partially oxidised. The remainder of the heat in the coker gas is recovered by generating steam. The energy efficiency can be further increased if the coke gas is combusted in a gas turbine of a combined cycle unit. See Section 4.10.
- As coke cutting from drums is not needed, emissions and dirty effluent generation are avoided, as opposed to delayed coking. Moreover, the sulphur components from the coke gas are easy to eliminate. Some 84 – 88 % w/w of the hydrocarbon feed is recovered as hydrocarbon product, the remainder is converted into CO, CO₂ and H₂O.
- The coke gas from the heater is passed through a cyclone set to remove the coarser coke particles and is subsequently cooled by the generation of high-pressure steam and by preheating boiler feed water. About 75 % of coke fines which pass through the two stages of heater cyclones are recovered in tertiary cyclones. Almost all the coke fines which escape the tertiary cyclones are scrubbed out in the venturi scrubber. The water slurry from the venturi scrubber is steam-stripped to remove absorbed hydrogen sulphide and ammonia.

Achieved environmental benefits

The environmental benefits from the described techniques include:

- an increase in the energy efficiency of the flexicoking process;
- less waste generated than delayed coking;
- prevention of particulate, hydrogen sulphide and ammonia emissions.

Cross-media effects

No data received.

Operational data

Some operational data for flexicokers can be found in Sections 2.7. and 3.7.

Applicability

Fully applicable. However, because the products from flexicoking are different than from other coking processes (e.g. no coke is produced), refinery product requirements should be considered when implementing this option.

Economics

Typical investment (based on US Gulf Coast 1996): USD 15100 – 19500 per m³/d.

Driving force for implementation

The implementation is mainly driven by the site production strategy.

Example plants

Many examples exist in Europe (The Netherlands, Greece), the US (Texas, California) and the rest of the world (Japan, Venezuela).

Reference literature

[183, HP 1998], [209, Pozo 2000].

4.7.5 Use of oily sludges and/or waste as coker feedstock

Description

In refineries with a coker, oily sludges, sludges from the waste water treatment, and waste can be destroyed in the coker (delayed, fluid or flexicoker). If coke is produced, the coke quality produced should remain acceptable (with respect to further use as fuel within/outside the refinery or as material for other purposes). Many oily sludges can be sent to a coking unit where they become part of the refinery products.

Achieved environmental benefits

Reduction of the amount of sludge and/or waste produced in the refinery. A refinery with a coker is able to greatly reduce its oily sludge production. High-quality coke requirements can, nevertheless, restrict its use.

Cross-media effects

Typically there is a reduction of the quality of the coke produced.

If sludges from the waste water treatment are included as feedstock to the coker, part of the water needs to be eliminated (e.g. by vacuum evaporation or in the blowdown system) if the amount of residues are to be maximised.

Applicability

A balance must be achieved between the amount of sludge waste sent to the coker and coke quality specifications. Coking operations can be upgraded, however, to increase the amount of sludge that they can handle.

The quantity of solids injected depends on the solids content of the slurry, typically being two to 10 %. Loading rates exceeding 40 kg of oil-free dry solids per tonne of coke are considered typical.

Generally cokers in general are an attractive process-integrated reprocessing outlet for oily sludges, provided the sludge-on-feed ratio is kept below 1 – 2 %, depending on the required coke quality. If that ratio is not achieved, neither the operability nor the coke quality is affected.

Economics

No information available

Driving force for implementation

Reduction of waste generation in the refinery.

Example plants

The use of sludge as a feedstock is, at the time of writing (2010), commonly carried out by refineries where no high quality coke is produced.

Reference literature

[174, HMIP UK 1995].

4.7.6 Water use in the cooling/cutting process

Description

Water used in the cutting/cooling operations is continuously recirculated with a bleed-off to the refinery waste water treatment. Settling and filtering over a vacuum filter enables the reuse of this water, resulting in a 'closed-water loop'. For water make-up to the quenching and for cutting the water loop, various effluent streams can be used. For this task, treated effluent could be used. Collected water from any condenser, and from the draining of wet green coke, should be reused for coke drum quenching or drilling. This type of cooling is not used in any other process in the refinery, because of environmental concerns. More information about direct cooling (quenching) is found in Section 2.8.

Achieved environmental benefits

Reduce consumption of water in the refinery.

Cross-media effects

Cutting and cooling processes result in vapour emissions (partially-recycled in the main fractionator), significant energy losses, large water use and severe water pollution. Bleeding of cutting water to the desalter has the potential to add solids to the effluent, so it is best to keep coker waters separate.

Operational data

The amount of make-up water required depends on the evaporation losses, loss with the coke product, and the bleed to other processes or to the waste water treatment plant, and is about 10 - 20 m³/h for a 10⁶ t/yr delayed coker unit.

Applicability

Applicable when delayed coking is used. Reuse of water is subject to restrictions of coke quality.

Driving force for implementation

Water reuse is typical in the delayed coking process and should be optimised as part of the site water management system.

Example plants

Many examples of this application exist worldwide.

Reference literature

[207, TWG 2001].

4.7.7 Handling and storage of the coke

Description

Several techniques are suitable to reduce particulate emissions that may occur during the handling of coke (green and calcined).

- Provided the green coke is kept wet, the handling between the discharge and the calciner feed hopper is not problematic. There is the possibility that parts of the receiving pit may dry out, although this is limited, as the coke is usually very wet and is covered with residual hydrocarbons which tend to make it stick together. The construction of wind-breaks around the pit might be considered. Careful design is essential, as bad design could make the situation worse. Complete enclosure of the pit and associated handling facilities is another possibility. The pits are very large and such an enclosure would be very expensive. A monitoring programme should be carried out to evaluate if this option is in fact necessary or desirable.
- Cutting the coke into a double-roll crusher, and conveying it to an intermediate storage silo is another technique. The railway wagons are then loaded from the storage silo. This approach would collect, filter, and dewater the coke prior to storage.
- Another option is spraying the calcined coke with a very fine layer of oil, which sticks the dust fines to the coke. The use of oil is limited by its acceptability in further processing. The oil option has the added advantage of reducing unloading problems.
- Covering and de-pressuring conveyor belts.
- Using aspiration systems to extract or collect dust.
- Using enclosed, hot blowdown system.
- Enclosing loading areas and maintaining positive/negative pressures, exhausting through bag filters. As an alternative, dust extraction systems can be incorporated with loading equipment.
- Conveying pneumatically collected fines from the cyclones to a silo with exhaust air filters. Dust collection systems are provided for handling, storage and loading, using bag filters. Collected fines are recycled to storage by enclosed means.

Achieved environmental benefits

Eliminates particulate matter releases to air of (containing metals) from this part of the process during routine operation, as well as from the storage of the coke.

Operational data

The storage silo provides a buffering capacity for process fluctuations and enables a controlled loading of railway wagons.

Applicability

Oiling coke (see Item 3 described above) is sometimes practised in fluid and calcined coke, but is rarely applied with delayed coke.

Collecting and recycling coke fines (see Item 8 described above) is mostly applicable to calciners, fluid cokers and flexicoking units.

Economics

Investment costs of about EUR 30 million for a typical coking unit with a capacity of 1.5 Mt/yr may be expected for the storage system.

Driving force for implementation

Reduction of coke spillage. If the petroleum coke is cut directly from the coking units into railway hopper wagons, it may cause overfilling of the wagons, degrading the quality of the

spilled coke, and increase the amount of solids entering the waste water treatment system. Reduction of particulate emissions from the storage system of the coker is another driving force.

Example plants

Many examples are available in European refineries.

Reference literature

[204, Canales 2000], [156, MCG 1991], [167, VDI 2000], [207, TWG 2001].

4.7.8 Techniques to reduce air emissions

This chapter mentions where the abatement techniques may be used and describes the techniques used for the abatement of air pollutants.

4.7.8.1 Particulate abatement in coking processes

Description

Flue-gases and coke gas from coking processes normally contain coke particulates (including metals). Dust collection systems are used in all appropriate sections of the coking processes, in order to ensure the cleaning of:

- coke gas;
- gas produced during the coke cooling in the calciner;
- incinerated exhaust gases from the calciner which also contain coke fines. Hot flue-gases pass through a waste heat boiler equipped with a dust collection system.

In addition to the particulate abatement technique used in the FCC (cyclones or ESP in Section 4.5.5), bag filters can also be used for coking processes.

Achieved environmental benefits

Achievable release levels of particulate matter (values based on averaged continuous monitoring) from calciners and coolers are generally reported in the range 20 –150 mg/Nm³ (see Table 4.33). Best-performing plants (e.g. OMV in Burghausen, DE) achieve 10 – 20 mg/Nm³ with electrostatic precipitators (ESP) [28, Tebert et al. 2009].

Cross-media effects

See Sections 4.5.5 and 4.23.4.

Operational data

See Sections 4.5.5 and 4.23.4. The application of an ESP for the control of particulate emissions from petroleum coke calciners has some difficulties in achieving the lower end of the range. The main reason is that coke is a very good conductor of electricity and consequently its surface is very difficult to electrically charge, and consequently difficult to catch by the ESP.

Applicability

See Sections 4.5.5 and 4.23.4. High-efficiency cyclones are easier to apply than ESPs.

Economics

Bag filters can be used at a cost of about EUR 5 million. Calciner boiler cyclones cost EUR 225 000 (1999). The economics for other types of systems are not available. An economic study done in a EU refinery in 1992 showed that the cost for an ESP for a calciner was high.

Driving force for implementation

To reduce the particulate emissions from the calciner.

Example plants

Many examples are available in European refineries: e.g. 4 cokers are installed in Germany, 4 coking units in Spain.

Reference literature

[174, HMIP UK 1995], [249, Balik et al. 1991], [221, Italy 2000], [210, Shawcross 2000], [167, VDI 2000], [207, TWG 2001], [28, Tebert et al. 2009], [77, REF TWG 2010].

4.7.8.2 SO₂ abatement techniques**Description**

Sulphur oxides are emitted during the coking processes, especially during the calcination processes. The principal option to reduce sulphur dioxide releases from the process is the use of the lowest possible sulphur-content feedstocks. In practice, low-sulphur feeds are typically used for product quality reasons, since a substantial part of the sulphur remains fixed in the product. However, this option is not always possible and emissions of SO₂ may be significant, especially during the calcining process. To control these sulphur oxide emissions, the same abatement techniques that may be used in the FCC may be also used in this process (see Sections 4.5.6 and 4.23.5.4), with the exception of the DeSO_x catalyst additive.

Achieved environmental benefits

SO₂ concentrations of 25 - 300 mg/Nm³ are achieved when the techniques mentioned in Sections 4.5.6 and 4.23.5.4 are used.

Cross-media effects

See Sections 4.5.6 and 4.23.5.4.

Operational data

No data from sites using calciners SO₂ abatement techniques has been reported. For other applications, see Sections 4.5.6 and 4.23.5.4.

Applicability

Normally applied to calciner flue-gases.

Economics

See Sections 4.5.6 and 4.23.5.4

Driving force for implementation

Reduction of SO₂ emissions.

Example plants

No examples of the use of these techniques and their associated emissions has been reported to the TWG.

Reference literature

[221, Italy 2000] and references in Section 4.5.10

4.7.8.3 NO_x abatement techniques

Description

As already stated in Section 4.7.3, the SCR technique (as described in Section 4.10.4.6) and SNCR technique (as described in Section 4.10.4.7) may be applicable to calcination off-gases for an efficient NO_x reduction. Nevertheless very few example data have been made available on this topic.

Operational data

No detailed monitoring data from sites using NO_x abatement techniques at the calciner have been reported.

Applicability and example plants

The use of SCR technique was not reported at calciners in the EU. One German refinery site reports the use of SNCR for two calciners.

4.7.8.4 Cleaning of the coking gas

Description

After the coking gas has been cleaned to remove particulates and to recuperate part of its heat, it is heated and passed over a catalyst bed in the COS converter, where COS is converted to H₂S. The gas is then cooled and most of the water is condensed. The H₂S is recovered from the coke gas in an amine treater for ultimate recovery of sulphur (see amine treating of refinery fuel gas in Section 4.23.5.1). Clean low-sulphur coking gas can either be used as a site fuel or can be sold as low calorific-value gas. Figure 4.30 shows a scheme of that process.

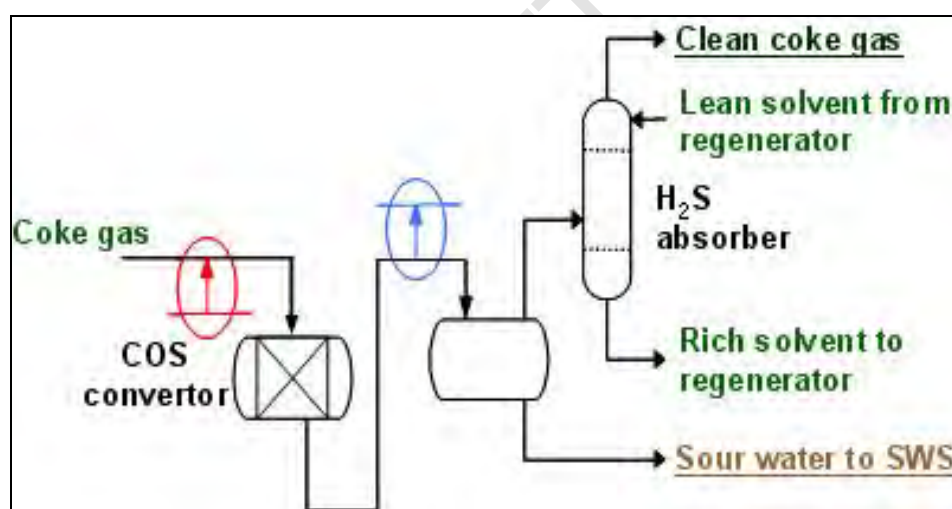


Figure 4.30: Coking gas treatment

Achieved environmental benefits

Reduction of emissions of H₂S (in the range displayed in Table 4.80) and COS.

Cross-media effects

Increased use of the amine scrubbing system and increased energy consumption of the COS converter.

Operational data

For amine scrubbing, see Section 4.23.5.1.

Applicability

Amine scrubbing is applied to all types of cokers. COS converters are applied to some units.

Economics

The economics data of the amine absorption of H₂S can be found in Section 4.23.5.1. For existing coking units, the applicability of the retrofit is reported to be limited due to the high investment and operational costs.

Driving force for implementation

Cleaning of the coke gas. Coke gas forms a main refinery gas source (after dust removal, COS conversion and amine treating for H₂S removal).

Example plants

These systems can be found in many cokers.

Reference literature

[168, VROM 1999], [146, TWG DE 2012].

4.7.9 Techniques to prevent emissions to water

This section analyses ways to prevent emissions to effluents. Techniques used in the final cleaning of the waters generated in the coking processes are found in Section 4.24.

4.7.9.1 Treatment of the waste water

In the coking processes, sour water is generated (steam condensate). Consequently, all water from the coking process is sent to the sour water stripper (Section 4.24) before being sent to the waste water treatment plant.

4.7.9.2 Separation of the oil/coke fines from the coke-cutting water**Description**

This technique consists of retrofitting the sump where the oil/coke fines are collected with an inclined plate separator to increase the separation efficiency.

Achieved environmental benefits

Coke fines and water generated from the coke-cutting operation enter a sump settled on the ground where the solids and water are separated by gravity. A refinery study indicated that this technique could prevent over twenty-five tonnes per year of coke fines entering the sewage system from that separator.

Cross-media effects

Additional oil/coke fines collected by the separator need suitable treatment or should be properly eliminated.

Applicability

The technique is fully applicable.

Economics

The annual cost savings associated with the increased recovery of product (coke) and the reduction in oil/water separation solids was approximately EUR 300 000 (7.5 Mt/yr refinery).

Driving force for implementation

Reduces the coke fines entering the sewage system and improves the maintenance of the sewage system and accordingly the quality of the raw effluents to the WWTP.

Example plants

No information received.

Reference literature

[249, Balik et al. 1991].

4.7.10 Techniques to reduce soil contamination

4.7.10.1 Control and reuse of coke fines

Description

Coke fines are often present around the coker unit and coke storage areas. The coke fines can be collected and recycled before being washed to the sewers or migrating off-site via the wind. Collection techniques include dry sweeping the coke fines and sending the solids to be recycled or disposed of as non-hazardous waste. Another collection technique involves the use of vacuum ducts in dusty areas (and vacuum hoses for manual collection), which run to a small baghouse for collection.

Achieved environmental benefits

Reduced soil contamination by coke particulates (including metals). Coke fines can be recycled for fuel use or can be sold (e.g. for cement production).

Cross-media effects

Electricity consumption by vacuum ducts/hoses.

Applicability

Fully applicable.

Driving force for implementation

Reduction of soil contamination.

Example plant(s)

The techniques is already in use in US refineries.

Reference literature

[249, Balik et al. 1991].

4.8 Cooling systems

The following topics of relevance to refineries are already described and analysed in the industrial cooling system BREF (ICS) [84, COM 2001]

- reduction of direct energy consumption
- reduction of water requirements
- reduction of entrainment
- reduction of emissions to water
- reduction of air emissions
- reduction of noise emissions
- reduction of risk of leakage
- reduction of biological risk.

The description and analysis includes an extensive discussion of the environmental benefits of systems, cross-media effects, operational data, applicability and economics. To avoid repetition, therefore, this section on cooling addresses only topics not covered by the ICS BREF.

4.8.1 Segregation of cooling and process waters

Description

Because process waters are normally more contaminated than cooling waters, it is important to maintain the segregation of the two. Only in cases where cooling waters need treatment (recirculation systems) should they be mixed, and then only at the right point (after the primary treatment of the process waters).

Achieved environmental benefits

Segregation reduces the contamination of cooling water by oil coming from other waters. It increases the recovery of oil by the waste water plant.

Cross-media effects

No cross-media effects have been found.

Operational data

No information received.

Applicability

Waste water treatment plants which were originally sized to jointly handle the process water flow and the cooling water flow may have to be modified after segregation in order to efficiently treat the resulting lower and more concentrated effluent.

Economics

Segregation can be very costly in some parts of existing installations.

Driving force for implementation

To prevent the contamination of cooling water by process waters, which are usually more contaminated, and to avoid the dilution of process waters before their treatment. Some of the topics dealing with pollution of water from cooling systems have already been studied in the OSPAR and HELCOM processes (North Sea and Baltic Sea region).

Reference literature

[160, Janson 1999]

4.8.2 Air cooling

Description

See Section 2.8 and the ICS BREF.

Achieved environmental benefits

The major advantage of using air coolers is that no additional medium is required.

Cross-media effects

Air cooling tends to produce more noise than water cooling. Noise production due to an air cooler fan measures 97 – 105 dB(A) at source.

Operational data

A major disadvantage is that normally a larger plot is required when compared to water coolers (5 – 30 m²/MW). It requires electricity but minimal maintenance costs.

Applicability

Air cooling can be sufficient for the cooling needs in some parts of the refinery process. Ambient conditions restrict the temperature levels that can be attained. Climatic conditions (hot climates or temperatures below 0 °C) typically restrict its use. Moreover, air fans cannot be located near buildings because air short-circuiting may occur.

Economics

Air coolers can be expensive. Minimal maintenance costs.

Example plants

Many examples exist in EU refineries.

Reference literature

[228, TWG 2000], [169, Bloemkolk et al. 1996], [69, European Commission 2001].

4.8.3 Prevention of oil leakages into cooling water

Description

Losses of oil through leaks can be minimised through continuous monitoring, associated with a leak detection and repair system (similar to the reference for VOC in Section 3.26.1.3).

The first step comprises monitoring the cooling water separators for oil build-up. If oil is observed, then it will be necessary to trace back through the system to identify the source of the leak so that corrective action can be taken. Detailed system drawings and flow charts are essential for this activity. Fingerprinting of the oil can also speed up identification of the leak.

This technique is better supported and more efficient when oil-in-water monitors are installed at various points in the cooling water system. This allows leaks to be detected rapidly and corrective action taken. For this procedure to be effective, sparing of critical heat exchangers will be required. More information is given in the ICS BREF.

Achieved environmental benefits

Reduction of oil leakages into cooling water.

Driving force for implementation

Detects and corrects oil leakages into cooling water.

Reference literature

[228, TWG 2000], [169, Bloemkolk et al. 1996].

4.9 Desalting

4.9.1 Good desalting practices

Description

A short description of desalters can be found in Section 2.9. Several good desalting designs have been included in this section and include:

1. multistage desalters and the combined use of AC and DC fields providing high desalting efficiencies as well as energy savings;
2. recycling, in multistage desalters, part of the brine effluent water of second stage desalters to the first stage, minimising the wash water quantity;
3. use of a low-shear mixing device to mix desalter wash water and crude;
4. avoiding turbulence in desalter vessels by using lower water pressure.

Achieved environmental benefits

Increased efficiency of desalters can reduce fresh wash water usage. Other environmental benefits could be energy savings, due to a more efficient electrical field.

Operational data

Two-stage processes achieve 95 % or better efficiency (more than 95 % of the salts/solids are removed from the crude oil). This high efficiency provides process benefits, as there is less corrosion in the topping units and less catalyst deactivation by e.g. sodium.

Applicability

Two-stage or even three-stage desalting is used either if the downstream process salt specification is very stringent or to prevent process upsets and functionality (e.g. when heavy residues are processed further in catalytic conversion processes).

Driving force for implementation

Increase the efficiency of the desalting process.

Reference literature

[164, Noyes 1993], [221, Italy 2000], [207, TWG 2001].

4.9.2 Enhance the oil/water separation before discharge to the waste water treatment plant

Description

Techniques that may be applied are the following.

- Transfer of the water effluent from desalting units to a settling drum where a further separation between oil and water can be achieved. The oil can be directly recovered in the slop system.
- Choice of optimum interface level controllers. As a function of specific gravity and range of crudes processed, it is possible to consider the most accurate level sensors among displacers, capacitance probes or radio wave detectors. The accuracy of interface level control is fundamental for the good operation of a desalter.
- A good improvement in oil/water separation can be achieved using 'wetting' agents, whose aim is to de-oil the solid contaminants that are usually responsible for a significant entrainment of oil in the water.
- Use of non-toxic, biodegradable, non-flammable specific demulsifying chemicals to promote coalescence of the water droplets.

Achieved environmental benefits

The systems described above enhance the oil/water separation, reducing the charge of oil to the waste water treatment and recycling it to the process, as well as reducing the oily sludge generation (see Section 4.9.3). With the application of the first technique mentioned above, some 10 - 20 % less oil is sent to the API separators. The second one can separate off some 5 - 10 % oil from the water phase.

Cross-media effects

Some of the techniques proposed require the application of chemicals.

Applicability

Fully applicable.

Driving force for implementation

Enhance the oil/water separation.

Reference literature

[221, Italy 2000].

4.9.3 Enhance the solid/water-oil separation

Description

Solids entering the crude distillation unit are eventually likely to attract more oil and produce additional emulsions and sludges. The amount of solids removed from the desalting unit should, therefore, be maximised. Thus the objective is to minimise solids leaving the desalter with the crude oil. A number of techniques can be used to accomplish this.

- Use low-shear mixing devices to mix desalter wash water and crude oil.
- Use low-pressure water in the desalter to avoid turbulence.
- Replace the water jets with mud rakes. They cause less turbulence when removing settled solids.
- The water phase (suspension) can be separated in a pressurised plate separator. Alternatively, a combination of a hydrocyclone desalter and a hydrocyclone de-oiler can be used.
- Evaluate the effectiveness of a sludge wash system. The sludge washing is a batch operation meant to stir the water phase in the desalter to suspend and remove the solids accumulated on the vessel bottom. This cleaning operation increases the efficiency of desalters during a normal run, particularly for long cycle runs.

Achieved environmental benefits

With the application of the techniques mentioned above, the content of oil in the generated sludges can be decreased and the separation of the sludges from the water phase can be enhanced.

Cross-media effects

The application of these techniques increases the sludge generation within the refinery. At a bottom sediment content of the crude of 0.015 % w/w, theoretically 1500 t/yr sludge can be collected in a 10 Mt/yr refinery.

Applicability

Where bottoms, sediments and water are critical in downstream process units, desalters are equipped with a bottom flushing system to remove settled solids.

Driving force for implementation

Enhances the separation of the oil and water phase by the removal of solids accumulated in the bottom of the desalter vessel.

Example plants

Desalters with desludging facilities are common. Atmospheric residue desalters are scarce, but their number is increasing with the increasing complexity of refineries with respect to residue conversion. In a few refineries, desalters have been equipped with a bottom flushing system (See Figure 2.11).

Reference literature

[221, Italy 2000].

4.9.4 Reuse of water for the desalter**Description**

The desalting process plays an important role in the waste water management of a refinery (see Section 4.15.4). The water used in other processes can be reused in the desalter. For instance, if stripped sour water is used as desalter wash water, the ammonia, sulphides and phenols that it contains can be reabsorbed by the crude to some extent.

The following process water streams can be suitable for use as desalter wash water.

- The accumulated water in the crude distillation unit overhead drum, usually 1 - 2 % w/w on crude feed from steam injection.
- The (unstripped) steam condensates from the light and heavy gas oil dryers and the vacuum distiller overhead (about 3.5 % w/w on feed).
- Stripped sour water and also other solid-free process water streams. Scrubber or quench water is dirty and requires oil and solids separation prior to biotreatment and/or reuse as desalter wash water. The sour water is routed to and stripped in a sour water stripper prior to reuse and/or final purification in effluent water treatment facilities.

Achieved environmental benefits

By using the water in this way, the refinery could reduce the hydraulic loading to the waste water treatment units and reduce the consumption of water.

Cross-media effects

Recycling of water streams that may form emulsions need to be avoided, because it results in deterioration of the oil/water phase separation in the desalter, which in turn leads to excessive oil carry over to water. High total dissolved solids (TDS) streams should not be used as desalter wash water, due to the reduced driving force to extract salt from the crude into the water.

Applicability

Examples of effluents that may form emulsions in the desalter are: bitumen blowing units, hydrocrackers, cokers (fines can stabilise emulsions), other deep conversion facilities (insoluble metal sulphides that can stabilise emulsions) and HF-Alkylation units (corrosive fluoride deposits). The possibility to reuse desalter water as desalter wash water is fully applicable to new refineries but more difficult to apply in existing refineries.

Economics

The costs of collecting, treating, pumping and piping these waters need to be considered.

Driving force for implementation

The refinery could reduce the hydraulic loading to the waste water treatment units and reduce the consumption of water.

Reference literature

[155, API 1993], [207, TWG 2001].

4.9.5 Stripping of the desalter brine

Description

This technique consists of stripping desalter brine for hydrocarbons, sour components and ammonia removal before sending brine to waste water treatment. Recovered hydrocarbons can be blended with several refinery streams. Acid injection can also be employed to enhance the stripping of oil from emulsions.

Achieved environmental benefits

Reduction of the hydrocarbon, sulphur or ammonia (depending of pH range) content of the waste water generated within the desalter. For example, benzene emissions can be reduced by 95 %.

Cross-media effects

This technique consumes steam, added acids, and other chemicals.

Applicability

Pretreatment of desalter brine is normally applied when processing a very heavy crude.

Operational data

In one 8.7 Mt/yr refinery, a waste water flow in the crude unit of 1.3 m³ per minute containing 90 kg/day of phenols is produced. The water discharge from the desalters contains a maximum of 20 ppm benzene, and the quantity of desalter wash water is equivalent to 4 - 8 % v/v of the crude charge. The discharge from the stripper bottoms, with benzene levels in the 20 ppb range, is then routed to the waste water treatment system. A brine de-oiling vessel is installed ahead of the stripping column to decant any free oil undercarry from the desalter. It is reported that in refineries, with this system, 90 % of the phenols can be reduced.\

Economics

No information received.

Driving force for implementation

This technique allows the reduction of waste water benzene, thereby reducing VOC emissions of benzene in the WWTP.

Example plants

No information received.

Reference literature

[164, Noyes 1993], [155, API 1993].

4.10 Energy system

As mentioned in the ‘Scope’, this document does not analyse energy production techniques that use conventional fuels. In other words, emission, consumption, cross-media effects, etc., related to commercial fuels (natural gas, fuel oil, etc) can be found in the LCP BREF [7, EC 2006].

The energy system is an important activity from the environmental perspective. Although heat-producing plants are an essential and integral part of most refining processes, the systems tend to be very similar and they are therefore dealt with in this horizontal section. This section includes a detailed analysis of the energy systems that are specific to refineries, i.e. only energy technologies that run (partially or totally) on refinery fuels. When a refinery uses a commercial fuel that can be found on the open market (e.g. natural gas, fuel oil) the emission levels that can be achieved by a certain energy technique (e.g. gas turbines, boilers) are found in the LCP BREF [7, EC 2006]. Techniques to reduce the energy consumption of a process or activity are addressed in each of the other sections of this document because the reduction of energy consumption is considered an environmental benefit. However, issues such as how the energy system can be integrated within a refinery and how the different processes/activities may share energy are addressed in this section.

Combustion improvement campaigns, the installation of alternative concepts (gas turbines, CHP, expanders, improved heat integration) and a switch to cleaner-burning fuels are some examples of techniques to consider in the determination of BAT. For example, a switch from liquid refinery fuel to natural gas as refinery fuel will reduce not only SO₂ emissions, but also particulates (including metals) and NO_x. All measures to reduce energy consumption will result in a reduction of emissions to air including CO₂. When end-of-pipe techniques to abate emissions lead the operator to higher energy consumption and increase of CO₂, this is addressed as a cross-media effect. This section has therefore been structured into four blocks of techniques. The first one includes the energy management systems, including general techniques to reduce energy consumption. The second one includes techniques to consider in the selection and cleaning of fuels that can be used in the refinery. The third block contains the techniques for energy production that can provide a good environmental performance using the different type of fuels as well as the utilities needed to run these techniques. The last block (4.10.4 to 4.10.6) includes the abatement techniques to control air emissions that are applicable to energy systems.

Table 4.35 summarises and shows the main impacts which may be connected to the techniques that have been considered in this section.

Table 4.35: Possible effect of the techniques to consider for the determination of BAT in the energy system on main pollutants emissions

Section	Techniques to consider in the energy system	CO ₂ ([*])	NO _x	PM (^{**})	SO ₂	Waste water	Residue	Energy
1	Energy management	↓	↓	↓	↓			↓
2	Refinery fuels: types and cleaning	↑	↓	↓	↓		↓	↑
3	Energy production techniques	↓						↓
4	Nitrogen oxide abatement techniques	↑	↓					↑
5	Particulate abatement techniques	↑		↓		↑	↑	↑
6	Sulphur oxides abatement techniques	↑			↓	↑	↑	↑

NB: ↓Reduction ↑ Increase
^{*} CO₂ emissions depend on the type of energy used but are generally expected to follow energy variations.
^{**} PM for total particulate matter, without specification of size.

4.10.1 Energy management

Good design and management of energy systems are important aspects of minimising the environmental impact of a refinery, bearing in mind the highly integrated and interdependent nature of most processes. The general aim is to continuously match the variable production and consumption of fuels in processes and utilities at the lowest economic and environmental cost. This section should be seen as an integration of all techniques proposed below, since an increase in the energy efficiency of a refinery can be achieved through energy conservation technique and heat integration/recovery techniques.

4.10.1.1 Energy efficiency management

4.10.1.1.1 Increasing energy efficiency

Description

The continuous matching of production and consumption at the lowest cost is to be performed at all organisational levels and to be assured at the highest management level. This energy management may be included in the site proper management system. In principle the ISO 14000 system series or EMAS [215, Demuyne 1999] and EN ISO 50001 on energy management systems provide an adequate framework. In order to ensure continuous improvement, formal reporting of energy consumption data to the authorities can be instigated. Energy audits are part of such a system and it is further recommended that, in the pursuit of continuous improvement, refineries learn from best practice by participating in ranking/benchmarking activities. An annual investment plan on energy consumption reduction is also to be included as a technique to consider in the determination of BAT.

Another way to match production and consumption is to try to improve the energy intensity within the refinery. More efficient refineries make better use of the energy produced within the refinery. To evaluate this, several methodologies exist, including the Solomon energy efficiency index (the most detailed one), specific energy consumption, and (less accurate and more simple) the index relating the energy consumption to the amount of feedstock processed (Methods described briefly in Section 3.10.1). Solomon data are also available in that section. Solomon data are available in a form, that only makes sense in its context, and one needs to understand certain underlying (benchmarking) concepts that are proprietary to Solomon.

Techniques to increase energy efficiency are available in the next sections of this chapter.

Achieved environmental benefits

An increase in the energy efficiency of a refinery has a direct impact on reducing air emissions and indirectly on the generation of waste water and waste. Lower consumption of fuels or more energy conservation increase the likelihood that the refinery gas supply will be sufficient for the whole refinery.

Cross-media effects

Some difficulties have been identified in the collection of Solomon energy intensity data from refineries. The main reason is that the figures are considered confidential by both refineries and the provider of the market study (Solomon Associates). Furthermore, Solomon Associates has not provided the TWG with data on the methodology used to calculate the figures. Moreover, it was identified that not all refineries participate in this benchmarking exercise, often for different reasons (e.g. cost, confidence in their figures not being high), and, not all refineries participate every year.

Applicability

Fully applicable. The wide range of energy consumption in refineries means that in certain refineries, a considerable reduction in energy consumption can be realised. A concerted and well-managed effort based on an integrated approach in reducing energy use, improved

operations, good housekeeping, adequate management and selective investment are good practices that are worth highlighting in this context.

Economics

Energy consumption may account for some 50-65 % of the total operating cost of refineries (50 % typical value for US operating costs on energy, 65 % is reported for some EU countries in the refining sector). As a consequence a reduction in the energy consumption, or an increase in the refinery efficiency reduce the total operating cost.

Driving force for implementation

Increasing the energy performance of the refinery is typically done because this reduces their operating cost.

Example plants

Many refineries have installed an energy management system; they issue annual reports on energy consumption performance and participate in benchmarking of energy consumption. Worldwide market studies of a wide variety of refineries (configurations/capacities) on the basis of Equivalent Distillation Capacities has proven useful in helping refineries compare their performance.

Reference literature

[168, VROM 1999], [228, TWG 2000], [77, REF TWG 2010], [68, Worrell et al. 2005].

4.10.1.2 Heat integration/recovery techniques

4.10.1.2.1 Design techniques

Description

Actions that can be taken to improve integration and recovery of heat and increase efficiency are addressed as a general matter in the Energy Efficiency (ENE) reference document. [66, EC 2009]. More specifically, techniques applicable to refineries include (non-exhaustive list):

- General measures to reduce energy consumption, such as optimised heat integration and improved furnace efficiency, combined with computer-controlled combustion. This will lead to lower fuel consumption per tonne of crude processed.
- Installation of waste heat boilers in heaters.
- Installation of expanders/power recovery e.g. in FCC unit (see section 2.5).
- Expanded heat exchanger areas in which cold streams are preheated by warm product streams directly from processes.
- Direct feed of 'semi-products' to processes without cooling and storage. It is always useful, from an energy conservation point of view, to recover the waste heat of hot products of the crude distillation unit, for instance, by later feeding them directly to the downstream units, rather than cooling them for storage and later feeding the downstream units from tankage.
- Balancing of vapour and refinery fuel gas systems.
- Optimisation of energy production (within see Section 4.10.3).

Achieved environmental benefits

Heat integration of process systems ensures that a substantial proportion of the heat required in various processes is provided by exchanging heat between streams to be heated and streams to be cooled. In a refinery, it is important to maximise heat integration in a plant to minimise heating and cooling duties. This way, substantial amounts of products can be sold instead of being burnt. Heat integration/recovery techniques directly result in lower emissions of CO₂, NO_x, particulates and SO₂ (see Section 3.10.3 for air emissions from energy system).

Cross-media effects

The interchange of heat between processes implies the transfer of disturbances from one process to another. This can affect safety, so stability control systems may be required.

Applicability

Waste heat is abundant at refineries, and so is low/medium pressure, low-temperature steam. Any effort to recover waste heat as low-pressure/low-temperature steam is pointless if there is no additional use for the extra steam produced. Options for using that heat need to be carefully quantified and qualified. Heat exchangers require space. The identification and use of opportunities or synergy for sharing use of energy outside the refinery is sometimes difficult and requires finding partners.

Economics

It makes economic sense to maximise heat integration in a plant, and as a result minimise heating requirements and the cooling system burden. Heat integration/recovery offers an opportunity for energy cost savings (50 % of total operating cost of refineries), but the cost of heat exchangers and piping need to be considered when heat integration is analysed.

Table 4.36 gives various examples of investments for increasing heat exchange surface areas ('add-ons') on existing units and, when available, related payback times.

Table 4.36: Examples of investments for increasing heat exchange reported in EU refineries

Ref (¹)	Type of units	Energy recovery	Investment cost (year) (EUR)	Payback time (years)
[14]	Atmospheric distillation	10 t/h of steam	1.2 million	-
[26]	Debutaniser overhead	5.3 MW	200 000 (2003)	<1.5
[39]	Diesel hydrotreating	2 000 TEP/yr	2.5 million (2006)	6
	Diesel hydrotreating	400 TEP/yr	400 000 (2006)	4
	Crude oil distillation	6 600 TEP/yr	3 million (2006)	6
⁽¹⁾ Site Questionnaire reference number.				

Driving force for implementation

Cost savings by reduction of the fuel consumption.

Example plants

Techniques are widely applied in refineries.

Reference literature

[160, Janson 1999], [168, VROM 1999], [207, TWG 2001], [66, EC 2009].

4.10.1.2.2 Process control and maintenance techniques**4.10.1.2.2.1 Steam Management and reduction of steam consumption****Description**

Steam used for stripping, vacuum generation, atomisation and tracing is usually lost to waste water and to the atmosphere. Steam used for mechanical and/or electrical energy generation and heating is usually recovered as condensate in the HP-, MP-, and LP-condensate systems and collected in the condensate storage tank. Several techniques can be implemented for optimising the use of steam and reducing steam consumption.

- Reducing the amount of steam stripping when not strictly necessary is not only part of a sound energy management, but also an option to reduce the generation of waste water. Stripping steam is normally used to meet flash point specification and to improve front end fractionation and yields distribution. In order to reduce the sour water loads to SWS strippers and reduce chemical treatments in the overhead systems, an option would be to

strip sidedraw products, particularly the lighter cuts, using reboiled sidestrippers instead of steamed strippers. However, the majority of steam is used to strip the column bottom, which could not be reboiled by any other means, so the reduction of condensed steam would be limited anyway; besides, the stripping is far better under vapour stream than under reboiling conditions, because the more volatile fraction distillates off.

- Where inert gas such as N₂ is available at an economic price, it can be an alternative to steam for stripping operations, especially for the lighter ends.
- Optimising steam production can also be achieved by waste heat recovery in waste heat boilers (WHB or CHP) from hot flue-gases (e.g. stacks) and hot product streams (related to the techniques shown in Section 4.10.1.2).
- Some sites report interesting initiatives related to systematic programmes for the verification of the very large number of steam condensate drain valves which are usually installed in refinery sites. These programmes consist of the ranking of all valves with regard to induced steam consumption, and the evaluation of all critical valves made on the process and economical points of view. Activities for leakage detection and repair are associated with the programme ('steam traps').

Achieved environmental benefits

Reducing steam consumption reduces the overall energy consumption, and minimises condensates, with a positive impact on waste water generation. The reduction of energy use in steam production will lead to a reduced energy requirement and therefore to lower emissions to air.

Cross-media effects

None in particular.

Operational data

On a French site, a 'steam trap' programme including the systematic mapping of drain valve systems was undertaken in 2008 and covers 20 000 pieces of equipment. At the date of writing (2010), around 30 tonnes of steam per hour have been saved since the programme started. The same approach has been followed on a British site, involving, since 2008, a dedicated team which has managed to reduce steam losses to atmosphere by around 50 000 t/yr.

Economics

The programme mentioned corresponds to a total annual investment estimated at EUR 450 000.

Driving force for implementation

Environmental driving force aimed at energy saving and related decrease of air and water emissions.

Example plants

Applications are found in some refineries.

Reference literature

[221, Italy 2000], [Questionnaires n° 16 and 45].

4.10.1.2.2.2 Other techniques

- Use of high-efficiency pumps and compressors.
- Use of heat pumps.
- Decreased film temperature and increased turbulence on heat transfer surfaces.
- Application of advanced process control to optimise energy utilisation use.

- Insulation of buildings and process units (minimisation of heat losses by thermal radiation).
- Optimisation of recycle gas rates, operating temperatures and pressures and steam pressure levels.
- Minimisation of slops production and their necessary reprocessing.
- Keeping heat exchanging surfaces clean or cleaning them regularly (good housekeeping - see Section 4.10.3.1)
- Repairing leaks and leaking steam traps (see Section 4.10.1.2.2.1).
- Increasing heat exchanger surface areas of new sections of existing plants (so called 'add-ons'). In the cases where more add-ons have been added to an existing plants: re-routing of intermediate process streams and re-definition of the number of steam pressure levels and steam duties.

4.10.2 Refinery fuels: types and cleaning

As mentioned above, this document offers a detailed analysis only of refinery fuels produced in the refinery. Whilst the use of marketable fuels such as LPG, commercial fuel oil and gas oil in refineries is a technique to consider that may be included in this chapter of the BREF, such use is extensively analysed in the LCP BREF [7, EC 2006], which also gives achievable emissions levels using these fuels.

4.10.2.1 Increase the use of gas

Description

An alternative to reducing SO₂, NO_x, CO₂ and metals emissions from a refinery would be to replace or decrease the use of liquid refinery fuel with LPG (often produced on site), refinery fuel gas (produced by some conversion techniques) or natural gas (from external supply). This increase of the use of gas is typically accompanied by a balance and control of the RFG system between suitable pressure limits to give the system flexibility, with RFG make-up available from clean fuels such as LPG or imported gas. In these cases, state-of-the-art controls optimise the performance of the RFG are necessary.

Achieved environmental benefits

Fired boilers and furnaces generate substantial CO₂, SO₂, NO_x and particulate emissions, particularly when heavy fuel oil is used. Gas-fired boilers generate hardly any dust and low SO₂ emissions when the refinery gases are cleaned in amine scrubbers. NO_x emissions are also much lower than those of oil-fired boilers.

Because of the low SO₂ concentrations in the flue-gases of gas-fired boilers, the emission temperatures at the stack can be lowered to 150 °C (dew point corrosion is less of or no longer a constraint). The lower flue-gas temperature represents a difference in energy efficiency and inherent CO₂ emission reduction.

A full switch to a 100 % gas-fired refinery would drastically reduce SO₂, CO₂ and NO_x emissions. Releases of heavy metals would also be slashed. Furthermore, the use of gas generates very little dust and very low SO₂ emissions, as part of the refinery gases are cleaned in amine scrubbers (see next section). Sulphur emissions are significantly lower when clean refinery fuel gas is used instead of a distillate such as automotive gas oil, i.e. 10 - 20 times better than low-sulphur (1 %) conventional fuel oil.

Gaseous fuels typically release less NO_x per unit of energy compared to liquid fuels, especially liquid refinery fuels. For gaseous fuels, usually only thermal NO_x is relevant; however NO_x emissions will depend on the gaseous fuel composition. Oil burning normally leads to higher

levels of NO_x releases for several reasons, especially due to fuel NO_x arising from the nitrogen content (see Section 4.10.2.3), the need to balance NO_x and particulate releases and the frequent design requirement for firing in combination with gas. More detailed information for achievable emission values can be found in Table 4.39 and Table 4.42.

As a matter of summary, the benefits for a switch to a 100 % gas-fired refinery are given below.

- SO₂ emissions from the energy system will be drastically reduced. These emissions will be very low from the refinery gas, and virtually zero for the natural gas. Contributions to the refinery bubble will be mostly attributed to emissions from other sources (SRU, FCC unit, flares, etc);
- Particulate emissions including heavy metals will be reduced.
- NO_x levels typically achieved by gas firing will be reduced to levels typically achieved for gas firing for energy production techniques, and consequently other sources such as catalytic crackers will become predominant emitters in the refinery.
- CO₂ emissions reduction is achieved mainly because of the lower carbon content of gas, its higher calorific value and in addition because of a higher attainable efficiency (stack gases can be cooled further).

Cross-media effects

It is acknowledged that the residual fuel replaced by gas results in a further surplus of residue, which has to be considered in any integrated solution for the fuel system of a refinery. Those residual fuels could be burnt improperly outside the refinery, so emissions produced in that way can be seen as merely an emission shift to outside rather than an elimination. Furthermore, the conversion of heavy fractions into light products and the targets for lower sulphur specifications of fuels require considerable extra energy. This will lead to an inevitable increase in CO₂ emissions, unless the CO₂ could be captured.

As a first approximation, NO_x emissions can be magnified by the use of hydrogen, the heaviest gaseous hydrocarbons, and residual fuels containing fuel-bound nitrogen. High-hydrogen fuels result in higher flame temperatures, which typically lead to higher NO_x levels. Although not all the fuel nitrogen ends up as NO_x emissions, the fuel NO_x contributions can range from non-existent, as in the case of natural gas fuelled equipment, to several times the thermal NO_x contribution of the equipment for refinery fuels. Refinery fuel gas may contain amines (nitrogen compounds) and other compounds. Adjustment factors for NO_x emissions as a function of the bound nitrogen content of heavy fuel oils are available in the literature. A well-recognised reference on this subject is provided by the 'Besluit Emissie-Eissen Stookinstallaties Milieubeheer A' (BEES) guidance document published by the Dutch competent authorities in 1987. The correlation factor (applying only to existing installations) proposed in the BEES is displayed in Figure 4.31.

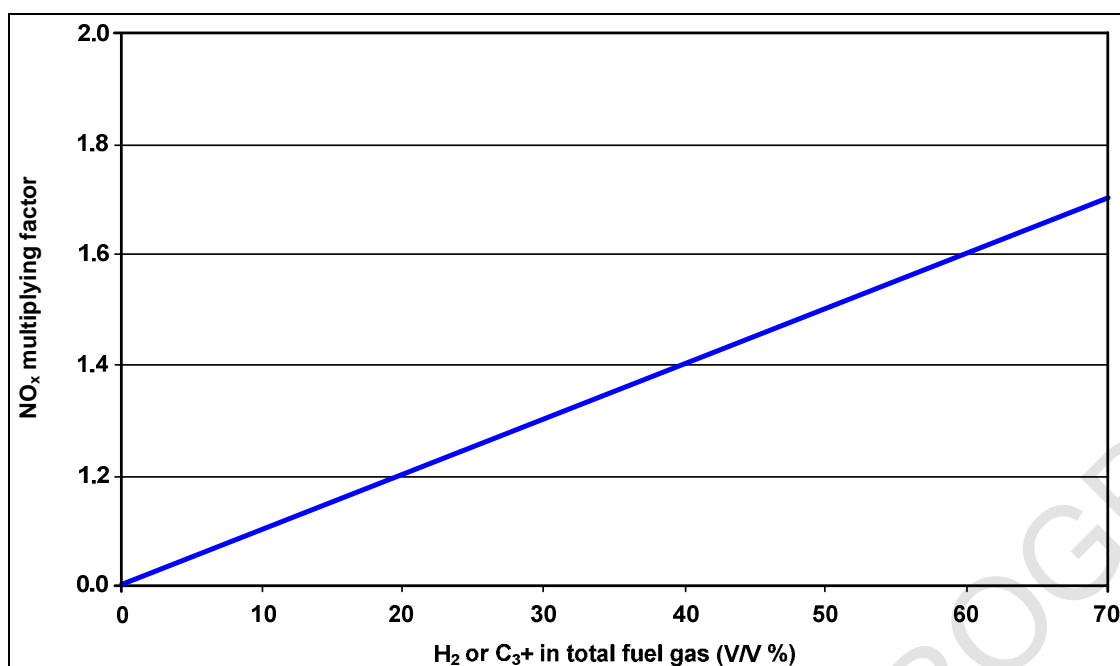


Figure 4.31: Effect of the refinery fuel gas composition on NO_x emissions (applying only to existing installations)

The adjustment factor proposed by the BEES document is made up with the combination of two factors multiplied together. The first accounts for the hydrogen content and the second is attributed to hydrocarbons having a carbon number greater than three.

Nevertheless, a linear relation of NO_x formation with hydrogen content of gaseous fuels cannot be straightforwardly applied: emissions variability is also linked to variation in gas quality and gas quantity and the various types of installations. [267, ECN 2012]

Further information on conversion techniques for heavy fractions to refinery fuel gas can be found in Section 4.10.3.4: the coking sections and the hydroconversion processes sections.

Applicability

The move from liquid to gas fuel would require process upgrades and gas grid connections. Some gases are used locally, i.e. in the process of origin or an adjacent process, but most refineries operate a common RFG mains into which most RFG is fed and transferred to gas users. In a modern refinery, the RFG mains is carefully 'balanced' with respect to supply and demand; necessary flexibility is achieved by control of production (i.e. reformer throughput, LPG evaporation). The relationship with the refinery flare system is important and RFG will normally include gas received from flare gas recovery. It may also release excess gas to flare if the upper pressure limit is exceeded. The application of energy conservation concepts (see Section 4.15.1.2) can help refineries to meet all their needs with refinery gas produced in-house.

The US EPA has recently reached a number of settlement agreements (referred to as Partnership Civil Judicial Settlements, or Consent Decrees) with major companies at the company or site level, in order to eliminate or minimise the use of solid and liquid fuels in all boilers and heaters operated in the refineries [25, Pham et al. 2009]. According to these settlement agreements, the use of solid/liquid fuels is only allowed during natural gas curtailment periods.

Nowadays, a number of European refineries have also switched to 100 % gas with similar operating conditions.

Operational data

Figure 4.32, a very clear correlation is displayed between the part of gaseous fuels burnt in the site energy mix and the specific NO_x and SO_2 emissions achieved by a sample of 55 European refineries during the period 2007 – 2008.

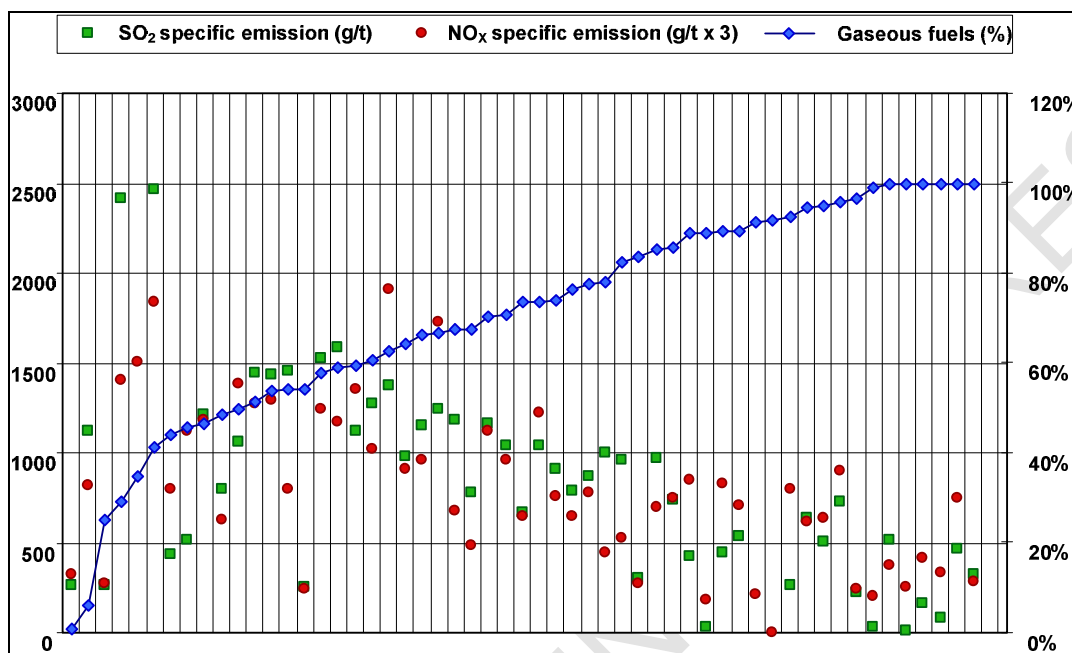


Figure 4.32: Relation between the fuel-mix part and specific NO_x and SO_2 emissions for a sample of European refineries

Figure 4.33 shows the current respective uses of gas and oil in the energy system for a sample of European refineries. From these data, in 2008, the median percentage of gas firing was around 75 % and liquid oil firing close to 25 %. For oil firing, the correspondent average sulphur content was 1.06 %.

This information is consistent with the CONCAWE survey on sulphur dioxide emissions ([139, CONCAWE 6/11 2011]) showing a decreasing oil use from 28.5 % in 1998 to 19.1 % in 2006, and an average sulphur content of 1.33 % in 2006.

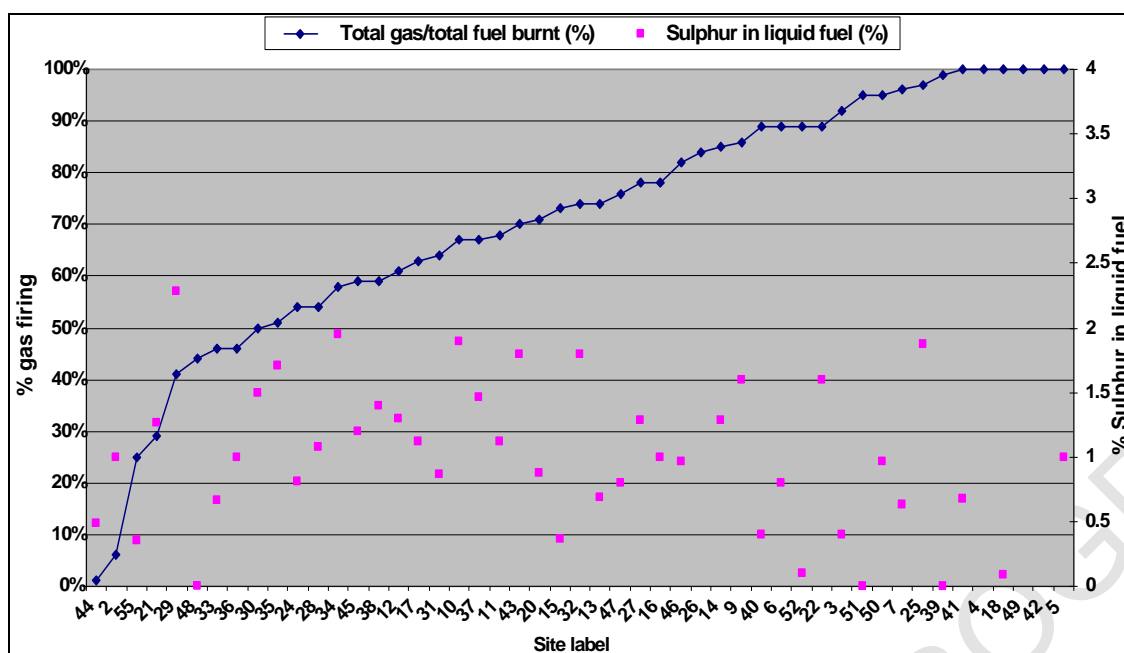


Figure 4.33: Percentage of gas firing and oil sulphur content in 2008 TWG data sample

Economics

The cost of switching to gas can be as high as EUR 30 million per year for a 10 Mt/yr refinery.

For the use of LPG in lieu of fuel oil, the approximate capital cost is small (some reburning) and the approximate operating cost per year is EUR 120 per tonne of fuel (cost differential between LPG and fuel oil). However, operating costs can vary significantly, depending on the season of the year and on the price of LPG on the market.

For the use of natural gas in lieu of fuel oil, the approximate capital cost of installation is around GBP 4 million. The approximate operating cost per year may vary from below EUR 50 per tonne to above EUR 100 per tonne (cost differential between natural gas and fuel oil). Again, operating costs can vary significantly depending on the season of the year and on the market. Cost data for switching to natural gas from CONCAWE 6/11 presented in Table 4.60 (for comparison with a wet gas scrubber) show a range to consider of 75 – 150 EUR/t.yr of fuel oil equivalent (FOE).

Driving force for implementation

Reduction of CO₂, NO_x, SO₂ and particulate emissions (including metals).

Example plants

In 2008, half of the EU refineries have a share of gas firing (RFG +NG) of more than 75 %.

Very few European sites rely upon more than 25 % of heavy liquid fuels for their own energy supply.

Reference literature

[168, VROM 1999], [218, HMIP UK 2000], [7, EC 2006], [193, BMUJF 1999], [207, TWG 2001], [64, CONCAWE 2010].

4.10.2.2 Cleaning of refinery fuel gas

Description

Some refinery fuel gases (RFG) may be sulphur-free at source (i.e. from catalytic reforming and isomerisation processes) or sulphur-containing at source (most other processes, i.e. from crude distillation, cracking and all hydrodesulphurising processes). In the latter case, the gas streams are normally treated by amine scrubbing to remove H₂S before being released to the refinery fuel gas system. More information about amine scrubbers can be found in Section 4.23.5.1.

Achieved environmental benefits

As shown in Table 4.80 of Section 4.23.5.1, amine-treated refinery fuel gases can be controlled to levels that range, depending on the amine scrubber pressure, from 2 – 15 to 20 – 220 mg H₂S/Nm³. These levels will lead to a range of 5-35 mg/Nm³ SO₂ at 3 % O₂ in flue-gases where upper level of H₂S is 220 mg/Nm³ and taking into account a maximum 45 % of hydrogen content (*Source*: CONCAWE 4/09).

Cross-media effects

Possibility of bottlenecking the amine scrubbing system. More information can be found in Section 4.23.5.1.

Operational data

See Section 4.23.5.1. In 2010, the amine cleaning of refinery fuel gases is adjusted to below 25 – 35 ppmv (annual average) in various US refineries [25, Pham et al. 2009] in order to meet the SO_x standards imposed for furnaces and boilers emissions.

It should be noted that fuel gas may contain other sulphur compounds such as mercaptans (from thermal cracking processes) or COS (from FCC and flexicoker units, see Section 4.7.8.4) which are not removed by amine scrubbers.

CONCAWE 04/09 identified that the composition of RFG (non-S compounds) influences the concentration of SO₂ measured in the flue-gas. The complete combustion products of a RFG are CO₂, H₂O and SO₂ and N₂ and the remaining O₂ from the combustion air. When SO₂ is measured in the flue-gas, it is done so on a *dry basis*. The volume of *water vapour is removed* and therefore the SO₂ concentration is higher. The RFG comprises mainly hydrogen and light hydrocarbons (C1,C2,C3) and as a consequence water is produced when it is burnt.

This means that, for a fixed concentration of H₂S in the RFG achieved by amine treating and/or blending, a different SO₂ concentration will be measured in the flue due to this formation of water during the combustion depending of the composition of the RFG (non-S compounds).

Applicability

Fully applicable.

Economics

See Section 4.23.5.1.

Driving force for implementation

To reduce the sulphur content of the flue-gas of the refinery.

Example plants

The treatment of refinery fuel gas in amine scrubbers is commonly used in all refineries.

Reference literature

[221, Italy 2000], [36, CONCAWE n°4/09 2009].

4.10.2.3 Hydrotreatment of liquid refinery fuels

Description

The nitrogen, sulphur, particulates and metals content of the fuel used in refineries are determined by the crude that is used at the refinery and by the process units it has passed through. Liquid refinery fuel streams originate from various processes such as crude distillation units, vacuum distillation, thermal cracking, cat cracking and hydrocracking of residues. Except for the latter, the sulphur content of these residues can only be controlled by feedstock choice. In general, the liquid refinery fuel may comprise one or more of the aforementioned fractions and the sulphur content can vary greatly. Table 4.37 shows the sulphur, nitrogen and metal content of different fractions suitable to be used as liquid refinery fuel.

Table 4.37: Sulphur, nitrogen and metal content of fractions suitable for liquid refinery fuels

Fraction suitable to be used as liquid refinery fuel	Crude oil origin	S (%)	N (%)	Metal content (%)
Atmospheric residue	North Sea	0.6 - 1.1	0.03 - 0.32	0.03 - 0.06
Atmospheric residue	Middle East	2.3 - 4.4		0.04 - 0.06
Vacuum residue	North Sea	1.1 - 1.8	0.18 - 0.58	
Vacuum residue	Middle East	3.6 - 6.1		0.07 - 0.13
Cracked residue	Middle East	3.5 - 6.5		

Based on hydrogenation reactions, the hydrotreatment of fuels can reduce the sulphur, nitrogen and metal content of the refinery fractions. The hydrotreatment of liquid fuels can reduce the sulphur content to 0.03 – 1 %. For more information on hydrotreatments, see Section 2.13. This technique is a pre-combustion operational change, treating the feed before it is used.

Achieved environmental benefits

Feed hydrotreating of fuels reduces the feed nitrogen, sulphur and metals content, which in turn reduces the SO₂, NO_x and particulate emissions. It has been calculated that by switching to fuel oil with a sulphur content of 1 % or less, UK refineries can reduce SO₂ emissions by 19 - 64 %. Another advantage of switching to low-sulphur fuel is that it reduces heat loss to the flue-gas stack (investment in extra heat exchangers or heat exchanger surface to be made) because dew point corrosion is minimised or is no longer a constraint.

Cross-media effects

The hydrotreatment of fuels is a very energy-intensive process, that consumes hydrogen with and consequently leads to increased CO₂ emissions. Moreover, effluent water and waste (used catalyst) are generated (see Section 3.13).

Operational data

Adjustment factors for NO_x emissions as a function of the bound nitrogen content of heavy fuel oils are available in the literature. A well-recognised reference on this subject is provided by the 'Besluit Emissie-Eissen Stookinstallaties Milieubeheer A' (BEES) guidance document published by the Dutch competent authorities in 1987. The correlation factor (applying only to existing installations) proposed in the BEES report is displayed in Figure 4.34.

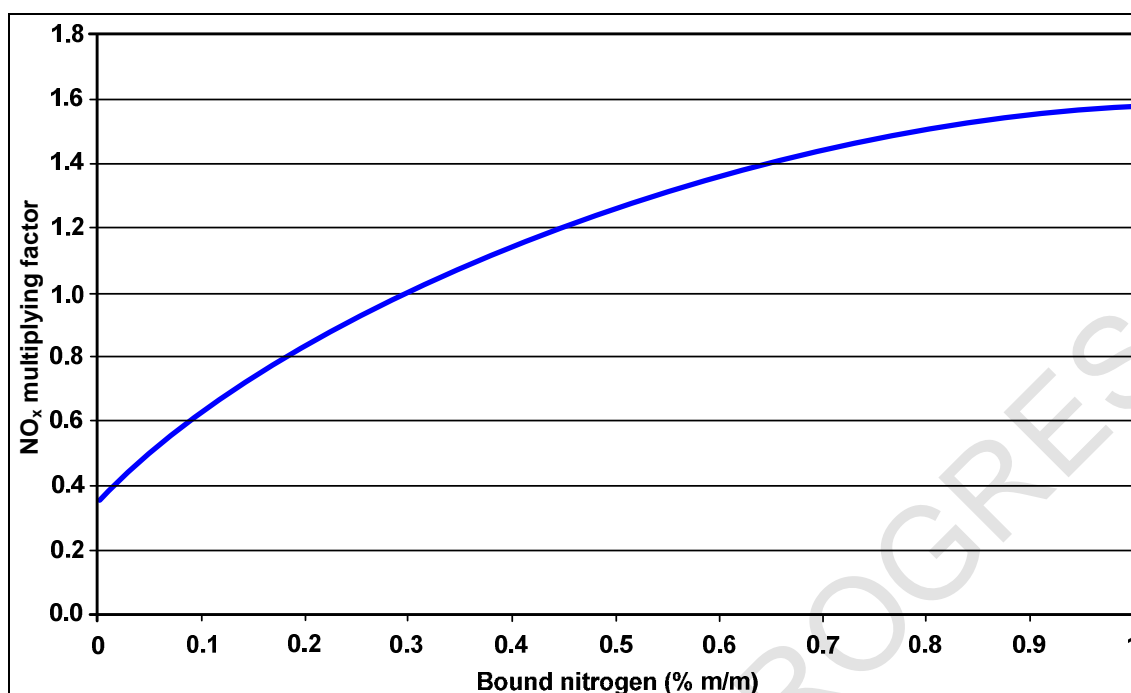


Figure 4.34: Effect of bound nitrogen concentration on NO_x emissions from fuel oil firing (Extract from BEES guidance (NL) applying only to existing installations)

Other information on the performance and consumption of hydrotreatments can be found in Sections 2.13 and 3.13.

Applicability

Fully applicable.

Economics

An intensive hydrotreatment is very expensive, increasing the cost of the liquid refinery fuel. Table 4.38 shows an example of the costs of liquid refinery fuel desulphurisation processes.

Table 4.38: Costs of a liquid refinery fuel desulphurisation

Capacity of the refinery	5 Mt/yr
Fuels used in the refinery	120 000 t/yr liquid refinery fuels 180 000 t/yr refinery fuel gas
Volume of flue-gas emitted	$1.68 \times 10^9 \text{ Nm}^3/\text{yr}$
Sulphur emission	5 000 mg/Nm ³ (for liquid refinery fuels with 3 % S) representing 8 400 t/yr (750 mg/Nm ³ with hydrotreatment)
Desulphurisation efficiency	Up to 85 %
Investment cost (EUR)	100 - 300 million
Operating costs (EUR/yr)	20 - 50 million

Driving force for implementation

Optimisation of the refinery configuration.

Example plants

The amount of refinery gas combusted by refineries compared to liquid fuel, in terms of megawatts fired, is typically 60 % refinery gas to 40 % liquid refinery fuel. However, data from the public register for 1996 in the UK show that in some refineries, the amount of fuel oil fired approached 60 %.

Reference literature

[151, Sema,Sofres 1991], [218, HMIP UK 2000], [168, VROM 1999], [192, Ademe 2001], [36, CONCAWE n°4/09 2009].

4.10.3 Energy production techniques

All types of energy production techniques found in refineries are included here. However, the emission levels associated with each technique are different from these included in Chapter 3 of this document, because only good performance levels are included in this section. Techniques to prevent emissions from these energy production techniques are also included.

4.10.3.1 Furnaces and boilers

Description

The primary measures considered in this section for furnaces and boilers are given below (see also the LCP BREF [7, EC 2006]):

- Installation of combustion air preheaters, which can increase the furnace efficiency significantly (by more than 5 %).
- Optimisation of furnace operations, and hence combustion efficiency, by an advanced control of the operations variables (air/fuel ratio for the fuel mix, avoiding sensible heat losses by optimising excess air).
- High thermal efficiency heater/boiler designs with good control systems (e.g. oxygen trim).
- Minimisation of heat losses via exhaust gas (e.g. minimisation of heat losses via unburnt gases (H₂, CO) or unburnt residues, i.e. ignition loss).
- Continuous monitoring of temperature and O₂ concentration of flue-gas for combustion optimisation. Monitoring of CO may be also considered.
- Maintaining a high boiler pressure.
- Preheating of fuel charged to the boilers.
- Preheating of boiler feed water with steam (see also Section 4.10.3.2).
- Prevention of the condensation of exhaust gas on surfaces.
- Minimisation of own requirements by high efficiency pumps, vents, and other equipment.
- Optimisation of combustion conditions.
- Techniques to control CO emissions such as:
 - good operation and control
 - constant delivery of liquid fuel in the secondary heating
 - good mixing of the exhaust gases
 - catalytic afterburning.
- Regular on-line heater hot tube descaling and hot convection cleaning (dry treatment).
- Regular cleaning of heating surface (soot blowing) for liquid fuel or mixed firing.
- Ceramic coatings for process tube protection against oxidation and prevention of scale build up.
- High emissivity refractories for radiant heat transfer improvement, e.g. by application of ceramic coatings.

Achieved environmental benefits

Table 4.39 to 4-46 provide the achievable emission levels when primary measures are implemented in furnaces and boilers for each air pollutant. Some specific techniques, such as low-NO_x, flue-gas desulphurisation and others are reviewed later in this chapter. Values in the tables are in mg/Nm³, attainable in continuous operation (half-hourly mean values) and are based on a 3 % oxygen volume in the waste gas, except where specified. For gas, the lower values in the ranges given below relate to natural gas firing. Liquid refinery fuel refers to thermal cracked residue, vacuum residue, etc.

Table 4.39: Expected CO emissions from furnaces and boilers with optimal burner and design

Source	Gas	Liquid refinery fuel (*)
Process furnaces	5 – 80	20 – 100
Boilers	5 – 80	20 – 100
Engines	10 – 150	

(*) For liquid firing, a concentration below 50 mg/Nm³ is achievable at temperatures above 800 °C, with sufficient retention delivery and retention time.
Source: [228, TWG 2000]

Table 4.40: Expected NO_x emissions from furnaces and boilers with optimal burner and design

Source	Gas	Liquid refinery fuel	
		0.3 % N	0.8 % N
Process furnaces	80 – 120 ⁽¹⁾	280 - 450	280 – 450
Boilers	250 in some case of retrofit in old installations ⁽²⁾	300 - 450	350 – 600
Engines	250 – 400	NA	NA

⁽¹⁾ TWG 2010 data collection (see also Table 4.46 for mixed firing)
Expected emissions result from multiple factors, including both burning optimisation and burners design.
⁽²⁾ TWG 2010 data collection questionnaire number 14 (See Table 4.46)

Table 4.41: Expected particulate emissions from furnaces and boilers with an optimal burner and design

Source	Gas	Liquid refinery fuel
Boilers and furnaces	< 1	20 - 250

Cross-media effects

Air preheating typically increases the production of NO_x. Adjustment factors for NO_x emissions as a function of preheated air temperature are available in the literature. A well-recognised reference on this subject is provided by the 'Besluit Emissie-Eissen Stookinstallaties Milieubeheer A' (BEES) guidance document published by the Dutch authorities in 1987. The correlation factor (applying only to existing installations) proposed in the BEES is displayed in Figure 4.35.

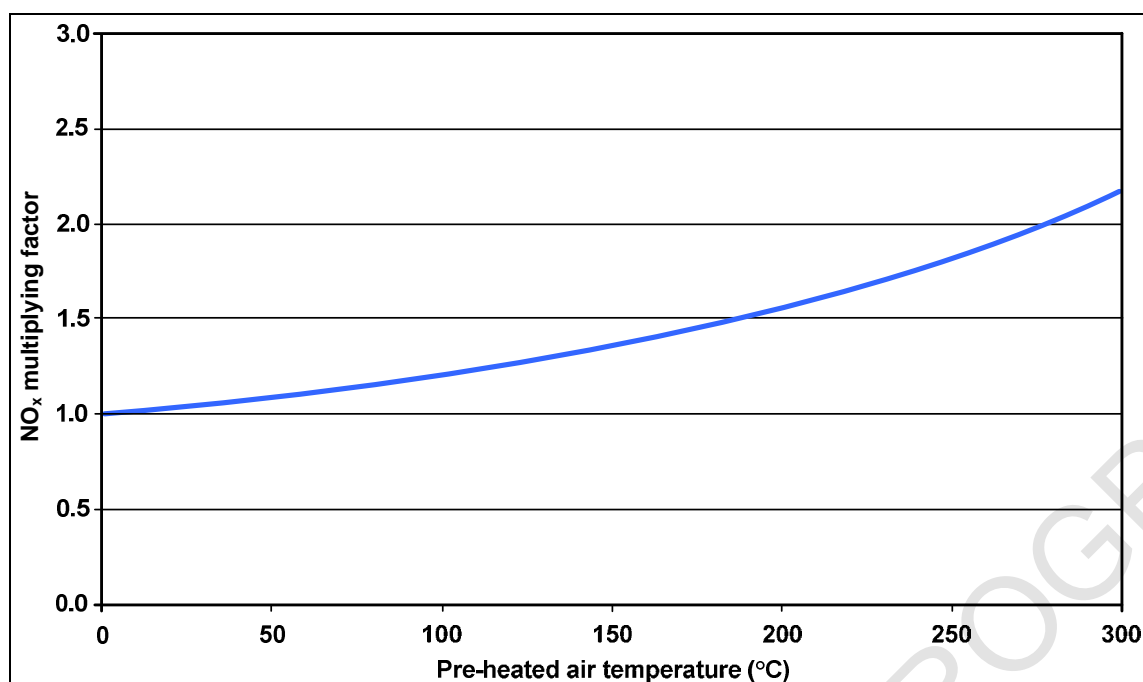


Figure 4.35: Effect of air preheating on NO_x emissions for fuel gas firing (applying only to existing installations)

This factor is applied directly for units fired with refinery fuel gas and addresses only the increase in thermal NO_x production. In the case of fuel oil or mixed liquid/gas fuel firing, this factor should be applied after first adjusting the bound fuel nitrogen to zero (see Figure 4.34 in Section 4.10.2.3), in order to avoid double counting the NO_x increase due to the fuel nitrogen conversion.

Operational data

Direct gas-fired heaters and boilers normally achieve thermal efficiencies of over 85 %. If air preheating is applied and the combustion products (flue-gas) are cooled close to their dew point, the thermal efficiency can be as high as 90 - 93 %.

An average fuel reduction of around 3 % has been achieved by retrofitting ceramic coatings on existing process furnace tubes (e.g. on catalytic reforming and vacuum distillation furnaces). A 2 % reduction was also observed after retrofitting high emissivity ceramic coatings on existing refractories of steam reformer furnace walls. In both cases, the related reduction of NO_x emissions could be estimated to 30 % for furnaces equipped with conventional burners, and 5 % for these equipped with low-NO_x burners.

Applicability

Most of the techniques mentioned in this section are generally applicable. However some restrictions to applicability for retrofitting existing units are to be taken into consideration. In the particular case of ceramic coatings, retrofitting this technique to furnaces fired with 100 % heavy liquid fuels is not advised.

Economics

The retrofitting of ceramic coatings on tubes and refractory walls of a 0.5 Mt/yr catalytic reforming furnace and a 2.1 Mt/yr vacuum distillation furnace costed around EUR 0.2 – 0.4 million per furnace (2004). The related payback time was estimated 6 months for the increased productivity (capacity and/or cycle run length) and at 2 years as far as energy consumption is strictly concerned.

Driving force for implementation

Reduction of energy consumption and related emissions from processes requiring heat or steam production.

Example plants

All techniques mentioned in this section are widely used in numerous process furnaces operated worldwide. In the particular case of tube and/or refractory ceramic coatings, more than 30 process furnaces have been treated since 2000 in Australia, Canada, Germany, Italy, Mexico, Japan and the US.

Reference literature

[167, VDI 2000], [177, WRA 1999], [151, Sema,Sofres 1991], [7, EC 2006], [193, BMUJF 1999], [221, Italy 2000], [168, VROM 1999], [207, TWG 2001], [Questionnaire n° 25], [36, CONCAWE n°4/09 2009].

4.10.3.2 Gas turbines

Description

A description of gas turbines can be found in the LCP BREF [7, EC 2006]. A brief description can also be found in Section 2.10. Some techniques that can be applied to gas turbines in order to reduce air emissions are listed below:

- steam injection;
- gas turbines with exhaust gas as combustion air;
- optimised transformation of steam into electrical energy (highest possible pressure difference in the steam turbine, generation of steam with high temperature and pressure, multiple reheating of the steam);
- other primary techniques such as dry low-NO_x burners cover in Sections 4.10.4.1 to 4.10.4.3;
- use high-efficiency turbines by, for example, optimisation of the design of the turbines, reducing as low as technically feasible the outlet steam pressure in the back-pressure turbine.

Achieved environmental benefits

Table 4.42 summarises the emission levels that can be achieved with the application of the primary measures for gas turbines.

Table 4.42: Expected air emissions from gas turbines with primary techniques

Pollutant	Gas ⁽¹⁾ (mg/Nm ³)	Liquid refinery fuel ⁽²⁾ (mg/Nm ³)
CO	5 – 100	<50
NO _x (as NO ₂) at 15 % O ₂	20 – 50 (new turbines) 20 – 90 (existing turbines ⁽³⁾)	200 (with water injection)
Particulates (at 15 % O ₂)		<5 – 30 with abatement
⁽¹⁾ The lower range relates to natural gas firing. ⁽²⁾ Gas oil/jet oil. ⁽³⁾ Lower range with dry low NO _x burners (DLN). Source: [7, EC 2006]		

Additional measures to abate NO_x emissions as low as 65 mg/Nm³ (15 % O₂) with, e.g. SCR, are also possible for existing gas turbines. See Section 4.10.4.7.

Environmental performance and operational data

The following Table 4.43 shows the achieved emissions values from a sample of gas turbines operated in some European refineries and using, at minimum, one of the techniques to reduce NO_x emissions as described previously. These data show the minimum and maximum monthly concentration of NO_x (at 15 % O₂ level) observed from continuous monitoring for a number of refinery gas turbines in Europe, the currently applied techniques and the operational conditions. [145, TWG CONCAWE 2012]

Table 4.43: Emissions of NO_x from gas turbines - Data from a sample of European refineries

Refinery Code	NO _x Min. Monthly	NO _x Max. Monthly	Techniques in place – Operational conditions
J2	40	70	Steam injection, RFG, SynGas, NG mixture changes
P	52	75	Steam injection, fired on FCCU off-gas
J1	40	80	Steam injection, RFG, Syn Gas, NG mixture changes
F	85	95	Steam injection, firing NG during data period
K	80	110	Steam injection peak shaving (high load factor change)
S	95	110	Four small 6 MW turbines fired on RFG/NG
M	110	120	SCR fitted. RFG fired
H	85	135	Steam injection varied over period. Fird on NG/RFG/middle distillate
V	130	160	Steam injection, NG(96 %)+RFG blend – the NO _x emission is affected by the crude being processed
W1	230	340	Partial load operation: 150 mg/Nm ³

NB: All concentration values expressed as mg/Nm³ @ 15 % O₂ content
Source: [145, TWG CONCAWE 2012]

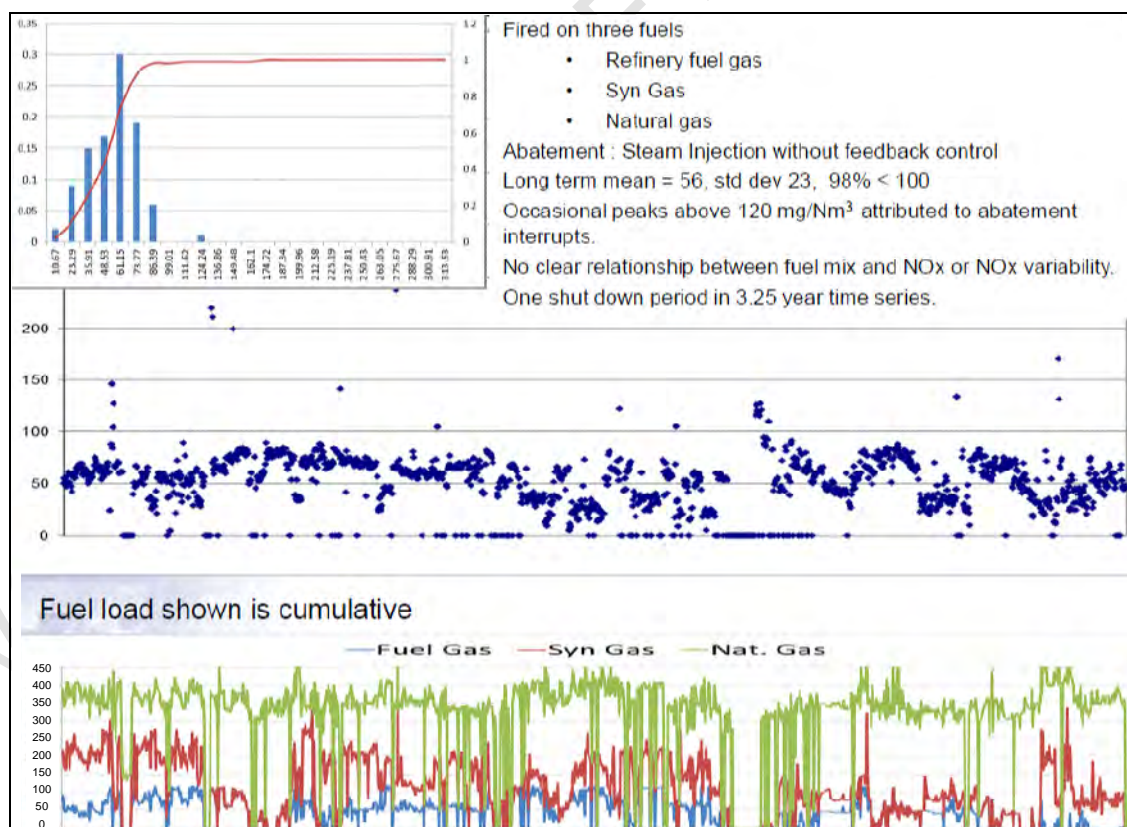


Figure 4.36: Daily variations of emissions to air from a gas turbines using three fuels (example from refinery J-GT A -170 MW)

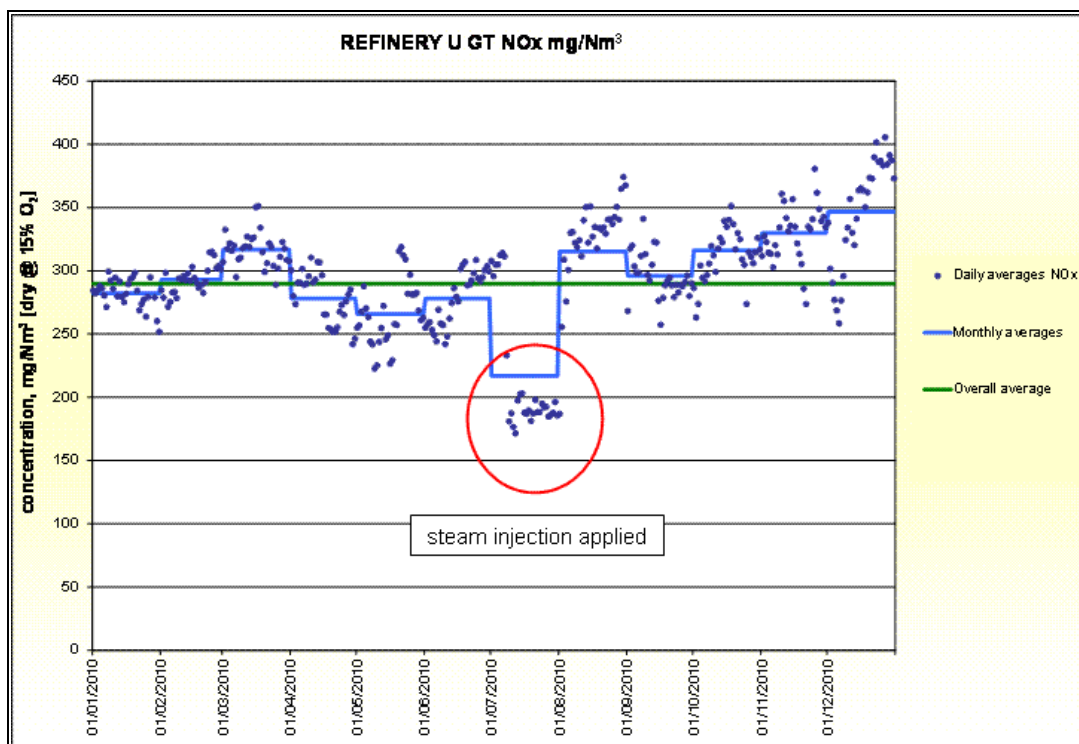


Figure 4.37: Effect of the application of steam injection to a gas turbine operating with a mixture of natural gas and refinery fuel gas (75 % RFG)

Cross-media effects

Steam injection typically generates higher emissions of CO and hydrocarbons. Steam should be produced if it is not available in the refinery.

Applicability

Fully applicable. Steam injection is particularly applicable where high hydrogen (H₂) content fuels are used. [145, TWG CONCAWE 2012], [266, Chiesa et al. 2003].

Economics

Steam injection applied to a 85 MWelec output turbine. Uncontrolled NO_x emissions of 500 mg/Nm³ at 15 % O₂ down to 50 – 80 mg/Nm³ at 15 % O₂. Investment cost (1998): EUR 3.4 million (including cost of steam production). Operating cost: EUR 0.8 million (excludes capital charge).

Driving force for implementation

Process technique used for the production of electricity.

Example plants

Many examples exist in refineries. A number of refineries have or are currently installing combined cycle gas turbines (CCGT) designed to produce steam and power for the refinery. This is usually done to replace, in whole or part, an old oil-fired boiler plant, to reduce operating costs and to decrease reliance on other power generators. A recent example (December 2011) for upgrading 6 gas turbines at Qatargas LNG plant (Qatar) shows a dry low NO_x system designed to achieve emissions levels of 25 ppm (<50 mg/Nm³).

Reference literature

[151, Sema,Sofres 1991], [168, VROM 1999], [166, CONCAWE 1999]. [7, EC 2006], [145, TWG CONCAWE 2012], [266, Chiesa et al. 2003].

4.10.3.3 Cogeneration plants (CHP)

Description

A brief description can be found in Section 2.10.

Achieved environmental benefits

For the combination refinery/other power generators (OPG), energy consumption and CO₂ emissions will be reduced by the application of the CHP concept. At the OPG, fuel consumption and all related emissions will be reduced but, at the refinery, fuel consumption and emissions may increase. A refinery that generates its own steam and electricity (no import from the OPG) can benefit from (enhanced) cogeneration. In these cases, the environmental benefit includes reduced fuel use and its related emissions.

Cross-media effects

No cross-media effects have been detected.

Operational data

Most turbines require a particularly stable mix of fuel in order to be sure of flame stability and are basically designed to burn natural gas. Refinery fuel gas components can vary considerably, especially when surplus hydrogen is produced, such as when a hydrotreatment unit is temporarily shut down, resulting in excess hydrogen being sent to the fuel gas system. However, these problems can usually be overcome, up to a limit of about 70 % hydrogen in the fuel.

Applicability

Generally applicable. The steam and power cogeneration concept can be also be applied to boilers firing, for instance, liquid refinery fuel. They can be designed to generate high-pressure steam and to let the pressure down over an expander/turbo-generator. Economisers and the optimisation of air-to-fuel control are also techniques applicable in cogeneration plants.

Driving force for implementation

For the production of steam and power to be used within or outside the refinery.

Example plants

A number of refineries have, or are currently installing, a combined cycle gas turbine (CCGT) or Combined Heat and Power (CHP) plant, designed to produce steam and power for the refinery. This is usually done to replace, in whole or part, an old oil-fired boiler plant, to reduce operating costs and to decrease reliance on other power generators.

Reference literature

[168, VROM 1999].

4.10.3.4 Gasification of heavy oils or coke (IGCC)

Description

Integrated gasification combined cycle (IGCC) is a technique whose purpose is to produce steam, hydrogen (optional) (see Section 2.14) and electric power from a variety of low-grade fuel types with the highest conversion efficiency possible. More information can be found in Section 2.10.

Achieved environmental benefits

Syngas produced in this process has a sulphur content of 0.01 – 0.05 % and could be used, as refinery fuel gas for hydrogen, fuel or chemical production. Water containing the soot particulates is filtered and the filter cake is subjected to a controlled burning process. The process is, in principle, autothermic; the heat of combustion being sufficient to evaporate the moisture content of the filter cake.

The IGCC is a highly-integrated and efficient process which can supply power, hydrogen and steam. Furthermore, it offers, in principle, an acceptable outlet for heavy residues and feedstocks or even refinery sludges, provided the latter are less than 1 % of feed. Hot gas clean-up systems have the potential to increase system efficiency and lower system costs. The achieved emissions to the atmosphere from that system are: SO₂: 50 mg/Nm³, NO_x: 65 mg/Nm³ at 3 % O₂, particulate matter: 5 mg/Nm³ and carbon monoxide: 10 – 30 mg/Nm³.

The emissions from the IGCC show a significant decrease compared with conventional power/steam plants. The SO₂ concentration in the refinery exhaust is reduced by 80 %, but CO₂ emissions increase.

The use of by-product and residual streams to meet the fuel requirement of refineries cannot only be cost-effective, but also is environmentally beneficial, in that it makes use of what would otherwise be a waste refinery stream that would be flared without recovering the energy content.

Cross-media effects

In some cases, some difficulties may occur in burning low-calorific-value gas produced. Water effluent is normally sent to the existing waste water treatment plant of the refinery. It may contain significant amounts of metals such as V, Cr or Ni and PAHs.

Operational data

Utility requirements for the gasification processes are 1800 – 4900 kWh/t of power and 1140 kg/t of steam consumption. The soot product is about 50 – 75 % w/w V₂O₅ residue, which can be sold to metal reclaimers. The IGCC complex is also equipped with all the necessary auxiliary systems, including cooling water (mixed system with an open seawater circuit for large users and a closed clean water circuit for the other users), demi-water, air, nitrogen, water and fuel gas networks, fire fighting, flare, storage, electrical distribution, buildings, etc.

IGCC is a technology with high flexibility in start-up, shutdown and part-load operation, depending on the level of integration between the different sections. Typically, systems that use heat exchange equipment are more efficient than those using quench cooling; however, the capital cost of the system with heat exchange is higher and there is a risk of fouling. The handling of the soot and filter cake should be done with care to avoid dust (even at 80 % moisture), due to the toxic properties of the residue.

Applicability

This technique can be seen as an alternative approach to removing sulphur using feed hydrotreatment (see Section 4.10.2.3). During normal refinery operation the gasifiers of the IGCC plant are able to convert almost any refinery residue (atmospheric residues, vacuum residues, visbroken or thermal tars, etc.) to heat and power. These feedstocks can have a high sulphur content.

Economics

Table 4.44 gives the economics of two examples of IGCC applied in European refineries.

Table 4.44: Economics of two IGCC plants of European refineries

Refinery capacity		Mt/yr
Fuel used in the refinery	120 000 liquid 180 000 gaseous	t/yr
Volume of flue-gas generated in the refinery	1.68×10^9	Nm ³ /yr
SO _x emissions (as SO ₂) before application of IGCC	5 000 (for liquid refinery fuels with 3 % S)	mg/Nm ³
SO _x emission load	8 400	t/yr
Efficiency of the process measured as sulphur content of the gaseous fuel	0.01	%
Investment cost	200 - 400	EUR million
Operating costs	20 - 40	EUR million/yr

Size of the IGCC	280	MW
Net cogeneration efficiency	47.2	%
Investment cost	648	EUR million
Characteristics of the feedstock used	Density: 1.05 - 1.1	kg/dm ³
	Viscosity: 100 - 3 500	cts at 150 °C
	Sulphur: 3.5 - 7	%
	Metals: 300 - 800	ppm
	Heating value: 8800 - 9 200	kcal/kg

Example plant(s)

The IGCC concept as such is quite a recent technological application for power stations. Although the main sections of an IGCC plant, i.e. gasification, air separation, gas cleaning and combined cycle are well known techniques that have previously been used separately for different applications and with different feedstocks. Integration (the 'I' in IGCC), though, is a more recent idea. Oil gasification is a process that has been applied for many years. Gasification of heavy residues, according to the principles of IGCC, is rather new. At least 4 IGCC plants are already in operation within European refineries and some others are in the design/construction phase. Coal gasification, also applying the IGCC concept, is new as well and a few plants are in operation.

Reference literature

[151, Sema,Sofres 1991], [221, Italy 2000], [232, Italy 1996].

4.10.3.5 Fluidised-bed boiler**Description**

An alternative method for the use of heavy residual oils or petroleum coke is combustion in a fluidised boiler with limestone injection for sulphur capture.

Achieved environmental benefits

About 90 % of the sulphur content of the fuel is captured and about 50 % of the calcium in the limestone is used in sulphur absorption.

Cross-media effects

The resulting calcium sulphate and unconverted calcium oxide, together with the nickel and vanadium in the fuel, are discharged from the boiler as a solid residue, which can be used as road aggregate or disposed of to landfill.

However, such schemes have a lower sulphur capture performance than gasification and they do not provide the option of producing hydrogen. There could also be environmental objections to the mining and transport of limestone and disposal of the residue. For these reasons, gasification may be generally more attractive in the long term.

Applicability

A combination of fluidised-bed boilers with upstream solvent deasphalting or delayed coking can be a cost-effective solution for refineries with existing FCC unit capacity and steam/power deficiencies.

Economics

Typically cheaper than gasification.

Driving force for implementation

Reduction of solid waste generation.

Reference literature

[168, VROM 1999].

4.10.4 Nitrogen oxide control and abatement techniques

Techniques to reduce NO_x emissions fall into two broad categories. Primary techniques that include NO_x control techniques, such as pre-combustion operational changes and combustion modifications. Secondary techniques that include the post-combustion flue-gas treatments or NO_x abatement techniques. More information about NO_x abatement techniques can be found in Section 4.23.3. Primary and secondary techniques are considered in this section. The types of NO_x control and abatement techniques to be considered in the energy systems are summarised in Table 4.45.

Table 4.45: NO_x control and abatement techniques considered for energy systems

Type of techniques	Fired heaters	Boilers	Gas turbines
Primary measures (control techniques)	Low-NO _x burners Ultra-low-NO _x burners Reburning	Flue-gas recirculation Ultra-low-NO _x burners Low-NO _x burners Reburning	Dry low-NO _x combustors Steam injection Water injection Low-NO _x combustors
Secondary measures (abatement techniques)	SCR SNCR	SCR SNCR	SCR

4.10.4.1 Low-NO_x burners and ultra-low-NO_x burners

Description

Low-NO_x burners, either air-staged or fuel-staged, have the aim of reducing peak temperatures, reducing the oxygen concentration in the primary combustion zone, and reducing the residence time at high temperatures, thereby decreasing thermally formed NO_x. Moreover, in the case of fuel-staged burners, the understoichiometric conditions created by the secondary flame after the fuel complementary addition creates a further chemical reduction of NO_x in N₂ by NH₃, HCN and CO radicals.

Ultra low-NO_x burners add the internal or external recirculation of flue-gases to the basic low-NO_x burner design, enabling the decrease of the oxygen concentration in the combustion area and a further abatement of NO_x, acting in particular on fuel-burn. Further information on various burner designs and features can be found in Section 3.4.1.6 of the BREF on Large Combustion Plants [7, EC 2006].

Achieved environmental benefits

When successfully implemented, low-NO_x burners can achieve NO_x reduction performances of 40 - 60 % for gaseous fuels and 30 - 50 % for liquid fuels compared to conventional burners of the same thermal capacity. Respectively, ultra low-NO_x burners successfully applied to gas-fired process heaters and boilers can achieve a 60 - 75 % reduction of NO_x emissions.

Based on the TWG 2008 data collection questionnaires (see Table 4.46), the following ranges have been reported from operational data at some EU 27+ refineries:

- 65 – 150 mg/Nm³ for gas fired in all cases, except for one old retrofit where a value of 253 mg/Nm³ has been observed
- 190 – 470 mg/Nm³ for mixed gas liquid fired (upper end reported for 50 % liquid firing).

The replacement of old burners with new low-NO_x burners, along with the air/fuel control system, may have also a positive effect on:

- process energy efficiency, as new burners are generally more fuel efficient;
- noise generated by the combustion plant, as a global improvement opportunity.

Cross-media effects

For heavy liquid fuel firing, there is a direct link between NO_x and particulates, i.e. reduction in NO_x as the flame temperature falls, will lead to an increase in particulates. CO emissions are also increased.

Operational data

Table 4.46 and Figure 4.38 give a selection of results reported by various European refineries within the data collection process launched for the BREF review (TWG 2008).

Table 4.46: Reported performance of low-NO_x burners in TWG site-level questionnaires

Reference [Questionnaire]	Type of fuel/burner	Emissions (daily average) mg/Nm ³ at 3 % O ₂	Available comments
[no 1]	Gas-fired LNB	<100	Process furnaces using generally RFG or NG Values < 150 for steam cracker
[no 13]	Gas-fired LNB	123	6 staged fuel burners - retrofit (2008) HDS unit – abatement achieved: 60 %
[no 14]	Gas-fired LNB	253 142 97	Retrofit (1991 – 2000) Retrofit (2006) Retrofit (2006)
	Mixed-fired LNB	297 191 315	Retrofit (1991 – 2000) 110 LNB out of 128 222 LNB out of 242
[no 16]	Gas-fired LNB	104 (monthly)	Max (spot): 194
	Mixed-fired LNB	317 (monthly)	Max (spot): 400
[no 20]	Gas-fired LNB	100	Average ranges achieved on 2 RFG-fired and 1 mixed-fired furnaces equipped with first generation LNB
	Mixed-fired LNB	300	
[no 22]	Gas-fired LNB	80 – 120	Average ranges achieved on a large number of furnaces equipped with LNB
	Mixed-fired LNB	200 – 250	
[no 26]	Gas-fired LNB	65	6 staged fuel burners - retrofit (2002) on a 20 MW furnace
[no 37]	Mixed-fired LNB	301 317 330 – 360 336 469 322	30/70 fuel to gas 34/66 fuel to gas 40/60 fuel to gas 45/55 50/50 58/42 (N content in liquid fuel: 0.6 %)
[no 38]	Mixed-fired LNB	435	50/50 fuel to gas N content: 2.44 % (liquid)/0.47 % (solid) H ₂ in fuel gas: 32 % (mass)
[no 39]	Gas-fired LNB	54	Concentration calculated from 15 mg/MJ Vacuum heaters – retrofit (1991) Achieved abatement: 80 %
	Gas-fired LNB	72	Concentration calculated from 20 mg/MJ Crude heaters - retrofit (1998) Achieved abatement: 65 %
[no 46]	Gas-fired LNB	<125	LNB burners Last generation of burners: 2000 Achievable with low throughput and low oxygen demand
	Liquid-fired LNB	<250	
[no 47]	Gas-fired LNB	93	Achieved with ULSG burners
	Mixed-fired LNB	340	Best boiler – 50/50 fuel to gas
	Mixed-fired LNB	220	Best furnace – 50/50 fuel to gas

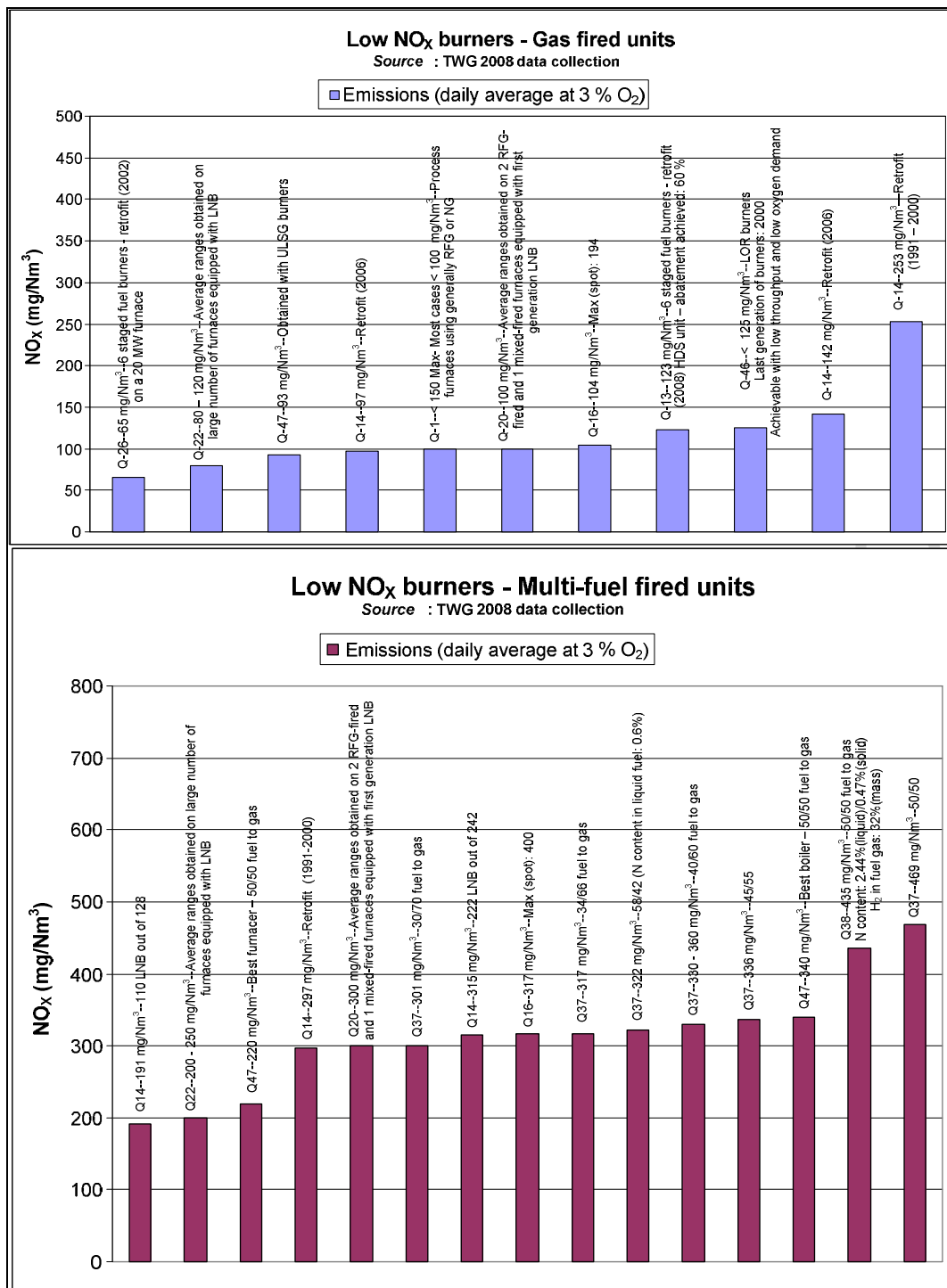


Figure 4.38: Reported performance of Low-NO_x burners for gas fired and multi-fuel fired combustion units (data from Table 4.46)

Extensive work has been undertaken to develop correlations that help explain how NO_x emissions relate to changes in operational parameters, e.g. fuel type and composition (in particular fuel bound nitrogen), combustion air preheat temperature, and fire box temperature. A good example is given by the set of adjustment factors developed in the Netherlands and provided as a national guidance for permit writers in 1987 [36, CONCAWE 2009 (Appendix 1)].

Table 4.47 shows a summary of typical ranges of NO_x emissions achieved in real refining operating conditions. These ranges cover a spectrum of different situations resulting from these

variable conditions, and are considered for air combustion converted back to ambient air temperature.

Table 4.47: Typical ranges of emission measured under various refining operating conditions in retrofit situations [36, CONCAWE n°4/09 2009]

Fuel	Type of burner	Emissions (daily average)	Comments
Refinery fuel gas	Low-NO _x burner with air or fuel basic staging	80 – 140 ⁽¹⁾	For combustion air at ambient temperature
	Ultra low-NO _x burner First generation	60 – 90 ⁽¹⁾	For combustion air at ambient temperature
	Ultra low-NO _x burner Latest generation	30 – 60 ⁽¹⁾⁽²⁾	For combustion air at ambient temperature and firebox temperature <900°
Mixed gas/liquid	Dual fired Low-NO _x burner (fuel staging for gas only)	200 – 350 ⁽¹⁾⁽²⁾⁽³⁾	For combustion air at ambient temperature. Lowest values achieved for 25 to 50 % liquid firing (0.21 – 0.5 % N content). Highest values achieved with 50-70 % liquid firing (0.4 – 0.55 % N content).

⁽¹⁾ Lower values are achievable with firebox temperature of <800°C and <10 % volume of hydrogen or C3 + in the refinery fuel gas composition.
⁽²⁾ Lower values are achievable with fuel gas containing no ammonia or other fuel-bond nitrogen.
⁽³⁾ Lower values are achievable with <0.1 % fuel-bond nitrogen mass content in the liquid fuel burnt.
 NB: Units in mg/Nm³ at 3 % O₂

For the gas refining sector in Norway, the following table shows recent examples of the use of ultra low NO_x burners.

Table 4.48: Recent example of ultra low NO_x burners in natural gas plants in Norway

Site	Thermal input capacity	Type of burner/fuel/year	NO _x emissions	Comments
Ormen Lange	2 x 42.1 MW	Ultra low-NO _x burner with flue-gas recirculation Natural gas/2007	20 mg/Nm ³	Measurements in 2008 in the range 20 – 90 mg/Nm ³ (30 to 10 MW) – NO _x emissions vary <i>inversely</i> to the MW of heat applied to the ovens
Kollsnes	18.4 MW	Ultra low-NO _x burner Natural gas/2012 ⁽²⁾	30 mg/Nm ³ ⁽¹⁾	

⁽¹⁾ Value guaranteed by supplier for 60-100 % operating duty range of the heater
⁽²⁾ Heater planned to be in operation in 2012 and used instead of existing one
 NB: Units in mg/Nm³ at 3 % O₂

Applicability

New installations

Apart from fuel-specific limiting conditions (see below), application is straightforward for new heaters and boilers.

Retrofitting existing installations

Compared to conventional burners, usual low-and ultra low-NO_x burners of the same thermal capacity tend to stretch the flame length up to 50 % and the flame diameter up to 30 – 50 %. They also need more space (internal and external area and volume) for being installed as their footprint is also increased, due to the presence of fuel injectors and/or the incorporation of furnace gas recirculation devices in and outside the burner tile. Finally, they usually offer a

lower flexibility ('turndown' capability ratio) between the highest and lowest accessible firing rate for given operating conditions, raising operating constraints and potential safety concerns. Therefore, some older-fired heaters are fitted with large high-intensity burners which cannot be easily retrofitted with new low-NO_x burners. As an illustration of this, some cases of disappointing results have been reported within the data collection process for the review of this BREF. Another example is the retrofitting of dual-fuel burners theoretically capable of operating with 100 % gas fuel, but with a practical restriction on the maximum amount of gas due to tube skin temperature limits in the primary and secondary super-heater section [Questionnaires n° 31, 32, 37, 45].

The retrofitting of low-NO_x burners is possible in general but will depend on site-specific conditions (such as furnace design and surrounding environment). Nevertheless, in some specific cases, it can lead to heavily modifying the technical integration of the furnace into the unit, or to changing the furnace.

Some state-of-the-art burners have been specifically designed for being retrofitted to existing plants, and may be very well adapted to the upgrading of oil refining gas-fueled heaters. They benefit from advanced computational fluid dynamics (CFD) modelling and show a higher compactness associated with an improved turndown capability.

Fuel-specific limiting conditions

The applicability for state-of-the-art gas-fired ultra low-NO_x burners is limited to fuel gases having a small amount of components heavier than propane and a low olefinic content. NO_x performance with ultra low-NO_x burners (ULNB) is more sensitive to excess oxygen. Therefore, this performance will depend on the feasibility and reliability of oxygen concentration control in the firebox (see Section 4.10.3.1 and Figure 4.35)

Economics

The following table gives different cost examples for the installation of low-NO_x burners, derived from various retrofitting projects in refineries.

Table 4.49: Specific cost examples for the retrofitting of low and ultra low NO_x burners

Project/reference	Investment cost	Comments
1/Reburning a typical crude oil furnace consisting of 40 forced-draught burners <i>No reference</i>	GBP 2 million (1998) Average per individual burner: GPD 50 000	Including the general upgrading of the furnace air, fuel and control systems likely to be carried out at the same time by a refiner
2/Retrofit several plants with gas-fired Low-NO _x burners as follows: - vacuum heaters - crude heaters [Site questionnaire n°39]	Total investments: - SEK 11 million (1991) - SEK 41 million (1998)	Assuming a 5-year operation life: - 25 000 SEK/t.yr (80 t/yr NO _x saved) - 34 000 SEK/t.yr (220 t/yr NO _x saved)
3a/Retrofit several process heaters operated within: - a CDU (10 Mt/yr – 20 burners) - a thermal cracker (3Mt/yr – 120 burners) - a HDS unit (12 burners) with: - gas-fired low-NO _x burners - ultra low-NO _x burners [Site questionnaire n°42]	Pre-evaluation step: average for the overall + project involving 152 burners (early 2007) Cost per individual burner: - GBP 16 200 - GBP 17 200	Does not include the general upgrading of the air, fuel and control systems. For the CDU unit: assumes a 5-year operation life: - GBP 639 /t.yr (141 t/yr NO _x saved) - GBP 472 /t.yr (202 t/yr NO _x saved)
3b/Retrofit several process heaters operated in units including finally: - a CDU (10 Mt/yr – 20 burners) - an alkylation unit (0.4 Mt/yr – 6 burners) - a VDU (7 Mt/yr – 16 + 13 burners) - HDS units (12 + 12 burners) with: - ultra low-NO _x burners [Site questionnaire No 42]	Updated evaluation step from 2A above (preliminary design): average for the overall final project involving 79 burners (early 2009) Cost per individual burner: - GBP 40 000	Include the general upgrading of the air, fuel and control systems For the CDU unit: assuming a 5-year operation life: - GBP 644 /t.y (202 t/yr NO _x saved)
4/Retrofit 20 low-NO _x burners on a visbreaker furnace in 2008 [Site questionnaire No 13]	Total burners cost alone: EUR 140 000 (EUR 7 000/burner) Total installation cost: EUR 756 000	Additional cost for burners installation: + EUR 37 800/burner in average (+ 540 % of burner individual cost)

The comparison between examples 2 and 3 in the table show very clearly that given the small cost difference, an ultra-low-NO_x burner can be an excellent cost-effective option when it is possible to retrofit on a high-power installation, compared to low-NO_x burners.

Potential investment and operational cost, expressed as total annual costs, for implementing this technique in 2007 on RFG and natural gas-fired process heaters in the Colorado refineries (US) were estimated as follows:

- For low-NO_x burners: EUR(*) 2 818 (USD 3 817) per year and tonne of NO_x, avoided, assuming a resulting NO_x emission decrease of 28 – 50 %;
- For ultra low-NO_x burners (first generation): EUR 4 087 (USD 5 536 - Based on currency conversion rate of 0.73822 on 1/07/2007) per year and tonne of NO_x, avoided, assuming a resulting NO_x emission decrease of 55 %;
- For ultra low-NO_x burners (last generation): EUR 613 to 908 (USD 831 to 1 230) per year and tonne of NO_x, avoided, assuming a resulting NO_x emission decrease of 75 – 85 %.

Driving force for implementation

Reduction of NO_x emissions, in combination with good cost-benefit conditions.

Example plants

There are many examples of applications in European refineries. At Preem Lysekil (SE), low-NO_x burners are used in 16 of 21 furnaces and boilers. For the Shell Gothenburg (SE) refinery, 85 % of the furnaces are equipped with low-NO_x burners.

Reference literature

[17, Jeavons and Francis 2008], [36, CONCAWE n°4/09 2009].

4.10.4.2 Dry low-NO_x combustors**Description**

More information can be found in the LCP BREF [7, EC 2006].

Achieved environmental benefits

A 90 % reduction in NO_x emissions in natural gas-fired gas turbine applications is possible. The main suppliers provide gas turbines equipped with dry low-NO_x combustors with a guarantee (for natural gas) of NO_x emissions ≤ 9 to 40 ppmv (18 – 80 mg/Nm³) at 15 % O₂ dry conditions.

Table 4.50: NO_x emissions achieved with dry low-NO_x combustors for different types of equipment

Type of fuel	Fired Heaters	Boilers	Gas Turbines
Refinery fuel gas or natural gas	NA	NA.	20 – 90(*)
NB: Data in mg/Nm ³ at 15 % O ₂ (g/GJ). n/a: not applicable. (*) Where DLN are applicable. Source [7, EC 2006], [264, G. Electric 2012], [265, Siemens 2012]			

Cross media effects

None in particular.

Operational data

Dry combustors differ from burners as their performance increases with higher loads.

Applicability

Applicable to gas turbines. Dry low-NO_x combustors are not available for gas turbines fired with refinery blend gas that contains more than 5 to 10 % v/v of hydrogen. When using a high hydrogen content RFG in gas turbines, additional techniques such as diluent injection may be needed. [264, G. Electric 2012]

Economics

The investment costs are: EUR 2.2 million (1998), and the operating cost is nil for an 85 MW_{el} output turbine.

Driving force for implementation

Reduction of NO_x emissions.

Reference literature

[166, CONCAWE 1999], [228, TWG 2000], [264, G. Electric 2012], [265, Siemens 2012]

4.10.4.3 Flue-gas recirculation

Description

External flue-gas recirculation (FGR) is applied to boilers and heaters to increase the diluent effect, hence to reduce the combustion temperature. Typically 20 % of the available flue-gas from the boiler stack is ducted to mix with fresh combustion air.

Achieved environmental benefits

Using recirculated flue-gas as part of the combustion air can further reduce NO_x formation.

Operational data

The process is difficult to control, especially during turndown.

Applicability

It is applied to boilers and fired heaters. In a retrofit (in particular boilers and furnaces in forced draught mode operation), FGR increases hydraulic loads, and shifts the heat load towards the convective section(s) and may not be practical.

Economics

Higher cost than other primary measures.

Driving force for implementation

To reduce the NO_x emissions from boilers and heaters.

Reference literature

[166, CONCAWE 1999], [228, TWG 2000].

4.10.4.4 Diluent injection

Description

Inert diluents, such as flue-gas, steam, water and nitrogen added to combustion equipment reduce the flame temperature and consequently the concentration of NO_x in the flue-gases.

Achieved environmental benefits

Control of NO_x in gas turbine combustors may be carried out by using steam/water injection, which can achieve reduction performances of 80 - 90 %. Detailed data of NO_x emissions to air from gas turbines are shown in Table 4.43. Based on these data from continuous monitoring of a sample of gas turbines operated at some European refineries, the corresponding achievable range when using diluent injection is reported in the following Table 4.51.

Table 4.51: NO_x emissions achieved by gas turbines with diluent injection

Type of fuel	NO _x emissions from gas turbines
Refinery fuel gas	40 – 120
NB: Data in mg/Nm ³ at 15 % O ₂	
Source: [145, TWG CONCAWE 2012]	

Cross-media effects

When extra energy is required to produce steam, it could result in higher emissions and reduction of the overall system efficiency. An example of the energy debit of increasing steam addition to significantly reduce NO_x concentrations is reported for a 109 MW unit: a steam consumption of 13.7 t/h requires 11 MW of fuel to produce it (at 3 GJ fuel per tonne of steam).

Operational data

The use of steam generates more corrosion in the system than the use of nitrogen.

The data from continuous monitoring of a sample of gas turbines operated on a variable mix of refinery fuel gas at some European sites and using steam injection, show an operational range of 40 – 120 mg/Nm³ at 15 % O₂. See Table 4.43.

Applicability

Steam and water injection is widely applied to gas turbines both in new installations and retrofits and is also applicable to fired heaters and boilers. There are technical difficulties in applying water injection in boilers and furnaces. Nitrogen dilution is only applied when nitrogen is already available in the refinery.

Economics

Capital costs of the steam and water injection are less than that of SCR, making the technology a good first choice for substantial levels of NO_x reductions, with SCR often added on if higher NO_x reduction is needed. Substantial recurring operating costs are, however, encountered for producing high-purity steam, and maintenance costs for re-blading may be high.

Driving force for implementation

Reduction of NO_x emissions.

Example plants

The nitrogen by-product from the air separation plant in refinery residue gasification projects has recently been proven commercially as a diluent for gas turbine NO_x reduction. Within the refining industry, steam injection predominates.

Reference literature

[163, FWE 1999], [166, CONCAWE 1999], [207, TWG 2001],
[145, TWG CONCAWE 2012].

4.10.4.5 Fuel staging (reburning)

Description

Fuel staging, also called reburning, is based on the creation of different zones in the furnace by the staged injection of fuel and air. The aim is to reduce NO_x emissions, which have already been formed back into nitrogen. This technique adds to the flame cooling, a reaction by which organic radicals assist in the breakdown of NO_x. More information is available in the LCP BREF [7, EC 2006].

Achieved environmental benefits

Achievable levels are < 200 mg/Nm³ NO₂ equivalent, especially for gas firing, for which the lowest levels are more easily achievable.

Cross-media effects

Additional energy consumption (estimated at around 15 %, without any complementary energy recovery).

Applicability

This technique is applied at the furnace or boiler level but it is strongly connected with the burner technique. It is widely used for gas firing. For mixed or liquid firing, a specific burner design is required.

Driving force for implementation

Reduction of NO_x emissions.

Reference literature

[163, FWE 1999].

4.10.4.6 Selective non-catalytic reduction (SNCR)

Description

See Section 4.23.3.2 below.

Achieved environmental benefits

In oil refining, reductions of NO_x from 25 % to 70 % have been demonstrated under favourable conditions for full-size combustion plants.

Cross-media effects

General cross-media effects are described in Section 4.23.3.2 below.

In the particular context of oil refining, effects given below are to be noticed:

- A side effect of particular concern is the formation of ammonium sulphates when firing sulphur-containing fuels such as liquid refinery fuel. Sulphate deposits give rise to the fouling and corrosion of cooler downstream equipment. Ammonium sulphate can also result in aerosol emissions from the stack and can contribute to PM emissions.
- The storage and use of gaseous or liquefied anhydrous ammonia has a great hazardous potential. If such storage is impossible to avoid, risk assessment should be carried out and appropriate prevention measures are required. When technically possible, a liquid solution of ammonia (25 %) should always be preferred. Flue-gas temperature drops after urea or ammonia injection, which penalise the energy recovery potential.

Operational data

Table 4.52 gives some illustrating examples of this, for 3 boilers operated in oil refineries.

Table 4.52: NO_x emissions achieved with retrofitted SNCR for different refinery boilers

Reference [Questionnaire]	Thermal capacity	Fuel type	% N in liquid fuel	% liquid fuel/total	Inlet concentration	% NO _x abatement	Comments
[no 13]	98 MW	Mixed	0.40 – 0.50	30 – 95	244 – 810	25 – 40	40 % only achieved for specific boiler load
[no 15]	45 MW	Mixed	0.34 – 0.45	80 – 95	667 – 877	25 – 30	Ammonia slip >15 ppm for >30 % abatement
[no 15]	45 MW	Mixed	0.34 – 0.45	70 – 90	568 – 780	25 – 30	

NB: Emissions in mg/Nm³ at 3 % O₂ (dry gas) - Continuous emission monitoring system for reference [13]
 Source: [36, CONCAWE 4/09 2009]

These figures are consistent with an urea test performed from 2008 – 2009 in a French refinery on a 99 MW boiler. In the 104 t/h flue-gas stream, containing 600 – 800 mg/Nm³ (3 % O₂ dry) of NO_x, the initial urea injection rate was 150 – 200 l/h, corresponding to approximately 1 kg urea per kg NO_x to be treated. The NO_x reduction achieved was 35 – 45 %, with concentrations in the range 380 – 400 mg/Nm³. However, after some tube perforations due to corrosion, the injection rate was reduced and then stopped for the injection conditions to be modified and optimised.

At the Gothenburg ST1 refinery (SE), it is reported that an SNCR operating at one boiler (45 MW) achieves the following reductions:

- from 300 to 150 mg/Nm³ for gas firing;
- from 1 100 to 550 for oil firing.

Applicability

SNCR requires temperatures within the following window:

- 850 – 1 000 °C, for ammonia and caustic ammonia (optimum 870 °C)
- 800 – 1 100 °C, for urea (optimum 1 000 °C).

Retrofitting to existing boilers and furnaces can be limited, as there may not be sufficient residence time (0.2 to 0.5 s in the region of injection) at the required temperature levels.

Thus, application of the SNCR technique in existing furnaces and boilers requires well chosen injection locations and a mixing region with an appropriate temperature and size to allow for sufficient NO reduction.

Application is also complicated when the flue-gases to be treated come from the combustion of high sulphur content heavy fuel oil for which ammonia slips can lead to the formation of ammonium sulphate deposits.

When retrofitting, new space requirements may be very limited, especially ammonia storage and injection equipment.

Economics

Table 4.53 shows the economics of the application of SNCR for the treatment of flue-gases coming from the combustion processes from different sources. Cost data for SNCR and SNCR used at combustion units for different sizes and abatement efficiencies are shown in Table 4.55.

Table 4.53: Examples and main cost factors for a Selective Non Catalytic Reduction (SNCR)

Values corresponding to a 100 GJ/h installation - retrofit of existing installation	Fired heaters and boilers firing refinery blend gas	Boilers firing residual fuel oil
Down to ppm at 3 % O ₂	50	100
Investment costs (1998) (EUR million)	0.4 - 0.5	0.4 - 0.9
Operating costs per year (excludes capital charge) (EUR million)	0.025	0.05 - 0.07

Capacity of the refinery	5	Mt/yr
Fuel consumption	120 000 (liquid refinery fuels) 180 000 (refinery fuel gas)	t/yr
Volume of the flue-gas	3 10 ⁹	Nm ³ /yr
Efficiency of the SNCR	60 - 80	%
NO_x emissions (as NO₂)	200	mg/Nm ³
Investment	3 - 5	EUR million
Operating costs	0.2 - 1	EUR million/yr

Cost parameters		EUR/unit	EUR/yr
Operating hours (h/yr)	8 000		
Investment (EUR)	1 090 093		
Input factors for annual expenditure:			
Number of years	15		
Interest rate (%)	6		
Annual repayment incl. Interest (EUR/yr)	112 239		
Proportional investment incl. Interest			112 239
Maintenance + wear and tear (% of investment costs)	2		
Maintenance + wear and tear (EUR/yr)	21 802		
Maintenance + wear and tear			21 802

Cost parameters		EUR/unit	EUR/yr
Electrical energy (kWh/h)	40	0.07 EUR/kWh	20 930
Air (Nm ³ /h)	1 200	0.01 EUR/Nm ₃	118 602
NH ₃ liquid (kg/h)	83.15	0.25 EUR/kg	169 201
Total cost			442 774
NB: Installation on a volume of exhaust gas of 250 000 Nm ³ /h after a power plant, in a refinery achieving a NO _x emission reduction of 500 mg/Nm ³ in relation to actual oxygen content and for a clean gas concentration of <200 mg NO _x /Nm ³			

Potential investment and operational costs for implementing this technique in 2007 on process heaters in the Colorado refineries (US) were estimated at EUR 3 644 (USD 4 936 - based on currency conversion rate of 0.73822 at 1/07/2007) per year and tonne of NO_x avoided, assuming a resulting NO_x emission decrease of 43 – 60 %. Another set of data gathered during an applicability test on a French refinery site (see details under operational data) gave less expensive costs, as shown in Table 4.54 below.

Table 4.54: Cost evaluation for urea SNCR retrofitting of a 99 MW refinery boiler (2009)

Urea SNCR retrofitting costs to a 99 MW boiler	Costs (EUR)	Comments
Investment cost	500 000	Project Year 2009
Operational costs:	539 000	(Excluding capital charges)
Including:		
Urea 200 l/h	376 000	EUR 190/t – 1980 t/yr
Equipment rental	100 000	
Energy for vaporisation (40 % urea in water)	55 000	180 kW estimated
maintenance	8 000	120 hours
Inlet concentration: 700 mg/Nm ³ Outlet concentration: 420 mg/Nm ³ Reduction 40 % NO _x : 330 t/yr		37.7 kg/h (Excluding capital charges)
Specific cost for 2009	EUR/t of NO _x 1 935	

Table 4.55: Cost data for combustion unit NO_x abatement techniques (SCR and SNCR)

NO _x Abatement on Combustion Units (Assuming SNCR Efficiency of 30%)																
Baseline					SNCR					SCR						
					Efficiency	ACC	Fixed OP	Variable OP	Efficiency	ACC	Fixed OP	Variable OP	Efficiency	ACC	Fixed OP	Variable OP
					%	%	%/y	k€/y	%	%	%/y	k€/y	%	%	%/y	k€/y
					30%	7.4%	4%	70	85%	7.4%	4%	64				
Heat Fired	Oil	Stack NO _x	Stack NO _x	NO _x Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to SNCR	Cost Effectiveness: Base to SNCR	Outlet NO _x	NO _x Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to SCR	Cost Effectiveness: Base to SCR	Incremental Cost Effectiveness: SNCR to SCR	Incremental Cost Effectiveness: SNCR to SCR		
MW	% Total MW	mg/Nm ³	mg/Nm ³	t/y	M€	k€/y	€/tNO _x	mg/Nm ³	t/y	M€	k€/y	€/tNO _x	€/tNO _x	€/tNO _x		
Unit 1	289	72%	450	315	328	2.9	730	2 225	70	924	18.3	2 445	2 645	2 876		
Unit 2	179	75%	450	315	204	2.2	496	2 434	70	574	13.7	1 788	3 117	3 492		
Unit 3	123	31%	356	250	111	1.7	368	3 318	55	312	10.9	1 401	4 491	5 136		
Unit 4	254	30%	351	245	225	2.7	657	2 923	54	634	16.9	2 247	3 546	3 889		
Unit 5	76	45%	425	298	81	1.3	251	3 099	66	229	8.2	1 025	4 483	5 245		
Unit 6	51	77%	450	315	58	1.0	187	3 218	70	163	6.5	799	4 890	5 811		
Unit 7	158	21%	305	213	122	2.0	448	3 684	47	343	12.7	1 649	4 807	5 425		
Unit 8	89	10%	250	175	56	1.4	285	5 075	39	158	9.0	1 138	7 185	8 346		
Unit 9	215	5%	227	159	123	2.4	573	4 658	35	346	15.3	2 010	5 804	6 434		
Unit 10	170	0%	200	140	86	2.1	475	5 533	31	242	13.3	1 728	7 142	8 028		
Unit 11	63	0%	200	140	32	1.2	219	6 873	31	90	7.3	915	10 173	11 989		
Unit 12	46	0%	200	140	23	0.9	172	7 438	31	65	6.0	746	11 453	13 662		
NO _x Abatement on Combustion Units (Assuming SNCR Efficiency of 40%)																
Baseline					SNCR					SCR						
					Efficiency	ACC	Fixed OP	Variable OP	Efficiency	ACC	Fixed OP	Variable OP	Efficiency	ACC	Fixed OP	Variable OP
					%	%	%/y	k€/y	%	%	%/y	k€/y	%	%	%/y	k€/y
					40%	7.4%	4%	70	85%	7.4%	4%	64				
Heat Fired	Oil	Stack NO _x	Stack NO _x	NO _x Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to SNCR	Cost Effectiveness: Base to SNCR	Outlet NO _x	NO _x Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to SCR	Cost Effectiveness: Base to SCR	Incremental Cost Effectiveness: SNCR to SCR	Incremental Cost Effectiveness: SNCR to SCR		
MW	% Total MW	mg/Nm ³	mg/Nm ³	t/y	M€	k€/y	€/tNO _x	mg/Nm ³	t/y	M€	k€/y	€/tNO _x	€/tNO _x	€/tNO _x		
Unit 1	289	72%	450	270	437	2.9	730	1 669	70	924	18.3	2 445	2 645	3 522		
Unit 2	179	75%	450	270	272	2.2	496	1 825	70	574	13.7	1 788	3 117	4 277		
Unit 3	123	31%	356	214	148	1.7	368	2 488	55	312	10.9	1 401	4 491	6 289		
Unit 4	254	30%	351	210	300	2.7	657	2 192	54	634	16.9	2 247	3 546	4 762		
Unit 5	76	45%	425	255	108	1.3	251	2 324	66	229	8.2	1 025	4 483	6 423		
Unit 6	51	77%	450	270	77	1.0	187	2 413	70	163	6.5	799	4 890	7 116		
Unit 7	158	21%	305	183	162	2.0	448	2 763	47	343	12.7	1 649	4 807	6 643		
Unit 8	89	10%	250	150	75	1.4	285	3 806	39	158	9.0	1 138	7 185	10 220		
Unit 9	215	5%	227	136	164	2.4	573	3 494	35	346	15.3	2 010	5 804	7 879		
Unit 10	170	0%	200	120	115	2.1	475	4 150	31	242	13.3	1 728	7 142	9 830		
Unit 11	63	0%	200	120	43	1.2	219	5 155	31	90	7.3	915	10 173	14 682		
Unit 12	46	0%	200	120	31	0.9	172	5 579	31	65	6.0	746	11 453	16 730		
NO _x Abatement on Combustion Units (Assuming SNCR Efficiency of 50%)																
Baseline					SNCR					SCR						
					Efficiency	ACC	Fixed OP	Variable OP	Efficiency	ACC	Fixed OP	Variable OP	Efficiency	ACC	Fixed OP	Variable OP
					%	%	%/y	k€/y	%	%	%/y	k€/y	%	%	%/y	k€/y
					50%	7.4%	4%	70	85%	7.4%	4%	64				
Heat Fired	Oil	Stack NO _x	Stack NO _x	NO _x Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to SNCR	Cost Effectiveness: Base to SNCR	Outlet NO _x	NO _x Removed (From Base)	Total Erected Cost (From Base)	Annualised Cost: Base to SCR	Cost Effectiveness: Base to SCR	Incremental Cost Effectiveness: SNCR to SCR	Incremental Cost Effectiveness: SNCR to SCR		
MW	% Total MW	mg/Nm ³	mg/Nm ³	t/y	M€	k€/y	€/tNO _x	mg/Nm ³	t/y	M€	k€/y	€/tNO _x	€/tNO _x	€/tNO _x		
Unit 1	289	72%	450	225	547	2.9	730	1 335	70	924	18.3	2 445	2 645	4 542		
Unit 2	179	75%	450	225	339	2.2	496	1 460	70	574	13.7	1 788	3 117	5 516		
Unit 3	123	31%	356	178	185	1.7	368	1 991	55	312	10.9	1 401	4 491	8 111		
Unit 4	254	30%	351	175	375	2.7	657	1 754	54	634	16.9	2 247	3 546	6 142		
Unit 5	76	45%	425	213	135	1.3	251	1 859	66	229	8.2	1 025	4 483	8 283		
Unit 6	51	77%	450	225	97	1.0	187	1 931	70	163	6.5	799	4 890	9 177		
Unit 7	158	21%	305	152	203	2.0	448	2 210	47	343	12.7	1 649	4 807	8 567		
Unit 8	89	10%	250	125	94	1.4	285	3 045	39	158	9.0	1 138	7 185	13 180		
Unit 9	215	5%	227	114	205	2.4	573	2 795	35	346	15.3	2 010	5 804	10 161		
Unit 10	170	0%	200	100	143	2.1	475	3 320	31	242	13.3	1 728	7 142	12 678		
Unit 11	63	0%	200	100	53	1.2	219	4 124	31	90	7.3	915	10 173	18 934		
Unit 12	46	0%	200	100	39	0.9	172	4 463	31	65	6.0	746	11 453	21 576		

Source: [CONCAWE 6/11]

Driving force for implementation

Reduction of NO_x emissions.

Example plants

This process has been applied to heaters and boilers of refinery plants. Experience of application of SNCR on oil-fired heaters is more limited. A US study reports that SNCR is used less frequently than SCR for the control of NO_x and that only 12 of the 150 boilers/heater

installations of 8 refineries use this type of technique. In the EU, for example, Shell refinery in Gothenburg (SE) operates an SNCR on one boiler.

Reference literature

[160, Janson 1999], [166, CONCAWE 1999], [151, Sema, Sofres 1991], [194, Winter 2000], [246, AL Group 2001], [17, Jeavons and Francis 2008], [36, CONCAWE n°4/09 2009], [Questionnaire n° 13].

4.10.4.7 Selective catalytic reduction (SCR)

Description

See Section 4.23.3.3 below.

Achieved environmental benefits

SCR is capable of reducing NO_x by 80 – 95 % in refining boilers and heater applications, as well as for gas turbine flue-gases.

Cross-media effects

Generic cross-media effects are described in Section 4.23.3.3.

In the particular context of oil refining, the effects given below are to be noted.

- As for the SNCR technique, a side effect of particular concern is the formation of ammonium sulphates when firing sulphur-containing fuels such as liquid refinery fuel. Sulphate deposits give rise to the fouling and corrosion of cooler downstream equipment. Ammonium sulphate can also result in aerosol emissions from the stack and contribute to PM emissions.
- As for the SNCR technique, the storage and use of gaseous or liquefied anhydrous ammonia has a great hazardous potential. If such storage is impossible to avoid, risk assessment should be carried out and appropriate prevention measures taken. When technically possible, a liquid solution of ammonia (25 %) is preferred.

Operational data

At Shell refinery (SE), an SCR unit has been installed at a 68 MW boiler (1998). Fuel oil is used and NO_x emissions are 16 mg/MJ (55 mg/Nm³, 3 % O₂). The NO_x reduction is about 94 % and the ammonia slip well below 5 ppm. Preem Lysekil (SE) has an SCR on the FCC (see Section 4.5.4.1). Preem refinery Gothenburg (SE) has two SCRs, on the reformer and one on one of the two crude distillation units.

At the STEAG power station (Total Raffinerie Mitteldeutschland in Germany), the three oil-fired heaters (each producing 160 t/h steam -100 bars - 505 °C, consuming 12 t/h of heavy fuel oil at 3.7 % S) are equipped with an SCR plant (high-dust); they have to reach NO_x emissions below 150 mg/m³. Table 4.56 below gives more data concerning this particular example.

Table 4.56: Gas concentration of the power plant of Total Raffinerie Mitteldeutschland

Parameters (yearly average 2009)	Raw gas	Clean gas
Flue-gas volume, wet (m ³ /h, 7 % O ₂)	171 690	188 249
Temperature (°C)	<180	<76
Dust (mg/Nm ³ , 3 % O ₂)	220	<10
NO _x as NO ₂ (mg/Nm ³ , 3 % O ₂)	800	<150
SO ₂ (mg/Nm ³ , 3 % O ₂)	<4 100	
SO ₃ (mg/Nm ³ , 3 % O ₂)	650	<10
SO _x as SO ₂ (mg/Nm ³ , 3 % O ₂)		<220

Moreover, CONCAWE reports two other data-sets of SCR in refineries, one covering a mixed gas/oil fired heater, and the other covering a common stack of four mixed gas/oil fired boilers. In both cases, a 80 – 82 % removal is shown, resulting in a 90 – 120 mg/Nm³ outlet concentration (3 % O₂).

Finally, one recent example of SCR has been reported for a 19 MW refinery gas turbine application in France. After the operation restarted in 2009, early results showed a 80 % NO_x decrease from concentrations registered before (max. 350 mg/Nm³) to new maximum concentrations measured below 65 mg/Nm³ (15 % O₂). A 2 % loss was reported of the generated power.

Applicability

Section 4.23.3.3 below gives general considerations on the usual constraints for the retrofitting of the SCR technique to existing combustion plants, notably in terms of space availability, temperature and pressure drop.

In the particular case of boilers and heaters of refineries fired with heavy fuels, fly-ash contains metal oxides, soot and coke. Unabated fly-ash concentrations are in the range of 100 – 600 mg/Nm³ (with the highest values corresponding to vacuum residues). SCR applied under these conditions may suffer from clogging by fly-ash and sulphates. The potential for sulphate precipitation is generally higher with vacuum residue, due to its high sulphur content (2.5 – 4 %).

NO_x removal efficiency will also depends on the NO_x inlet concentration to be abated, because even under optimal thermal conditions, there is a lower limit to the technically achievable reduction yield and outlet concentration, due to the particular mixing conditions and chemical kinetics.

Economics

The costs of SCR vary, depending on the fuels, exhaust volume and required NO_x reduction. For new power generation installations, the cost range may be EUR 25 – 110/kW. Maintenance costs are minimal, the bulk of which are from NH₃ consumption.

For retrofitting situations, two examples of the application of SCR in refinery power plants are shown in Table 4.57 and

Table 4.58. The use of an SCR unit for treating the power plant flue-gas has been estimated in raw gas (

Table 4.58) and clean gas (Table 4.57) operation mode. These two cost tables refer to the Total Raffinerie Mitteldeutschland project in the two cases already mentioned, for which performance data are provided in Table 4.56.

Table 4.57: Main cost factors for a Selective Catalytic Reduction (SCR) on clean gas operation

Cost details (clean gas operation) in 1998	Quantity	EUR/unit	EUR/yr
Operating hours (h/yr)	8 000		
Investment (EUR)	3 270 278		
Input factors for annual expenditure:			
Number of years	15		
Interest rate (%)	6		
Annual repayment incl. Interest (EUR/yr)	336 717		
Proportional investment costs incl. interest			336 717
Volume of catalyst (m ³)	20		
Endurance (years)	15		
Renewal of catalyst (m ³ /yr)	1.33	14 535 EUR/m ³	
Average renewal of catalyst (EUR/yr)	19 379		
Catalysts			19 379
Maintenance + wear and tear (% of investment costs)	2		
Maintenance + wear and tear (EUR/yr)	65 406		
Maintenance + wear and tear			65406
Pressure drop (mbar)	35		
Energy for reheating (MJ/h)	11 806.67	3.63 EUR/GJ	343 210
Electrical energy (kWh/h)	610	0.07 EUR/kWh	319 187
NH ₃ liquid (kg/h)	46.20	0.25 EUR/kg	94 001
Total costs (1998)			1 177 900
NB: Installation on a volume of exhaust gas of 250 000 Nm ³ /h in the dedusted off-gas after a power plant, in a refinery achieving a NO _x mission reduction of 500 mg/Nm ³ in relation to actual oxygen content and for a clean gas concentration of <100 mg NO _x /Nm ³ .			

Table 4.58: Main cost factors for a Selective Catalytic Reduction (SCR) on raw gas operation

Cost details (raw gas operation) in 1998	Quantity	EUR/unit	EUR/yr
Operating hours (h/yr)	8 000		
Investment costs (EUR)	2 180 185		
Input factors for annual expenditure:			
Number of years	15		
Interest rate (%)	6		
Annual repayment incl. interest (EUR/yr)	224 478		
Proportional investment costs incl. interest			224 478
Volume of catalyst (m ³)	35		
Endurance (years)	8		
Renewal of catalyst (m ³ /yr)	4.38	14 535 EUR/m ³	
Average of catalyst (EUR/yr)	63 589		
Catalysts			63 589
Maintenance + wear and tear (% of investment costs)	2		
Maintenance + wear and tear (EUR/yr)	43 604		
Maintenance + wear and tear			43 604
Pressure drop (mbar)	8		
Energy for reheating (MJ/h)	0	3.63 EUR/GJ	0
Electrical energy (kWh/h)	160.07	0.07 EUR/kWh	83 753
NH ₃ liquid (kg/h)	46.20	0.25 EUR/kg	94 001
Total costs (1998)			509 425
NB: Installation (raw gas) on a volume of exhaust gas of 250 000 Nm ³ /h after a power plant, in a refinery achieving a NO _x emission reduction of 500 mg/Nm ³ in relation to actual oxygen content and for a clean gas concentration of <100 mg NO _x /Nm ³ .			

Table 4.59 illustrates another retrofitting cost example for the reformer furnace of the Swedish Preem refinery, also in 1998.

Table 4.59: Investment costs for a SCR retrofitting to a reformer furnace (1998)

	Data	Comments
Capacity	68 MW	Total reformer thermal capacity
Efficiency (design)	90 %	Designed for low temperature: 185 °C Ammonia slip of 5 ppm
Efficiency (operational)	91 %	Achieved value until 2009 In 2009: 75 % including one month out of operation for revision
Investment cost (1998)	EUR 3.2 million	

Cost data for SCR and SNCR used at combustion units for different sizes and abatement efficiencies are shown in Table 4.55.

Moreover, potential investment and operational costs for implementing this technique in 2007 on existing boilers and process heaters in Colorado refineries (US) were estimated at a range of EUR 2 000 to 6 054 (USD 2 708 to USD 8 201) per year and tonne of NO_x avoided, assuming a resulting NO_x emission reduction of 70 – 90 % (currency conversion rate of 0.73822) at 1/07/2007).

For retrofitting a 19 MW refinery gas turbine in France, the following costs were reported:

- total construction cost (2008): EUR 7 million;
- annual cost: EUR 200 000.

Driving force for implementation

Reduction of NO_x emissions.

Example plant(s)

Concerning refinery energy systems, SCR has been applied to gas turbines, process boilers, process heaters such as naphtha reformers, steam reformers, crude and vacuum distillation units, thermal cracking and hydroprocessing units. A report on US refineries shows that 20.7 % (or 31 boilers/heaters) of 150 boiler/heater installations at 8 refineries employ SCR as a control technique. The same study shows that three SCR installations have been applied to the four turbines found in the eight refineries analysed.

Reference literature

[181, HP, 1998], [160, Janson 1999], [151, Sema,Sofres 1991], [194, Winter 2000], [166, CONCAWE 1999], [246, AL Group 2001], [17, Jeavons and Francis 2008], [36, CONCAWE n°4/09 2009], [Questionnaire n° 9].

4.10.4.8 Low temperature oxidation

Description

See Section 4.23.3.1.

Achieved environmental benefits

Reduction of NO_x emission by 90 – 95 %, with an outlet concentration reduced to 10 ppm.

See Section 4.23.3.1.

Cross-media effects

Low temperature oxidation (LoTO_x) should be necessarily associated with a new or existing scrubbing unit, which generates waste water to be treated properly. An increase in nitrate load to the existing WWTP might have to be considered, together with the associated cost to control nitrates. Nitric acid is produced and needs to be neutralised with an alkali used in the scrubbing section.

In order to oxidise the NO_x to soluble higher oxides, ozone is required and should be generated on site using an ozone generator, which consumes oxygen and electrical energy.

Operational data

NO_x removal performance is directly linked to the ozone injection rate. It can be regulated on a real-time basis in relation to the NO_x outlet concentration target. The outlet NO_x can be adjusted by varying the set point on the system controller. Reported values show that the control level was set up in order to respect the permit conditions of 20 ppm.

Applicability

The LoTO_x process operates optimally above 150 °C and does not require heat input to maintain operational efficiency, enabling maximum heat recovery from the flue-gas. Applicable to both new and retrofitted applications.

In the case of retrofitting, a separate tower may have to be built in order to provide the required additional ozone injection and reaction stage. Ozone slip out of the stack will be associated with this technology. Appropriate design for additional processes related to ozone generation and personnel safety have to be taken into account.

The applicability may be limited by the need for additional waste water treatment. It should also be taken into consideration that an appropriate supply of liquid oxygen for ozone generation is needed. The applicability of the technique may also require significant space availability.

Economics

No data available.

Driving force for implementation

Demands for very low-NO_x emissions in the case of installations either already equipped with a wet scrubbing system or aimed at being treated with such.

Example plants

There have been examples of applications since 1997 in the US for two small gas-fired boilers (California) and one coal fired 25 MW power plant (Ohio).

Reference literature

[18, Confuorto 2007].

4.10.4.9 Catalytic reduction of CO and NO_x**Description**

The technology uses a single platinum-based catalyst coated with potassium carbonate (K₂CO₃) that operates in two cycles: oxidation/absorption and regeneration. The catalyst works by simultaneously oxidising CO to CO₂, NO to NO₂, and then absorbing NO₂ onto its surface through the use of a potassium-carbonate absorber coating. The regeneration of the catalyst is accomplished by passing a controlled mixture of regeneration gases across the surface of the catalyst in the absence of oxygen. The regeneration gases are steam, hydrogen and carbon dioxide. Consequently the nitrates are reduced to nitrogen. An additional catalyst layer is required to reduce SO₂ emissions and preserve the CO- and NO_x-reducing catalyst when sulphur is present in the fuel.

Because the regeneration cycle should take place in an oxygen-free environment, a section of catalyst undergoing regeneration must be isolated from exhaust gases. This is accomplished using a set of louvers, one upstream of the section being regenerated and one downstream. During the regeneration cycle, these louvers close and a valve opens, allowing regeneration gas into the section.

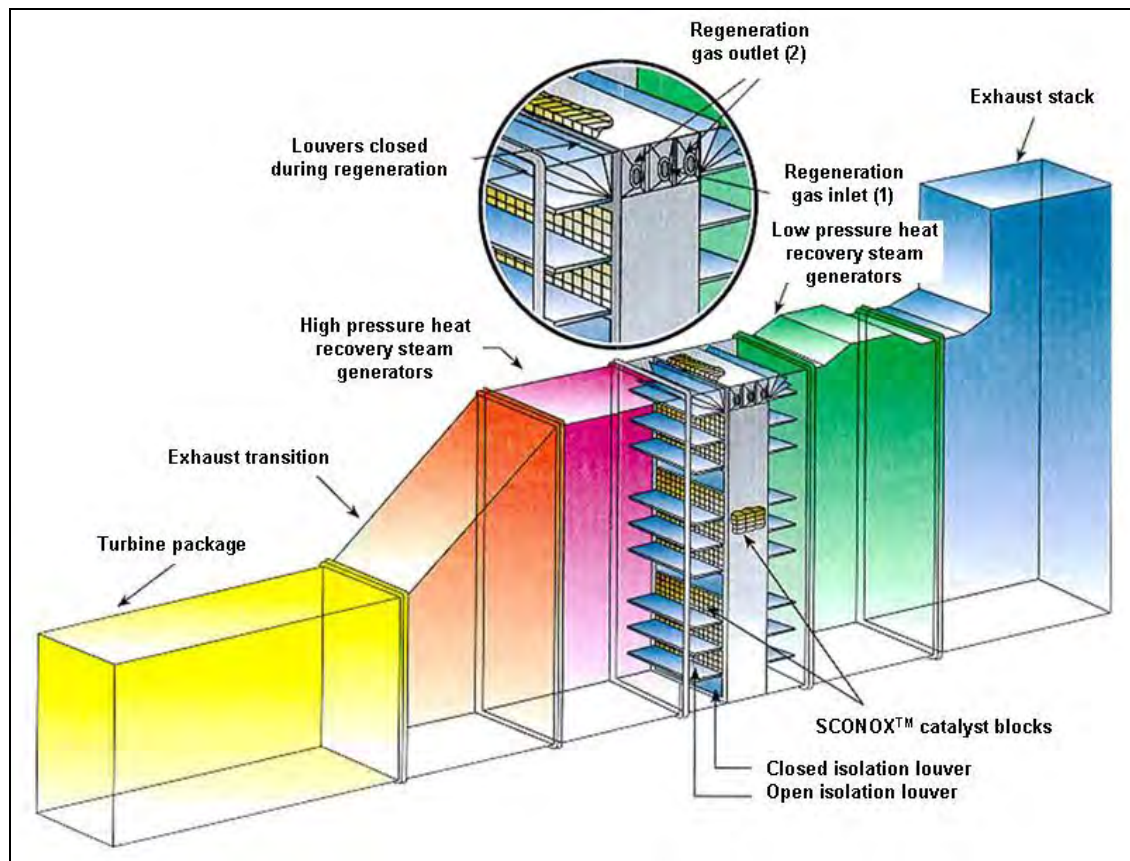


Figure 4.39: Schematic presentation of the catalyst system

Achieved environmental benefits

By using this technique, combined cycle gas turbines can be operated with very low- NO_x emissions levels. At the same time, the system reduces emissions of CO and non-methane volatile organic compounds. It uses no ammonia. In conjunction with a sulphur-removal catalyst technique this system can also be used for reducing sulphur compounds from exhaust gas if required. Achievable levels are the following:

- NO_x emissions below 2 ppm (4 mg/Nm³ as NO_2 at standard conditions 0 °C; 1 013 mbar);
- conversion rate of CO into CO_2 is 90 %;
- destruction of non-methane volatile organic compounds (NMVOC) greater than 90 % at 315 °C;
- destruction of formaldehyde and acetaldehyde, measured at 97 % and 94 % respectively at 150 °C.

Cross-media effects

The catalyst is very susceptible to fouling by sulphur in the flue-gas and may need an additional specific sulphur absorption catalyst. The system emits CO_2 , H_2O , N_2 and trace levels of SO_2 to the stack. Due to the masking and poisoning of the catalyst, annual or every 6 months catalyst cleaning is required with de-ionised water and a potassium-carbonate solution (K_2CO_3). The spent cleaning fluids can be neutralised and disposed of through the sewerage system and

are harmless to the water and soil. Precious metals on the spent catalyst have a residual value and can be reclaimed. There is no waste disposal issue caused by spent catalyst.

Operational data

This system requires electricity for control systems, valves and actuators, natural gas for regeneration gas production and steam both for regeneration gas production and as a dilution carrier. The typical pressure drop is between 8.5 mbar and 15 mbar. The system can operate effectively at temperatures ranging from 150 °C to 370 °C. The utility requirements for a 25 MW gas turbine are steam (333 to 389 °C): 1590 kg/h and natural gas: 14 kg/h.

The US EPA has stated its concerns (19 November 1999 letter) over the technical uncertainties of such a technique, especially about applying it to large combined cycle turbines.

Applicability

Applicable to both new and retrofitted applications, the system can operate effectively at temperatures ranging from 150 °C to 370 °C and does not limit gas turbine performance. Such a unit can be installed at the back of the boiler or in the heat recovery steam generator within the same envelope reserved for a conventional SCR system.

Economics

The estimated cost presented refers to a typical 400 MW size combined-cycle gas-fired power plant. The cost estimate numbers below are based on 8000 h/yr of operation and a NO_x reduction from 25 ppm to 5 ppm (50 to 10 mg/Nm³ as NO₂ at standard conditions 0 °C; 1013 mbar), which equals approximately 666 tonnes annually of NO_x removed. Included in the numbers are investment costs, operational and maintenance costs and indirect annual costs.

Cost	EUR million	Including
Investment	19.2	Delivery, erection and commissioning/start-up
Operation and maintenance	1.6	General maintenance; Steam and natural gas consumption in the regeneration cycle; Pressure drop across the unit (approx. 10 mbars) (converted to power consumption); Average cost/yr for catalyst replacement (7 year catalyst life for leading row); Catalyst disposal/refund.
NB: Additional indirect annual costs to the contractor are not included.		

A reduction of NO_x from 25 ppm to 2 ppm (50 to 4 mg/Nm³ as NO₂ at standard conditions 0 °C; 1 013 mbar) will contribute to an increase in the investment due to the need for additional catalyst. It will also somewhat increase the operation and maintenance costs due to the increased consumption of natural gas and steam and increased pressure drop.

A second example gives an installation cost of EUR 6.2 million for the application of this technique to a gas turbine of 25 MW. The operating costs are estimated to be approximately EUR 0.42 million/yr, including maintenance, steam and natural gas, pressure drop through the system, and the cost of catalyst replacement.

Driving force for implementation

Demands for very low NO_x emissions and limitations of air pollution control equipment utilising ammonia, especially for plants situated in densely populated areas.

Example plants

There are example applications in the US in small gas power plants. For example, a combustion turbine of 32 MW is operating at the Federal Cold Storage Cogeneration facility in California.

Reference literature

[211, Power 2000], [207, TWG 2001] [91, JEA 2008].

4.10.5 Particulate abatement techniques

Particulate loads (containing metals) from refinery combustion plants are normally fairly low, unless heavy residues are burnt. These particulates may be abated using a number of methods, including electrostatic precipitators (ESP), bag filters and wet scrubbing, as described in Section 4.23.4.

4.10.5.1 Switching to low-ash content fuels

Description

Refinery fuel gas and hydrotreated liquid refinery fuels contain lower particulate loads than heavy liquid refinery fuels. Switching to these fuels has a positive impact on the reduction of particulates emissions. The achieved emission particulate levels, as well as cross-media effects, operational data, applicability and economics have already been described in Section 4.10.2. and 4.10.3.1).

4.10.5.2 Steam atomisation for liquid fuel

Description

Steam injection while burning the liquid refinery fuel leads to atomisation and to lowering the particulate concentration.

Achieved environmental benefits

In the flue-gas of the firing liquid refinery fuel of older furnaces, the PM content may range from 500 – 1 000 mg/Nm³. For new optimal burner designs with steam atomisation, this can be in the range of 20 – 250 mg/Nm³ (see Section 4.10.3.1). For boilers, all these figures are, on average, lower. The range of 150 - 500 mg/Nm³ represents the current typical range with liquid fuels employed (ash contents) and burners installed (Low-NO_x with steam atomisation).

Cross-media effects

Improved fuel oil atomisation reduces the droplet size and leads to an increase in the intensity of combustion. This results in higher flame temperatures and can lead to increased NO_x emissions.

Applicability

Steam injection in fired furnaces/boilers is widely practised with liquid fuel.

Driving force for implementation

Reduction of particulate emissions.

Reference literature

[168, VROM 1999].

4.10.5.3 Electrostatic precipitator (ESP)

Description

For more information, see Section 4.23.4.2.

Achieved environmental benefits

ESPs can achieve particulates matter (PM) emissions of <10 – 50 mg/Nm³ with up to 95 % reduction. Soot blowing is an operation that is carried out at regular intervals to remove soot that has accumulated on the furnace equipment and which has hampered proper functioning. During this operation, the PM content of the exhaust gas can reach values of 2 000 mg/Nm³. ESPs and similar dust removal techniques installed for normal operations are effective in

reducing the PM emissions to the accepted level. Thus, ESPs working on process furnaces normally yield higher average concentrations due to soot blowing.

Cross-media effects

Electricity consumption, dust disposal and, in some cases, ammonia emissions. For more information see Section 4.23.4

Operational data

More information in Section 4.23.4

Applicability

ESPs are widely applied in FCC units, in thermal power plants and in incinerators. ESPs may not be applicable for some particulates with high electric resistance. They can be installed both in new and existing plants. They require space for their application.

Economics

Typical installed capital costs for ESPs are from EUR 1 million to 3.8 million.

Driving force for implementation

Reduce emissions of particulates and metals or other hazardous substances contained on them.

Examples

Wet ESPs are the most common type used for the abatement of particulates in heavy fuel oil combustion processes. In refineries, ESPs are both used on FCC units and on heavy oil and residue cracker units. They can be used to treat emissions from heavy liquid or solid fuel combustion.

Reference literature

[191, UBA Austria 1998], [151, Sema,Sofres 1991].

4.10.6 Sulphur oxides abatement techniques

The release of sulphur dioxide is directly linked to the sulphur content of the refinery fuel gas and fuel oils used. Techniques to reduce sulphur oxide emissions are fuel optimisation, fuel desulphurisation (hydrotreatments described in Section 4.10.2.3) or flue-gas desulphurisation. The lower the sulphur content of the fuel, the lower the emission of sulphur dioxide. In this section, techniques for the capture of SO₂ from the flue-gas after combustion or flue-gas desulphurisation techniques and the use of additives are included. More general information on these techniques is given in Section 4.23.5.4.

4.10.6.1 Additives to fuels

Description

- Technique 1: Use of lime or limestone as an additive to fuels to capture the sulphur oxides.
- Technique 2: Use of magnesium-based additives for the inhibition of the SO₂ to SO₃ oxidation. Magnesium combines with the vanadium pentoxide generated during the heavy liquid fuels combustion.

Achieved environmental benefits

- Technique 1: This technique abates the SO₂ release by about 90 %. 100 % limestone in excess of the stoichiometric quantity is required.
- Technique 2: The purpose of this technique is not to reduce SO_x emissions, but to reduce the amount of SO₃ in the plume for mitigating its visibility.

Cross-media effects

- Technique 1: A limestone/gypsum mixture has to be disposed of.
- Technique 2: No noticeable effects to be mentioned.

Operational data

Technique 2: The injection rate used has been around one litre for every 5.6 tonne of liquid fuel burnt.

Applicability

- Technique 1: For conventional refinery boiler and furnaces, the injection of lime or limestone into the furnace for sulphur capture cannot be applied. If the heaters and boilers are fluidised-bed or circulating fluid boilers to burn petroleum coke or heavy bitumens resulting from solvent deasphalting, then lime/limestone injected into the furnace as abatement would be practical.
- Technique 2: This technique was applied as a trial (2008) in a European refinery to reduce the visible plume from two out of the six boilers. In 2010, the technique was out of service, as the site was not able to quantitatively prove the improvements achieved.

Driving force for implementation

Reduced sulphur oxide emissions.

Reference literature

[151, Sema,Sofres 1991], [Questionnaire No 45].

4.10.6.2 Flue-gas desulphurisation processes

Description

The techniques that may be considered for application to the flue-gas desulphurisation are e.g.: Wet limestone scrubber, the Walther process, the Wellman-Lord process, the SD-process, the AI process, the SNO_x process and seawater scrubbing. Detailed information about these processes can be found in Section 4.23.5.4.

Economics

Recent costs data for the use of a wet gas scrubber compared to fuel substitution (natural gas replacing refinery fuel oil) are presented in the following Table 4.60 (data from [139, CONCAWE 6/11 2011]).

Table 4.60: Cost data for combustion units SO₂ abatement techniques: comparison between wet gas scrubber and substitution of refinery fuel oil (RFO) by natural gas

SO₂ Abatement on Combustion Units (NG to RFO Spread at net 75€tFOE)															
Baseline		Substitution of Refinery Fuel Oil with Natural Gas							Installation of Wet Gas Scrubber						
Heat Fired	MW	% Total MW	% \$ in Oil	Stack SO ₂ mg/Nm ³	Stack SO ₂ mg/Nm ³	SO ₂ Removed (From Base) t/y	Total Erected Cost (From Base) M€	Annualised Cost: Base to NG k€/y	Cost Effectiveness: Base to NG €/tSO ₂	Stack SO ₂ mg/Nm ³	SO ₂ Removed (From Base) t/y	Total Erected Cost (From Base) M€	Annualised Cost: Base to WGS k€/y	Cost Effectiveness: Base to WGS €/tSO ₂	Variable OP (50MW)
															Efficiency %
Net Cost of Natural Gas (Cost-Value of Displaced RFO €tFOE)									75	%	%	%TEC/y	k€/y		
(Includes annualised cost of project to supply NG to Refinery)										90%	7.4%	4%	433		
Unit 1	289	72%	1.8%	2 616	484	5 180	N/A	12 091	2 334	262	5 721	34.4	6 422	1 123	
Unit 2	179	75%	1.7%	2 282	165	3 194	N/A	7 812	2 446	228	3 098	25.8	4 497	1 452	
Unit 3	123	31%	3.9%	2 222	163	2 133	N/A	2 251	1 056	222	2 072	20.6	3 416	1 649	
Unit 4	254	30%	0.9%	569	118	964	N/A	4 473	4 642	57	1 095	31.8	5 832	5 326	
Unit 5	76	45%	0.9%	777	102	429	N/A	1 991	4 642	78	444	15.4	2 408	5 418	
Unit 6	51	77%	0.4%	531	10	224	N/A	2 284	10 212	53	205	12.2	1 828	8 901	
Unit 7	158	21%	0.5%	191	16	232	N/A	1 938	8 337	19	228	24.0	4 103	17 961	
Unit 8	89	10%	1.1%	209	21	141	N/A	522	3 714	21	141	17.0	2 705	19 179	
SO₂ Abatement on Combustion Units (NG to RFO Spread at net 100€tFOE)															
Net Cost of Natural Gas (Cost-Value of Displaced RFO €tFOE)									100	%	%	%TEC/y	k€/y		
(Includes annualised cost of project to supply NG to Refinery)										90%	0	4%	433		
Unit 1	289	72%	1.8%	2 616	484	5 180	N/A	16 121	3 112	262	5 721	34.4	6 422	1 123	
Unit 2	179	75%	1.7%	2 282	165	3 194	N/A	10 416	3 261	228	3 098	25.8	4 497	1 452	
Unit 3	123	31%	3.9%	2 222	163	2 133	N/A	3 002	1 407	222	2 072	20.6	3 416	1 649	
Unit 4	254	30%	0.9%	569	118	964	N/A	5 964	6 189	57	1 095	31.8	5 832	5 326	
Unit 5	76	45%	0.9%	777	102	429	N/A	2 654	6 189	78	444	15.4	2 408	5 418	
Unit 6	51	77%	0.4%	531	10	224	N/A	3 045	13 617	53	205	12.2	1 828	8 901	
Unit 7	158	21%	0.5%	191	16	232	N/A	2 584	11 116	19	228	24.0	4 103	17 961	
Unit 8	89	10%	1.1%	209	21	141	N/A	696	4 951	21	141	17.0	2 705	19 179	
SO₂ Abatement on Combustion Units (NG to RFO Spread at net 150€tFOE)															
Net Cost of Natural Gas (Cost-Value of Displaced RFO €tFOE)									150	%	%	%TEC/y	k€/y		
(Includes annualised cost of project to supply NG to Refinery)										90%	0	4%	433		
Unit 1	289	72%	1.8%	2 616	484	5 180	N/A	24 181	4 669	262	5 721	34.4	6 422	1 123	
Unit 2	179	75%	1.7%	2 282	165	3 194	N/A	15 624	4 892	228	3 098	25.8	4 497	1 452	
Unit 3	123	31%	3.9%	2 222	163	2 133	N/A	4 503	2 111	222	2 072	20.6	3 416	1 649	
Unit 4	254	30%	0.9%	569	118	964	N/A	8 946	9 284	57	1 095	31.8	5 832	5 326	
Unit 5	76	45%	0.9%	777	102	429	N/A	3 981	9 284	78	444	15.4	2 408	5 418	
Unit 6	51	77%	0.4%	531	10	224	N/A	4 568	20 425	53	205	12.2	1 828	8 901	
Unit 7	158	21%	0.5%	191	16	232	N/A	3 875	16 673	19	228	24.0	4 103	17 961	
Unit 8	89	10%	1.1%	209	21	141	N/A	1 044	7 427	21	141	17.0	2 705	19 179	

Source: [CONCAWE 6/11]

4.10.7 Combustion units abatement techniques performance and emissions variability

Table 4.61 shows the achieved emissions values expressed as minimum and maximum monthly concentration (at 3 % O₂ level) observed from continuous monitoring for a number of refinery combustion units in Europe for SO₂, NO_x and dust and the determining conditions of run or the currently applied techniques at these units.

The data summarised in Table 4.61 are based on daily values from time-series for periods from one to up to four years, generally including 2011. [145, TWG CONCAWE 2012]

From these data and the conditions of run and techniques in use, the main factors influencing the emissions to air of the combustion units are the following:

- For SO₂ emissions, the main driver is the fuel sulphur content: the sulphur (S) going into the combustion units is the result of the combination of:
 - the sulphur content in oil (the fuel oil sulphur content can vary over time);
 - the sulphur content in gas;
 - the ratio of oil to gas.
- For NO_x emissions, several factors need to be considered:

- the burner and furnace conditions (e.g. burner design, furnace rating, air preheat);
 - the firing duty (firing rate/design rate);
 - the fuel composition (e.g H₂ content, heating value);
 - the fuel nitrogen (N) content for oil firing;
 - the abatement technique in place.
- Dust emissions are mainly affected by:
 - the type of fuel;
 - the burner and furnace conditions;
 - the firing duty.

In addition, a survey carried out in 2012 on a number of multi-firing combustion units (of more than 50 MW) currently operating at refineries in Italy, confirms that the day-to-day variability of SO₂ and NO_x emissions is directly linked to the percentage of use of fuel oil to refinery fuel gas due to the adjustment of the refinery to the energy balance needs and to the sulphur content of the fuel oil.

According to this survey, the variability of the ratio of use of fuel oil/fuel gas changes from site to site and from plant to plant, consequently leading to a broad daily variability of the emissions to air of SO₂ and NO_x. [278, TWG-IT 2012]

Table 4.61: Emission data from a sample of combustion units at some European refineries

Site and unit	Shared Stack	Rating, MW	Fuel	H ₂ content of RFG %v	Technique	NO _x		SO ₂		Dust		Comments
						Min monthly	Max monthly	Min monthly	Max monthly	Min monthly	Max monthly	
Site J Furnace B	yes	130	Gas	0 - 90	Air staged LNB	200	250					Variable fuel properties and firing duty. The furnace is connected to a common stack but has a separate analyser for NO _x . Variable operating conditions affect the NO _x concentration: <u>large variations</u> in duty firing (50 %-100 %) and in overall fuel gas composition: H ₂ content (0 %-90 % H ₂).
Site J Furnace A		160	Gas	5 - 26	LNB	80	90					
Site J Furnace E		66	Gas	12 - 47	LNB	200	300					NO _x changes with air-preheat temperature and load and with fuel hydrogen content. Fuel Hydrogen changes not available
Site J Furnace F		66	Gas	12 - 47	LNB	180	300					Idem previous comment - J Furnace E
Site J Furnace G		55	Gas	12 - 47	LNB	140	300					Idem previous comment - J Furnace E
Site J Furnace H		66	Gas	12 - 47	LNB	70	250					Idem previous comment - J Furnace E
Site J Furnace I		66	Gas	12 - 47	LNB	120	180					Idem previous comment - J Furnace E
Site J Furnace J		66	Gas	12 - 47	LNB	60	230					Idem previous comment - J Furnace E
Site J Furnace K		55	Gas	12 - 47	LNB	80	130					Idem previous comment - J Furnace E
Site J Furnace P		37	Gas	30-60	LNB	70	140					Idem previous comment - J Furnace E
Site J Furnace Q		40	Gas	30-60	LNB	140	180					Idem previous comment - J Furnace E
Site J Furnace R		40	Gas	30-60	LNB	60	130					Idem previous comment - J Furnace E
Site G	several		Gas		LNB, Conventional	200	250					Common stack shared by several furnaces. Refinery fuel gas being fired.
Site B Stack 1	8 furnaces	296	Gas	20 - 45	LNB and/or ULNB	80	100					The averaging effect of combining flue-gas from 8 furnaces may account for the low variability in the NO _x concentration.

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Site and unit	Shared Stack	Rating, MW	Fuel	H ₂ content of RFG %v	Technique	NO _x		SO ₂		Dust		Comments
						Min monthly	Max monthly	Min monthly	Max monthly	Min monthly	Max monthly	
Site B Stack 3	5 furnaces	86	Gas	22.5 - 50.5	LNB and/or ULNB	180	220					No information on the actual variation over the period. Suspect that fuel is reason for higher emissions in first half (averaging in stack would compensate individual furnace condition changes).
Site B Stack 2	5 furnaces	90.2	Gas	22.5 - 50.5	LNB and/or ULNB	230	290					
Site B Stack 4	3 furnaces	112	Gas	22.5 - 50.5	LNB and/or ULNB	160	210					Shared stack. 3 furnaces (20.8, 25.7 and 66 MW). Lower NO _x concentration found when the largest furnace is at low load.
Site B Stack 5	3 furnaces	110	Gas	22.5 - 50.5	LNB and/or ULNB	120	155					
Site B Stack 6	1	6	Gas	22.5 - 50.5	LNB and/or ULNB	90	175					
Site B Stack 7	1	21.5	Gas	22.5 - 50.5	LNB and/or ULNB	180	300					
Site B Stack 8	1	10	Gas		LNB and/or ULNB	135	230					
Site B Stack 9		24	Gas	22.5 - 50.5	LNB and/or ULNB	180	335					
Site B Stack 10		18	Gas	22.5 - 50.5	LNB and/or ULNB	170	220					
Site B Stack 11	1	16	Gas		LNB and/or ULNB	230	305					
Site B Stack 12	1	29	Gas		LNB and/or ULNB	100	125					
Site B Stack 13	1	106	Gas		LNB and/or ULNB	190	235					Oscillations at the beginning of the year unexplained by load, operating conditions or fuel quality.
Site V Unit 4			Gas		LNB	40	70					No information on load or operating conditions is available
Site V Unit 5			Gas		LNB	50	90					No information on load or operating conditions. Load is expected to be variable and includes an out-of-service interval.
Site V Unit 6			Gas		LNB	105	145					Unit operating on low load.

Site and unit	Shared Stack	Rating, MW	Fuel	H ₂ content of RFG %v	Technique	NO _x		SO ₂		Dust		Comments
						Min monthly	Max monthly	Min monthly	Max monthly	Min monthly	Max monthly	
Site W Plant 5			Gas		LNB	120	200					Operating through the overall combustion plant shutdown so possibly supplying steam requirement
Site W Plant 6			Gas		LNB	135	200					
Site W Plant 7			Gas		LNB	130	160					
Site N		164	RFO+VRO			420	510					NO _x trends follow changes in amount if oil firing. VRO is vacuum residue oil
Site G	4		VGO+RFG		Standard burners	250	370	120	650			VGO is vacuum gas oil
Site AZ	3	185	1-3 %S oil, 0.015 %S gas					400	1 500			Monitoring: Calculated from Fuel S content
Site AY CDU furnace	1	254	oil 0.75-3 % gas 0.03 %					750	1 700			Monitoring: Calculated from Fuel S content
Site AY Boiler 7			oil 0.75-3 % gas 0.03 %					< 100	1 500			Monitoring: Calculation associated with measure of sulphur content of the fuel or CEM both systems
Site AY Boiler 5		49	oil 0.75-3 % gas 0.03 %					<100	1 550			Monitoring: Calculation associated with measure of sulphur content of the fuel or CEM both systems
Site AZ		200	oil 0.75-1 % gas 0.05 %					600	1 000			Monitoring: Calculation associated with measure of sulphur content of the fuels
Site N		164	25-50 % oil firing VRO+RFG					900	1 250			Fuel oil S content and amount of fuel oil fired determine the SO ₂ emission,
Site U Unit 1		100	83 % oil fired, 1.9 %S, 0.3 %N			250	480	1 500	2 800	25	70	<u>Suspect data error in June</u> as SO ₂ is high and NO _x is low at the same time. Dust concentrations are lower and less variable in second half of year. SO ₂ and NO _x are also lower: could reflect a difference in fuel mix or recalibration of opacity meter.
Site U Unit 2		164	Oil between 13-35 %			180	315	750	1 300	10	55	August SO ₂ looks affected by zero data. Three periods of different oil/gas ratio are

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Site and unit	Shared Stack	Rating, MW	Fuel	H ₂ content of RFG %v	Technique	NO _x		SO ₂		Dust		Comments
						Min monthly	Max monthly	Min monthly	Max monthly	Min monthly	Max monthly	
			over period									reflected in the SO ₂ , NO _x and Dust concentration time-series
Site U Unit 3		280	61 %FO 1.9 %S 03 %N			350	550	1 600	2 300	35	65	Time series suggest changing fuel mix
Site V Unit 1		34	19 % Oil, RFO: 1.77 % w S			47	325	177	1 210	25	48	Corrected data (original monthly averages included missing data as zero concentration)
Site V Unit 2		321	typical 14 % fuel oil - 86 % gas, RFO: 1.77 % w S			72	265	55	415	1	13	Unit switched to gas part way through year. Corrected data (original monthly averages included missing data as zero concentration). Reported PM and SO ₂ values are very low after switch to gas firing possibly this reflects problems in the analyser or calibration for high amounts of oil firing.
Site V Unit 3		337	25 % RFO- 75 % RFG, RFO: 1.77 % w S			150	360	450	1 100	2	45	Time series suggest a switch to higher (or complete) switch to RFG firing after April (cf V unit 2).
Site W Unit 1			60 % RFO		LNB	380	490	-	-	-	-	
Site W Unit 2			33 % RFO			280	360	-	-	-	-	
Site W Unit 3			40 % RFO			320	400	400	1 100	19	44	SO ₂ time series added and monthly averages checked for influence of missing/zero values.

Source: [145, TWG CONCAWE 2012]

4.11 Etherification

4.11.1 Catalytic distillation

Description

The catalytic distillation process combines reaction and fractionation into a single unit operation. It requires a two-reactor design, where one is a boiling-point fixed-bed reactor, followed by final conversion in a catalytic distillation column. Reactors use an acidic ion exchange resin catalyst. For more information see Section 2.11.

Achieved environmental benefits

The increased conversion process efficiency decreases the energy consumption within the system per tonne of product manufactured.

Cross-media effects

This technique requires an additional reactor. Catalyst handling in elevated places during installation and catalysts change may cause safety risks.

Operational data

The advantages of the process where the reaction catalyst is within the distillation column include essentially complete isoolefin conversions. Etherification can be applied for MTBE, ETBE or TAME production. Conversions of 98 % of isobutylene are typical for refinery feedstocks. Conversion is slightly less for ETBE than for MTBE. For TAME, isoamylene conversions of >95 % are achievable.

Typical utility requirements, per m ³ of product	Range depending on the technology licensor	Units
Electricity	1.3 – 3.1	kWh
Steam (10.3 barg)	600 – 1 150	kg
Steam (3.4 barg)	100 – 1 150	kg
Water cooling ($\Delta T=17$ °C)	1.5 – 4	m ³

Economics

Investment costs: EUR 18 850 per m³/d of MTBE product.

(Costs calculation based on 1999 rate EUR = 1.1680 USD, for a 1 500 bpsd capacity unit and a cost of 3 500 USD per bpsd of MTBE)

Example plants

This technique is widely applied.

Reference literature

[183, HP 1998], [76, Hydrocarbon processing 2011].

4.11.2 Prevention of upsets in the waste water biotreater

Description

Water effluents from MTBE and TAME production contain releases of methanol, formic acid and ethers. These compounds or their degradation products can be toxic for the fauna of the biotreater. Therefore, high concentrations of these components need to be prevented from entering the bioreactor. This can be easily controlled by the use of a storage tank or by the planning of production in order to dosify the right flow to the waste water treatment.

Achieved environmental benefits

The methanol, formic acid and ethers content of the waste water generated in the etherification processes need to be controlled to prevent upsets in the waste water biotreater.

Applicability

Fully applicable.

Economics

The implementation of this technique is not expensive.

Driving force for implementation

To avoid upsets of the biotreater.

Reference literature

[210, Shawcross 2000].

4.11.3 Prevention of leaking of water-soluble compounds

Description

Ethers produced in the etherification processes are highly soluble in water. If they leak, they may contaminate the soil, rainwater and groundwater. This may a part of a programme for prevention, detection and control of the soil and groundwater (see Section 4.25.1).

Achieved environmental benefits

Reduction of the risk of contamination of water by ethers and alcohols used in these processes.

Driving force for implementation

To avoid contamination of groundwater and surface water by ethers.

Reference literature

[247, FEI 2001].

4.12 Gas separation processes

The gas plant is a relatively simple process and the temperature levels are not high enough to create the opportunity for steam generation. No great efficiency improvements are to be expected within a gas plant, but heat integration with upstream plants will normally make use of e.g. reboiling heat available from upstream plant streams, saving direct heating capacity in the gas separation plant. More information on energy management is available in Section 4.15.1.2.

4.12.1 Fugitive emissions reduction

Description

Gas plants process light compounds and are consequently more likely to produce fugitive emissions. The use of dual mechanical seals on pumps, compressors and agitators can reduce VOC emissions. Use of low-leaking valves also can contribute to reducing VOC emissions. This topic is described as an integrated measure within Section 4.23.6.1 as fugitives emissions occur in all refinery processes, but it is mentioned here explicitly because the light compounds used lead to a relatively high level of fugitive emissions.

Achieved environmental benefits

Applying these techniques, fugitive emissions such as VOC, H₂S and other sulphur compounds can be reduced considerably.

Cross-media effects

See Section 4.23.6.1.

Operational data

See Section 4.23.6.1.

Applicability

See Section 4.23.6.1.

Economics

See Section 4.23.6.1.

Driving force for implementation

To reduce product loss.

Example plants

Programmes of minimisation of VOC emissions can be found in many European and non-European refineries.

Reference literature

See Section 4.23.6.1.

4.12.2 Prevention of emissions of LPG odorant

The storage and handling of odorants used in LPG production will be covered in the EFS BREF [5, EC 2006]. However, the dosing of odorant to the LPG product needs to be handled in a proper way to prevent emissions to the environment. This technique is included in Section 2.21.

4.13 Hydrogen-consuming processes

4.13.1 Hydrodesulphurisation processes

Description

See Section 2.13.

Achieved environmental benefits

The reduction of sulphur content of the different fractions. Modern techniques can reduce the sulphur content of distillates to less than 10 ppm. For example, the application of one-step hydration by means of a Co/Mo catalyst (30 - 40 bar) to middle distillates reduces the sulphur content by more than 90 % (down to some 100 ppm), depending on the product, the S-content of the feed, and the reaction conditions. If demand for diesel fuel increases, additional compounds (e.g. LCO from the FCC) have to be used in its production. However, these feedstocks contain a variety of aromatic compounds, which have to be hydrated under severe conditions (high temperature, high pressure, highly active catalysts, two-step processes).

Current diesel specifications can be met in conventional single-stage hydrotreating units by lowering liquid hourly space velocity (LHSV) from 3.7 in conventional units to 0.8 – 1.1, by implementing a reactor in series to the existing ones and applying the latest catalyst generation available for gas oil hydrotreating units. Processing a Russian export blend with 1.3 % w/w S and an intermediate sulphur content ahead of the final desulphurisation unit of 0.12 % S, a final sulphur content of 8 ppm S in the raffinate can be achieved during normal operation.

Cross-media effects

Energy consumption, waste generation, effluent water and air emissions.

Operational data

Gas oil hydrotreating units need the additional measure of a high-pressure amine washer in the hydrogen recycle stream to maintain hydrogen purity in the recycle stream with hydrocarbons from fresh feed. The unit will operate at 45 bar, utilising 40 Nm³ hydrogen/t of gas oil feed and anticipating a run length of 30 months.

Applicability

Applicable to distillates from naphtha to heavy residues.

Economics

The estimated installation costs for a reduced-crude desulphurisation process (based on 132 m³/h unit) is EUR 47 million. Another estimated investment summary for a residue desulphurisation system hydrotreater to prepare residue fluid catalytic cracking feed is shown below.

Feed rate, Mt/yr	3.8
Run length, days	335
Operating factor	0.92
On-plot investment, in million EUR	272
Total off-plot cost (30 % of on-plot), in million EUR	82
Catalyst cost per charge, million EUR	10
NB Basis: second quarter 1995 US gulf coast	

Driving force for implementation

To reduce the sulphur content of the feedstock to achieve EU specifications: the current value for sulphur is 10 mg/kg (10 ppm) according to Directive 2009/30/EC.

Example plants

Many desulphurisation processes exist in refineries.

Reference literature

[175, Meyers 1997].

4.13.2 Catalytic distillation**Description**

Catalytic distillation for desulphurisation of gasoline in a two-stage process.

Achieved environmental benefits

Reductions of more than 95 % of sulphur content in FCC gasoline containing 1 800 ppm of sulphur have been achieved. This type of technique consumes less energy than traditional desulphurisation processes.

Cross-media effects

Energy consumption, waste generation, effluent water and air emissions.

Applicability

Fully applicable. This technique may also be used for the reduction of benzene in the reformat.

Economics

A two-stage process is designed to treat 7 950 m³/d of FCC gasoline containing 1 800 ppm of sulphur. Its efficiency has been reported as 95 % and its investment costs are approximately EUR 20 million.

Driving force for implementation

To reduce the sulphur content of gasoline to reach EU specifications: the current value for sulphur is 10 mg/kg (or ppm) according to Directive 2009/30/EC.

Example plants

At least one catalytic distillation plant for desulphurisation of 7 950 m³/d of FCC gasoline is available in Europe. In 2010, in the Russian Federation, a 1.26 Mt/yr FCC unit was designed with a catalytic distillation patented process to meet Euro-5 emissions requirements.

Reference literature

[191, UBA Austria 1998].

4.13.3 On-stream catalyst replacement technology for processing high-metal feeds**Description**

While the main objective of this process is to extend catalyst life in a downstream fixed-bed reactor by maintaining high hydrodemetallisation performance, the catalyst also achieves high hydrodesulphurisation/hydrodemetallisation and hydrodesulphurisation Conradson carbon removal/hydrodemetallisation activity ratios.

Achieved environmental benefits

On-stream catalyst replacement technology improves the residual desulphurisation in the refinery, thereby decreasing the waste generation.

Operational data

The reactor typically operates at 390 °C and 138 bar (2 000 psia).

Applicability

Fully applicable.

Driving force for implementation

To extend the catalyst life of the hydrotreatment processes.

Example plants

Until 1997, there were 15 on-stream catalyst replacement techniques worldwide.

Reference literature

[175, Meyers 1997].

4.13.4 Hydrogenation of light dienes

Description

The hydrogenation of light dienes serves the purpose of producing a more stable refinery stream, reducing upstream gum formation. The process converts dienes into useful olefins. For more information see Section 2.13.

Achieved environmental benefits

The process helps reduce acid losses in downstream processes (e.g. alkylation). Typical product diene levels from the selective hydrogenation process unit may range from 25 to 1 ppm.

Cross-media effects

Low energy consumption.

Operational data

Low temperature, liquid-phase operation means that no utilities are required in most cases if the feed and hydrogen are both available at suitable conditions. Heating or cooling duties are limited to cases with relatively high diene concentrations in the feed. Commercial operation for a period of more than two years without the need to regenerate or replace the catalyst is typical.

Applicability

The design of the unit is simple. Most of the units are designed for diene reduction to less than 5 ppm in the product.

Economics

The design of the units is simple and requires low capital and nominal operating costs. The cost of the catalyst is low compared with the installation cost. The capital investment, including the catalyst for the unit is small, usually within the range of EUR 0.6 million – 1.2 million. The investment based on a recent project is some EUR 3 million for a plant of 100 000 t/yr capacity.

Driving force for implementation

To reduce gum formation in downstream operations. The flexibility and minimal cost of this technique make the unit a valuable processing tool.

Reference literature

[175, Meyers 1997], [204, Canales 2000].

4.14 Hydrogen production

For SO₂ emissions reduction, hydrogen gains increasing importance as a key reacting agent for the supply of hydrotreating units that are now crucial to the desulphurisation and upgrading of intermediate feedstocks and final products

Hydrogen production using a hydrocarbon-rich feedstock requires, as a first step, the conversion of the feedstock into a carbon oxides and hydrogen rich synthesis gas. The synthesis gas generation can be conducted by different techniques, such as steam reforming (see Section 4.14.1), gas heated reforming (GHR)(see Section 4.14.2) and partial oxidation (see 4.14.3).

An additional purification step is then needed (see Section 4.14.4). Figure 4.40 shows the H₂/CO ratio for various hydrogen production techniques available.

As mentioned in Section 2.14, the production of hydrogen is not exclusive to the refinery sector. Therefore the sector-specific information contained in this chapter can be completed as necessary by the information available in the other BREF documents, e.g. LVIC-AAF [92, EC 2007]

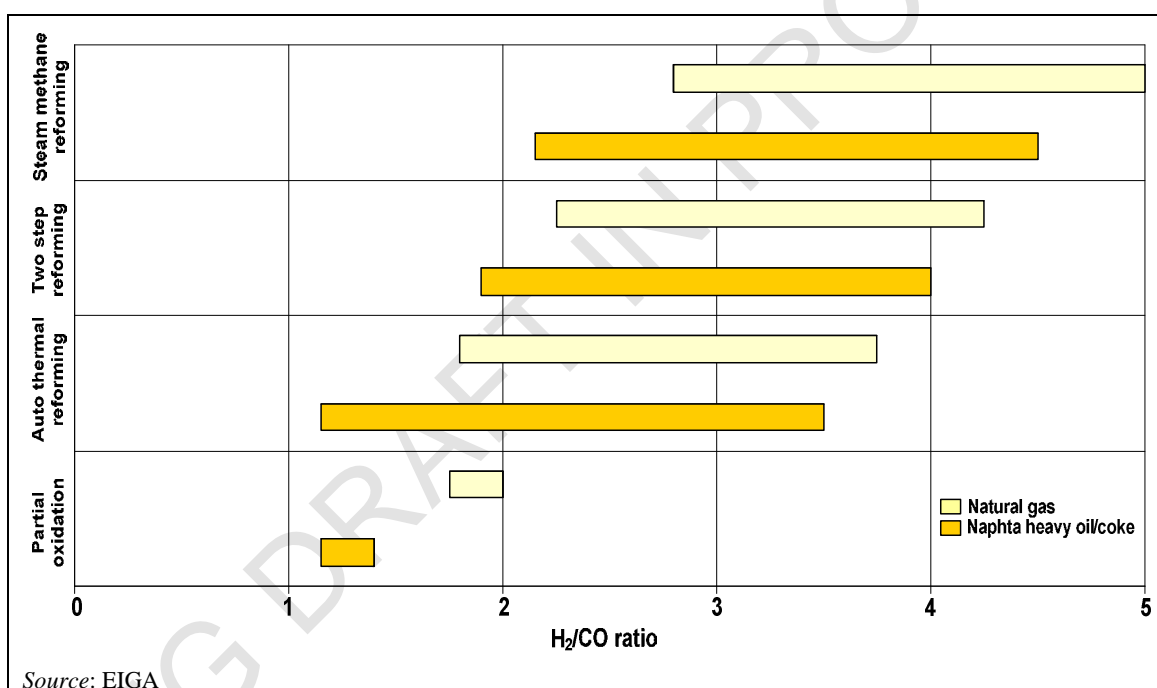


Figure 4.40: H₂/CO ratio for hydrogen production processes available in a refinery

4.14.1 Steam methane reforming

Description

A description of this most commonly used process is given in Section 2.14.

The steam reformer has to supply a large amount of heat at a high temperature for the steam reforming reaction by burning fuel, with the result that a large amount of heat is potentially lost in the flue-gas. As a result, many refineries recover heat as part of their heat integration. However, the values displayed in Figure 4.40 do not take into consideration, as a more general approach, the potential reduction of air emissions that can be achieved from co-production synergies. All of the processes in Figure 4.40 can be used within a refinery to export steam as a valuable product, thereby eliminating the need for dedicated steam production elsewhere and translating directly into energy and CO₂ emissions savings. Furthermore, if there are CO₂ customers there may be some demand such as agriculture, the food and beverage industry, or

other chemical facilities nearby, and there may be demand for carbon dioxide which can be productively used instead of being emitted as CO₂.

Achieved environmental benefits

- Either exclusively or primarily as a hydrogen production process, steam methane reforming is intrinsically advantageous from both a product yield and an energy consumption point of view (see Figure 4.40 showing product yield ranges, as hydrogen to carbon monoxide ratio, for different process). In addition, steam methane reforming reduces the potential for CO₂ emissions with its requirement for lighter feed stocks
- Steam methane reforming of natural gas typically has a small carbon footprint. When available, maximising the use of external methane imported to the refinery for hydrogen production instead of thermal power generation could be seen as a preferable option when hydrogen production needs to be increased.
- Steam methane reforming typically requires 10 – 15 % excess air with the minimum value being limited by safety considerations. This relatively small quantity is an intrinsic primary measure for the reduction of NO_x emissions.
- As it is a closed loop process, the obligation to thoroughly monitor the excess O₂ and/or CO content in the SMR flue-gas also provides the opportunity for the enhanced control and the reduction of CO and unburnt hydrocarbon emissions.
- The steam methane reforming process requires a very deep desulphurisation of the feed so as to prevent catalyst poisoning. As a result, the tail gas from the PSA is virtually free of sulphur. As it forms up to 90 % of the fuel, SO_x emissions are correspondingly reduced and will only depend on the sulphur content of the supplementary fuel.

Cross-media effects

The choice of heat recovery system can have a major effect on NO_x production, since both the amount of fuel fired and the flame temperature will be affected. Preheating combustion air will reduce firing, but since NO_x formation increases with flame temperature, there will be an overall increase of NO_x concentration, limiting the overall NO_x mass flow reduction. Other methods of reducing firing, such as pre-reforming or gas heated steam reforming (see Section 4.14.2) do not affect the flame temperature and will reduce the overall required firing duty without increasing the NO_x concentration, and therefore will reduce NO_x production. The production of CO₂ is also important. For every tonne of H₂ produced, some 10 tonnes of CO₂ are also produced including the amount related to steam production. Such value may vary widely depending upon the strategy for conducting the steam production. Other impacts, such as SO_x or water emissions, are minimal, because low-sulphur fuel is typically used.

Operational data

The combination of high temperature and pressure imposes severe demands on the steam reformer tubes, which must be fabricated from expensive alloys. The furnace box must be large to obtain the high rates of heat transfer from the flue-gas to the tubes. These combined factors make the steam reformer the largest and single most expensive piece of equipment in a hydrogen plant. The large size of the unit means that it takes a long time to heat up and cool down, and this makes it the most time-consuming part of the start-up and shutdown procedure.

Applicability

Fully applicable.

Economics

The operating expenses are dependent on the type of feed used and a typical specific energy consumption (feed + fuel – export steam) range is between 3 and 3.4 Gcal/1 000 Nm³ (12.5 to 14.2 kJ/Nm³)

Driving force for implementation

The need for additional sources of hydrogen is increasingly a crucial requirement for maximising the hydrotreatment capacity in the refinery and meeting SO_x challenges and the sulphur level enforced in the final product quality standards.

Example plants

There are many examples of steam methane reforming plants in operation associated with European oil refineries.

Reference literature

[163, FWE 1999], [56, EIGA 2009], [76, Hydrocarbon processing 2011].

4.14.2 Gas Heated Reforming (GHR)**Description**

The gas heated reforming (GHR) technique generally uses a compact unit heated by high temperature waste heat from the raw synthesis gas, often by means of a heat exchanger-type reactor downstream of the conventional synthesis gas generator. In other examples, the GHR can also be fully integrated into the synthesis gas generator.

The recovered heat is used in the GHR to drive the endothermic reforming reactions instead of solely using this heat for steam generation in a steam boiler. Consequently, a hydrogen production plant with a GHR unit produces less excess steam than a conventional synthesis gas production plant based on a steam reformer or partial oxidation reactor.

Achieved environmental benefits

Gas heated steam reforming reduces the energy consumption of the synthesis gas production process itself. It is especially appropriate for refineries where high pressure steam is not strictly needed for operating other production units.

Cross-media effects

When GHR is applied, little or even no steam is produced from the hydrogen plant. Depending on the specific configuration of the site energy system, the steam production in other units may need to be increased. The benefits from the application of GHR must then be balanced with the associated steam reduction demanded by the industrial steam network and/or the additional energy consumption and air emissions that would accompany the increase of steam production outside the hydrogen production plant.

Operational data

GHR recovers sensible heat from the process gas to drive the endothermic reforming reaction in an additional reactor. Many different possibilities to design a GHR exist, and many only use a small additional feed (i.e. 10 – 20 %) as a fraction of the total feed. The resulting economics can vary widely. One exemplary embodiment of the GHR application is essentially a special heat exchanger filled with highly active catalyst.

The severe operating conditions (high temperature) require very careful design. Because of the higher wall temperatures of the heat exchange surface compared to conventional steam boilers and the reducing gas atmosphere, severe and instantaneous corrosion of particularly high-alloyed materials by the metal dusting corrosion phenomena are highly likely. Besides the risk to operation by failure of the heat exchange equipment, the resulting metal and carbon particles accumulate in the process condensate and can have an impact on the plant operation. Therefore, specific HSE and reliability/availability requirements will have to be taken into account for application of the GHR technology.

The integration of the GHR technology into a synthesis gas plant requires special procedures for start-up, operation and shutdown and consequently requires operational effort to maintain the catalyst lifetime.

Applicability

Fully applicable. However, the application of GHR as a steam reduction process technology must be evaluated against other design options which may include using the excess steam for

power generation or mechanical power in rotating equipment. Gas heated steam reforming may represent an attractive alternative process technology if high pressure steam cannot be consumed by other units outside the synthesis gas generation unit.

Economics

Economics depend strongly on specific site configuration. Because of the severe conditions of gas heated steam reforming (high temperature, corrosive atmosphere), the typical embodiment as described above - a special heat exchanger filled with highly active catalyst - represents a significant capital expenditure.

Driving force for implementation

Hydrogen is increasingly needed for hydrotreatments performed in the refinery.

Example plants

GHR is a new alternative, already proven commercially for a few applications, e.g. in ammonia and methanol production. As far as refining is concerned, GHR is typically applied to debottleneck existing conventional SMR-based hydrogen plants.

Reference literature

[56, EIGA 2009].

4.14.3 Partial oxidation

Description

The IGCC plant can also function as a hydrogen supplier, in which case hydrogen is removed from the syngas (after the sulphur removal) where the feed reacts at high temperatures with oxygen. For more information see Sections 2.14, 2.10 and 4.10.3.4.

Achieved environmental benefits

Coke gasification

A fixed-bed desulphurisation system using regenerable zinc ferrite as the sorbent has been tested as a continuation of the gasification exhaust gas treatment. Sulphur levels of 10 - 20 ppm in the treated gas were achieved in this system. The product gas also contains traces of ammonia (less than 5 %) and hydrogen cyanide (HCN), derivatives of the nitrogen in the feed. Using limestone in the gasifier tends to reduce the level of these components. Ammonia is not removed by zinc ferrite in the external desulphurisation process. If there is any alkali in the feed, some of it may vaporise in the gasifier and may have to be removed by an alkali sorbent or by cooling the gas going to the filter. The particulates in product gas are removed in the barrier filter to a level of less than 5 ppm.

Heavy oil gasification

Another environmental benefit of gasification is that it reduces heavy oils which, when used in another way, may pollute the environment much more. See also Section 4.10.3.4.

Cross-media effects

Partial oxidation requires an oxygen plant (95 - 99 % purity), which increases costs.

Operational data

Normally, an IGCC plant includes a water purification section with the following units:

- soot recovery, either by washing with naphtha and recycling of the naphtha/soot mixture to the gasification section and/or by filtration;
- water pretreatment, to remove solids (carbon, metals, salts) by filtration before final treatment in biological plant e.g. a grey water treatment (GTW).

Grey water treatment (GWT) is designed to treat water blowdown from a carbon extraction unit with syngas condensate and possibly the amine regeneration overhead system; water from grey water treatment is finally sent to biological treatment. The GWT may employ physical and chemical treatment for cyanide destruction and the removal of heavy metals, followed by a sour water stripper, which removes sulphides, ammonia, and carbon dioxide from the water.

The gaseous streams are totally washed to remove any contaminant and the process normally includes the following ancillary units for gas purification:

- washing with water and sometimes oil to remove soot and particulate;
- reactor for COS or cyanides by hydrolysis;
- sour gas absorbing with amine or equivalent system and the production of elemental sulphur from H₂S in the Claus unit.

Applicability

Relative hydrogen production costs are primarily a function of feedstock cost. The main problem with investment in a gasification plant is its capital and operating cost. To be attractive commercially it usually needs to be undertaken on a large scale. Typical requirements for chemicals production are the generation of more than 200 MW_e of electrical power through IGCC or the use of hydrogen, carbon monoxide and steam on a large scale.

Economics

Generally accepted investment costs for an oil gasification-based combined cycle plant in the 200+ MW_e range are EUR 1 300 – 1 700 per kW installed, with a thermal efficiency of around 40 % and close to 99 % sulphur emission abatement. On average, electrical demand in a refinery is usually less than 80 MW_e, the investment in IGCC often depends on the opportunity to export the surplus of electrical power generated. However, high pressure steam can also be a valuable gasification product and there are examples of much smaller gasification units that fit in well with a refinery.

Relative hydrogen production costs of the process are primarily a function of feedstock cost. Steam reforming of methane usually produces hydrogen at lower costs than the partial oxidation of fuel oil.

Driving force for implementation

The production of hydrogen costs, the reduction in heavy oils produced, power export and the synthesis gas produced as feed for petrochemistry are the driving forces for the implementation of gas-heated steam reforming.

Example plants

At least five gasification processes are currently running in European refineries.

Reference literature

[175, Meyers 1997], [221, Italy 2000].

4.14.4 Purification of hydrogen

Description

Information about the processes of purification can be found in Section 2.14. Some techniques that may be applied to the hydrogen purification units to achieve better environmental performance are given below.

- Use of several adsorber beds periodically switching the gas flow from one vessel to another to allow regeneration of the adsorbent by pressure reduction and purging, thus releasing the adsorbed components. The desorbed gas is used as fuel at a convenient location.
- Use of PSA systems only for purification of hydrogen to reduce air emissions.
- Use of the PSA tail gas as refinery fuel gas in the reforming furnace instead of higher C/H ratio fuels.
- Use of membranes technique which can achieve purification ratios of 80 % v.

Achieved environmental benefits

Reuse of waste fuel gas as a fuel within the process.

Cross-media effects

Because of the loss of hydrogen to the PSA tail gas, the reformer and front end of a PSA plant are larger than in a wet scrubbing plant. However, a PSA plant uses less process steam and does not require heat for the reboiler. PSA is a high energy consumer due to the high vacuum/pressure systems that it uses.

Operational data

The PSA system is completely automatic and offers a higher purity product. The PSA unit is simpler to operate than a wet scrubbing system, since it has no rotating equipment or circulating solutions. The conventional process produces a hydrogen product of maximum 97 - 98 % v/v purity, while the pressure swing adsorption process produces a very pure hydrogen product between 99.9 % v/v and 99.999 % v/v. The residual constituents of the product gas are mainly methane and less than 10 ppm CO. Some data on the utility consumption of the PSA system are for example: 3 700 Nm³/h with a H₂ content of at least 85 % and a pressure between 37 and 47 bar. Product-stream: 2 400 Nm³/h purified H₂ with a concentration of at least 99.5 %, temperature: 45 °C, pressure: 35 bar; waste gas: 1 300 Nm³/h, P: 3 bar, T: 30°C, contains 60 % H₂, 1.4 % H₂S and 40 % C₁-C₆ compounds with higher boiling points.

Driving force for implementation

To purify the hydrogen. The choice between the PSA system and the scrubbing system depends on the product purity required, reliability and process economics. The extra investment for the PSA system for large plant capacities can normally be offset by the lower operating cost. Also a PSA system will yield a higher H₂ purity.

Example plants

Many examples exist as PSA is commonly used.

Reference literature

[175, Meyers 1997], [221, Italy 2000], [182, Ecker 1999].

4.15 Integrated refinery management

This section is structured in the same way as Chapter 2 and 3 and contains these integrated refinery management activities that are not included in other sections. The first techniques to consider are environmental management activities and other utility management techniques.

4.15.1 Environmental management tools

4.15.1.1 Environmental management system

Description

A formal system to demonstrate compliance with environmental objectives.

Technical description

The Directive defines ‘techniques’ (under the definition of ‘best available techniques’) as ‘both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned’.

In this respect, an environmental management system (EMS) is a technique allowing operators of installations to address environmental issues in a systematic and demonstrable way. EMSs are most effective and efficient where they form an inherent part of the overall management and operation of an installation.

An EMS focuses the attention of the operator on the environmental performance of the installation; in particular through the application of clear operating procedures for both normal and other than normal operating conditions, and by setting out the associated lines of responsibility.

All effective EMSs incorporate the concept of continuous improvement, meaning that environmental management is an ongoing process, not a project which eventually comes to an end. There are various process designs, but most EMSs are based on the plan-do-check-act cycle (which is widely used in other company management contexts). The cycle is an iterative dynamic model, where the completion of one cycle flows into the beginning of the next (see Figure 4.41).

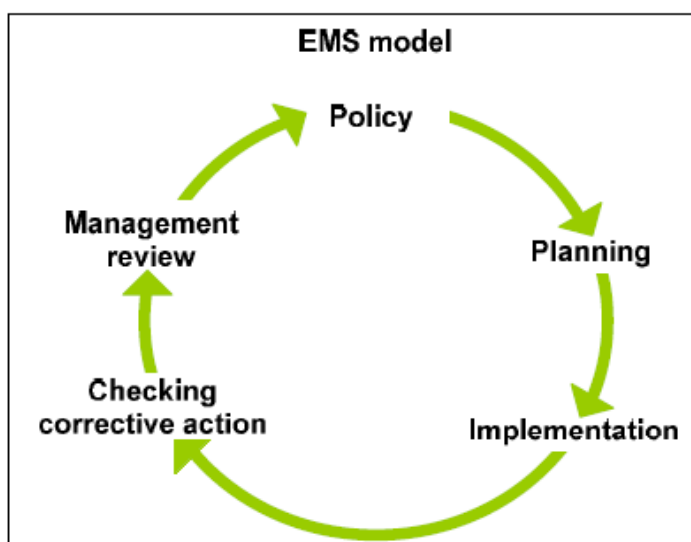


Figure 4.41: Continuous improvement in an EMS model

An EMS can contain the following components:

1. commitment of management, including senior management;
2. definition of an environmental policy that includes the continuous improvement of the installation by the management;
3. planning and establishing the necessary procedures, objectives and targets, in conjunction with financial planning and investment;
4. implementation of procedures paying particular attention to:
 - (a) structure and responsibility
 - (b) training, awareness and competence
 - (c) communication
 - (d) employee involvement
 - (e) documentation
 - (f) efficient process control
 - (g) maintenance programmes
 - (h) emergency preparedness and response
 - (i) safeguarding compliance with environmental legislation;
5. checking performance and taking corrective action paying particular attention to:
 - (a) monitoring and measurement - see also the document on the General Principles of Monitoring [46, EC 2003].
 - (b) corrective and preventive action
 - (c) maintenance of records
 - (d) independent (where practicable) internal and external auditing in order to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained;
6. review of the EMS and its continuing suitability, adequacy and effectiveness by senior management;
7. preparation of a regular environmental statement;
8. validation by a certification body or an external EMS verifier;
9. following the development of cleaner technologies;
10. consideration for the environmental impacts from the eventual decommissioning of the installation at the stage of designing a new plant, and throughout its operating life;
11. application of sectoral benchmarking on a regular basis.

Achieved environmental benefits

An EMS promotes and supports the continuous improvement of the environmental performance of the installation. If the installation already has a good overall environmental performance, an EMS helps the operator to maintain the high performance level.

Environmental performance and operational data

Cross-media effects

None reported. The systematic analysis of the initial environmental impacts and scope for improvements in the context of the EMS sets the basis for assessing the best solutions for all environmental media.

Technical considerations relevant to applicability

The components described above can typically be applied to all installations within the scope of this document. The scope (e.g. level of detail) and nature of the EMS (e.g. standardised or non-standardised) will be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

Economics

It is difficult to determine accurately the costs and economic benefits of introducing and maintaining a good EMS. There are also economic benefits that are the result of using an EMS and these vary widely from sector to sector.

External costs relating to verification of the system can be estimated from guidance issued by the International Accreditation Forum.

Driving forces for implementation

The driving forces for the implementation of an EMS include:

- improved environmental performance
- improved insight into the environmental aspects of the company which can be used to fulfil the environmental requirements of customers, regulatory authorities, banks, insurance companies or other stakeholders (e.g. people living or working in the vicinity of the installation)
- improved basis for decision-making
- improved motivation of personnel (e.g. managers can have confidence that environmental impacts are controlled and employees can feel that they are working for an environmentally responsible company)
- additional opportunities for operational cost reduction and product quality improvement
- improved company image
- reduced liability, insurance and non-compliance costs.

Example plants

EMSs are applied in a number of installations throughout the EU.

Reference literature

[96, Reg. 1221/2009], [93, DG Environment 2010], [95, ISO 2004], [94, ISO 2010]

4.15.1.2 Energy conservation techniques

A concerted and well-managed effort based on an integrated approach to reduce energy use, improve operations, maintain good housekeeping, and management and selective investments are the best practices worth highlighting here. There follows a list of techniques that are considered for the determination of BAT in the refinery sector. As can be seen, some of them are related to others in some way.

Description of the technique	Performance and remarks
To have a management focus on energy	To ensure that decisions are made on a process-integrated basis
To instigate an energy consumption reporting system	To measure progress and ensure that targets are met
To instigate an incentive scheme for energy savings	To promote identification of improvement areas
To carry out energy audits on a regular basis	To ensure activities are in conformance with instructions
To have a formal energy consumption reduction plan	To set targets and strategies for improvements
To carry out combustion improvement campaigns	To identify areas of improvement (e.g. air/fuel ratio, stack temperature, burner configuration, furnace design)
To participate in ranking/benchmarking activities in energy consumption	Verification by an independent body
To review the integration between and within units and systems	Heat integration between units in the refinery can be sub-optimal. 'Pinch' studies

Achieved environmental benefits

All measures to reduce energy consumption will result in a reduction of all emissions to air, including CO₂. Any energy conservation action has an impact on pollution due to the marginal fuel consumption.

Applicability

Especially applicable to these refineries with very high specific energy consumption (see Section 3.10.1).

Reference literature

[221, Italy 2000], [168, VROM 1999].

4.15.2 Production planning and control

Description

To ensure the full use of key abatement techniques (for both availability and capacity), some procedures can be defined for specific conditions where the operating parameters of a waste gas or waste treatment system may have a significant effect on the overall achieved removal efficiency (e.g. quantity of alkaline reagent, working temperature, waste gas flow, by-pass operations, etc.).

Special procedures can be defined for specific operating conditions, in particular :

- start-up or shutdown operations;
- other special operations which could affect the proper functioning of the system (e.g. regular and extraordinary maintenance work and cleaning operations of the furnace and/or of the waste gas treatment system, or severe production change);
- insufficient waste gas flow or temperature which prevents the use of the system at full capacity.

4.15.3 Safety management

Safety management in a refinery is mainly addressed through the requirements of Seveso II and Seveso III Directives (respectively 96/82/CE and 2012/18/EU).

4.15.4 Water management

4.15.4.1 Water stream integration (WSI)

Description

Similar to the identification of energy-saving opportunities, water pinch studies can be carried out to identify process water integration options and water reduction and reuse opportunities. In most refineries, some internal water streams are commonly used as desalter wash water, such as condensate water and steam-stripped sour water. There is scope for increased water reduction and reuse in refineries, which will lead to reduced size and costs of both water make-up and end-of-pipe treatment facilities.

Technical description

Purpose and principle

The purpose of water stream integration (WSI) is the reduction of process water produced for final treatment prior to discharge, in order to save operational costs. It saves high-quality potable and demineralised water, which can be expensive at some locations; it reduces the size, investment and running costs of the water supply and effluent treatment facilities. Moreover, it reduces the size and the environmental impact of effluent discharges.

The principle of WSI is to use, when possible, prevention, reduction, recycling and reuse of process water, rainwater, cooling water and sometimes contaminated groundwater with the aim of reducing the amount of process water for end-of-pipe treatment. WSI needs to be carried out as part of a water master plan for the refinery. This plan aims at the optimisation of the use and reuse of all water streams in the refinery.

The water used for the process in a refinery is of the magnitude of 0.1 to 0.6 m³ per tonne of feed. Some techniques to consider for the reduction of freshwater consumption, can be, but are not limited to, the following:

- reusing unstripped/stripped sour water as wash water
- use of rainwater as process water.

Concept description

The concept or methodology to design an effluent/water integration system for a refinery is to take an inventory of water demand and effluent production for each refinery unit operation and to assess the water losses. This inventory provides the water balance across the refinery. It is recommended to visualise the water balance by a block scheme as presented as an example in Figure 4.42. The next step is to identify all possibilities to reduce the amount of water required and to reuse as much as possible by matching (quantity and quality) effluents by means of a water optimisation scheme. This 'water-pinch' methodology includes giving consideration to the reuse of treated effluent. The WSI concept aims at 'closing the water loop'.

WSI is mainly dependent on the refinery configuration, location, availability and type of raw water, the crude quality and the level of desalting required, the cost of potable water, the type of cooling water system and the availability of rainwater. Within a refinery, a number of standard process-integrated effluent/water treatment provisions are available as well as a number of standard possibilities for water reduction and reuse.

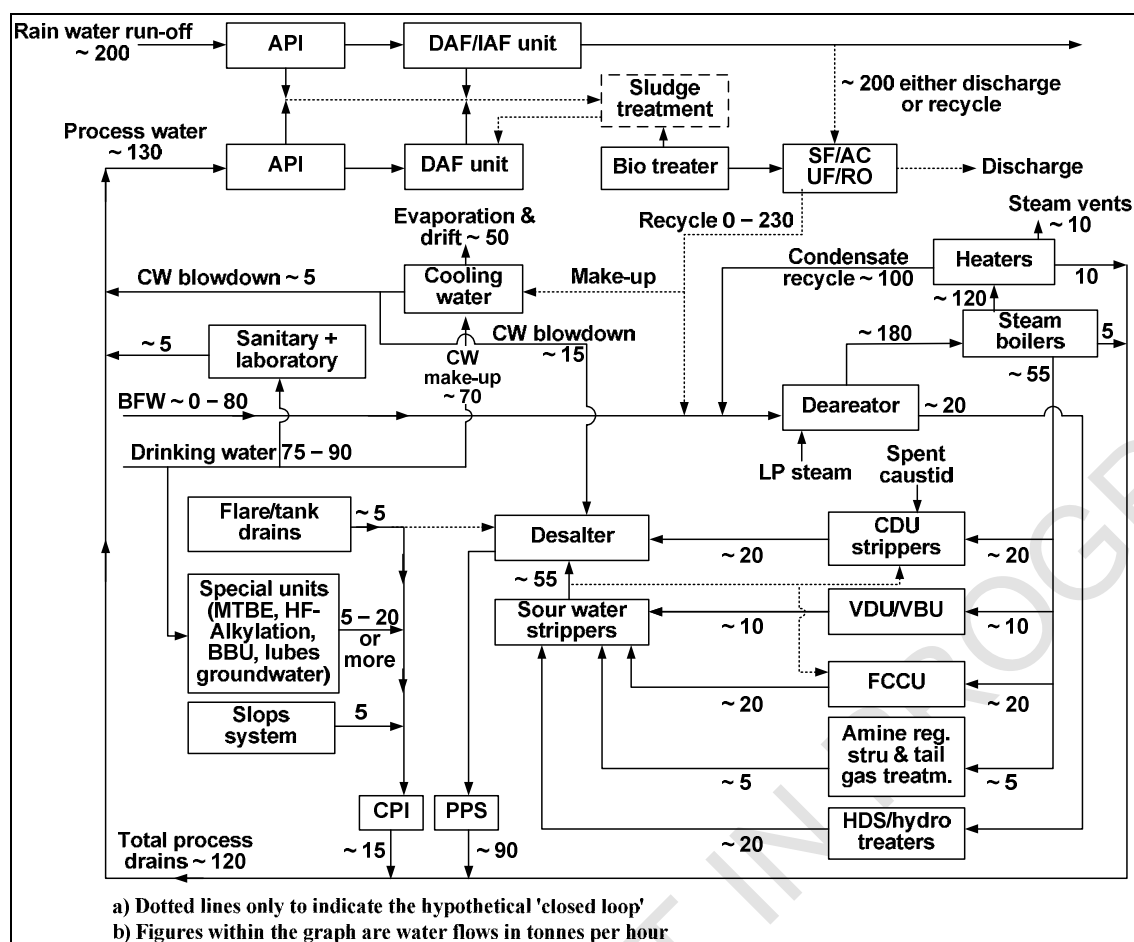


Figure 4.42: Example of a process water integration scheme for a catalytic cracker refinery configuration (10 Mt/yr)

Achieved environmental benefits

Water stream integration mainly aims at reducing the consumption of fresh water. The environmental implications of the conceptual approach of a process water integration scheme are favourable. Enclosed systems and closed-water loops limit the hydrocarbon emissions to air and discharges to surface water, and also lead to the reduced generation of waste in the form of sludges. The quantification of the reductions of the water used (and products lost) vary from location to location but can be substantial (>50 %).

Environmental performance and operational data

Reducing the volume of water discharged reduces the size of the effluent treatment plant required, the amount of energy and chemicals used, and the quantity of pollutants discharged to the environment. Data on actual fresh water usage are included in Section 3.1.1.2, Table 3.3 and Section 3.15. Based on the TWG data collection, specific consumption mainly ranges between 0.2 and 25 m³/t of feedstock, the largest part still being used for cooling and returned to fresh-water bodies.

Cross-media effects

Reducing the water volume can lead to increased pollutants concentrations entering the waste water treatment plant but the process, if properly designed, can generally deal with this issue. This rise might put the value for one or several priority substances beyond the environmental quality standard (EQS) of the water framework Directive (WFD). Specific attention should be paid to these cases and could justify the handling of a specific study

Technical considerations relevant to applicability

Generally applicable to existing plants, but when included in the initial design it can lead to even higher efficiency.

Economics

No data.

Driving force for implementation

The reduction of fresh water use is a goal for most refineries for two main reasons. First, fresh water, particularly high quality water, is a valuable resource which in many parts of Europe is becoming increasingly scarce. Where water of lower quality is used, treatment to acceptable standards also requires the use of energy and chemicals. Secondly, water used has to be discharged.

Example plants

A newly built refinery in Thailand generates only 40 t/h process water at a crude throughput of 8 Mt/yr due to such an approach. Values of 0.5 m³ per tonne of crude oil have been also achieved within Europe.

Reference literature

[168, VROM 1999], [164, Noyes 1993], [207, TWG 2001], [167, VDI 2000], [77, REF TWG 2010]

4.15.4.2 Water and drainage system**Description**

Flexibility is needed in water and drainage systems to cope with changing circumstances, such as sudden rainfall, firefighting, process upsets, process changes, additional plants, capacity extensions and new regulatory demands. A basis for integrated water management is also needed, including spill prevention and potential reuse of water streams without or after treatment. The principle is based on a thorough qualitative and quantitative analysis of the various water and effluent streams, the assessment for reuse potential with maximum reliability and environmental protection. A flexible water and drainage design allows for water integration and allows for short-term and long-term changes at optimised cost. An enclosed sewerage system for the transfer of contaminated water from tanks and processes to separation facilities is also a technique to consider.

Technical description

A water and drainage system of an industrial site is the result of a conceptual design of many unit operations lined up in such a way that water management can be optimised. The basis of the concept is segregation of the different water streams into oil-free water streams, accidentally oil-contaminated (AOC) streams and continuously oil-contaminated (COC) streams. The latter may be subdivided into low and high BOD streams with the possibility for biotreatment, effluent polishing and reuse (see Figure 4.43).

The application of a segregation concept takes a certain level of housekeeping and operational discipline into account. The decision to choose a different route for a certain type of effluent would be based on the monitoring of water qualities, both internal streams and the collective discharge. The environmental performance and the effluent management of the refinery requires a constant level of alertness and dedication, sufficient training and motivating instructions and an extensive monitoring (sampling and analysis) scheme. The concern is mainly with the first flush, which entails the collection, separation and treatment of the first charge of rainwater from the potentially contaminated refinery surface. After the first flush the rest of the rainwater is collected, analysed and discharged without treatment, if acceptable.

Achieved environmental benefits

Prevention of pollution due to discharge without appropriate treatment of water coming from the whole refinery drainage system.

Environmental performance and operational data

No data.

Cross-media effects

Energy requirements are mainly for pumping the waste waters and are system and site-dependent.

Technical considerations relevant to applicability

A number of elements of the current design approach for a new water and drainage system can be considered for implementation in existing refineries. However, as the overall drainage systems of old refineries have remained unchanged, the applicability of segregation of drainage streams may be limited.

Economics

No data.

Driving force for implementation

Source reduction and spill prevention by good housekeeping are also essential elements for VOC and odour emission reduction at CPI, API, DAF units and biotreaters.

Example plants

Not many refineries have segregated process water and rainwater run-off. If they do, these streams are routed to separate and dedicated treatment systems. The extent of segregation varies from refinery to refinery (by design or retrofit). Most refineries use stripped sour water and/or some condensate streams as desalter wash water (see Section 4.9). Reuse of treated effluent (biotreatment, filtration followed by reversed osmosis) as a source for boiler feed water is technically feasible. Reuse of treated effluent as cooling water make-up is done at several locations. First flush treatment is applied in several refineries. Some refineries employ an H₂S oxidation tank to prevent toxic and odorous emissions from process water prior to DAF and biotreatment.

Figure 4.43 shows a block diagram of an example of an optimised water/effluent routing for a refinery.

Reference literature

[223, Bakker et al. 1994], [168, VROM 1999], [148, Irish EPA 1993].

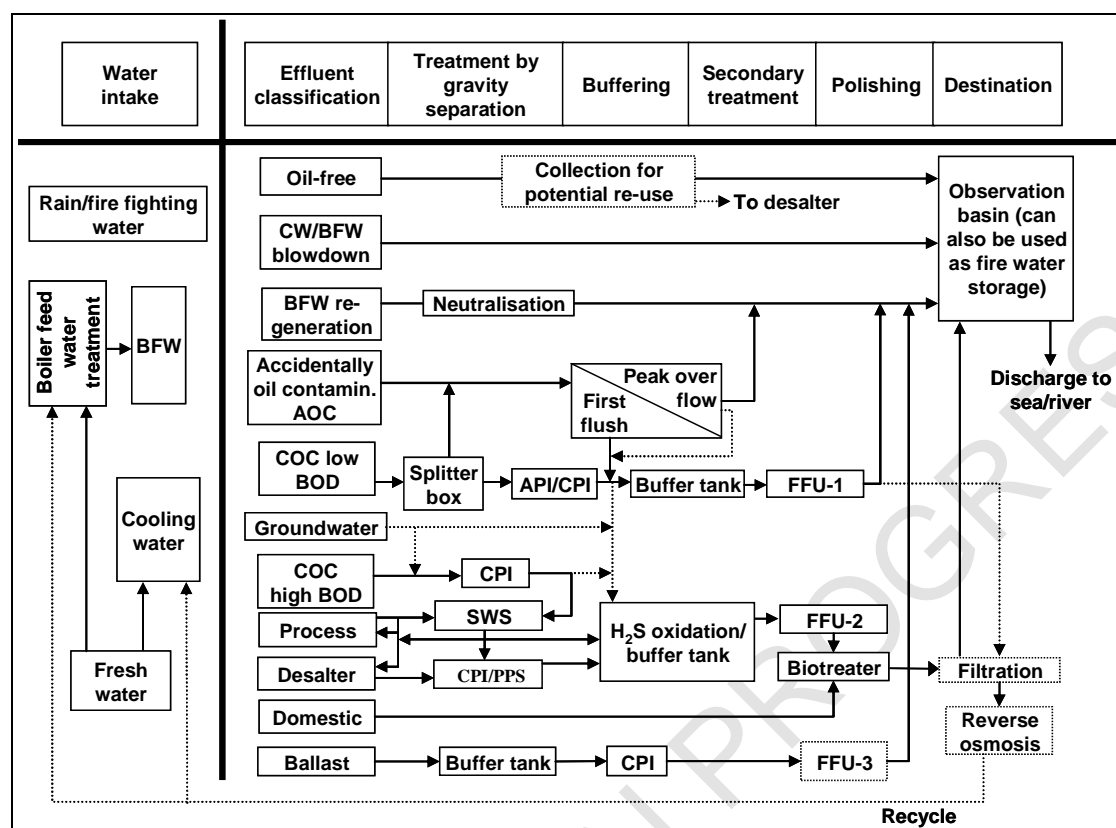


Figure 4.43: Block diagram of an example of an optimised water/effluent routing for a refinery

4.15.4.3 Rainwater

Some techniques that may be applied to rainwater are given below:

- Surface water run-off or rainwater can be segregated into oil-free, accidentally oil-contaminated, and continuously oil-contaminated effluents. These effluents may require treatment. Rainwater on contaminated surfaces may lead to effluent to be treated in a CPI/API.
- In specific situations, rainwater may be a useful source of raw water for the preparation of process water make-up, boiler feed water and cooling water.
- Some refineries have segregated effluent and drainage systems. In a number of refineries, the water and drainage system includes a segregation of process water, condensate blowdowns, rainwater and cooling water, in order to reduce the environmental impact of effluent discharges at minimum cost. Moreover, adequate process water integration and water management measures will include a review of all options to recycle water streams, with the aim of achieving a significant reduction of end-of-pipe treatment. Segregation of the process water discharges, surface water run-off, cooling water and boiler feed water blowdowns and other effluents may be considered. Separation of storm water and other effluents of different origins in order to permit appropriate treatment options may be considered. In some cases, retrofitting costs can be very high.

Reference literature

[168, VROM 1999], [164, Noyes 1993].

4.15.4.4 Ballast water

Ballast water is typically discharged at a very high rate, provoking the generation of high-volume waste water peaks, which can contain high salt concentrations (seawater), and a high content of oil. It can easily lead to an upset of existing effluent treatment systems. Therefore the use of ballast water tanks is an important equalisation tool for feeding the water in a controlled way to the waste water treatment plant, if the COD is lower than 100 ppm. Because of this, (and because jetties are often remote from the rest of the refinery), ballast water is often treated in a separate plant dedicated to that. As more and more crude tankers are equipped with double hulls, the ballast water problem is slowly phasing out.

4.15.4.5 Firefighting water

Some techniques to consider are:

- The firefighting water system can sometimes be a water reuse sink within the refinery.
- Provision should be made to reduce the potential for pollution as a result of firefighting activities (e.g. to collect firefighting water in a basin). Serious pollution can be caused by the release of firefighting water in an emergency. Design of Containment Systems for the Prevention of Water Pollution from Industrial Accidents can be found in the Construction Industry Research and Information Association Report 164 1996.

4.15.4.6 Priority substance-driven management

Description

Within the framework of European legislation (specifically Directive 2000/60/EC, the water framework Directive) this technique is a strategy to identify and reduce the water releases of substances classified as 'priority substances'.

An appropriate strategy could be implemented and include the following steps:

- establishing a list of substances that may be released by the refinery sites;
- setting sampling prescriptions for monitoring normal operating conditions (temporary or permanent plan);
- determining the most relevant period for a temporary monitoring plan, e.g. a 6 month period or yearly in case that the values are very low, and carrying it out;
- analysing the results and establishing a concrete action plan for reducing emissions of the corresponding substances to be included in the EMS. This could result, e.g. in adding substances to the regulatory monitoring plan.

Achieved environmental benefits

According to the water framework Directive, progressive reduction of priority substances discharge from refineries. For priority hazardous substances, cessation or phasing-out of discharges.

Operational data

Based on the results from the French monitoring campaign, the following table may be used to determine the substances to be monitored monthly during a six month transitory plan. In the last step, a relevant list of substances to monitor for each plant will be defined. When appropriate, specific actions will have to be carried out by operators in order to achieve reduction under the control of the local authorities.

Table 4.62: Example of hazardous substances tracking in refineries discharges

Substances	CAS ⁽¹⁾ number	WFD ⁽²⁾ number	Limit of quantification (µg/l)	Transitory monitoring ⁽³⁾
Benzene	71 – 43 – 2	4	1	Systematic for benzene production sites only
Xylenes (o,m,p)	1330 – 20 – 7		2	Systematic
Anthracene	120 – 12 – 7	2	0.01	Systematic
Fluoranthene	206 – 44 – 0	15	0.01	Systematic
Naphtalene	91 – 20 – 3	22	0.05	Systematic
Benzo (a) pyrene	50 – 32 – 8	28	0.01	Systematic
Benzo (b) fluoranthene	205 – 99 – 2	28	0.01	Systematic
Benzo (g,h,i) perylene	191 – 24 – 2	28	0.01	Systematic
Benzo (k) fluoranthene	207 – 08 – 9	28	0.01	Systematic
Indeno (1, 2, 3-cd) pyrene	193 – 39 – 5	28	0.01	Systematic
Cadmium and compounds	7440 – 43 – 9	6	2	Systematic
Lead and compounds	7439 – 92 – 1	20	5	Systematic
Mercury and compounds	7439 – 97 – 8	21	0.5	Systematic
Nickel and compounds	7440 – 02 – 0	23	10	Systematic
Arsenic and compounds	7440 – 38 – 2		5	Systematic
Zinc and compounds	7440 – 66 – 6		10	Systematic
Copper and compounds	7440 – 50 – 8		5	Systematic
Chromium and compounds	7440 – 47 – 3		5	Systematic
Biphenyl	92 – 52 – 4		0.05	Additional
Tributyl phosphate	126 – 73 – 8		0.1	Additional
Hexachlorobenzene	118 – 74 – 1	16	0.01	Additional
Chloroform	67 – 66 – 3	32	1	Additional
Perchloroethylene	127 – 18 – 4		0.5	Additional

⁽¹⁾ CAS Chemical Abstract Service.
⁽²⁾ WFD: Water Framework Directive.
⁽³⁾ Additional means case-by-case approach.
Source: [263, TWG 2010] FR French Strategy to reduce discharges of dangerous substances.

Applicability

Applicable to existing installations.

Economics

Costs may vary greatly depending on the total number of substances monitored and on the duration of the transitory monitoring programme put in place, which are very site specific. It may be necessary in some cases (e.g. where ubiquitous substances are detected) to also measure these substances in the raw water uptaken by the refinery, eventually increasing the number of samples and analyses. The cost for an analysis of a dozen substances is estimated (2010) as between EUR 1 500 and 3 000.

Driving force for implementation

Community legislations.

Example plants

In France, 13 refineries were concerned.

4.15.4.7 Site-level management of air emissions: the 'bubble approach'

Description

Refineries meet some or all of their energy needs with a variety of gaseous and liquid fuels that are by-products of the various processes. In this respect, refineries differ from other industries that generally buy all their specified fuels from outside. Another particularity of the refining sector is the recognised complexity of refineries. Aspects of this complexity include, in a modern refinery, numerous emission points interrelationships between feedstock, types of processes and variations in different operating conditions in relation to product slate and product quality requirements. Furthermore, a refinery operates using, at different plants and at different times, the various fuels it produces in-house.

One of the most used techniques for site level management of air emissions is known as the 'bubble approach' and can be described as follows.

The 'bubble approach' is a generic tool for expressing and comparing the level of emissions achieved or expected at refinery site level, from a clearly identified set of combustion and process units, and for a given substance or parameter. As represented in Figure 4.44, this approach consists of considering all concerned emissions together, as emitted through a 'virtual single stack'.



Figure 4.44: The single 'virtual chimney stack' of a 'bubble approach'

This approach is considered especially suitable to oil refining, where some flexibility is needed for expressing or evaluating the environmental performance at the site level. This flexibility is notably justified by the following factors:

- the recognised complexity of refining sites, with multiplicity of combustion and process units, often interlinked for their feedstock and energy supply;
- the frequent (e.g. weekly or even daily) process adjustments required in function of the quality of the crude received;
- the technical necessity for many sites to keep burning a part of their internal residues as energy fuels, and to frequently adjust the site fuel mix according to process requirements;
- the need for enabling, quantifying and monitoring a net site-level emission reduction for sites where some key specific installation controls have been duly justified as not being possible and have to be compensated elsewhere.

Based on the exchange of information within the TWG, a proposal for a harmonised methodology for the bubble calculation is provided in Annex 9.6. This example enables to set a site level air emission value based on BAT. It provides a method for calculations of SO₂ and NO_x equivalent concentration (mg/Nm³) and can also be used for setting global loads (e.g. tonnes per year). This approach assumes, as a prior condition, that the global result on the environment should be at least as efficient as if BAT-AELs were achieved for every individual process.

This ensemble of techniques consists of setting, in the refinery management system appropriate targets, dedicated procedures and specific monitoring instruments in order to allow the operator:

- to set clear emission targets at the site level;
- to monitor permanently the site environmental performance against the set targets;
- to optimise together possible site energy requirements with their related air emissions;
- to identify the most cost-effective places for the application of new primary or end-of-pipe techniques for further reduced emissions;
- to better prepare and anticipate retrofitting difficulties;
- to maximise the availability and stability of abatement processes and equipment.

Technical description

Focusing on the most used technique for site level management the 'bubble approach', as described in Annex 9.6 is based on the main items given below.

Bubble perimeter

The exact bubble perimeter to be considered for a given site will depend on the purpose the bubble tool is used for. For the purpose of applying BAT, the proposal methodology provided in Annex 9.6 is designed to cover, as necessary, all sources of permanent emissions of a refinery: i.e. combustion plants, catalytic crackers, sulphur recovery units, coke calciners and other processes where appropriate.

Bubble substances or parameters

Some competent authorities have considered covering simultaneously all usual main parameters (CO, PM, NO_x, SO₂ and eventually VOC) in a bubble approach, with the aim to address site energy consumption and air emissions in a consistent way, and to introduce the same site-level flexibility for all these parameters which are very often interdependent.

In the context of the work undertaken for the revision of this document, SO₂ and NO_x have been recognised as the two parameters which deserve priority in a BREF common methodology for a site-level bubble-expressed AEL calculation, and for which enough supporting information and data have been provided.

Therefore, the methodology developed in Annex 9.6 focuses on SO₂ and NO_x and is based on the available data provided. Nevertheless, extensions to other pollutants (e.g. PM, CO) are not excluded.

Bubble averaging period

The averaging period to be considered will depend on the purpose the bubble tool is used for. In the particular context of this document, the methodology proposed has been based primarily on a yearly average, since a long-term period has been considered as the most appropriate for reflecting best performances achievable in normal operating conditions, and giving enough time and flexibility to integrate necessary feedstock, process and fuel adjustments.

However, the efficient control of a yearly bubble requires a very frequent or continuous monitoring regime of all emissions concerned. A shorter term bubble can be derived from the long term bubble using monitoring results.

Bubble calculation

The site-level bubble is a sum of two terms.

A first term related to the energy system, including at least all furnaces, stand-alone boilers, central CHP or conventional power plants, and gas turbines. This term is driven by suitable AEL concentration ranges expected on each category of installations when BAT is applied. A second term related to the process units including at least an FCC UNIT if any, and an SRU. This term should be driven by suitable AEL concentrations or specific emission ranges expected on each of them when BAT is applied.

In the context of this document, and for the purpose of expressing meaningful AELs at the site or partial site level, the bubble determination should always be based on concentration and specific emission ranges expected on all concerned installations when BAT is applied, and should involve the following steps:

- Step 1: exhaustive identification and geographical mapping of all included sources
- Step 2: determination of the offgas volumetric contributions expected from all included sources
- Step 3: determination of the mass contributions expected from all included sources
- Step 4: Determination of the bubble-associated monitoring regime

The actual details of the calculation and necessary information on each of these steps are given in Annex 9.6.

Achieved environmental benefits

By allowing flexibility in how to reduce refinery emissions, the bubble approach puts the focus on environmental benefit (decreasing overall emissions) rather than on individual source compliance.

Examples of how to achieve environmental targets by various reduction means are made available under the following heading.

Environmental performance and operational data

Example 1 is a refinery with a small FCC unit which currently uses 32 % of liquid fuel firing and has a SRU unit that operates at a recovery efficiency of 98 %. The options considered potentially viable to reduce sulphur emissions are:

- to replace a fraction of the liquid fuel firing with natural gas;
- to use sulphur reducing additives (SRA) in the FCC unit;
- to install a wet gas scrubber on the FCC unit;
- to upgrade the sulphur recovery tail gas treatment unit which could be to two levels corresponding to the process chosen.

The current total site bubble (SO_2) is $1\,165 \text{ mg/Nm}^3$ (at 3 % O_2), with contributions:

- of 795 mg/Nm^3 from the combustion system;
- $2\,500 \text{ mg/Nm}^3$ from the FCC;
- and $19\,000 \text{ mg/Nm}^3$ from the SRU.

The combustion system contributes 88 % of the flue-gas, the FCC 11 % and the SRU 1 %.

By mass emission the combustion system contributes 60 %, the FCC 24 % and the SRU 16 % of total SO_2 .

Table 4.63 shows the effect of applying different control options. In this refinery, the base capacity of the SRU is limited and this imposes a maximum use of SRA in the FCC which has to be regenerated. Two degrees of substitution of the liquid fuel are considered to reflect the fact that this is not a commercial fuel and conversion would have to be considered.

Option 1 considers measures on all three sources (Combustion, FCC and SRU) substituting part of the liquid firing, introducing SRA to 30 % removal and upgrading the SRU tail gas unit to a sub-dewpoint system. The reason for this choice is that the existing unit is a 2 bed Claus unit which does not offer an economic advantage to the installation of a SuperClaus unit. This achieves a 31 % reduction in mass emissions.

Option 2 focuses on eliminating liquid firing only. It achieves a 42 % reduction in emissions. Option 3 focuses on upgrading the SRU tail gas unit to a SCOT plant but achieves only a 16 % reduction in emissions.

Option 4 focuses on scrubbing emissions from the FCC unit and achieves a 21 % reduction in emissions.

Options 5, 6, 7 and 8 consider combined actions based on a full fuel switch to natural gas firing supplemented by actions on the FCC (5), SRU (6,7) and both FCC, SRU (8). The incremental improvements in mass reduction range from 7 % (5) to 15 % (7) over the fuel switch alone.

Table 4.63: Example of options for SO₂ emissions reduction with site level management

% Flue-gas volume	100 %	88 %	11 %	1 %	Combination
	Total bubble mg/Nm ³	Combustion mg/Nm ³	FCC mg/Nm ³	SRU mg/Nm ³	
Current situation	1 165	795	2 500	19 000	FCC: 32 % liquid fuel firing -SRU 98 %
Option 1	802	583	1 750	9 700	Partial fuel switch + FCC SRA 30 % + SRU 99 %
Option 2	675	239	2 500	19 000	Full fuel switch
Option 3	984	795	2 500	990	SRU 99.9 %
Option 4	917	795	250	19 000	FCC Scrubber 90 % SO ₂ Removal
Option 5	593	239	1 750	19 000	Fuel switch and FCC SRA 30 %
Option 6	582	239	2 500	9 700	Fuel switch and SRU 99 %
Option 7	495	239	2 500	990	Fuel switch and SRU 99.9 %
Option 8	500	239	1 750	9 700	SRU 99 % and FCC SRA 30 % and fuel switch
NB: Example 1: 32 % oil firing, small size FCC, SRU 98 % Source: [125, CONCAWE 2011]					

Example 2 shows how NO_x control options might be considered. The refinery combustion system comprises many small units ducted to common stacks. The flue-gas temperature at the stacks is too low for SCR to be technically applicable to the combustion system. There are negligible NO_x emissions from the SRU. In this case, controls on the combustion system comprising a complete switch to gas-firing and upgrading the burner system (Option 1) would reduce NO_x emissions by 58 %. Measures on both NO_x sources (Option 3) comprising a partial fuel switch and application of SNCR to the FCC unit would achieve a reduction of 35 %. Measures on the FCC alone (Option 2) are ineffective resulting in a reduction of 11 %.

Table 4.64: Example of options for NO_x emissions reduction with site level management

	Total bubble mg/Nm ³	Combustion mg/Nm ³	FCC mg/Nm ³	
Current situation	501	492	600	
Option 1	210	161	600	Liquid fuel substitution + LNB
Option 2	446	492	100	FCC SCR 84 %
Option 3	327	332	300	Partial fuel switch + LNB + FCC SNCR (50 %)
NB: Example 2: 32 % oil firing, small size FCC. Source: [125, CONCAWE 2011]				

These two examples show that the several ways to reduce overall emissions from a refinery can differ in their effectiveness.

Cross-media effects

When the optimisation process is only challenged and evaluated through equivalent concentrations set up at the site level rather than at the unit level, it can theoretically lead to possible concern linked to, higher emissions at the lower stacks (e.g. SRU). Nevertheless, although all sources are inside the bubble there may be additional constraints on specific source emissions, e.g from low stacks, to be limited for local air quality requirements.

Technical considerations relevant to applicability

This technique is fully applicable, provided that emitting units and processes are equipped with appropriate continuous monitoring systems, including emissions measurements or process parameters monitoring (see Annex 9.6).

Economics

Monitoring for emissions to a site-specific bubble limit is not different to monitoring for individual sources. It serves two purposes:

- to ensure a better protection for the environment as a whole by being continuously aware of total emissions and enabling to control them;
- and to provide measurement/calculation data to evidence compliance with individual limit values where set.

Monitoring for a bubble requires that all the information needed to assess sitewide emissions is brought together in an automated way, so that an accurate picture is gained. This involves combining different types of information achieved in different ways, e.g. analytical samples, continuous sensor output, discrete measurements with interpolating calculations.

This requires that the site data collection system can assemble this information and generate appropriate management reports at timely intervals, enabling dynamic management. This is very much the same sort of system that should be in place for individual source permitting.

Therefore the extra costs of monitoring for a bubble should be small and related to the generation of formal informational data that can be used for site reporting, alongside the real time picture of site emissions.

Driving force for implementation

Management and reduction of air emissions and related cost effectiveness.

Example plants

A number of European refineries have already implemented a full scale management and monitoring system for the site-level management of emissions of SO₂, NO_x, PM, CO.

Examples of air emission site management of two Belgium refineries are described in EIPPCB report dated 17/05/2011. The UK approach to define SO₂ air emissions values based on short term requirement for air quality is illustrated through EIPPCB report dated 16/11/2011.

Reference literature

[65, EC 2003], [77, REF TWG 2010], [97, CONCAWE 2011], [90, EIPPCB 2011], [98, EC EIPPCB 2010], [125, CONCAWE 2011], [126, CONCAWE 2011], [127, France 2010].

4.15.4.8 Anticipation and adaptation to unfavourable meteorological conditions

Description

Directive 2008/50/EC on ambient air quality and cleaner air for Europe defines and establishes objectives for ambient air quality designed to avoid, prevent or reduce harmful effects on human health and the environment as a whole and also ensures that such information on ambient air quality is made available to the public. In certain unfavourable meteorological conditions, pollutant concentration peaks may be detected in the surroundings of refineries even when they are normally operated, using properly all expected primary and abatement techniques according to their permit. In such conditions, specific measures and tools can turn out to be necessary to anticipate, and further manage and reduce emissions as necessary, in order to guarantee that concentration limit values in the ambient air around the site are being respected.

Two examples of such tools are described in more detail in the Operational Data section. They only concern the management of SO₂ emissions.

- The first example, applied by the Total refinery in Donges (France), is based on a daily prediction of the concentrations likely to be reached at most exposed urban areas. A specific dispersion model fitted to the local conditions was developed for this purpose.
- The second example relates to the specific organisation set out for the anticipation of pollution peaks in the surrounding of the ExxonMobil refinery in Notre Dame-de-Gravenchon (France). This organisation is based on the evolution of real time ambient concentration measured in several locations distributed according to most exposing wind directions.

In each case, when the tool predicts the likely occurrence of excessive ambient concentrations, appropriate actions are taken at the site level. As a first step, a progressive switch to low sulphur fuels is required on key energy consuming units. If needed, a further step consists of a progressive production slow down or shutdown.

Achieved environmental benefits

A meteorological model-based system has been implemented for the Donges refinery since the end of 2006. Between 2007 and 2008, five meteorological episodes with SO₂ ambient air concentrations over the limit values have been reported, compared to 28 episodes recorded between 2002 and 2005.

Environmental performance and operational data

In the case of Donges

The system is predictive and follows the steps illustrated in the local weather forecast handled as a minima on a daily basis, using a dedicated software that actually adjusts and refines by physical calculation the spot meteorological conditions in particular areas of interest. The model has been initially configured with local historical and physical data. Concentrations are predicted by dispersion modelling based on these calculated meteorological conditions, where all main emission contributing sources are physically described and separately addressed. The results are used by the scheduling department of the refinery for daily adjustment of the operational planning.

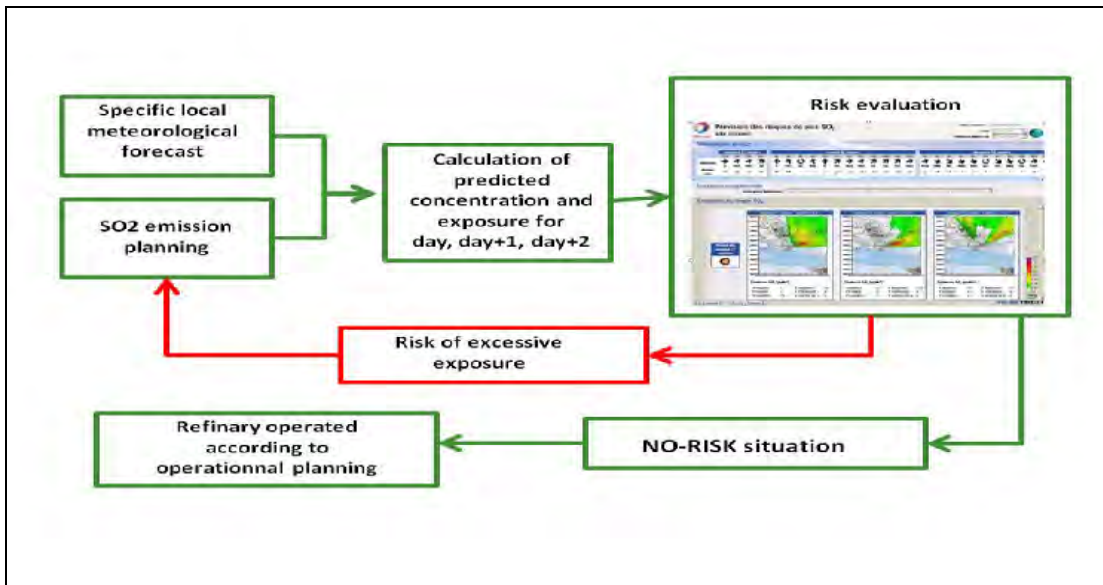


Figure 4.45: Flowchart of an emission management system for anticipating unfavourable meteorological conditions-Example of Total refinery in Donges

In the case of Rouen

The system is reactive and based on an existing network of 15 permanent multi-parameter automatic measuring devices settled all over the Rouen urban and industrial harbour area, is handled and maintained by a local air-monitoring non-profit organisation. Two of these measuring devices have been selected due to their geographical location, the results of them being processed according to the two following procedures as displayed in Figure 4.46.

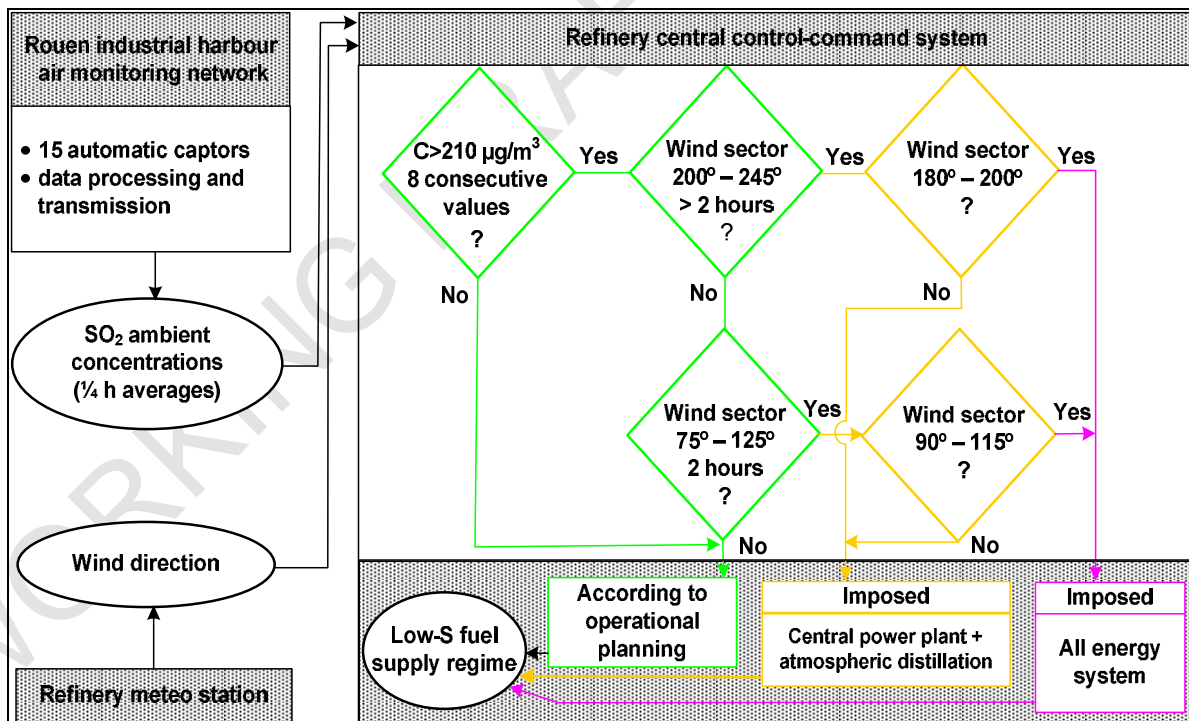


Figure 4.46: Flowchart of an emission management system for anticipating unfavourable meteorological conditions - Esso refinery in Notre Dame de Gravenchon

Cross-media effects

No data submitted.

Technical considerations relevant to applicability

Systems based on local modelling require the existence of public or private meteorological services which are able to provide the necessary forecast data on a continuous basis. The applicability of systems based on a continuous measuring of ambient air concentrations in urban target areas is significantly facilitated when they can rely upon an existing air quality monitoring organisation which already operates and maintains a network of appropriate sensors.

Economics

In the case of Donges, the initial investment for the system development and basic configuration is around EUR 0.45 million (2006). The annual operating costs are evaluated at EUR 0.1 million/yr, covering software and hardware maintenance, as well as the acquisition of daily meteorological forecasts at the appropriate frequencies and geographical scales for providing, as necessary, calculation starting conditions to the system. As such, the measures actually taken for the SO₂ reduction by itself during concerned meteorological episodes are highly variable by year. They were in the range 1 – 6 million EUR/yr in 2006, 2007 and 2009.

Driving force for implementation

Prevention or limitation of potential exposure to ambient air concentrations over limit values, by anticipation or early detection of unfavourable meteorological episodes, in order to prevent and reduce health and environmental impacts.

Example plants

A number of both kinds of systems are implemented by refineries in France (see above). In Italy, similar systems have existed for more than 15 years in the province of Siracusa (East Sicily) a densely populated area with 4 refineries, and several chemical and power plants. The system works with a permanent monitoring network of 24 fixed stations (SO_x, NO_x, PM, VOC, Benzene, ...). It includes a permanent meteorological station equipped to predict the thermal inversion conditions and worsening of the air quality. In south of Spain, the Cepsa La Rabida Refinery uses a model taking into account real time and meteorological data.

Reference literature

[39, French contribution to TWG (item 4) 2009].

4.16 Isomerisation

4.16.1 Active chloride promoted catalyst isomerisation process

Description

More information can be found in Section 2.16.

Achieved environmental benefits

Higher process efficiencies compared with the zeolitic catalysts and lower reaction temperatures (less energy consumed).

Cross-media effects

The chloride promoted, chlorinated alumina catalyst (containing platinum) requires the addition of very small amounts of organic chlorides to maintain high catalyst activities. This is converted to hydrogen chloride in the reactor. The chloride-promoted catalyst cannot be regenerated.

Operational data

The highly active chloride promoted-catalyst, and the chlorinated-alumina catalyst (containing platinum), operate at a relatively low temperature (150 – 175 °C and 20 barg) and give the highest octane improvement. In such a reactor, the feed must be free of oxygen and sulphur sources, including water to avoid deactivation and corrosion problems. The oxygen deactivation is not reversible, nevertheless the sulphur can be desorbed from the catalyst surface. This desorption process of sulphur species from the catalyst consumes utilities and energy.

Applicability

This catalyst is very sensitive to sulphur, so deep desulphurisation of the feed to 0.5 ppm is required.

Economics

Investment estimated (based on ISBL, US Gulf Coast 1998) EUR 4 150 – 10 400 per m³/d. Investment for installation (based on: 2Q98 US Gulf Coast) were evaluated for 1590 m³/d of fresh feed capacity of EUR 8.8 million (±50 %).

Driving force for implementation

Production process.

Reference literature

[183, HP 1998], [228, TWG 2000].

4.16.2 Zeolitic isomerisation process

Description

More information is given in Section 2.16. Some refiners need more octane from the light straight run naphtha fraction than is possible from the O-T zeolitic isomerisation process. Adsorption technology can then be used to remove the unconverted normal paraffins. The utilities needs for that process are quite low.

Achieved environmental benefits

No chloride compounds are used in these types of processes. The zeolite and sulphated zirconia catalyst can be regenerated several times before sending the catalyst to a reclaimer to recover the platinum.

Cross-media effects

Higher temperature of the process, requiring more heating.

Operational data

The zeolite catalyst operates at significantly higher temperatures (250 - 275°C and 28 barg) and is much more tolerant to contaminants, though the resulting octane improvement is lower.

Applicability

The zeolite catalyst is mainly used for non-hydrotreated feedstreams. Lower reaction temperatures are preferred to higher temperatures because the equilibrium conversion to isomers is enhanced at the lower temperatures.

Refiners with idle hydroprocessing equipment, such as old catalytic reformers or hydrodesulphurisation units, can consider converting this equipment to the once-through zeolitic isomerisation process. With isomerisation, a 10 to 12 octane-number increase for the C₅ - 71 °C light naphtha can be achieved.

Economics

Estimated cost of the reaction process is EUR 4 654 per m³/d. For the absorption process, the investment is EUR 18 900 – 25 160 per m³/d. The catalyst and adsorbent cost is around EUR 1 700 per m³/d.

Driving force for implementation

Production process. Selection of a once-through or recycle scheme depends on factors such as quantity of light naphtha to be blended in the gasoline pool, the required octane number of the gasoline pool and the availability of other high-octane gasoline blend components. If the isomerate product has an octane number exceeding 87, a recycle scheme is the only option. Selection of a fractionation-based scheme or an absorption-based scheme is dependent on feed composition and to a certain extent on the product requirements. In general it can be said that the fractionation-based scheme is lower in investment but significantly higher in operating costs as a result of high energy requirements.

Reference literature

[175, Meyers 1997], [183, HP 1998], [228, TWG 2000].

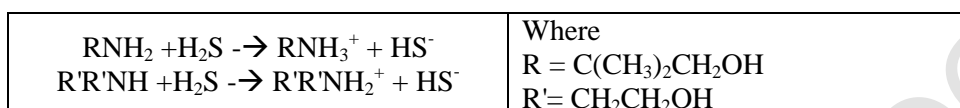
4.17 Natural gas plants

As mentioned in the Scope and in Section 2.17, the processes treated in this section are these used in the refining of natural gas. As with mineral oil refineries, the processes used on production platforms are not included in this BREF.

4.17.1 Amine sweetening of natural gas

Description

Many reactions may take place in the process where H₂S is absorbed into an aqueous blended amine solution, mainly by proton transfer as given below.



Technical description

The process is illustrated in Figure 4.52 of Section 4.23.5.1.

If the recovered H₂S gas stream is not to be used as a feedstock for commercial applications, the gas is usually passed to a tail gas incinerator in which the H₂S is oxidised to SO₂ and is then released to the atmosphere via a stack. More information can be found in Section 4.23.5.1.

Achieved environmental benefits

Reduction of H₂S concentration in natural gas.

Environmental performance and operational data

See Section 3.17

Cross-media effects

See Section 4.23.5.1.

Operational data

The recovered hydrogen sulphide gas stream may be:

- vented
- flared in waste gas flares or modern smokeless flares,
- incinerated or
- used for the production of elemental sulphur or sulphuric acid.

Technical considerations relevant to applicability

Fully applicable.

Economics

Section 4.23.5.1.

Driving force for implementation

To comply with sulphur specifications of natural gas.

Example plants

At present, the amine process (also known as the Girdler process) is the most widely used method for H₂S removal.

Reference literature

[172, MRI 1997], [173, HMIP UK 1997], [99, Mandal et al. 2005].

4.17.2 Sulphur recovery unit

Extensive information can be found in Section 4.23.5.2.

4.17.3 Techniques to reduce VOC emissions

During the routine operation of natural gas terminals and other processes, it is necessary to prevent releases to air of natural gas. Techniques to consider to reduce these emissions are given below:

- Minimise the frequency of sphere pigs use by operating sealines at a high velocity, i.e. use 'mist flow' conditions.
- Minimise the recovery of spheres by use of receivers holding several devices
- Use vent receivers of high-pressure gas to a low-pressure part of the process for gas recovery by recompression, before opening for access to sphere pigs
- Minimise the occasional shutdown and venting of process plant (when necessary, e.g. for maintenance, upset and changeover purposes) by appropriate plant selection and design.
- Avoid the use of refrigerants for gas dew point control that are of significant environmental concern (CFCs).
- Condense and incinerate overheads and any gas vented from storage and glycol and methanol regeneration units.
- Apply leak detection and repair (LDAR) programme (see Section 4.23.6.1).
- Maintain VOC emissions, including fugitives, within a range of 200 to 250 kg/h (300 - 350 kg/MNm³).

Reference literature

[173, HMIP UK 1997], [207, TWG 2001].

4.17.4 Techniques to reduce NO_x emissions

NO_x emissions come from the combustion processes applied in the natural gas plant. The techniques that can be applied for the control and abatement of NO_x are the same as those applied to refinery fuel gas. See Sections 4.10.4 and 4.23.3 for a detailed explanation.

4.17.5 Techniques to reduce water emissions

Description

Prevention techniques that may be applied to reduce the releases to water can be:

- Minimise and control, if possible, the quantity and contamination level of waste water to be treated on-shore 'at source', i.e. waste water coming from off-shore activities;
- Use of a three-phase separator on the liquids from the slugcatcher to control and minimise the hydrocarbon content of the aqueous phase;
- Treat sour water in a sour water stripper unit. see Section 4.24.2;
- Keep process effluent from glycol or methanol regeneration plants and any other high BOD/COD effluents separate from other streams, e.g. surface water, and treatment before discharge to the site effluent system;
- Apply water management techniques (See Section 4.15.4).

The techniques that may be used in the waste water treatment are described in Section 4.24.

Achieved environmental benefits

The achievable emission levels for a well-performing waste water treatment within a natural gas plant are shown in Table 4.65.

Table 4.65: Typical WWTP performance in natural gas plants

Water parameter/compound	Concentration (ppm)	Load (kg/MNm ³ feedstock)
Waste water		160 m ³ /MNm ³
Total oil content	0.1 – 5	0.4 – 0.6
TOC	60 – 100	3.5 – 12
COD	400	
Suspended solids	25	
Phenol	0.1 - 0.5	
NB: Values in this table are daily averages.		

Reference literature

[173, HMIP UK 1997], [207, TWG 2001], [77, REF TWG 2010].

4.17.6 Techniques to reduce waste generation**Description**

Techniques that may be applied to reduce waste generation are:

- Returning catalysts, absorbents, adsorbents, etc. to the manufacturers for recycling.
- Desalination of glycol purge stream which will give rise to solids for disposal and ensuring any residual glycol should first be reduced to a low-level.
- Some of the gas fields contain mercury vapour in very low concentrations. This mercury is removed from the gas in a 'cold trap' (e.g. by gas expansion) and recovered as a mercury-containing sludge. A specialised company processes this sludge by treatment in a vacuum distillation unit.

Reference literature

[173, HMIP UK 1997], [207, TWG 2001].

4.18 Polymerisation

4.18.1 Reduction of emission and use of catalyst within the process

Description

More information is given in Section 2.18.

Achieved environmental benefits

Reduction of the process emissions and reduction of acid consumption and consequently waste. Good polymerisation units can reduce the phosphoric acid consumption to levels of 0.1 - 0.2 gr/t of polymer produced. Another source relates that the typical catalyst consumption (H_3PO_4 + support) is around 1.18 kg catalyst per tonne of polymer produced.

Cross-media effects

No cross-media effects.

Operational data

Available data is provided in Table 4.66.

Table 4.66: Typical utility consumption of a polymerisation plant

Utilities	
Electric power (kW/tonne of C_5+ product)	20 – 28
Steam (t/tonne of C_5+ product)	0.7 – 1.1
Cooling (m^3 /tonne of C_5+ product)	4.4 – 6.0

Applicability

Commonly used as a production process.

Economics

The catalytic condensation process is relatively simple to operate and requires minimum labour. Its simplicity is reflected in the operating requirements summarised in Table 4.67.

Table 4.67: Typical operating costs of a catalytic condensation process

Catalyst and chemical cost (EUR/tonne of C_5+ product)	5.00 – 8.20
Labour and operating cost (workforce)	1 operator-helper
Typical operating cost (EUR/t C_5+ product)	20 – 30
Investment (EUR1 995/(t/yr) of C_5+ product)	50 – 95

Only one operator is required. Overall, the cost of operating a catalytic condensation unit ranges from EUR 16 – EUR 22.6 per m^3 of C_5+ polymer gasoline. This cost includes utilities, labour, catalyst, chemicals, and an allowance for process royalty, but does not include any direct or indirect capital-related costs.

Driving force for implementation

Production process.

Example plants

Some polymerisation processes are running in European refineries. Nowadays alkylation units are more predominant than polymerisation units, even though polymerisation units are cheaper.

Reference literature

[175, Meyers 1997], [183, HP 1998], [207, TWG 2001].

4.18.2 Management and reuse of the catalyst

Description

Two techniques can be applied to minimise the impact of catalyst disposal.

- The catalyst to be disposed of from the process is potentially pyrophoric and requires special treatment. However, removal by steam/water prevents any risk of fire. The catalyst solidifies in situ, and removal is achieved manually under nitrogen purge, or more recently by 'explosive' steam decompression with steam suppression to a catchment system. The catalyst may then be sent for either off-site disposal as special waste or to on-site treatment. On-site treatment involves neutralisation and fixing with cement. The material may then not be classified as special waste.
- The spent catalyst can be reused as fertiliser or as phosphorous feed to the biotreater.

Achieved environmental benefits

Reduction of risk of fire due to the pyrophoric characteristics of the catalysts and reduction of waste generation.

Cross-media effects

No cross-media effects.

Operational data

Disposal frequencies of up to 12 times per year may be expected.

Applicability

Fully applicable.

Driving force for implementation

Treatment of catalyst and reuse of phosphorous compounds within the refinery.

Example plants

No detailed data.

Reference literature

[149, Ministero dell'Ambiente 1999].

4.19 Primary distillation units

As mentioned in Section 3.19, the atmospheric and vacuum distillation units are large consumers of heat. The techniques to consider for application to the crude oil furnaces are these described in the section dealing with the energy system (Section 4.10).

4.19.1 Progressive distillation unit

Description

A progressive distillation unit with integrated CDU/HVU, which saves up to 30 % on total energy consumption for these units. The technique includes atmospheric distillation (topping), vacuum distillation, gasoline fractionation, a naphtha stabiliser if required and a gas plant.

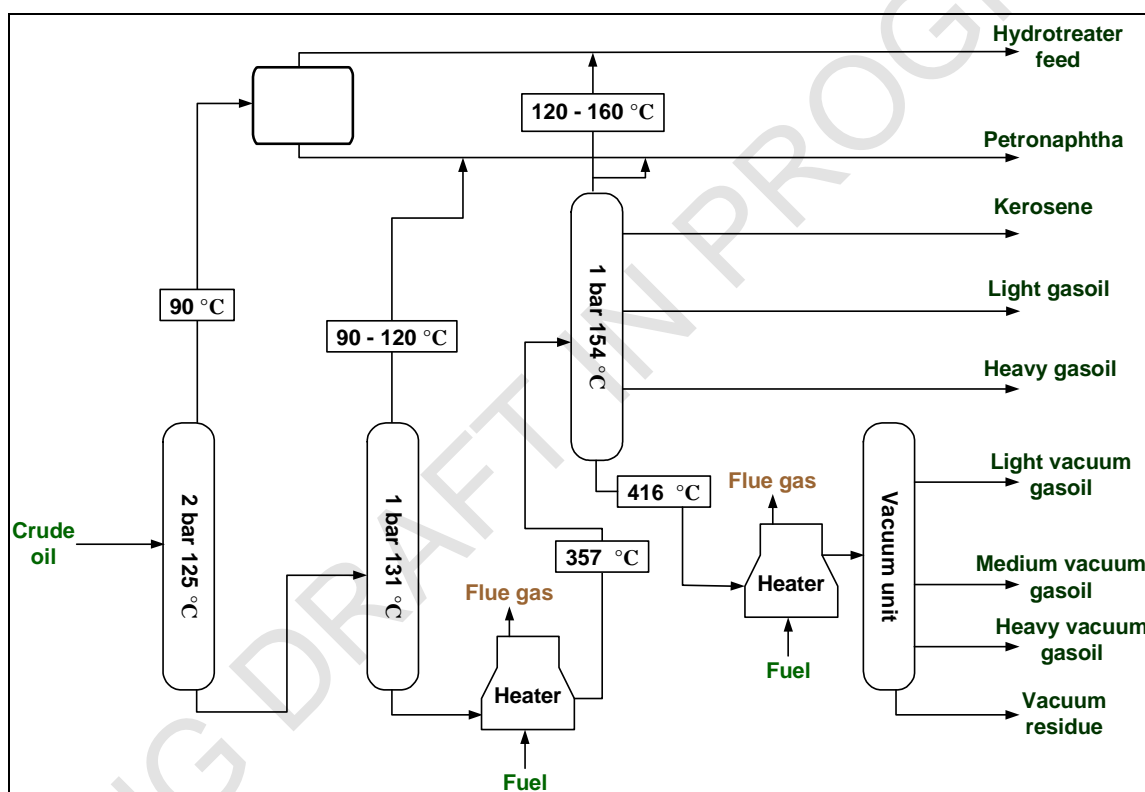


Figure 4.47: Process flow diagram of a progressive distillation unit

Achieved environmental benefits

The heater process duty (MWh/100 tonnes of crude) of a distillation capacity of 10 million tonnes per year is around 17.3 for an Arabian light crude. Using progressive crude distillation it is reduced to 10.1. The specific energy consumption (overall energy consumption in tonnes of fuel equivalent per 100 tonnes of crude) for a distillation capacity of 10 million tonnes per year is 1.7 - 2.0 for an Arabian light crude, whereas using the progressive distillation unit only consumes 1.15. The energy savings for a 9 700 000 tonnes/yr refinery is in the range of 50 000 tonnes heavy fuel compared to conventional techniques.

Total primary energy consumption

For Arabian light or Russian export blend: 1.25 tonnes of fuel per 100 tonnes of crude.

For Arabian heavy: 1.15 tonnes of fuel per 100 tonnes of crude.

Progressive distillation is the extreme of heat integration between atmospheric and vacuum distillation. It also prevents the superheating of light cuts to temperatures higher than strictly

necessary for their separation and it prevents degrading the thermal levels associated with the drawing-off of heavy cuts.

Cross-media effects

No cross-media effects identified.

Environmental performance and operational data

Table 4.68: Energy consumption of the progressive crude distillation when the same plant is used to process two types of crude oil

	Heavy Arabian (887 kg/m ³) 6.5 Mt/yr			Ekofisk (810 kg/m ³) 5 Mt/yr		
	Consumption	TOE/h	TOE/100 t	Consumption	TOE/h	TOE/100 t
Fuel (MWh/h)	67.5	5.81	0.75	67.5	5.81	1.04
Steam (tonnes/h)	15.95	0.8	0.11	21.0	1.05	0.19
Electricity (MWh/h)	6.4	1.41	0.18	6.4	1.41	0.25
TOTAL		8.02	1.04		0.27	1.48

NB: The energy consumption is defined according to the following hypothesis:
 TOE (tonne of oil equivalent) = 11.6 MWh.
 kg of low-pressure steam = 0.581 kWh.
 Yield of the electrical power plant = 39 %.
 Products are sent to storage (cold temperature).

Table 4.69: Utility requirements typical per tonne of crude feed in the US

Utility requirements typical per tonne of crude feed		Units
Fuel fired	107 – 140	kWh
Power	6.6 - 8.8	kWh
Steam, 4.5 barg	0 - 17	kg
Water cooling ($\Delta T = 15\text{ }^{\circ}\text{C}$)	1.4 – 2.8	m ³

NB: Data converted using average value of 1 tonne for 7.3 barrels of crude oil.

Technical considerations relevant to applicability

The process is applicable to all or part of these units when being constructed and can also be used in revamps for debottlenecking. It includes, for example, adding a preflash column to reduce the fuel consumption.

Economics

Reduced fuel consumption can be achieved and thus reduced operating costs of the distillation units.

Investment (based on 11.45 Mt/yr including atmospheric and vacuum distillation, gas plant and rectification tower): EUR 41 000 – 55 000 per t/yr (US Gulf Coast 1998).

Driving force for implementation

To reduce fuel consumption in refineries.

Example plant(s)

Some European refineries employ a progressive distillation unit with an integrated CDU/HVU.

Reference literature

[177, WRA 1999], [183, HP 1998], [191, UBA Austria 1998].

4.19.2 Heat integration of crude distillation units

Description

There is a tendency towards improved heat integration with crude and other units. The high energy consumption of the CDU makes heat integration very relevant. To optimise heat recovery from the atmospheric distillation column, two or three reflux streams are normally kept in continuous circulation at several points per top and middle pumparounds. In modern designs, integration with the high vacuum unit and sometimes the thermal cracker is achieved. Some techniques applied are given below:

- Optimise the heat recovery, studying and implementing the optimal energy integration. In this context, major progress has been made in recent years in understanding the design of efficient heat recovery networks. Pinch analysis has emerged as a tool for the evaluation of total systems designs, helping to balance investments against energy savings.
- Apply pinch analysis to the crude preheat train heat integration. Increase crude preheat temperature and minimise heat losses to air and cooling water.
- Increase crude distillation column pumparounds from two to four. Reboil sidestrippers with a heat transfer oil rather than by steam stripping.
- Heat transfer in the crude preheating can be improved using specific antifouling treatments in the crude heat exchanger train. Antifoulants are available from many chemical companies and, in many applications, are efficient in increasing the run cycle length of the exchangers; an antifoulant can help prevent the plugging of tube exchangers, improving heat recovery and preventing hydraulic losses, depending on the nature of the fouling. Service factors of the various units/trains, as well as heat recovery (energy efficiency) increase at the same time.
- The application of advanced process control to optimise the energy utilisation within the crude unit.

Achieved environmental benefits

Reduced fuel consumption in distillation columns.

Cross-media effects

In the case of highly heat-integrated units, the refinery complex as a whole becomes more susceptible to unstable conditions arising in an individual unit.

Applicability

Integration in retrofitting applications will normally depend on the plot space available and the possibility to execute these modifications in the available shutdown time. Except in a very few cases, this technique is commonly applicable.

Driving force for implementation

Reduced energy consumption and the associated CO₂ emission within the refinery.

Example plants

Heat integration procedures are extensively applied in crude units. Progressive distillation is the stream of heat integration between atmospheric and vacuum distillation.

Reference literature

[174, HMIP UK 1995], [155, API 1993], [221, Italy 2000].

4.19.3 Heat integration of the vacuum distillation units

Description

The number of side-streams in a high vacuum unit is chosen to maximise heat integration for producing streams at different temperatures, rather than to match the number of products required, with the exception of the lube oil vacuum distillation units. Heat integration with the

crude units can be achieved. The atmospheric residue is then taken directly from the crude distillation unit to the vacuum furnace, and the product streams and circulating refluxes of the high-vacuum unit are cooled against the crude oil.

The main feed stream to the high-vacuum unit is the bottom stream of the crude oil distillation unit, referred to as atmospheric or long residue, which is either supplied directly hot or (relatively) cold from storage tanks. The latter option requires higher energy consumption.

The application of advanced process control to optimise the energy utilisation within the crude unit.

Achieved environmental benefits

Reduction of fuel consumption in the refinery.

Cross-media effects

In the case of highly heat-integrated units, the refinery complex as a whole becomes more susceptible to unstable conditions arising in an individual unit.

Applicability

Integration in retrofitting application will normally depend on the plot space available and the possibility to execute these modifications in the available shutdown time. Except in a very few cases, this technique is commonly applicable.

Driving force for implementation

To reduce fuel consumption and the associated CO₂ emission within the refinery.

Example plants

Heat integration procedures are extensively applied in vacuum units. Progressive distillation is the stream of heat integration between atmospheric and vacuum distillation.

Reference literature

[174, HMIP UK 1995], [155, API 1993], [221, Italy 2000].

4.19.4 Use of vacuum pumps and surface condensers

Description

This technique consists of the use of vacuum liquid ring compressors instead of steam ejectors.

Achieved environmental benefits

Vacuum pumps and surface condensers have largely replaced barometric condensers in many refineries to eliminate this oily waste water stream. Replacing the steam ejectors by vacuum pumps will reduce the sour water flow from 10 to 2 m³/h. The vacuum may be generated by a combination of vacuum pumps and ejectors to optimise energy efficiency. Other benefits are linked with cross-media effects.

Cross-media effects

Replacement of the steam ejectors by vacuum pumps will increase the electricity consumption for vacuum generation, but will reduce the heat consumption, the cooling water consumption, the electricity consumed for cooling pumps and the consumption of agents used for the conditioning of cooling water. Within the refinery, there are many processes where surplus steam can be recovered and used for the production of vacuum. However, an energy management analysis will help to decide whether the use of surplus steam for steam ejection instead of applying vacuum pumps is more efficient than using surplus steam for other purposes. The reliability of both systems are also to be taken into account, as usually steam ejectors are more reliable than vacuum pumps.

Operational data

The use of vacuum pumps consumes electricity.

Applicability

May not be applicable in retrofit cases. For new units, vacuum pumps either in or not in combination with steam ejectors to achieve a high vacuum (10 mm Hg), are needed as well as a spare in case the vacuum pump fails.

Driving force for implementation

To reduce the production of waste water.

Example plants

At present, vacuum pumps are used more often than ejector sets.

Reference literature

[155, API 1993], [207, TWG 2001].

4.19.5 Reduction of the vacuum pressure in the vacuum distillation unit

Description

Lowering the vacuum pressure, e.g. down to 20 - 25 mm Hg, will allow a reduction in the furnace outlet temperature, while maintaining the same target cut-point of the vacuum residue.

Achieved environmental benefits

This technique would provide some benefits, both in terms of energy conservation and pollution reduction. The environmental benefits are:

- a lowered potential for cracking or coking at furnace tubes;
- a reduced cracking of feed to lighter products;
- a lowered furnace fired duty and hence lowered fuel consumption.

Cross-media effects

Energy (electricity or steam) is necessary to generate the vacuum.

Applicability

Applicability is usually limited by the tower capacity, the condensing fluid temperature, or other material restrictions.

Driving force for implementation

Reduce the heat duty of the vacuum distillation process.

Reference literature

[221, Italy 2000], [155, API 1993].

4.19.6 Treatment of non-condensables from the vacuum ejector set condenser

Description

These techniques to control releases from vacuum units include processes such as amine scrubbing (see Section 4.23.5.1), compression into refinery fuel gas and burning in adjacent process furnaces, or combinations thereof. The gases from some units may contain significant amounts of air and such gases are normally combusted best locally. Amine scrubbing techniques may need to be applied carefully, as hydrocarbon contamination could cause foaming problems in amine regeneration units.

Non-condensables from overhead condensers can be passed to light ends treatment or recovery systems or refinery fuel gas systems; sour incondensable gases vented from sealed barometric pumps of vacuum distillation units should be extracted and dealt with in a manner appropriate to the nature of the sour gas.

This is a control technique applicable to the non-condensable emissions vented from the vacuum ejectors or pumps, consisting of venting into blowdown systems or refinery fuel gas systems and incineration in furnaces or waste heat boilers.

Achieved environmental benefits

Vacuum distillation column condensers may emit 0.14 kg/m³ of vacuum feed and can be reduced to negligible levels if they are vented to the heater or incinerator. Pollution reduction is achieved if vacuum gaseous streams (vent gas) are routed to an appropriate amine scrubbing unit instead of being directly burnt in the process heater. Vacuum vent gas routing to scrubbing requires significant investment due to compressor costs.

The efficiency of incineration control techniques is generally greater than 99 % as regards NMVOC emissions.

Cross-media effects

In the incineration technique, the combustion products have to be accounted for. Reuse of waste water generated by the overhead reflux drum might have an effect on the desalter pH and the desalted yield of some components.

Applicability

Fully applicable.

Operational data

Questionnaire 15 reports that the non-condensable streams from vacuum distillation, currently routed to furnace, involve typically a small flowrate with high concentration of H₂S. It is estimated to represent close to 15 % of the total sulphur refinery emissions. A project is ongoing for treating these streams through an amine unit to therefore reduce these emissions. Similar projects are reported for other refinery sites.

Driving force for implementation

To reduce the emissions of pollutants, for example in the context of a 'bubble' approach.

Example plants

Applied in some European refineries.

Reference literature

[172, MRI 1997], [171, UN/ECE 1998], [Questionnaire 15]

4.19.7 Waste water treatment and reuse

Description

This topic is also treated in Section 4.15.4. Techniques to consider are the following:

- Reuse of waste water generated by the overhead reflux drum. This water can be reused as a desalter wash water.
- Passing sour water from atmospheric and vacuum unit condensates to a stripper in enclosed systems.
- Optimising water reuse by application of side-stream softening to blowdown streams.

Achieved environmental benefits

Reduction of water consumption and reabsorption pollutants.

Applicability

Fully applicable.

Driving force for implementation

Reduce water consumption.

Reference literature

[155, API 1993].

4.19.8 Other techniques to consider in the atmospheric units**Description**

Some other techniques to consider are given below.

- Where applied, ammonia injection should be handled in enclosed systems. Alternative neutralising techniques are available and can reduce the ammonia/ammonium load on sour water and sulphur recovery systems.
- De-coking vents need to be provided with suitable knock-out and dust suppression facilities; suitable methods for preventing emissions during clean-out procedures need to be used.
- Many oily sludges can be sent to crude distillation (or an alternative to the coking unit. See Section 4.7.5) where they become part of the refinery products. This technique typically implies sending the light slops to floating roof tanks (double sealed), and the heavy slops typically to fixed roof tanks. Typically the heavy slop after settling is blend with liquid fuel. The blended light slops after enough settling may also be blended with liquid fuel or sent to the crude distillation at a mixing rate to avoid fouling.
- Pressure relief valves on column overheads; relief from overhead accumulator should be piped to flare, as should the vent points.
- Use of spent caustic instead of fresh caustic for corrosion control on distillation unit. (for more information see Section 4.20.2).
- New additives (amines) can substitute caustic for corrosion control.
- Special additives (thiophosphates) can be used for treating naphthenic crudes.
- Online cleaning (wet or dry) of heater convection sections.
- Floating pressure control: operating the column at the minimum possible pressure minimises the energy cost of separation and improves tray efficiencies and latent heating from vaporisation. The disadvantage is that the operating temperature is no longer an indication of composition.

Operational data

The process of oily sludges in the crude distillation may generate problems in the desalter or may foul up the heat exchangers of the distillation column.

Reference literature

[155, API 1993], [207, TWG 2001].

4.20 Product treatments

A brief explanation on which kind of processes are included within this section is given in Section 2.20 and within the Scope.

4.20.1 Cascading of caustic solutions

Description

An overall reduction in the caustic consumption of wet treating units can be achieved if semi-spent caustic from one treating unit can be reused in another one. A typical example of this procedure is the use of the bleed of regenerated caustic (e.g. in mercaptan treaters for catcracked gasoline or for the removal of H₂S or thiophenols) in a pre-wash step of the non-catalysed cat cracked gasoline sweetening processes. An example of a caustic integration scheme is given in Figure 2.31.

Achieved environmental benefits

Reduction of the use of caustic solutions.

Operational data

Systems handling spent caustic require particular care regarding sulphur compounds.

Economics

Table 4.70: Data on costs associated with various gasoline and distillate sweetening processes

Product	Types of gasoline sweetening processes	Estimate capital cost EUR million	Est. operating cost, EUR/m ³
LPG	Extraction ⁽¹⁾	2.2	0.05
Light naphtha	Minalk	1.1	0.04
	Caustic-free	1.1	0.15
Heavy naphtha and kerosene	Conventional fixed-bed	2.6	0.18
	Caustic free	2.6	0.40

⁽¹⁾ Include pretreating and post-treating facilities.
Sample economics of the MEROX process on the basis of 1 590 m³ per stream day capacity for various applications. The capital costs are for modular design, fabrication and erection of MEROX plants. The estimated modular cost is inside battery limits, US Gulf coast, FOB point of manufacturer. The estimated operating costs include catalysts, chemicals, utilities and labour.

Sweetening treatment is much cheaper than hydrotreating, both in terms of capital investment and operational costs. The caustic is normally almost fully regenerated and only a small bleed results.

Reference literature

[166, CONCAWE 1999], [175, Meyers 1997], [158, CONCAWE 1990].

4.20.2 Management of the spent caustic

Description

Caustics are used to absorb and remove hydrogen sulphide, mercaptans and phenol contaminants from intermediate and final product streams. Spent caustic solutions from some sweetening units are odorous and need to be handled in enclosed systems and treated as necessary before release at a controlled rate to the effluent system. Several techniques exist to

maximise the reuse of caustics within a refinery. They include recycling within the refinery or outside the refinery or destruction within incinerators.

Techniques to consider are:

- Neutralisation and stripping.
- Incineration which can be an appropriate alternative to waste water treatment because of the very high concentration of cresylics, naphthenes, mercaptans and other organic compounds in spent caustic solutions (COD>>>50 g/l).
- Handling and disposing of dry spent caustic in a manner that prevents dust generation. It should not be disposed of to the land.
- Reuse of spent caustic within the refinery.
- Corrosion control on crude distillation units using spent caustic rather than fresh caustic. Unstable chloridic (magnesium) salts that are not extracted from the crude oil in the desalter will decompose upon heating to the crude distiller and cause chloridic corrosion. To prevent corrosion of the exposed equipment, small quantities of caustic (sodium) are injected in the crude oil feed by which the chloridic components are neutralised due to the formation of stable sodium chloride. For the purpose of the neutralisation of chloridic decomposition products, often spent caustic can be used, which is recommended as well to minimise waste generation.
- Recycling to downstream of the crude desalter or sour water strippers.
- Addition to biotreaters for pH control.
- Recycling caustics containing phenols on-site by reducing the pH of the caustic until the phenols become insoluble thereby allowing physical separation. The caustic can then be treated in the refinery waste water system.
- Reusing spent caustic (generally classified into: sulphidic, cresylic and naphthenic) outside the refinery:
 - In paper mills (sulphidic caustic only);
 - As raw material for Na_2SO_3 (may require segregation of various caustics).
 - In chemical recovery companies if concentrations of phenol or hydrogen sulphide are high enough. Process changes in the refinery may be needed to raise the concentration of phenols in the caustic to make recovery of the contaminants economical.
- Regenerating or oxidising spent caustic by:
 - treatment with hydrogen peroxide.
 - fixed-bed catalyst.
 - pressurised air: 120 – 320°C; 1.4 - 20.4 MPa.
 - biological system.

Achieved environmental benefits

Reduction of odour emissions and caustic use.

Cross-media effects

The cross-media effects found in the different techniques mentioned above are given below.

- The presence of caustic within the crude unit may enhance the coke formation within downstream units.
- The increase of phenols and BTX loads to waste water treatment. As a consequence, the degradation efficiency of the biotreater can be adversely affected or the emissions from the waste water treatment plant for these components can increase. Mercaptans, cresyls, and naphthenes can have an adverse impact on the biotreatment system.

Operational data

Systems handling spent caustic require particular care regarding sulphur compounds.

Driving force for implementation

To reduce caustic use.

Example plants

A number of refineries are able to regenerate their spent caustic, but others have to dispose of some excess quantities, mainly from caustic pre-wash activities. Usually these quantities are small and can be managed within their effluent treatment system or, if this is not the case, they are disposed of via contractors for use as a bleaching agent in the paper and pulp industry. Some refineries sell their concentrated phenolic caustic for the recovery of cresylic acids. Some refineries work up the phenolic caustics themselves. From the extraction process, the disulphide recovered can be sold as product, or be recycled to a hydrometer or incinerator.

Reference literature

[166, CONCAWE 1999], [202, Dekkers 2000], [207, TWG 2001].

Description

Foul air vented from sweetening processes contains sulphur compounds that typically have a strong odour. The range of quantity of sulphur in the foul air vented from the sweetening processes is around 0.7 – 7 kg/day (disulphide concentration can be as high as 400 ppm) for a 10 000 t/d crude unit and the percentage contribution it makes to the stack gases where it is incinerated has been estimated at 0.16 – 2.48 %. For this reason, the abatement prior to incineration is not justified and the foul air vented from sweetening processes is incinerated in local furnaces.

Reference literature

[207, TWG 2001].

4.20.3 Replace clay filtration with hydrotreating

Description

Where a need to remove colour bodies and olefins exists, hydrotreating replaces clay filtration as the method of choice. Hydrotreating does a better job of improving colour and increasing stability against oxidation, and has no yield loss (the oil measured in the spent filter clay represents a loss of some of the most valuable products produced in a refinery). It also eliminates the problem of spent clay disposal.

Achieved environmental benefits

Reduction of waste generation.

Cross-media effects

Need for hydrogen and energy consumption. See Section 4.10.2.3.

Operational data

See Section 4.10.2.3

Economics

See Section 4.10.2.3.

Driving force for implementation

Product requirements.

Reference literature

[164, Noyes 1993].

4.20.4 Catalytic dewaxing

Description

The removal of wax is necessary to produce lubricating oil which meets desired low temperature properties. Many processes require solvent, chilling and filtration stages for separation.

Catalytic dewaxing processes, based on selective molecular sieve-based catalyst, typically produces a lower-pour product than solvent dewaxing. This system produces fuel components instead of waxes. A short description of the technique can be found in Section 2.20.

Achieved environmental benefits

The foul odours and the sulphur content of the products produced with this technique are lower than with solvent dewaxing. The products generated by the cracking of the wax remain as part of the product.

Cross-media effects

Hydrogen consumption, typically 20 – 62 m³/tonne feed (100 – 300 scf/bbl).

Applicability

Fully applicable for new units. Catalytic dewaxing is unlikely to be retrofitted on another type of dewaxing process because it is a completely different process. Catalytic dewaxing has a pour point advantage, but has a viscosity index disadvantage compared to solvent dewaxing.

Economics

Table 4.71 compares the relative cost of debottlenecking a 300 kt/yr solvent extraction complex to 500 kt/yr with the cost involved in the construction of a new 200 kt/yr solvent extraction complex and hybrid debottlenecking with a catalytic dewaxing.

Table 4.71: Cost data for a 200 kt solvent extraction dewaxing unit

Cost parameters	New solvent extraction (200 kt/yr) (% of the total cost)	Hybrid desbottlenecking (from 300 to 500 kt/yr) (% of the solvent extraction cost)
Capital change	36	24 – 36
Fixed costs	20	7 – 9
Variable costs	8	8
Hydrocarbon cost	35	11
Total	100	50 – 64
NB: Investment based on: 795 m ³ /day of lube base oils excluding fuels hydrocracker. Total amount (1998 US Gulf Coast): USD 80 million.		

Driving force for implementation

To produce distillate with a low wax content.

Example plants

One EU refinery has been identified that uses this process to produce distillates with a low wax content.

Reference literature

[183, HP 1998], [191, UBA Austria 1998], [207, TWG 2001].
[76, Hydrocarbon processing 2011].

4.21 Storage and handling of materials

As mentioned before, more information on techniques to consider regarding the storage and handling of materials can be found in the EFS BREF [5, EC 2006]. Among them, the following techniques are these used in the refinery industry.

4.21.1 Underground caverns

Description

More information on all types of caverns can be found in Section 2.21 and in the EFS BREF.

Achieved environmental benefits

- VOC emissions from underground storage caverns are very low or are non-existent. The main reasons are: the temperature of the cavern is low and stable, the product is under pressure and the breathing gases from the cavern are not led to atmosphere but to another cavern.
- The land above caverns is free for other purposes.
- Improves safety.

Cross-media effects

Groundwater leaking into the cavern must be removed and treated with other oily waters.

Applicability

The geology of the site should be adequate to install a cavern: non-porous rock.

Economics

The construction costs of storage caverns are markedly lower than for above-ground tank farms. In Finland, profitability begins at 50 000 m³ under favourable conditions (depends highly on the rock type and the hydrocarbon product to be stored). Maintenance costs have been calculated to be one-sixth these of above-ground tanks.

Driving force for implementation

Prevention of visual intrusion, the reduction of energy consumption, saving of land surface and economic forces for large storage systems. This technique is one of the safest way of storing large amounts of hydrocarbon products.

Example plants

Used in some European countries.

Reference literature

[199, Lameranta 2000], [5, EC 2006].

4.21.2 Internal floating roof tanks

Description

As described in the EFS BREF, an internal floating roof tank (IFRT) has both a permanent fixed roof and a floating roof (or deck) inside. The deck in an IFRT rises and falls with the liquid level and either floats directly on the liquid surface (contact deck) or rests on pontoons several centimetres above the liquid surface (non-contact deck). Contact floating roofs can be:

- aluminium sandwich panels that are bolted together, with a honeycomb aluminium core;
- pan steel decks with or without pontoons;
- resin-coated, fibreglass reinforced polyester (FRP), buoyant panels.

The majority of direct contact floating roofs currently in service are aluminium sandwich panel type or pan steel type.

More information can be found in Section 2.21 and in the EFS BREF.

Replacement of primary/secondary seals with tighter seals which can reduce VOC emissions; might be also applied to IFRTs.

Achieved environmental benefits

Reduction of VOC emissions. Conversion of fixed roof tanks to internal floating roof and seals to minimise evaporation of the product being stored. The control efficiency of this method ranges from 60 to 99 %, depending on the type of roof and seals installed and the true vapour pressure of the liquid stored. The EFS BREF reports that emission reductions potential for installing an IFRT with a primary seal ranged from 62.9 to 97.4 % (estimated using the EPA AP-42 method).

Cross-media effects

The net storage capacity of a fixed roof tank is reduced by approximately 10 %. There is a need to consider flammable atmosphere problems as part of the design.

Operational data

Performance data on emissions and other useful information about IFRT are available in [100, API 2002].

Applicability

IFRTs are widely used in the petroleum industry, however, they are only applicable to vertical fixed roof tanks. An IFRT is less effective in tanks with a small diameter because of the poor effectiveness of the rim seal in small tanks. There are possible compatibility issues between stored products and the IFRT construction materials, e.g. aluminium sheets/pontoons and gasket/sealing materials. Where caustic treatment is included downstream of the process, corrosion on the IFRT might give rise to problems of applicability. Floating suction in existing tanks, high filling rate regimes, mixers and other protuberances all present difficulties in retrofits.

Economics

The costs of retrofits are given in Table 4.72. Costs are dependent on the tank diameter.

Table 4.72: VOC controls in storage

Emission source Control technology	Refinery storage		
	Internal floating roofs in fixed roof tanks	Secondary/double seals on floating roof tanks	Other roof fitting emission controls (roof legs, still wells) and options (tank paint)
Efficiency	90 – 95 %	95 %	Over 95 % when together with secondary seals
Investment costs (EUR million)	0.20 → 0.40 for 20 - 60 metres diameter tanks ⁽¹⁾	0.05 – 0.10 for 20 - 50 metres diameter tanks ⁽²⁾	0.006 for 50 metre diameter tank ⁽¹⁾
Operating costs	Minor	Replacement every 10 years	Minor
Other impacts comments	Requires tank to be taken out of commission reduces the net storage by 5 – 10 %	Can reduce maximum storage capacity of tank	Not suitable for high sulphur crude oils due to pyrophoric scale possibility
References: (Installed and retrofitted)			
⁽¹⁾ UN-ECE/IFARE, and Industry Proprietary Information.			
⁽²⁾ UN-ECE/IFARE and Industry Proprietary Information (UN-ECE EC AIR/WG6/1998/5).			

Driving force for implementation

European Directive 94/63/EC (Stage 1) prescribes either fixed roof gasoline storage tanks are fitted with internal floating roofs (with a primary seal in existing tanks and with secondary seals in new tanks) or are connected to a vapour recovery unit. Vapour destruction is also a technically viable option which may be applied, e.g. when vapour recovery is unsafe or technically impossible because of the volume of return vapour.

Reference literature

[151, Sema,Sofres 1991], [171, UN/ECE 1998], [100, API 2002], [207, TWG 2001], [5, EC 2006].

4.21.3 Fixed-roof tanks

Description

The fixed-roof tank (FRT) can give rise to emissions in the way described below.

- Filling losses; during tank filling the existing tank vapour space, which is more or less saturated with vapour, is expelled to the atmosphere, while when a tank is emptied the incoming air is slowly saturated with vapours, which are then expelled by subsequent filling and/or breathing. Generally these emissions are greater than standing emissions. A technique to reduce VOC from these tanks is to increase the storage pressure by blanketing.
- Breathing losses; during storage of the liquid there will be vapour emissions from tank breathing caused by the difference in night and day temperatures and by changes in atmospheric pressure. To a certain extent, installing pressure/vacuum relief valves and reducing thermal effects by painting the tank a light colour or fitting insulation can reduce breathing losses
- Vapours released during water draining.

The technique that is considered to reduce emissions from fixed roof tanks is to install an internal floating roof.

It is to be noted that blanketing tanks by introducing inert gas is a safety measure to avoid explosive atmosphere but does not prevent the product from evaporating.

Achieved environmental benefits

The installation of an internal floating roof in fixed-roof tanks can reduce VOC emissions up to 90 – 95 % (see Table 4.72)

Cross-media effects

The installation of an internal floating roof in a fixed roof tank requires the tank to be taken out of commission and reduces the net storage by 5 - 10 %.

Operational data

Performance data on emissions and other useful information about FRT are available in [100, API 2002].

Applicability

Fixed roof tanks are typically used for low-or non-volatile material with true vapour pressures (TVP) at less than 14 kPa, e.g. kerosene, heating oil. These tanks can be retrofitted to internal floating roof tanks, but are not suitable for all products, e.g. bitumen tank with an internal floating roof will not work due to bitumen solidifying in the gap between the wall and the internal floating roof.

Economics

The investment for installing internal floating roofs in fixed roof tanks can be EUR 0.2 - 0.4 million for tanks 20 - 60 metres in diameter.

Driving force for implementation

Reduction of VOC emissions.

Reference literature

[160, Janson 1999], [166, CONCAWE 1999], [207, TWG 2001], [100, API 2002].

4.21.4 External floating roofs**Description**

External floating roof tanks (EFRT) are used to store crudes, light products and intermediate stocks having a vapour pressure of more than 14 kPa but less than 86 kPa at normal storage temperature. More information can be found in Section 2.21 and in the EFS BREF.

With external floating roof tanks (EFRT), filling and breathing losses are greatly diminished in comparison with fixed roof tanks. However, the vapour losses described below are inherent to this type of tank and should be minimised:

- Rim seal and roof-fitting emissions, which result from stock vapour pressure changes due to temperature, and pressure variations, but more importantly wind effects as well as openings in the roof. Standing emissions on external floating roof tanks are generally much more significant than withdrawal emissions.
- Wetting losses by evaporation of liquid from the wet wall, when the level of the liquid is lowered by discharge.
- Vapours released during water draining.
- In many cases, for an external floating roof tank, the emissions through fittings can exceed the rim seal losses especially on tanks with secondary seals. In terms of fitting losses, the major source is from the slotted stillwell (sample well or dipping well).

Techniques to minimise emissions of external floating roof tanks include but are not limited to the following:

- installing improved primary seals at the floating deck, e.g. from a vapour mounted to a liquid mounted seal;
- installing sleeves around the pipe, incorporating still well wipers;
- installing floats with wipers inside the slotted pipe;
- landing the floating roof tanks as infrequently as possible to avoid unnecessary vapour releases;
- sealing of all floating roof openings (e.g. gauging poles, support legs) with appropriate wrappings, sleeves or compensators;
- installing secondary or tertiary seals between tank walls and roof (Section 4.21.6);
- designing drains on floating roof tanks appropriately to avoid hydrocarbon contamination of rainwater.

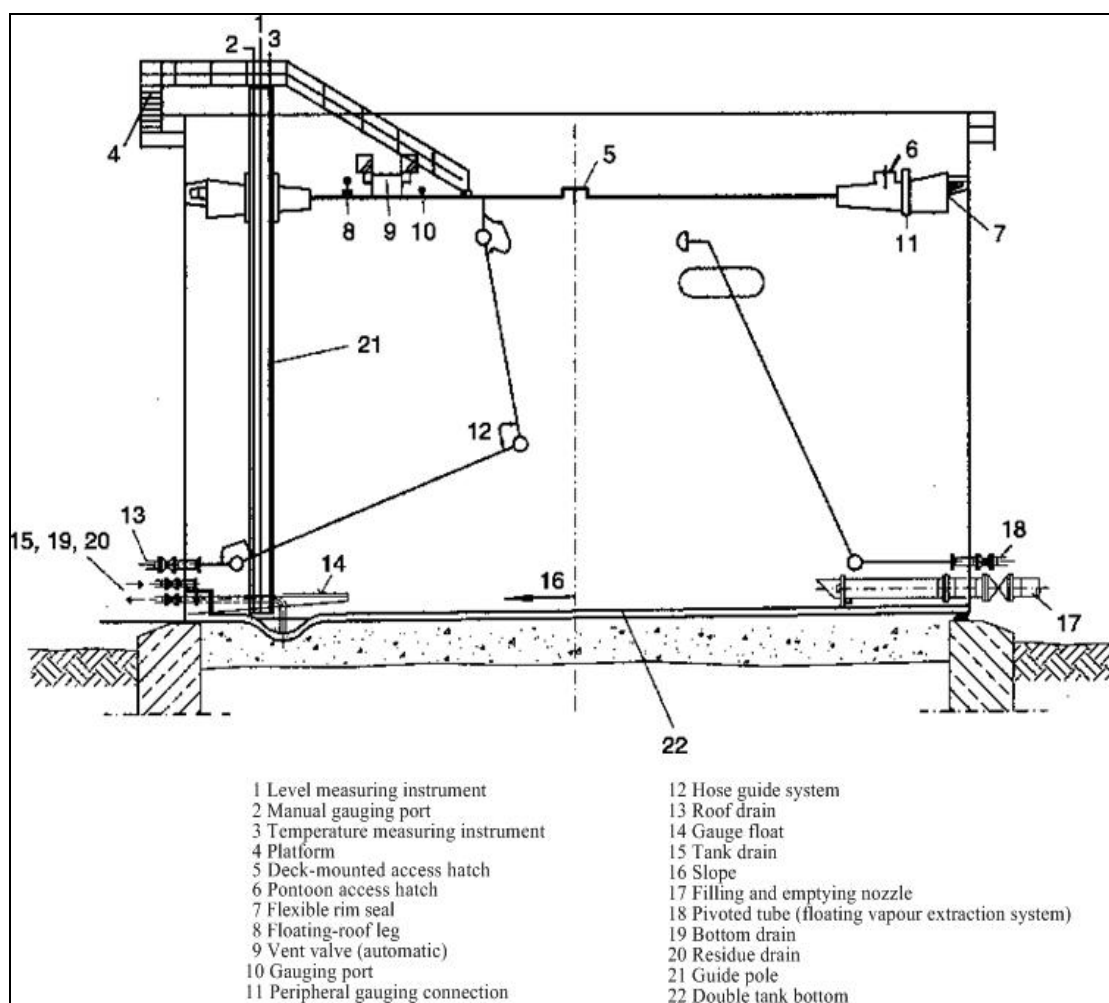


Figure 4.48: Example of a floating roof tank

Achieved environmental benefits

For the same substance, e.g. gasoline, EFRTs have the advantage over fixed roof tanks of significantly lower emissions to the atmosphere of e.g. VOCs. An EFRT can avoid 95 % of the losses from a fixed roof. Product savings give operating benefits.

Cross-media effects

They have potentially more emissions to water than fixed roof tanks, since it is possible for rainwater to enter the tank past the roof seal. Any such water needs to be drained before dispatch of the product to a customer since the quality of the product can be seriously jeopardised.

Operational data

Performance data on emissions and other useful information about EFRT are available in [100, API 2002]. Examples of emissions reduction efficiency (compared to fixed roof tank) when retrofitting external floating roofs are given in the following tables [77, REF TWG 2010].

Table 4.73: Tank construction working hypothesis

Product	Diameter (m)	Height (m)	Calculated annual emissions (kg/yr) ^(*)
Naphtha, heavy	23	14.5	3 942
Naphtha, light	30	17	2 492
Crude oil	57	16.5	5 519
(*) Based on rim seal area, dipping wells/still wells, roof fitting penetrations, without wetting losses Source: TWG 2010 DE			

Table 4.74: Option of sealing and correspondent expected efficiency

	Seal construction	Efficiency (%)		
		Naphtha, heavy	Naphtha, light	Crude oil
Case 1	Double rim seal (fitted secondary seals) dipping wells/still wells not sealed roof legs not sealed	51.8	50	95.7
Case 2	Double rim seal (fitted secondary seals) dipping wells/still wells sealed roof legs sealed	92.5	92	98.3
Case 3	Double rim seal (fitted secondary seals) dipping wells/still wells sealed inkl. helicoat roof legs sealed	93.3	93	98.8
Case 4	Double rim seal (secondary seal with access to ponton) dipping wells/still wells sealed roof legs sealed	95.6	96.1	98.9
Case 5	Triple rim seal dipping wells/still wells sealed roof legs sealed	97.1	97.5	99.1
Case 6	Triple rim seal dipping wells/still wells sealed + helicoat roof legs sealed	97.9	98.1	99.6
Source: TWG 2010 DE				

Applicability

In retrofit situations where a change in the service of the tank is desired, an acceptable alternative to an EFRT is to retrofit a fixed roof tank with an internal floating cover.

Economics

Investment costs for the retrofitting of a fixed roof tank to a EFRT is EUR 0.26 million per tank of diameter 20 m. An operator is necessary for tank draining, giving rise to some operating cost.

Driving force for implementation

Directive 94/63/EC (Annex 1) defines an appropriate floating roof tank as one having at least a VOC release efficiency of 95 % as compared with a fixed roof one with no vapour-containment controls (that is a fixed-roof tank with only a vacuum/pressure relief valve).

Reference literature

[151, Sema,Sofres 1991],[196, CONCAWE 2000],[201, Manduzio 2000],[100, API 2002], [207, TWG 2001],[5, EC 2006],[77, REF TWG 2010],[142, TWG DE 2012].

4.21.5 Pressurised vessels

Pressurised vessels such as bullets and spheres are often fitted with pressure relief valves, which vent to atmosphere or flare. VOC emissions can occur if these valves or bypass block valves have internal leaks. See EFS BREF.

4.21.6 External floating roof seal systems

Description

Two or three seals at the external floating roof rim provide a multiple barrier to control VOC emissions from storage tanks. Fitting secondary and tertiary roof rim seals are efficient techniques for emission reduction. When retrofitting rim seals to floating roof tanks for non-waxy products, the second or third seal can be equipped with a contact element for draining the inner tank wall (additional weather seal function). Rim-mounted seals (as opposed to shoe-mounted seals) are favoured, since the former offer emission control if the primary seal fails.

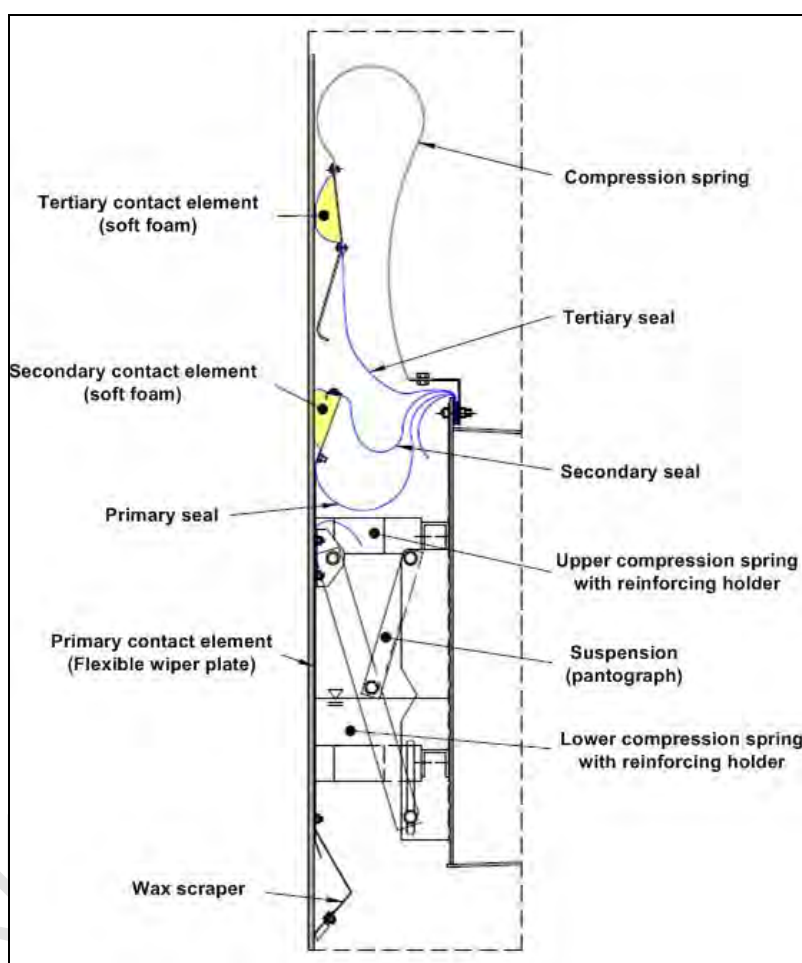


Figure 4.49: Example of multiple seal for external floating roof tank used in a German refinery

Achieved environmental benefits

VOC emissions can be significantly reduced by installing secondary and tertiary seals on storage tanks. The Amoco/US EPA joint study estimated that VOC losses from storage tanks could be reduced by 75 to 95 % compared to emissions generated by a fixed-roof tank of the same capacity without any floating roof. Tertiary seals can achieve up to a 99 % reduction (see Section 4.21.2). When they are applied to EFRT, secondary seals also reduce the likelihood of rainwater ingress into the tank. Secondary seals for gasoline storage can reduce VOC emissions by up to 95 %.

Cross-media effects

Retrofitting seals usually results in a loss of operating capacity by about 5 %.

Operational data

Performance data on emissions and other useful information about rim seals are available in [100, API 2002].

Applicability

Multiple seals can be readily installed in new units (named double or triple seals) and can also be generally retrofitted (as secondary seals). It is reported to be generally difficult to retrofit tertiary seals.

Economics

Equipping an average tank with a secondary seal system was estimated to cost about USD 20 000 (1991). Investment costs: EUR 0.05 - 0.10 million for tanks with a 20 - 50 metre diameter. Operating costs: replacement likely every 10 years.

Driving force for implementation

European Directive 94/63/EC (Stage 1) prescribes secondary seals for external floating roof tanks and for new internal floating roof tanks for gasoline storage in refineries and terminals.

Example plants

Secondary seals are of common use worldwide. In Sweden, all tanks with light products (Reid vapour pressure higher than 27 kPa) are equipped with double seals roofs. Tertiary seals are used in several refineries and depots in Germany.

Reference literature

[151, Sema,Sofres 1991], [196, CONCAWE 2000], [100, API 2002], [207, TWG 2001], [28, Tebert et al. 2009].

4.21.7 Storage strategy**Description**

The need for certain tanks can often be eliminated through improved production planning and more continuous operations. This technique is closely related to Section 4.15.2. An example is the implementation of an in-line blending system (see Section 4.21.14).

Achieved environmental benefits

Since storage tanks are one of the largest sources of VOC emissions, a reduction in their number contributes to a reduction of VOC emissions. By minimising the number of storage tanks, tank bottom solids and decanted waste water may also be reduced.

Applicability

The reduction in the number of tanks typically requires a full change in the management of product and intermediates. As a consequence, this technique is more easily applied to new units.

Driving force for implementation

Space usage can be improved by reducing the number of storage tanks in operation.

Reference literature

[207, TWG 2001].

4.21.8 Prevention of leakage through tank bottoms

This follows techniques to consider in the determination of BAT for the prevention of leakage through tank bottoms. This topic is well documented in EEMUA publication 183 'Guide for the Prevention of Bottom Leakage from Vertical, Cylindrical, Steel Storage Tanks'.

4.21.8.1 Double bottoms tank

Description

Double bottoms can either be retrofitted to existing tanks or incorporated into the design of new tanks. If retrofitted, the existing tank bottom is normally used as the secondary flooring, and sand, gravel or concrete can be installed between the new primary and the secondary floors. In this case, it is general practice to keep the interstitial space to a minimum and therefore the secondary bottom should slope in the same way as the primary bottom. The slopes to the base of tanks can be either straight, cone-up (sloping from the centre down to the tank perimeter) or cone-down (sloping downward from the tank perimeter). Nearly all tank floors are made of carbon steel. If a double bottom is to be installed (either retrofitted or newly built), there are choices in material selection for the new floor. A second carbon steel floor can be utilised or a more corrosion-resistant stainless steel floor can be installed. A third choice is to use a glass fibre-reinforced epoxy coating over the steel.

The use of double bottom tanks allows a vacuum system to be installed, and in this case the space between the lower and upper floor is not filled, but retained as an air space using steel spacers (which can typically be made of steel reinforcement mesh). In this more recent system, the space between the floors is kept under a vacuum that is continuously monitored. Any leak in the primary or secondary floor will dissipate the vacuum and trigger an alarm. A further test of the extracted air will indicate an upper floor failure if product or vapours are present, or a lower floor failure if neither product nor vapours are present (subject to any previous underfloor contamination).

Achieved environmental benefits

Installing a second impervious bottom to a tank provides a measure of protection against non-catastrophic releases due to corrosion, faulty weld joints, or flaws in the bottom material or the construction details. In addition to containment, the secondary bottom provides a means of allowing detection of a bottom leak which is not obviously visible to an operator, as a similar shell defect would be.

Cross-media effects

In the case of retrofitting, the application of this technique may prolong the outage time of tanks during the installation of the double tank bottom. Its application can reduce the capacity of the tank.

Operational data

By installing double tank bottoms, the time between inside inspections and the number of annual tank cleaning procedures are decreased.

Applicability

Applicable to either retrofitted or newly built tanks.

Economics

Typical retrofitting costs for double tank bottoms, as quoted from German or Swiss suppliers, are as follows and include the provision of a vacuum leak detection system:

- carbon steel: EUR 110/m²
- stainless steel: EUR 190/m²
- glass fibre-reinforced epoxy: EUR 175/m²

A UK refinery reported that the actual cost of installing a double bottom on a 10 340 m³ tank was EUR 600 000.

Driving force for implementation

Prevention of leaks from storage tanks.

Reference literature

[197, MWV 2000], [163, FWE 1999].

4.21.8.2 Impervious membrane liners**Description**

The impervious membrane liner is a continuous leak barrier under the entire bottom surface of the tanks. It can be an alternative to a double tank bottom or it can be added as an extra measure of safety below the double tank bottom. Like the double tank bottom, it is primarily intended to arrest the small but persistent leak rather than address a catastrophic failure of the entire tank. The key to an effective liner is that the seams need to be liquid-tight against either the steel shell of the tank or the concrete wall that supports and surrounds the tank. The minimum thickness of the flexible membrane is 1 mm, although 1.5 to 2 mm thick sheets are commonly used. The membrane needs to be chemically resistant to the product stored in the tank.

Achieved environmental benefits

Prevention of leaks from storage tanks.

Cross-media effects

Prolonged tank outage if the liner has to be retrofitted to an existing tank.

Applicability

Impervious membrane liners can be installed either in a new-build design or as a retrofitted design, especially during the overhaul of a tank, and they generally include a leak detection system.

Economics

Recently updated costs data (2011) from UK operators (*Source*: UKPIA) are shown in Table 4.75.

Table 4.75: Estimated costs for retrofitting impervious membrane liners to different tanks

Small tanks		Medium tanks		Large tank	
3 small tanks (22 m (dia), 20 m (h), sharing a bund)		3 medium tanks (48.5 m (dia), 20 m (h), sharing a bund)		1 large tank (81m (dia), 20 m (h), dedicated bund)	
Tank volume m ³ (single tank)	7 603	Tank volume m ³ (single tank)	36 949	Tank volume m ³	103 060
Tank footprint m ² (single tank)	380	Tank footprint m ² (single tank)	1 847	Tank footprint m ²	5 153
Required bund area (all tanks, 2m wall height)([^])	4 942	Required bund area (all tanks, 2m wall height) ([^])	24 017	Required bund area (2m wall height) ([^])	56 683
Cost for installing membrane under the tank floor					
	EUR([^])		EUR([^])		EUR([^])
Lining of bund floor	317 755	Lining of bund floor	1 672 754	Lining of bund floor	4 787 890
Lining bund walls	282 575	Lining bund walls	621 892	Lining bund walls	1 038 379
Lining under tanks	110 079	Lining under tanks	535 644	Lining under tanks	498 195
Jacking	680 904	Jacking	1 021 356	Removing and replacing tank floor	907 872
Total per bund	1 391 314	Total cost per bund for a typical installation	3 851 647	Total per bund	7 232 335
Total per tank	464 150	Total cost per tank for a typical installation	1 284 639	Total cost per tank for a typical installation	7 232 335
Cost for replacing tank floor, installing new tank foundation					
Lining of bund floor	317 755	Cost of lining of bund floor	1 672 754	Lining of bund floor	4 787 890
Lining bund walls	282 575	Cost of lining bund walls	621 892	Lining bund walls	1 038 379
Installing new foundation and replacing tank floor	1 429 898	Cost of installing new foundation and replacing tank floor	2 859 797	Installing new foundation and replacing tank floor	1 815 744
Total per bund	2 030 229	Total cost per bund for a typical installation	5 154 443	Total per bund	7 642 013
Total cost per tank for a typical installation					
Small tank	676 743	Medium tank	1 718 148	Large tank	7 642 013
^(^) EUR Costs based on currency conversion from GBP of 1.13484 on 25/07/2011. NB: Required bund area is based on 110 % of the tank rated capacity for the largest tank in the bund Costs related to project management and design, tank emptying and cleaning are excluded , but expected to be 10-15 % of total cost per tank. For large tanks >48.5m in diameter, tank jacking is not an option, therefore costs are based on an estimate for removing and replacing tank floor. Costs related to the need to hire tank space during extended outage to complete works (likely to be 9 months per tank) are also excluded . The lining of bund walls includes fixing at the top of the bund wall, and sealing it to existing bund flooring (where applicable). Installing a new tank foundation after removing the existing tank floor may be a more effective solution where the ground is too permeable or where there is concern that the liner may not remain intact following replacement of the tank. No account has been taken of the increase in business rates following secondary and tertiary containment upgrades. Bund wall lengths are likely to increase depending upon the shape of the bund, also bund height of 2m does not take into account the slope of the bund wall, which will increase the area. Source: CONCAWE/UKPIA 2011					

Driving force for implementation

To prevent soil contamination.

Example plant(s)

Impervious membrane liners are used in lieu of double bottoms in a number of non-European countries.

Reference literature

[151, Sema,Sofres 1991], [207, TWG 2001].

4.21.8.3 Leak detection

Description

As with sewers, one way to protect against soil and groundwater contamination is by detecting leaks at an early stage. Leaks through a tank bottom can be detected by a leak detection system. Conventional systems include inspection ports, inventory control and inspection wells. More advanced systems include electronic sensing probes or energy pulse cables whereby product that comes into contact with the probe or cable will alter its impedance and trip an alarm. In addition, it is common practice to use a variety of inspection procedures on tanks at intervals to prove their integrity. See also Section 4.23.6.1 LDAR programme. Some techniques to consider are:

- equipping storage tanks with overflow alarms and, if appropriate, automatic pump shut-offs;
- installing double bottoms with integrated leak detection systems on tanks where practicable.

It is to be noted that, based on past incidents, a systematic risk analysis is needed to apply the appropriate recommendations to avoid overfilling tanks.

Relief valves on pressurised storage should undergo periodic checks for internal leaks. This can be carried out using portable acoustic monitors or, if venting to atmosphere with an accessible open end, tested with a hydrocarbon analyser as part of an LDAR programme.

Achieved environmental benefits

Prevention of soil and groundwater contamination.

Applicability

Probes and cables have to be packed pretty densely if the leak to be detected is small. Consequently, inspection, where possible, may in some cases be more reliable than probes.

Economics

One refinery reported that the installation of a leak detection system on a group of four 12 m diameter tanks cost a total of EUR 55 000 with an operating cost of EUR 4 000 per year. The routine inspection of tanks at another refinery was quoted as EUR 2 000/tank per year.

Driving force for implementation

To prevent soil and groundwater contamination.

Reference literature

[197, MWV 2000].

4.21.8.4 Cathodic protection

Description

To prevent corrosion on the underside of the tank bottom, tanks can be equipped with cathodic corrosion protection.

Achieved environmental benefits

Avoidance of soil and groundwater contamination and air emissions due to the prevention of corrosion.

Cross-media effects

Electricity is needed when impressed current cathodic protection (ICCP) requires a DC power source.

Driving force for implementation

To prevent the corrosion of tanks and pipes, and to reduce the maintenance costs.

Reference literature

[197, MWV 2000], [101, INERIS 2008].

4.21.9 Tank farm bund containment

Description

Whereas double tank bottoms or impervious liners protect against the small but incessant leak, a tank farm bund is designed to contain large spills (for safety as well as for environmental reasons), such as caused by a shell rupture or a large spill from overfilling. The bund consists of a wall or dyke around the outside of the tank to contain all or part of the tank contents in the event of a spill, and (in some cases) an impermeable ground barrier between the tank and the dyke to prevent infiltration of the product into the ground. The dyke is typically constructed of well-compacted earth or reinforced concrete. The height is normally sized to accommodate the maximum contents of the largest tank within the volume enclosed by the dyke. If, due to the local soil conditions, there is risk of material loss to the substrate then an asphalt, concrete or high density polyethylene liner may be used to provide a barrier.

Achieved environmental benefits

Containment of large spills from liquid storage tanks.

Cross-media effects

This technique might call for the soil to be compacted, which may be seen as a negative impact. A study in the United States has concluded that the effectiveness of liners in protecting the environment is limited because of their unreliability and the difficulty in inspecting or testing their integrity. Also, there are few releases that would be contained by such liners, and moreover, they are expensive to install. Because of this, it was concluded that other preventative measures are more effective in protecting the environment and are more cost-effective in the long run.

Applicability

In some cases, retrofitting may not be possible.

Economics

Some refineries have quoted the total cost for installing concrete paving under 6 large tanks at EUR 1.3 million (0.22 million per tank), the cost of sealing the bund dyke walls with asphalt (around 10 tanks) at EUR 0.8 million, and the cost of concrete paving bunds at EUR 70 - 140/m². One refinery quoted the cost of installing 200 m of impermeable HDPE barrier along the site boundary at 150 000 EUR (EUR 750/m).

Driving force for implementation

Containment of large spills that may occur from liquid storage tanks is normally regulated by national laws. In Italy, current legislation foresees for some liquids a volume of the bund less than 100 % of the tank volume. French regulation requires any liquid storage to be associated with a containment volume superior to the highest value from:

- 100 % biggest tank volume;
- 50 % total capacity of associated tanks.

Reference literature

[174, HMIP UK 1995].

4.21.10 Reduction of the generation of tank bottoms

Description

Minimisation of tank bottoms can be carried out through careful separation of the oil and water remaining in the tank bottom. Filters and centrifuges can also be used to recover the oil for recycling. Other techniques to consider are the installation of side entry or jet mixers on tanks or the use of chemicals. This means that basic sediment and water is passed on to the receiving refineries.

Achieved environmental benefits

Tank bottoms from crude oil storage tanks constitute a large percentage of refinery solid waste and pose a particularly difficult disposal problem due to the presence of heavy metals. Tank bottoms are comprised of heavy hydrocarbons, solids, water, rust and scale.

Cross-media effects

Passing the sediments and water from the crude oil tanks to the refinery means that they will most probably show up in the desalter.

Reference literature

[174, HMIP UK 1995].

4.21.11 Tank cleaning procedures

Description

For routine internal tank inspections and for the purpose of repair, crude oil and product tanks have to be emptied, cleaned and rendered gas-free. A technique to clean tank bottoms includes dissolving the majority of the tank bottom content (>90 %) with hot diesel fraction at temperatures of around 50 °C, where it dissolves most of the tank bottom contents and they can be blended after filtration to the crude tanks. Oil tank cleaning is traditionally performed by workers entering the tank and removing sludge manually, thus they are exposed to potentially explosive and toxic atmospheres. Fully automated techniques of tank cleaning are also available typically using the following procedures.

- Installation of the process equipment: low pressure/high impact nozzles are installed either in the tank roof or through the existing wall manholes and operated over the liquid surface.
- Tank blanketing: an inert gas is injected and monitored to maintain an oxygen level below 8 %, securing non-igniting conditions.
- Desludging and cleaning: the sludge is sucked out and recirculated via the cleaning nozzles, using the oil in the tank as a cleaning agent. If needed, crude oil or gas oil is added and/or the recirculated media is heated to lower the viscosity.
- Oil separation and recovery: part of the sludge is mechanically separated (decanter) without the addition of chemicals.
- Water wash: final wash with hot water is performed and finally the inert gas is vented.

Achieved environmental benefits

Emissions during the cleaning of tanks arise during natural or mechanical ventilation. With specific measures, e.g. installation of mobile flares, which are currently under development for cleaning crude oil and product tanks, further emission reductions of VOC of up to 90 % can be expected. Automated tank cleaning techniques working in closed-loop systems, where the atmosphere from the oil tank is degassed, reduce the venting of VOC to the ambient air.

Cross-media effects

When natural or forced ventilation is used, VOC emissions may be significantly higher during tank cleaning when compared to VOC emission from normal operation of an oil tank. Due to the recirculation of water, automated cleaning achieves savings of fresh water and reuse of the

oil as a cleaning agent. Electricity consumption for the cleaning process and generation of inert gas is higher than for manual cleaning. Solid and liquid waste is reduced by using automated cleaning. Closed loop systems under inert conditions lead to safer conditions, as risk of explosion and human exposure to hazardous substances are reduced.

If the refinery operates its own sludge incineration plant, cleaning residues can be supplied to it.

Operational data

The emissions arising during the cleaning of crude oil tanks and the reduction of these emissions are exhaustively described in [222, UBA 2000]. The use of hot diesel to clean up the tank bottoms requires heating. The corresponding consumption is strongly dependent on the type and size of tank and the type of residues processing. According to information from a supplier of automated tank cleaning [102, ORECO 2011] the following operational data are reported.

Table 4.76: Typical crude oil tank cleaning utility requirements

	Automated cleaning	Manual cleaning
Hydrocarbon emissions	1 to 2 tonnes	30 to 50 tonnes
Fuel consumption	30 000 to 70 000 litres depending on the need for heating	20 000 to 25 000 litres
Waste for incineration	20 to 50 m ³	2 000 to 5 000 m ³ depending on the volume used for cleaning
Waste water	20 to 50 m ³	Approx. 500 m ³
NB: Crude oil tank: diameter 50 to 80 m - floating roof - 2 000 m ³ oil sludge		

Applicability

Tank cleaning procedures are generally applicable. Applicability may nevertheless be limited by the type and size of tanks and the type of residues processing.

Economics

According to the operational costs given in Table 4.77 are typical for crude oil tank cleaning [102, ORECO 2011].

Table 4.77: Typical crude oil tank cleaning estimated costs

	Automated cleaning	Manual cleaning
Direct cleaning cost	300 000	200 000
Waste transportation	5 000	100 000
Waste disposal or processing	10 000	200 000
Overall costs (EUR)	315 000	500 000
NB: Crude oil tank: diameter 50 to 80 m - floating roof - 2 000 m ³ oil sludge.		

Driving force for implementation

To reduce VOC emissions and tank bottom content.

Example plants

Examples exist of applications in many EU refineries and tank farms.

Reference literature

[167, VDI 2000], [228, TWG 2000], [222, UBA 2000], [170, REPSOL 2001],
[102, ORECO 2011].

4.21.12 Colour of tanks**Description**

It is preferable to paint tanks containing volatile materials a light colour for the reasons given below.

- To prevent increasing the evaporation because of increased product temperature.
- To prevent increasing the breathing rate of fixed roof tanks. A total heat reflectance coefficient of a minimum of 70 % is recommended. This coefficient can be achieved by using colours with a low-coating factor, e.g. white (1.0) or aluminium silver (1.1). On the contrary, any of the other colours usually used, including light grey, show significantly higher factors (>1.3), which does not allow to achieve the coefficient mentioned above.

Achieved environmental benefits

Reduction of VOC emissions.

Cross-media effects

Depending on the geographical landscape context, painting in light colours can result in tanks being more 'visible' but can have a negative visual effect. Emissions may occur while painting is taking place.

Applicability

Painting the roof and the upper part of the shell of a tank in the middle of a tank farm can be almost as effective as painting the entire tank.

Driving force for implementation

Using this technique is also a requirement of Directive 94/63/EC for gasoline tanks, except where there are derogations for visually-sensitive areas.

Reference literature

[205, Jansson 2000], [207, TWG 2001], [222, UBA 2000], [28, Tebert et al. 2009].

4.21.13 Other good storage practices**Description**

Proper material handling and storage minimises the possibility of spills, leaks and other losses which result in waste, air emissions and emissions to water. Some good storage practices are listed below (other useful information is available in the EFS BREF [206, EIPPCB 2001]):

- Use larger containers instead of drums. Larger containers are reusable when equipped for top and bottom discharge, whereas drums have to be recycled or disposed of as waste. Bulk storage can minimise the chances of leaks and spills as compared to drums. In terms of applicability: safe disposal of non-refillable large containers can be a problem.
- Reduction of the generation of empty oil drums. Bulk purchasing (via tank trucks) of frequently used oils and filling tote bins as intermediate storage. Personnel could then transfer the oils from the tote bin to reusable drums, buckets, or other containers. This would reduce the generation of empty drums and their associated handling costs.
- Storage of drums off the floor to prevent corrosion through spills or concrete 'sweating'
- Keeping containers closed except when removing material.
- Practise corrosion monitoring, prevention and control in underground piping and tank bottoms (related to the Sections 4.21.8).

- Tanks for storage of ballast water may cause large VOC emissions. They can be therefore equipped with a floating roof. These tanks are also relevant as equalizing tanks for the waste water treatment system.
- Passing of vents from sulphur storage tanks to sour gas or other arrestment systems.
- Vent collection and ducting from tank farms to central abatement systems.
- Installation of self-sealing hose connections or implementation of line draining procedures.
- Installation of barriers and/or interlocking systems to prevent damage to equipment from the accidental movement or driving away of vehicles (road or rail tank cars) during loading operations.
- Implementation of procedures to ensure that arms are not operated until inserted fully into the container to avoid splashing where top loading arms are used.
- Application instrumentation or procedures to prevent overfilling of tanks.
- Installation level alarms independent of the normal tank gauging system.

Achieved environmental benefits and Economics

Techniques	Emission factor for NM VOC (g/t throughput)	Abatement efficiency (%)	Size (diameter in m)	Cost (EUR)
Fixed roof storage tanks (FRT)	7 – 80			
External floating roof tank (EFRT)	7 – 80			
Internal floating roof tank (IFRT)	2 – 90			
External paint finish in a lighter shade		1 – 3 FRT	12	3 900
			40	25 400
Installation of an internal floating roof in existing fixed-roof tank		97 – 99 FRT	12	32 500
			40	195 000
Replacement of a vapour-mounted primary seal with a liquid-mounted primary seal		30 – 70 EFRT 43 – 45 IFRT	12	4 600
			40	15 100
Retrofitting secondary seals on an existing tank		90 – 94 EFRT 38 – 41 IFRT	12	3 400
			40	11 300
Improvement of primary seal, plus secondary seal and roof fitting control (pontoon and double deck)		98 EFRT 48 – 51 IFRT	12	200
			40	200
Installation of a fixed roof on an existing external floating-roof tank		96 EFRT	12	18 000
			40	200 000

NB: Columns for abatement efficiency, size and cost are related to the techniques and not to each other. Costs are average costs for the two diameters and abatement efficiencies are ranges for the technique applied to different types of tanks.

Reference literature

[171, UN/ECE 1998], [207, TWG 2001], [196, CONCAWE 2000], [148, Irish EPA 1993], [205, Jansson 2000], [206, EIPPCB 2001].

4.21.14 In-line blending

Description

Figure 4.50 shows a scheme of an in-line blending system for gas oils.

Achieved environmental benefits

The energy savings realised by in-line blending compared to batch blending can be substantial, especially in electric power consumption. Using in-line blending reduces the total number of handling operations with respect to feed and product streams—less filling and emptying of tanks and thus reduces total emission to atmosphere. The numerous valves and pumps can be provided with dual mechanical seals and can be regularly maintained in order to minimise fugitive VOC emissions. In-line blending generally creates more flexibility towards product specifications and product quantities, and represents a large savings by avoiding intermediate storage.

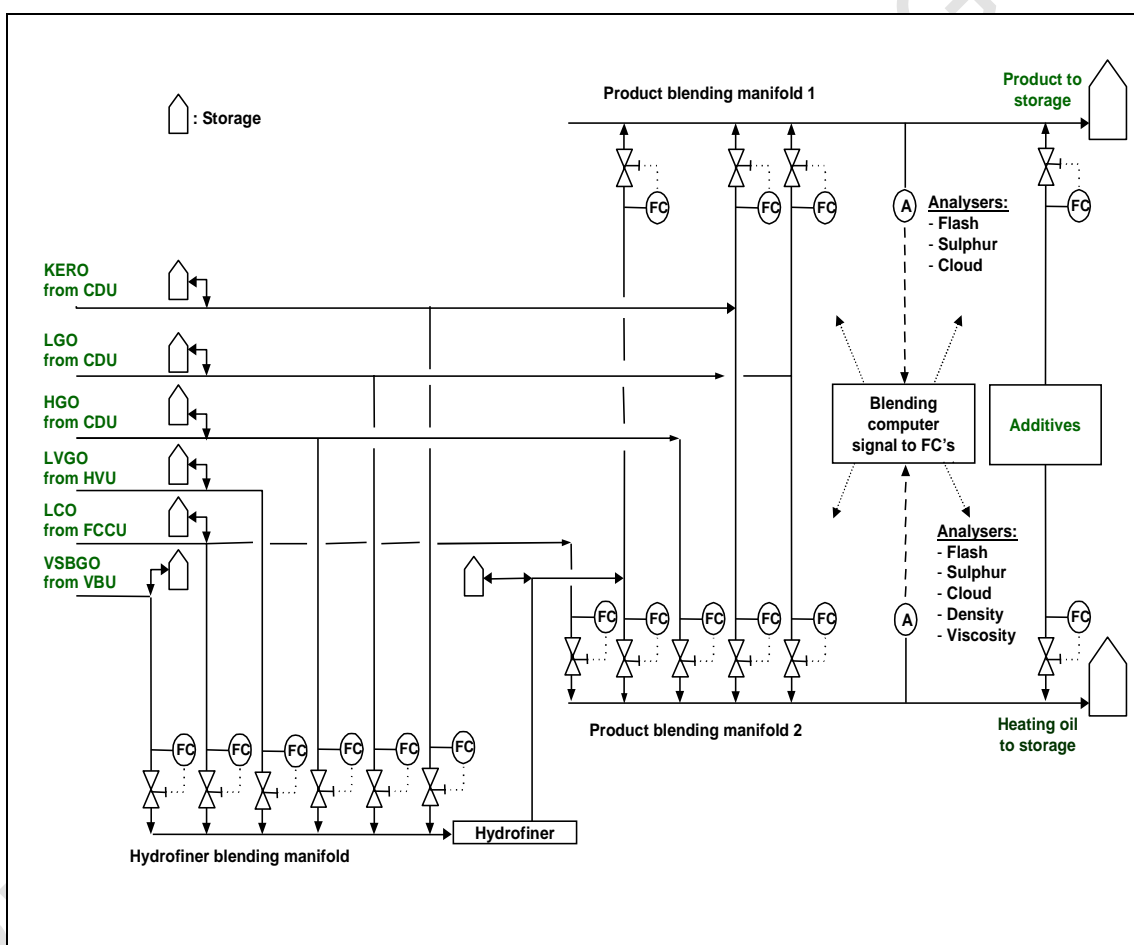


Figure 4.50: Simplified scheme of an in-line blending system for gas oils (automotive diesel and heating oil)

Cross-media effects

In-line blending systems contain many flange connections and valves, which could be sources of leakage, particularly during maintenance.

Operational data

Extreme care has to be taken to in-line quality analysers to ensure the quality of the blended product.

Applicability

Optimising the blend ratios to meet all critical specifications is, to a certain extent, a trial-and-error procedure which is most economically accomplished with the use of a computer. There are usually a number of comparable solutions that give roughly equivalent total overall cost or profit. Optimisation programs allow the computer to provide the optimum blend to minimise costs and maximise profit.

Example plants

In-line blending systems are normally applied for high volume feed and/or product streams.

Reference literature

[168, VROM 1999].

4.21.15 Batch blending

Description

See Section 2.21.

Applicability

The reasons for batch blending are the minimum storage requirements for strategic reasons, fiscal and tax control, operating flexibility and tank dimensions.

Example plants

For the reasons mentioned above, under 'applicability', batch blending of feed and product is still done to a certain extent.

4.21.16 Vapour balancing during loading processes

Description

In order to prevent emissions to atmosphere from loading operations, several options are available. Where loading takes place from fixed roof tanks, a balance line can be used. The expelled mixture is then returned to the liquid supply tank and so replaces the pumped-out volume. Vapours expelled during loading operations may be returned to the loading tank, if it is of the fixed roof type, where it can be stored prior to vapour recovery or destruction. This system can also be used for vessels and barges.

Achieved environmental benefits

Vapour balancing greatly reduces the vapour volumes expelled to atmosphere. It can reduce VOC emissions by up to 80 %

Cross-media effects

Due to evaporation in the receiving vessel during transfer (vapour evolution by splashing), there is usually a surplus volume of vapours compared to the displaced liquid volume. The balancing line is not considered an efficient means of VOC abatement for the most volatile liquids.

Operational data

Where explosive mixtures can occur, safeguards should be implemented to limit the risk of ignitions and ignition propagation. Tanks should remain closed to prevent emissions, so they may operate under a low pressure and ullaging and sampling should not be undertaken through open dispatches. Detonation arrestors require regular cleaning when vapours contain particulates (e.g. soot from badly-operated cargo tank inerting systems).

Applicability

Not all vapours can be collected. May affect loading rates and operational flexibility. Tanks which may contain incompatible vapours cannot be linked. Can only be used where the product is pumped out of a fixed roof tank fitted with pressure/vacuum relief valves.

Economics

The investment required is EUR 0.08 million per tank and the operating costs are low.

Driving force for implementation

Reduce VOC emissions.

Example plant(s)

LPG loading. Subsequent loading of transport containers is carried out by means such as closed loop systems or by venting and release to the refinery fuel gas system.

Reference literature

[166, CONCAWE 1999], [207, TWG 2001].

4.21.17 Bottom loading measures**Description**

The loading/unloading pipe is flange-connected to a nozzle situated at the lowest point of the tank. A vent pipe on the tank can be connected to a gas balancing line, VRU or to a vent. In the last case, VOC emissions can occur. The flange connection in the filling line has a special design ('dry connection') which enables it to be disconnected with minimum spillage/emissions.

Achieved environmental benefits

VOC emissions reduction.

Driving force for implementation

Directive 94/63/EC on the control of VOC emission requirements for gasoline loading for road tankers.

Reference literature

[156, MCG 1991], [207, TWG 2001].

4.21.18 Tightly sealed floors**Description**

The handling of materials used in the refinery may result in accidental spills that could contaminate the soil, surface water or groundwater. Paving and kerbing the area where materials are handled, for the collection of the possible spilled material.

Achieved environmental benefits

Prevention of soil pollution and directing any spillage of product to the slops.

This minimises the volume of waste generated and allows for the collection and reclamation of the material.

Driving force for implementation

To prevent soil and rainwater contamination.

Example plants

Many examples can be found in European refineries.

Reference literature

[156, MCG 1991].

4.22 Visbreaking and other thermal conversions

4.22.1 Visbreaking

4.22.1.1 Hydrovisbreaking

Achieved environmental benefits

A modern technique, which increases the conversion rate of the feed by the addition of H-donators and water without reducing the stability of the process.

Economics

Investment (based on: 750 kt/yr of topped heavy Canadian crude; battery limits including desalting, topping and engineering; 1994 US Gulf Coast). Information is given in Table 4.78.

Table 4.78: Cost comparison between normal and hydrovisbreakers

Process alternative	Normal visbreaker	Hydro visbreaker
EUR per t/yr	85 000	115 000
Utilities, typical per m ³		
Fuel oil fired (80 % effic.) kg	15.1	15.1
Electricity, kWh	1.9	12.0
Steam consumed (produced), kg	15.1	30.2
Water, process, m ³	nil	nil
Hydrogen consumption, Nm ³	NA	30.2

Example plants

Hydrovisbreaking was tested in a 2 Mt/yr visbreaker in a refinery in Curaçao.

Reference literature

[183, HP 1998], [194, Winter 2000].

4.22.1.2 Soaker visbreakers

Description

In this process, a soaker drum is added after the furnace, so the cracking takes place at lower furnace outlet temperatures, and over a longer residence time.

Achieved environmental benefits

The product yields and properties are similar but the soaker operation with its lower furnace outlet temperatures has the advantages of lower energy consumption (30 – 35 %) and longer running times before shutting down to remove coke from the furnace tubes (running times of 6 – 18 months versus 3 – 6 months in coil cracking).

Cross-media effects

The advantage of reducing the number of clean-ups for soaker visbreakers is at least partially balanced by the greater difficulty in cleaning the soaking drum.

Operational data

Run times of 3 – 6 months are common for furnace visbreakers and 6 – 18 months for soaker visbreakers. Fuel consumption is around 11 kg FOE/t. Power and steam consumption is similar to the coil one. Operating temperature is 400 – 420 °C at the soaker's exit.

Example plants

Some soaker visbreakers exist in European refineries.

Reference literature

[221, Italy 2000], [207, TWG 2001].

4.22.2 Thermal gas oil unit (TGU)**Description**

For complete description see Section 2.22.2 on the thermal gas oil unit.

The thermal gas oil unit (TGU) allows the conversion of the vacuum distillation residue by using a two-step thermal cracking and subsequent distillative separation into the gas oil and naphtha cuts produced.

Achieved environmental benefits

Compared to a conventional visbreaker, the TGU process allows for a significantly higher conversion of the vacuum residue into lighter products. The conversion yield reaches about 40 % weight instead of 15 %, and the resulting products can be directly valorised in cut streams used for diesel, gasoline and naphtha production.

Cross-media effects

This process increases the site energy consumption and the related air emissions. The net energy necessary for the conversion of the vacuum residue is high. It also generates additional heavily hydrocarbon-contaminated waste waters to be treated in the WWTP.

Operational data

A TGU unit has been operated at the OMV refinery in Schwechat since Spring 2009. The unit treatment capacity is 2 000 t/day. The heat required for the process is provided by a natural gas-fired gas turbine with a rated thermal input of about 80 MW, which delivers a 27 MW_e of additional electrical energy to the refinery grid, together with some process steam generated in the heat recovery unit of this plant.

Applicability

This process is fully applicable for new plants. On the contrary, the retrofitting of such process on existing visbreaking units is not possible.

Economics

The investment amounts to USD 2 400 to 3 000 (EUR 1 900 – 2 500) per bpd (barrel per day) installed, excluding treatment facilities and depending on the capacity and configuration (basis Europe: 2004).

Driving force for implementation

Maximisation of the site conversion ratio towards a 'no residue' refining.

Example plants

Approximately 12 units are installed worldwide. One plant has been operated since 2009 by OMV in Schwechat (Austria)

Reference literature

[228, TWG 2000], [54, Gallauner et al. 2009], [76, Hydrocarbon processing 2011].

4.22.3 Sour gas and waste water management**Description**

The gas generated in the visbreaking may be sour and contain sulphur compounds, in which case, a gas-sweetening operation, typically amine scrubbing, should be applied before the gas is recovered into products or used as refinery fuel gas. Visbreaking gas, apart from being amine scrubbed to remove H₂S, is further treated to remove approximately 400 to 600 mg/Nm³ of

mercaptan sulphur (depending on the feed), in order to meet the refinery fuel gas sulphur-content specification.

The aqueous condensate is usually sour, and should be passed to the sour water stripper in an enclosed system.

Achieved environmental benefits

Reduction in the sulphur content of products.

Cross-media effects

Need for chemicals and utilities to run the processes.

Driving force for implementation

Sulphur specifications of the products.

Example plants

Sour gas use and waste water management are applied in many refineries.

Reference literature

[228, TWG 2000].

4.22.4 Reduction of coke formation in visbreakers

Description

During thermal cracking some coke formation is produced and deposits itself onto the furnace tubes. The coke should be cleaned when necessary. Additives are available on the market to control the sodium content within the feedstock. The control of the addition of caustics or specific additives to the feedstock upstream can also be used.

Achieved environmental benefits

Reduction of the coke formation and as a consequence, reduction of cleaning waste.

Driving force for implementation

This technique is typically applied to prevent cleaning.

Reference literature

[207, TWG 2001].

4.23 Waste gas minimisation and treatments

This section is complementary to previous sections of Chapter 4 related to individual production processes or units. It gives sector-specific information on key management, reduction and abatement techniques that are or may be implemented for air emissions from oil and gas refining.

For a given technique, the information provided here aims at completing, broadly, the operational data and material that have already been provided in previous sections where only specific results achieved from the application of this technique to a particular process or unit are reflected. Consequently, general information on environmental benefits, cross-media effects, operational data, and applicability, which have not appeared in other sections will be found in this section. Complementing these techniques that may appear within the production activities, this section and the next one also contain end-of-pipe processes which concern the whole refinery and have also to be considered for the determination of BAT. Under this category are the sulphur recovery units, flares, and amine treatment and the waste water treatments. These techniques are only discussed here.

4.23.1 CO-abatement techniques

Description

CO boilers and catalyst reduction of CO (and NO_x). Good primary measures for the CO reduction are:

- good operational control;
- constant delivery of liquid fuel in the secondary heating;
- good mixing of the exhaust gases;
- catalytic afterburning;
- catalysts with oxidation promoters.

Achieved environmental benefits

Reduction of CO emissions. Emissions after the CO boiler: <100 mg/Nm³. In the case of conventional firings, a CO concentration below 50 mg/Nm³ is achievable at temperatures above 800 °C, at sufficient air delivery and sufficient retention times (see Table 4.39).

Applicability

FCC and in heavy residues fired. (Sections 4.10.4.9 and 4.5.5).

Reference literature

[228, TWG 2000].

4.23.2 CO₂ emission control options

For more information see also Chapter 6 on emerging techniques.

Description

Unlike SO₂, NO_x or particulates treatments flue-gases, a feasible abatement technology for CO₂ is not available. CO₂ separation techniques are available but the problem is the storage and the recycling of the CO₂. Options for the refiner to reduce CO₂ emissions are:

- effective energy management (see Section 4.15.1.2), including:
 - improving heat exchange between refinery streams;

- integration of refinery processes to avoid intermediate cooling of components (e.g. Section 4.19.1 Progressive distillation unit);
 - recovery of waste gases and their use as fuels (e.g. flare gas recovery);
 - use of the heat content of flue-gases;
- use of fuels with high hydrogen contents (topic discussed in Section 4.10.2);
 - effective energy production techniques (see Section 4.10.3). This means the highest possible recovery of energy from fuel combustion;
 - the capture, transport and sequestration (CCS - Carbon Capture and Storage) of CO₂ emissions (see Chapter 6 Emerging Techniques).

As the CCS option is not yet available at site scale, choices for abatement techniques should be made taking into account the possibility to further use the CO₂.

Achieved environmental benefits

Reduction of CO₂ emissions.

Cross-media effects

The use of fuels with high hydrogen contents reduce CO₂ emissions from the refineries but overall will not reduce CO₂ as these fuels will not then be available for other uses.

Operational data

Rational energy use requires good operation to maximise heat recovery and process control (e.g. O₂ excess, heat balances between reflux, product temperature to storage, equipment survey and cleaning). To get optimum results, repeated operator training and clear instructions are necessary.

Reference literature

[196, CONCAWE 2000], [207, TWG 2001], [77, REF TWG 2010].

4.23.3 NO_x-abatement techniques

The NO_x emission level of an oil refinery or a natural gas plant is influenced by the refining scheme, the type of fuels used and the abatement techniques implemented. As the number of emission sources and their contribution to the overall emission level may vary greatly, one of the first techniques to consider is the precise quantification and characterisation of the emission sources in each specific case. For more information, see Section 3.26.

See also Section 4.23.8 for information on the SNO_x combined technique.

4.23.3.1 Low-temperature NO_x oxidation

Description

The low-temperature NO_x oxidation process injects ozone into a flue-gas stream at optimal temperatures below 150 °C, to oxidise insoluble NO and NO₂ into highly soluble N₂O₅. The N₂O₅ is removed in a wet scrubber by forming dilute nitric acid waste water, that can be used in plant processes or be neutralised for release.

Achieved environmental benefits

Low-temperature NO_x oxidation can achieve 90 – 95 % removal of NO_x, with consistent NO_x levels as low as 5 ppm. Additional benefits are the heat-recovery from the fuel gas, which remains fully possible. The entire process is controlled to produce no secondary gaseous emissions. Because ozone is used as an oxidising agent, emissions of CO, VOC and ammonia are also reduced.

Cross-media effects

Ozone should be produced on site, on demand, from stored O₂. There is a risk of ozone slip.

Low temperature oxidation (LoTO_x) should be necessarily associated with a new or existing scrubbing unit, and generates waste water to be treated properly. An increase in nitrate load to the existing WWTP might have to be considered, together with the associated cost to control nitrates. Nitric acid is produced and needs to be neutralised, with an alkali used in the scrubbing section.

Operational data

The use of ozone and the low optimal temperatures of the process provide stable treatment conditions. Energy consumption for the production of ozone range from 7 – 10 MJ/kg (2 – 2.8 kWh/kg) of ozone produced, with a concentration of 1 – 3 % w/w with dry oxygen feed. Temperatures should be below 150 °C to minimise ozone decomposition. Heavy particulate-laden fuels may require additional equipment.

Applicability

This process has been developed and is known as SNERT (scrubber-based NO_x emissions reduction technology). The NO_x-removal performance is directly linked to the ozone injection rate and its real-time regulation in relation to the NO_x outlet concentration target. The outlet NO_x can be adjusted by varying the set point on the system controller.

This process can be used as a stand-alone treatment system or can follow other combustion modifications and post-combustion treatment systems, such as low-NO_x burners, SCR or SO_x removal, as a final polish step, including the treatment of ammonia slips. It can be easily retrofitted to an existing plant.

Economics

This technique requires low maintenance and low operator interface. The relative capital costs and operating costs given by the technology providers claim that they are equal to, or less than SCR-type systems.

A prospective study for the potential control of existing major SO₂ and NO_x industrial sources in Colorado (US) provides accumulative capital and operational annual cost data expressed per tonne of abated NO_x for some industrial sectors. In refineries, the quoted application (using updated economic data from US-EPA of 2005) concerns FCC units with costs ranging from 1 391 – 1 595 (*) EUR/tonne (1 884 – 2 161 USD/tonne 2007 values - currency conversion rate of 0.73822 on the 1/07/2007). As a comparison, other cost ranges are available for wet kilns 2 303 – 2 454 EUR/tonne (3 102 – 3 324 USD/tonne) and dry kilns 1 717 – 1 963 EUR/tonne (2 327 – 2 659 USD/tonne) in the cement industry.

Example plants

The process is in use in US commercial installations in sectors such as acid pickling, lead smelting, steam boilers and coal fired boilers. Also a number of FCC units have been notably retrofitted with such a technique in the US (see Section 4.5.4.5).

Driving force for implementation

To reduce NO_x emissions.

Reference literature

[181, HP, 1998], [242, Crowther 2001], [207, TWG 2001], [17, Jeavons and Francis 2008]

4.23.3.2 Selective non-catalytic reduction (SNCR)

Description

SNCR is a non-catalytic process for removing nitrogen oxides from combustion flue-gases by gas phase reaction of ammonia or urea at high temperatures (generally between 850 and 1 100 °C). This technique, also called thermal DeNO_x, reduces NO_x to nitrogen and water. To achieve a good mixing, the small amount of reactant is injected along with a carrier gas, usually air or steam. General information about this technique can be found in the CWW BREF [6, EC 2003] and in the LCP BREF [7, EC 2006].

Achieved environmental benefits

Reductions of 25 – 70 % can be achieved, giving values of less than 200 mg/Nm³.

Cross-media effects

An intrinsic limitation of the SNCR technique is the emission of a small amount of unreacted NH₃ (ammonia slip) in the flue-gas stream. The ammonia slip is typically in the range of 5 – 20 ppm (3 – 14 mg/Nm³), the higher values being associated with higher NO_x reduction. The US EPA identified ammonia as the single largest precursor of fine particulate (air pollution (2.5 microns and smaller) in the country.

A side effect of particular concern is the formation of ammonium sulphates when firing sulphur-containing fuels such as liquid refinery fuel. Sulphates give rise to the fouling and corrosion of downstream equipment.

Aqueous ammonia, anhydrous ammonia, or urea can be used as a reactant in the SNCR system. The storage of gaseous or liquefied anhydrous ammonia has a great hazardous potential. Therefore, whenever possible, after an appropriate evaluation of the risks, a liquid solution of ammonia (25 %) or urea should generally be used.

N₂O is a by-product formed when SNCR is used. Urea-based reduction generates more N₂O than ammonia-based systems. At most, 10 % of the eliminated NO_x is formed into N₂O in the urea based systems [103, EPA 2002].

Operational data

The NO_x reduction rate depends very much on the possibility of matching the following temperature windows together with an minimum residence time of 0.2 – 0.5 s in the temperature window:

- 850 – 1 000 °C, for ammonia and caustic ammonia (optimum 950 °C);
- 800 – 1 100 °C, for urea (optimum 1 000 °C).

Injection of reagent below this temperature window results in excessive ammonia slip. Injection of reagent above the temperature window results in increased NO_x emissions. In some applications, it has been suggested that chemical enhancers, such as hydrogen, are needed to help the reaction at lower temperatures, but this type of application is not reported within the refining industry.

The ammonia produced in the sour water stripping (see Section 4.24.2) can be used as a DeNO_x agent.

It also depends on the NO_x inlet concentration to be abated, because even under optimal thermal conditions, there is a lower limit to the technically achievable reduction yield and outlet concentration due to the particular mixing conditions and chemical kinetics.

Applicability

SCNR is typically applied to flue-gases from heaters and boilers. There are only very small space requirements mainly concerning NH₃ storage.

In some cases, operating and physical constraints can make retrofitting difficult: e.g. temperature window required may occur in the middle of the boiler tube bank and could lead to impingement of the injected chemical against the tubes.

Economics

Cost considerations include the initial capital costs for modifying the furnace or boiler, piping to inject the reactant, the reactant supply system, and the recurring cost for ammonia or urea to react with the NO_x. For specific cost effectiveness data, see Sections 4.5.4.2 and 4.10.4.6.

Driving force for implementation

To reduce nitrogen oxide emissions.

Example plants

Applied to FCC units, process furnaces and boilers.

Reference literature

[182, Ecker 1999], [222, UBA 2000], [166, CONCAWE 1999], [181, HP, 1998], [191, UBA Austria 1998], [207, TWG 2001], [104, Tayyeb Javed et al. 2006], [103, EPA 2002].

4.23.3.3 Selective catalytic reduction (SCR)**Description**

Also known as catalytic DeNO_x. The ammonia/urea vapour is mixed with the flue-gas through an injection grid before being passed through a catalyst to complete the reaction. Various catalyst formulations are available for different temperature ranges: zeolites for 300 – 500 °C, traditional base metals employed between 200 – 400 °C, and metals and activated carbon for the lowest temperature applications 150 – 300 °C. More information about this technique can be found in the CWW BREF [6, EC 2003] and the LCP BREF [7, EC 2006].

Achieved environmental benefits

SCR is especially suitable for situations where emission standards are strict. With SCR, removal efficiencies of 80 to 95 % can be achieved generally for inlet concentration over 200 mg/Nm³. Residual NO_x stack levels of 10 – 20 mg/Nm³ can be achieved by application of SCR in gas-fired boilers and furnaces. When firing heavy residues, emissions of <100 mg/Nm³ (3 % O₂, half-hourly mean value, efficiencies of up to 90 %) can be achieved.

Cross-media effects

The main cross-media effects can be summarised below:

- As with SNCR, an intrinsic limitation of the SCR technique is the emission of a small amount of unreacted NH₃ (ammonia slip) in the flue-gas stream. The ammonia slip is typically in the range of 2 – 10 ppm (1.4 – 7 mg/Nm³ at 25 °C), the higher values associated with higher NO_x reduction and, more specifically, to catalyst end-of-run conditions. It should be noted that ammonia slip is dependent on many factors, including NH₃ injection rate, catalyst activity, flue-gas distribution, process controllability.
- The spent catalyst should be disposed of properly.
- As for SNCR, aqueous ammonia, anhydrous ammonia, or urea can be used as a reactant in the SCR system. The storage of gaseous or liquefied anhydrous ammonia has a great hazardous potential. Therefore, whenever possible, after an appropriate evaluation of the risks, a liquid solution of ammonia (25 %) or urea is generally preferred.

- A small amount of SO₂ is oxidised to SO₃ over the SCR catalyst. In sufficient amounts, SO₃ in flue-gas may impact plume opacity.
- Additional fuel consumption may be needed to increase the furnace flue-gas temperature to reach the one required by the catalyst. In this case, additional CO₂ emissions will be produced (see under Operational data and Economics).

Operational data

The theoretical amount of reducing agent for removing 1 kg of NO_x is dependent on the ratio of NO to NO₂ in the combined NO_x concentration, as reaction stoichiometry requires one mole of ammonia to reduce one mole of NO and two moles for one mole of NO₂. Attention is required for applications where fouling substances like SO₃ and soot or dust are present in the off-gas. The presence of SO₃ and ammonia can lead to the formation of ammonium sulphates if the flue-gas temperature drops below the ammonium salt deposition temperature. Ammonium sulphates may have a detrimental effect on the catalyst due to the masking of active sites and can lead to fouling of downstream heat exchangers. Catalyst deactivation can be mitigated by ensuring that the process unit is operated above the ammonium salt deposition temperature.

The catalyst has a general lifetime of 4 to 7 years for oil firing, and 7 to 10 years for gas firing, but shorter lifetimes have been reported in particularly unfavourable conditions. For the multifuel SCR catalyst, the catalyst life is likely driven by the most severe fuel. The pressure drop of the catalyst bed will lead to a minor amount of additional power consumption from fans in the system or loss of efficiency in the case of a gas turbine application (equivalent to 0.5 - 1 % of the heat input).

Flue-gas reheat may be required if the SCR is located downstream of wet scrubbing processes or in applications with low flue-gas temperatures. Minimum operating temperature for an SCR unit is dependent on catalyst type and composition and will be application specific. According to a study at API refinery (Italy), the fuel gas required to increase the temperature (to around 270 °C) could lead to additional CO₂ emissions, in the order of magnitude of 5 750 tonnes/yr for 100 tonnes of NO_x abated.

At Preem Gothenburg Refinery (SE), the SCR used at the reformer unit is of low temperature type (185 °C) and achieve 90 % reduction of NO_x. At Preem Lysekil Refinery (SE), the SCR used at the FCC unit reports a NH₃ slip < 5 ppm (< 3.5 mg/Nm³), based on a continuous monitoring from 2010-2011.

Applicability

(SCR) has been applied to combustion flue-gases or process off-gases (e.g. FCC). The introduction of an SCR system into an existing installation is a challenge due to space, pressure and temperature problems. Creative solutions can often be found to reduce the retrofit costs. Higher operating temperatures reduce the catalyst size and costs but introduce retrofit complexity. Lower operating temperatures increase the required catalyst volume and costs but often allow for a more simple retrofit.

So far, operating temperatures between 200 and 450 °C prevail. These temperatures are normally available before the economiser section or the air preheater of a boiler. Gas-fired refinery furnaces generally have a stack temperature of 150 – 300°C. Dependent on the flue-gas sulphur content, a medium temperature (MT) or low temperature (LT) catalyst can be applied in tail-end configuration. Zeolite-type catalysts have reached the market place. In the US, a number of gas turbines have been fitted with these catalysts.

Combined techniques for both SO₂ and NO_x removal use also such a catalyst: e.g. the DeSoNO_x process [7, EC 2006]. As for oil firing, only MT catalysts can be applied, because of the presence of sulphur and particulates. MT catalysts have been widely applied in coal-fired power plants predominantly under conditions where the flue-gas still contains all the fly-ash and SO₂ from the boiler. Two other configurations are low dust/high SO₂ level and low dust/low SO₂ level (tail-end configuration).

There is little experience of the use of SCR for units applying vacuum residue as fuel. However, the power plant of the TOTAL Mitteldeutschland refinery in Germany uses vacuum residue, visbreaker residue and FCC slurry as fuel in its three oil-fired heaters. An SCR plant in high dust configuration is installed after the heaters, cleaning the gas of the NO_x to concentrations lower than 150 mg/Nm³ (see Section 4.10.4.7 for detailed data-sets). Unabated fly-ash concentrations for oil firing are in the range of 100 – 600 mg/Nm³ (with the highest values for vacuum residues). SCR applied under these conditions may suffer from clogging by fly-ash and sulphates. The potential for sulphate precipitation is generally higher with vacuum residue, due to its high sulphur content (2.5 – 4 %).

Pressure drop can be important when considering whether SCR can be applied to a flue-gas system. For this reason natural draft furnaces could probably not be fitted with it. See Section 4.23.8 for information on the SNO_x combined technique.

Economics

See applications in each section (Section 4.10.4.7 for the energy system, 4.5.4.1 for FCC units and Section 4.5.4.1, Section 4.7.8.3 for cokers). The investment of new SCR system depend largely on the flue-gas volume, its sulphur and dust content and the retrofit complexity. For existing installations, the possible location of the catalyst bed is often constrained by space limitations, which will lead to additional retrofitting costs.

The installation of two SCR units were studied in 2007 at the API refinery (Italy) with the objective of reducing NO_x emissions from gas furnaces: one at the thermal cracking unit, for an estimated investment cost (ammonia system, compressor, design and installation) of EUR 2.2 million, and the other one at the pipestill furnaces, for EUR 3 million. Both SCR had designed performances of 85 – 87 % NO_x abatement (from average 120 mg/Nm³, with current low NO_x burners, to 15 mg/Nm³) and a flue-gas flow around 55 000 Nm³/h. The project was not completed.

Table 4.79 gives cost effectiveness of the use of SCR under different conditions:

Table 4.79: Data on the cost effectiveness of SCR retrofitting for various refining units

SCR	Cost effectiveness in EUR/tonne NO _x removed (includes capital charge of 15 %)
Heaters and boilers firing refinery blend gas	8 300 – 9 800
	12 000
	4 200 – 9 000
Boilers firing residual fuel oil	5 000 – 8 000
	4 500 – 10 200
Gas turbines firing natural or refinery blend gas	1 700 – 8 000
Fluid catalytic cracking units	2 800 – 3 300
N.B: Details on the conditions are given in Annex IV.	

Driving force for implementation

To reduce NO_x emissions.

Example plants

SCR has been applied to FCC off-gases, gas turbines, process boilers and process heaters. It has been applied successfully on a large variety of applications: coal and oil-fired power plants, waste incineration plants, diesel and gas engines, gas turbine plants, steam boilers and refinery furnaces (such as naphtha reformers, steam reformers, crude and vacuum distillations units, thermal cracking and hydroprocessing units) and FCC plants. There has been less experience with flue-gas from firing high-sulphur residual oil.

SCR is used extensively on power plants in Japan, Germany, Austria and on gas turbine plants in the Netherlands, and in California in the US. SCR are also widely used in waste incineration

plants. To date, SCR has been successfully applied worldwide in refinery processes as power plants and FCCs. For example, at refineries in Japan, SCR applications are common. In European refineries, more than 6 applications have been found (Austria, the Netherlands and Sweden).

Reference literature

[222, UBA 2000], [182, Ecker 1999], [168, VROM 1999], [200, Gilbert 2000], [176, R. E. Constructors 1998], [181, HP, 1998], [166, CONCAWE 1999], [207, TWG 2001], [77, REF TWG 2010] [105, EPA 2002].

4.23.4 Particulates

Particulate Matter (PM) emissions from refinery units entail particles present in the flue-gas from furnaces, particularly soot, catalyst fines emitted from FCC regeneration units and other catalyst-based processes, from the handling of coke and coke fines and ash generated during the incineration of sludges. Particulates generated in the refinery contain metals. Therefore, a reduction in the particulates content reduces the metal emissions from the refinery. The particles may range in size from large molecules, measuring a few tenths of a nanometer, to the coarse dusts arising from the attrition of catalyst. Distinction is usually made between aerosols, <1 - 3 μm and larger dust particles. The avoidance of fine particulates <10 μm (PM_{10}) is particularly important for health reasons.

The available dust removal techniques can be subdivided into dry and wet techniques or a combination of the two. The usual techniques applied at refineries for dust emission reduction are briefly discussed below. The main dedusting processes dry techniques include cyclones, electrostatic precipitators and bag filters. Some wet techniques such as scrubbers may also be used mainly as finishing treatment.

4.23.4.1 Cyclones

Description

The principle of cyclone separation is based on centrifugal force, whereby the particle is separated from the carrier gas. More information can be found in the CWW BREF [226, EIPPCB 2001]. Data on application of cyclones to FCC units is available in Section 4.5.5.1.

Achieved environmental benefits

Cyclones are used to reduce dust concentrations in the 100 - 500 mg/Nm^3 range. A novel cyclone design, called the rotating particulate separator (RPS), is able to effectively remove particles of >1 μm ; this design, however, has a limited capacity compared to the conventional cyclone. Third cyclones achieve a 90 % reduction of particulate emissions (100 - 400 mg/Nm^3). Modern multicyclones used as third-stage cyclones achieve an 80 % reduction of particulate emissions to about 50 mg/m^3 .

Cross-media effects

By nature, cyclones are efficient for larger particulates but do not separate and retain the finest part of emitted dust. Furthermore, a reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift of an air emission problem to a waste problem.

Operational data

Cyclones can be designed for high temperature and pressure operation. Dust collection equipment is normally simple to operate and fully automated. For dry separation, no utilities are needed. For dust removal normally no additives are used. Sometimes the collected dust needs rewetting to prevent the spreading of dust during handling.

Applicability

Multi-cyclones as employed in FCC units or cokers are not able to remove fine particulate matter (PM_{10} = dust $<10 \mu\text{m}$) and therefore they are mainly used as a pre-separation step.

Driving force for implementation

Process gas streams must often be cleaned up to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as to compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal-containing catalytic fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants

In refineries, multi-cyclones are employed, often together with ESPs, in FCC and RCC units.

Reference literature

[194, Winter 2000], [168, VROM 1999].

4.23.4.2 Electrostatic precipitator (ESP)**Description**

The basic principle of operation for electrostatic precipitators (ESP or electrofilter) is simple. Flowing gas is ionised as it passes between a high-voltage electrode and an earthed (grounded) electrode. The dust particles become charged in the electric field that is generated and are attracted to the earthed electrode. The precipitated dust is removed from the electrodes mechanically, usually by vibration force (dry ESP), or by water wash (wet ESP).

Achieved environmental benefits

ESPs are capable of collecting bulk quantities of dust including very fine particles at high efficiencies. ESPs can achieve values of $<10 - 50 \text{ mg/Nm}^3$ (95 % reduction or higher with higher inlet concentrations only). However, a penetration 'window' exists in the submicron ($0.1 - 1 \mu\text{m}$) size range where the collection efficiency lowers.

Cross-media effects

Electricity consumption, dust disposal, and in some cases ammonia emissions. In addition the high voltage in an ESP introduces a new hazard in refineries. For some installations, ammonia may be injected to improve ESP performance. For these installations, ammonia emissions result from ammonia slip through the ESP. The dust collected in an ESP requires disposal if a useful outlet is not found.

Operational data

An ESP uses some electricity. For dust removal, normally no additives are used. Sometimes the collected dust needs rewetting to prevent the spreading of dust during handling.

Applicability

The application of ESPs can be found in FCC units, FGD processes, power plants and incinerators. It may not be applicable for some particulates with high electric resistance. They typically can be installed in new and existing plants.

Economics

Some recent examples of ESP costs for FCC units are available in Section 4.5.5.2. Generally fines disposal costs are not included and need to be taken into account for the total cost.

Driving force for implementation

Process gas streams must often be cleaned to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as to compressors. Toxic and other hazardous

substances (e.g. coke fines and heavy metal-containing catalyst fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants

In refineries, multi-cyclones and ESPs are employed in FCC units and in heavy oil and residue cracker units.

Reference literature

[194, Winter 2000], [168, VROM 1999], [106, Bong-Jo Sung et al. 2006].

4.23.4.3 Filtration

Description

Fabric and solid bundle blow-back filters (see also Section 4.5.5.3.).

Achieved environmental benefits

Fabric and solid bundle blow-back filters can achieve values less than 5 mg/Nm³. They are more efficient than cyclones and ESPs on the finest particulates. Solid bundle filters can allow a filtration guaranteed for particulates above a minimal granulometry of 0.8 – 1 µm.

Cross-media effects

As for all other dry separation techniques, a reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift from an air emissions problem to a waste problem. In the case of conventional fabric bundles, filter material life is limited (1 - 2 years) and may create a disposal problem. In the case of solid ceramic/alloy bundles, the lifetime is much longer but bundles may need a chemical cleaning from time to time if an eventual progressive increase of the pressure drop due to plugging is experienced, generating another issue of waste elimination.

Operational data

Dust collection equipment is normally simple to operate and is fully automated. For dry separation, limited utilities are needed.

Applicability

Fabric filters are effective, except in applications with sticky dust or at temperatures of over 240 °C. Depending on the flowrate design parameters, they can reach significant volumes and space needs.

Solid bundle filters are much more compact, and can resist much higher temperatures, up to 800 °C, depending on the metallurgy of the bundles constituent.

Filters are typically used for the cleaning of flue-gases with an output of <50 000 Nm³/h, even if they are also used for the treatment of much higher flowrates in the metallurgy. They are well adapted for processes likely to deliver variable flue-gas flows and dust concentrations.

Driving force for implementation

Process gas streams must often be cleaned to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as to compressors and turbo expanders. Toxic and other hazardous substances (e.g. coke fines and heavy-metal containing catalyst fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Reference literature

[194, Winter 2000], [168, VROM 1999].

4.23.4.4 Wet scrubbers

Description

In wet scrubbing, the dust is removed by countercurrent washing with a liquid, usually water, and the solids are removed as slurry. Venturi and orifice scrubbers are simple forms of wet scrubbers. The electro dynamic venturi (EDV) washer reduces the dust emission to 5 mg/Nm^3 . The technique combines venturi with electrostatic dust separation. EDV is reported to be used in the flue-gas treatment of combustion installations and incinerators. More information is available in the WI BREF [82, COM 2006].

Achieved environmental benefits

A hypothetical curve (US-EPA) illustrating particle size and collection efficiency for wet scrubber is shown in Figure 4.51. Wet scrubbers reduce between 85 and 95 % of the particulates and can achieve values of particulate concentration of $<30 - 60 \text{ mg/Nm}^3$. In addition to solids removal, wet scrubbers can be used to simultaneously cool the gas and neutralise any corrosive constituents. The collecting efficiency can be improved by the use of plates or packings at the expense of a higher-pressure drop.

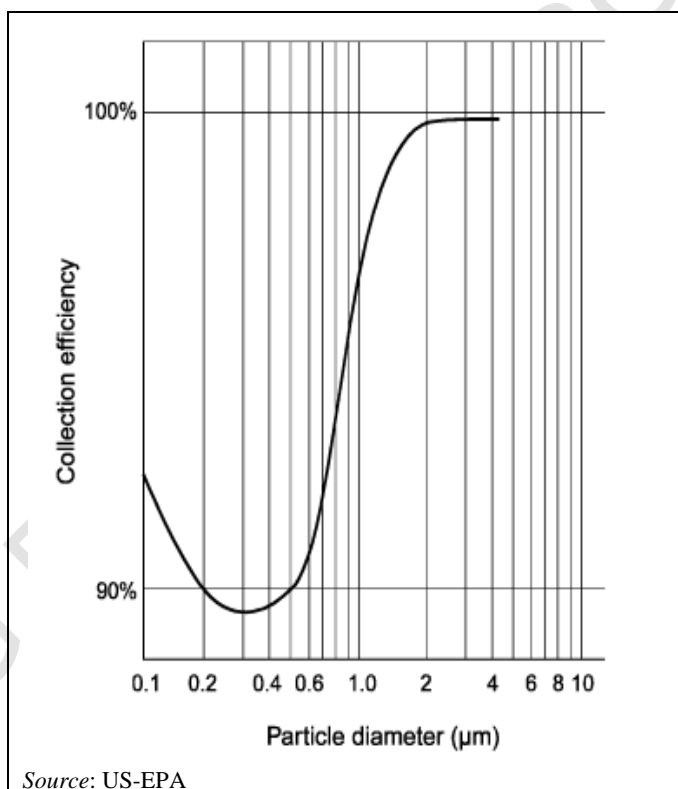


Figure 4.51: Wet scrubber collection efficiency

Cross-media effects

A reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift from an air emissions problem to a waste problem. Cross-media issues related to water also need to be considered. Scrubbers for dust removal may also be effective for SO_2 reduction. Wet scrubbing requires pumping energy as well as water and alkali.

Operational data

Dust collection equipment is normally simple to operate and is fully automated.

Applicability

Spray towers have a low pressure drop but are not suitable for removing particles below 10 μm . Venturi and packed bed washers have been installed for sludge incinerators.

Economics

Operating costs are in the order of EUR 0.5 to 10 per 1 000 Nm^3 treated flue-gas.

Driving force for implementation

Process gas streams must often be cleaned to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal-containing catalyst fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants

Some FCC units are equipped with scrubbers.

Reference literature

[194, Winter 2000], [168, VROM 1999]

4.23.4.5 Other wet techniques

Description

Centrifugal washers combine the cyclone principle and an intensive contact with water, like the venturi washer.

Achieved environmental benefits

Dust emissions can be reduced to 50 mg/Nm^3 and below if very large quantities of water are used, such as in an absorber used for a two-stage scrubbing system.

Operational data

Dust collection equipment is normally simple to operate and is fully automated.

Venturi washers need to be operated at sufficient pressure and at full water saturation of the gas phase to reduce the dust emission. For SO_2 removal scrubbing at $\text{pH} \pm 6$ with caustic or lime is necessary.

Applicability

Wash columns, or absorbers with packing are applied in various processes.

Driving force for implementation

Process gas streams must often be cleaned up to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as to compressors. Toxic and other hazardous substances (e.g. coke fines and heavy-metal-containing catalyst fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants

Venturi washers are mostly applied for the removal of a combination of dust, acidic components (HCl and HF) at for example cokers and incinerators.

Reference literature

[168, VROM 1999]

4.23.4.6 Combination of particulate abatement techniques

Often a combination of techniques is applied, such as cyclone/ESP, ESP/venturi/wash column or a cyclone/venturi/absorber leading to more than 99 % dust elimination.

4.23.5 Techniques for sulphur recovery and SO₂ abatement

Sulphur is an inherent component of crude oil. Part of this sulphur leaves the refinery in its products, part of it is emitted to the atmosphere (already described in all the processes) and part of it is recovered by some processes located in the refinery for this purpose (more information about the sulphur split in a refinery can be found in Section 1.4.1). Sulphur is an environmental issue that cannot be addressed in an integrated manner if the sulphur coming out with the products is not considered. In other words, decreasing emissions from a refinery may result in the production of fuels (products) that may later be burnt in a way that is not environmentally efficient, thereby jeopardising the environmental effort made by refineries. This is addressed through other types of both European and national legislations.

Because it is such an integrated issue, proper sulphur management should also consider other topics that may not be within the objectives of this document. For example, a global environmental impact assessment of sulphur dioxide emissions should consider items listed below:

- Atmospheric emissions from processes generating SO_x (furnaces, boilers, FCC, etc.). These issues are in fact included in this document in each of the process sections.
- Atmospheric emissions from sulphur recovery units or of gases containing sulphur in an H₂S form before incineration. This category of sulphur is normally recovered, as shown in Section 4.23.5.2.
- Atmospheric emissions generated by sulphur contained in products for which more stringent specifications already exist, such as gasolines, gas oils, etc. These emissions cannot be considered here because they do not fall within the scope of the IED legislation, but they should be considered as part of an integrated approach.
- Atmospheric emissions generated by products with less stringent specifications (bunkers, coke, heavy fuel oil). Typically, these products (heavy residues) contain high quantities of sulphur. If they are not used in a proper way from an environmental point of view, the emissions can jeopardise the integrated approach to reducing sulphur emissions from the refinery sector. Another threat to this integrated approach is the exporting of these products to countries with less environmental control.
- Sulphur contained in non-fuel products such as bitumen or lubricants is typically not identified as a problem.

In order to reduce the SO₂ emissions at the refinery level, the operator needs to set a global strategy and may have recourse to combinations of the following types of actions:

- selection of fuels and raw materials with low sulphur content, such as:
 - increasing the use of non or low-sulphur-containing gas (LPG, natural gas, etc.): see Section 4.10 on Energy systems;
 - using low-sulphur crudes (Sections 4.10).
- increase the efficiency of the various abatement techniques, such as:
 - SRU (see Section 4.23.5.2);
 - Fuel gas desulphurisation (H₂S reduction with amine-treating -see Section 4.23.5.1) or other techniques for FGD (see Section 4.23.5.4 and Sections 4.5.6 FCC units and 4.10.6 Energy system), gasification (see Section 4.10) or hydrotreatment (see Section 4.13.1).

In this section, only those processes dealing with the recovery of sulphur are considered. See also Section 4.23.8 for information on the SNO_x combined technique.

4.23.5.1 Amine-treating

Description

Before elemental sulphur can be recovered in the SRU, the fuel gases (primarily methane and ethane) need to be separated from hydrogen sulphide. This is typically accomplished by dissolving the hydrogen sulphide in a chemical solvent (absorption). Solvents most commonly used are amines. Dry adsorbents such as molecular sieves, activated carbon, iron sponge and zinc oxide may also be used. In the amine solvent processes, amine solvent is pumped to an absorption tower where the gases are contacted and hydrogen sulphide is dissolved in the solution. The fuel gases are removed for use as fuel in the process furnaces of other refinery operations. The amine-hydrogen sulphide solution is then heated and steam stripped to remove the hydrogen sulphide gas. In Figure 4.52 a simplified process flow diagram of an amine treating unit is shown.

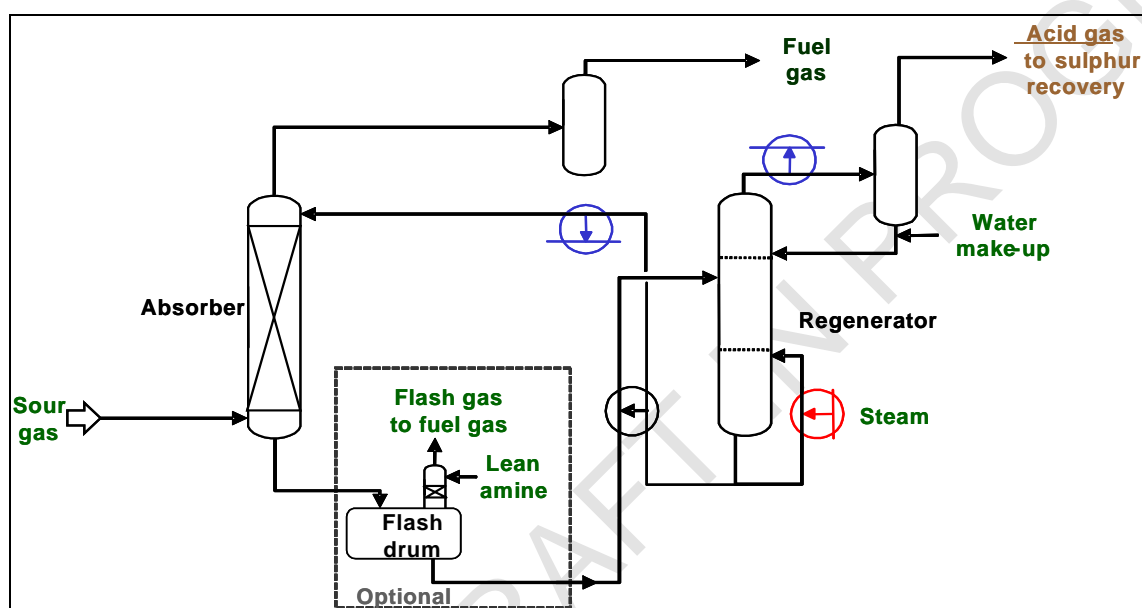


Figure 4.52: Simplified process flow diagram of an amine-treating unit

Online analysis of the H_2S content of the RFG leaving the absorber is fed back into the system process control to optimise the performance of the absorber.

The main solvents used are MEA (monoethanolamine), DEA (diethanolamine), DGA (diglycolamine), DIPA (diisopropanolamine), MDEA (methyl diethanolamine) and a number of proprietary formulations comprising mixtures of amines with various additives. One important issue concerning the selection of the type of amine is the selectivity concerning H_2S and CO_2 .

- MEA has had widespread use, as it is inexpensive and highly reactive. However, it is irreversibly degraded by impurities such as COS, CS_2 and O_2 , and therefore is not recommended when gases from cracking units are present.
- DEA is more expensive than MEA but is resistant to degradation by COS and CS_2 and has achieved widespread use.
- DGA is also resistant to degradation by COS and CS_2 but is more expensive than DEA and has the disadvantage of high hydrocarbon solubility into the solution.
- DIPA, which is used in the ADIP process, licensed by Shell. It can be used for selective H_2S removal in the presence of CO_2 and is also effective in removing COS and CS_2 .
- MDEA is nowadays most widely used, and has a similar characteristic to DIPA, i.e. it has a high selectivity to H_2S , but not to CO_2 . As MDEA is used as a 40 - 50 % solution (activated MDEA) in water, this also has the potential energy savings. Because of the low selectivity for CO_2 absorption, DIPA and MDEA are very suitable for use in

ClausTail gas amine absorbers, as these do not tend to recycle CO₂ over the Claus unit. MDEA is applied as a single solvent or as in proprietary formulation comprising mixtures.

Achieved environmental benefits

Sulphur is removed from a number of refinery process off-gas streams (sour gas or acid gas) in order to meet the SO_x emission limits of the applicable regulation and to recover saleable elemental sulphur. The amine-treating unit produces two streams for further use/processing in downstream units:

- the treated gas stream with a residual H₂S content normally in the ranges displayed in Table 4.80 and
- the concentrated H₂S/acid gas stream, which is routed to the SRU for sulphur recovery (discussed in Section 4.23.5.2).

Table 4.80: Residual H₂S concentration achievable in the refinery fuel gas

Typical amine-scrubbing pressure (absolute bar)	Residual H ₂ S concentration (mg/Nm ³)
3.5	20 – 220
20	4 – 40
50	2 – 15
<i>Source: CONCAWE 4/09 report-Daily average values</i>	

Cross-media effects

They are summarised in Table 4.81. Energy consumption must also be considered (see above).

Table 4.81: Overview of the cross-media effects related to some aspects of amine treating

	Source	Flow	Composition	Comments
Effluent: amine blowdown	Amine regenerator	10 – 50 t/yr for a 5 Mt/yr refinery	Decomposed amine up to 50 % in water	In order not to disturb the biotreater operation and to meet effluent discharge specifications on N-Kj a storage tank or production planning can be used to control very small flow to the WWTP. The WWTP microbiology requires acclimatisation time to be able to biodegrade amines - MDEA requires several days, for MEA it is shorter
Waste 1:	Amine filter cleaning residue	Plant specific	FeS and salt deposits	Removed by a skid-mounted unit operated by a specialised contractor (usually the filter supplier)
Waste 2:	Saturated activated carbon from skid- mounted unit	Plant specific	Decomposition products, heavy ends and amine emulsions	The saturated activated carbon filling has to be replaced occasionally for disposal or regeneration

Operational data

The use of selective amines should be considered, e.g. for a stream containing carbon dioxide. Measures should be taken to minimise hydrocarbons entering the sulphur recovery system; the

operation of regenerator feed drums should be controlled to prevent hydrocarbon accumulation in, and sudden release from, the amine regenerator, as this is likely to lead to an emergency shutdown of the SRU.

Utility consumption per tonne of H₂S removed in an amine-treating unit is approximately the following:

Electricity (kWh/t)	Steam consumed (kg/t)	Cooling water (m ³ /t, ΔT =10 °C)
70 – 80	1 500 – 3 000	25 – 35

Usually a fresh solvent make-up rate of 10 - 50 t/yr is required to maintain solvent strength for a 5 Mt/yr refinery.

Amine solutions should be reused wherever possible and where necessary, suitably treated before being properly disposed of. Recycling of monoethanolamine-solutions: corrosive salts, which concentrate during recycling, can be removed via ion exchange or thermal reclaiming techniques. Some proprietary solutions may be biodegradable under suitable conditions.

It is also important that the amine processes have sufficient capacity to allow for maintenance activities and upsets. This sufficient capacity can be achieved by having redundancy equipment, or by applying load shedding, emergency amine scrubbers or multiple scrubber systems.

Applicability

Process off-gas streams from the coker, catalytic cracking units, hydrotreating units and hydroprocessing units can contain high concentrations of hydrogen sulphide mixed with light refinery fuel gases. Additional treatment, such as COS converter, is necessary to ensure appropriate sulphur removal in off-gas from cokers (see Section 4.7.8.4). Emergency H₂S scrubbers are also important.

Economics

The cost of upgrading the refinery amine-treatment system (2 %) to meet 0.01 to 0.02 % v/v of H₂S in fuel gas is around EUR 3.75 to 4.5 million. This cost is battery limit costs based on 1998 prices and include items such as equipment, licence fees, foundations, erection, tie-ins to existing plant and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plant could have a significant impact. In some cases, these factors might be expected to increase the costs by some 50 %.

Driving force for implementation

To reduce the sulphur content of flue-gases.

Example plant(s)

Common technique used all over the world.

Reference literature

[168, VROM 1999], [182, Ecker 1999], [148, Irish EPA 1993], [207, TWG 2001]

4.23.5.2 Sulphur recovery units (SRU)

H₂S-rich gas streams from amine-treating units (see Section 4.23.5.1) and sour water strippers (see section 4.24.2) are treated in a sulphur recovery unit (SRU), which most often consists of a Claus process for bulk sulphur removal and subsequently a tail gas treatment unit (TGTU) for the remaining H₂S removal. Other components entering the SRU may include NH₃, CO₂ and, to a minor extent, various hydrocarbons.

4.23.5.2.1 Increased efficiency of the Claus Process

Description

The Claus process consists of the partial combustion of the hydrogen-sulphide-rich gas stream (with one-third of the stoichiometric quantity of air) and then reacting the resulting sulphur dioxide and unburnt hydrogen sulphide in the presence of an activated alumina catalyst to produce elemental sulphur. As shown in Figure 4.53, the Claus unit then consists of a reaction furnace followed by a series of converters and condensers, where:

- the partial combustion and a part of the sulphur formation ($2\text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{SO}_2 + \text{S} + 2\text{H}_2\text{O}$) occurs in the primary reactor;
- the main of Claus reaction for sulphur formation ($2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$) takes place in the different catalytic converters;
- and liquid elementary sulphur is collected from the various condensers in a common pit, as shown in Figure 4.53.

Side reaction effects also occur that produce carbonyl sulphide (COS) and carbon disulphide (CS₂), which have raised problems in many Claus plant operations because they cannot be easily converted to elemental sulphur and carbon dioxide.

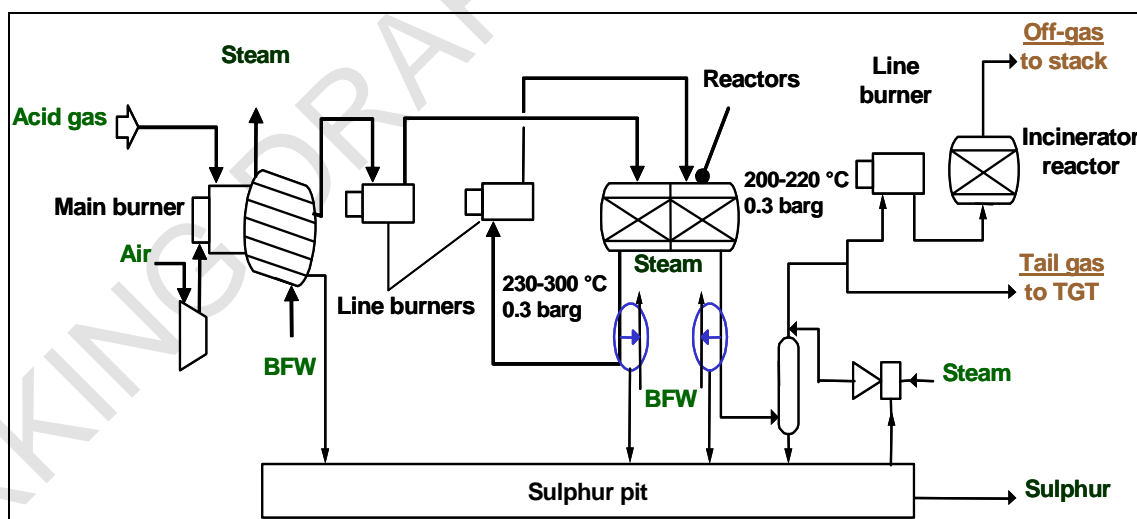


Figure 4.53: Simplified process flow diagram of a sulphur recovery unit (Claus process)

The overall capacity of the Claus plants can be increased with the use of oxygen enrichment technologies (e.g OxyClaus process). However, this has not had any beneficial effect in the sulphur-recovery efficiency of the Claus plant. The use of this process can increase the unit capacity up to 200 % in existing Claus sulphur-recovery units, or can be an option for a more economical design for new Claus sulphur units.

The techniques given below can be used and retrofitted to existing SRUs for increasing the Claus process efficiency.

- An improved unique burner system and enhanced combustion conditions to reach a minimum temperature of 1350 °C, which allows a better destruction of ammonia and mercaptans in the combustion chamber, and a reduction of the Claus catalytic bed plugging by ammonium salts [Questionnaire n° 31].
- High-performance catalysts process (e.g. Selectox), which can be used in combination with the first stage of the Claus unit to promote the oxidation of H₂S to SO₂ without the use of a flame. They allow for a significant increase in the sulphur-recovery efficiency.
- An automated control of the air feed to the Claus reaction furnace optimises sulphur recovery.

Achieved environmental benefits

The SRU is characterised by its sulphur-recovery efficiency, calculated as the fraction of sulphur in the feed which is recovered in the liquid sulphur stream routed to the sulphur collection pits. This fraction includes the dissolved H₂S (typically 200 – 500 ppm weight) which must be removed from the liquid sulphur at a later stage of the process (see Section 4.23.5.2.4 on sulphur degassing).

The sulphur-recovery efficiency of an SRU closely depends on the number of Claus reactors that are operated in series in the sulphur recovery unit chain, as shown in Table 4.82.

Table 4.82: Sulphur-recovery efficiency of Claus process SRUs in European sites

Number of Claus reactors	Number of data-sets	Sulphur recovery efficiency (% H ₂ S converted)		
		Observed range	Median	Typical
1	NA	NA	NA	90
2	87	92.4 – 97.8	96.1	95 – 96.5
3	27	96.0 – 98.4	97.0	96.5 – 98
<i>Sources: [36, CONCAWE n°4/09 2009]</i>				

Most recent or recently refurbished units have 3 – 4 stage units (including SuperClaus), meaning that they have 3 to 4 sets of converters and condensers.

Furthermore, state-of-the-art oxidation catalysts (e.g. Selectox or Criterion – these types of catalysts are suitable for promoting the Claus reaction) have been used in North American refineries with significant increased efficiency rates reported [25, Pham et al. 2009] specifically:

- from 90 to 97 %; at 1st Claus stage level;
- from 96 – 97 % to 99.8 – 99.9 %; for a full three-stage Claus unit followed by a tail gas treating unit that reduces sulphur components to H₂S and recover H₂S with amine treating. [261, Criterion 2006].

Cross-media effects

The reduction of SO₂ leads to an increase of the CO₂ emission. For example, for a 100 t/d sulphur Claus plant, the application of three reactors would lead to an emission of 4.8 tonnes of sulphur per day at a cost of 8.5 tonnes of CO₂ per day. Table 4.83 shows indicative estimates of the incremental emission of CO₂ which will be associated with the marginal incremental reduction of SO₂ achieved for various SRU+TGTU configurations. It is assumed that the low pressure steam generated on the SRU can be fully valorised as energy, which goes against the amine-based TGTU, but this does not necessarily reflect real case situations.

Table 4.83: CO₂ incremental emissions for the main categories of SRU+TGTU techniques

SRU technology	Incremental t CO ₂ per incremental t SO ₂ reduced (compared to a base two stage Claus ⁽¹⁾)
Two-stage Claus + 3rd stage Claus	0.25
Two-stage Claus + Superclaus	0.25
Two-stage Claus + Catalytic Oxidation	0.31
Two-stage Claus + sub-dewpoint TGPU	0.55
Two-stage Claus + amine based TGPU	0.75
⁽¹⁾ Based on a 100 t/d SRU fed with 80 % acid gas feed (95 % H ₂ S) and 20 % gas from the sour water stripper (56 % H ₂ S, 43 % NH ₃).	

Operational data

- Feed/air ratio control, temperature control of the furnace, reactors and condensers and good demisting of liquid sulphur, especially from the final condenser exit gas stream are important parameters in achieving maximum sulphur recovery. Good control and availability is crucial as a technique, to deliver any design targets. In this line, the use of state-of-the-art control and monitoring systems can be seen as an important technique. Use of a tail gas analyser linked to the process control system (feedback control) will aid optimum conversion during all plant operating conditions, including changes to sulphur throughput.
- To have an SRU configuration with sufficient capacity for the H₂S feed to the unit including the sourest crude oil to be used is important. The duplication of the SRU capacity is important to consider to obtain low sulphur emissions. This should also be large enough to allow the scheduled maintenance activity to proceed every two years, without a significant increase of sulphur emissions.
- To have utilisation factors close to 100 % increases how efficiently the units are used. These capacity factors must also include the impact of major turnaround maintenance.
- Use a good furnace burning-zone design and effective furnace temperature and oxygen control systems where sour water stripper off-gases are a feed stream, because the process must also be designed and operated to complete the destruction of ammonia. Ammonia breakthrough may lead to deposition and blockages of catalyst beds by ammonium salts (e.g. carbonate/sulphate) and these SRUs need to be monitored for avoidance of this.

Typical emissions and utilities necessary for a 20 000 t/yr SRU are summarised in Table 4.84 and Table 4.85.

Table 4.84: Typical emissions of a 20 000 t/yr SRU

Emissions based on a 20 000 t/yr SRU				
Type	Source	Flow	Composition min/max	Comments
Air emissions: CO ₂ SO ₂ NO _x	Incinerator off-gas	0.2 % of the total H ₂ S-load to the SRU	SO ₂ : 1 500 mg/Nm ³ Through presence of NH ₃ non-catalytic deNO _x ing takes place	Amount of SO ₂ released depends on total sulphur production and overall sulphur recovery or conversion
Liquid effluents:	Knock-out drum for water in SWS off-gas	0.02 m ³ /h	H ₂ S: 50 mg/l; Phenol: 100 mg/l; NH ₃ : 2 000 mg/l	To be treated in the SWS
Solid waste:	Spent SRU catalyst	Plant specific	Mainly Al ₂ O ₃ , depending on the catalyst composition	

Table 4.85: Typical utility consumption

Fuel (MJ/t)	Electricity (kWh/t)	Steam produced (kg/t)	Cooling water (m ³ /t, ΔT=10 °C)
1 000 – 1 600	60 – 75	1 500 – 2 000	0 – 20

In some cases, the SRU needs a pilot flame to co-fire natural or fuel gas when the H₂S concentration is so low that a stable flame cannot be achieved.

Applicability

Fully applicable. The OxyClaus process and other oxygen enrichment technologies increase the plant flexibility, as they allow the treatment of feed gases for a wide H₂S content range of 20 – 100 % (volume). Temporary higher, lower or fluctuating amounts of hydrogen sulphide can be handled by automatic changeover from air to oxygen operation and vice versa. Higher hydrocarbon contents can also be processed, and an almost complete combustion of the ammonia contained in sour water stripper off-gases, provided the reaction furnace temperature is above 1 350 °C, adequate residence time, and a properly designed burner.

Economics

Table 4.86: Cost examples of two typical upgrading projects for an existing two-stage 100 t/d SRU

Upgrading project	Plant size range	Approximate capital cost (EUR million installed)	Approximate operating cost per year (EUR million)
Upgrade SRU with O ₂ enrichment to increase throughput from 100 t/d to 170 t/d ⁽¹⁾	100 t/d	2.1 – 5.3	1.6 (oxygen consumption)
Addition of a 3rd stage Claus reactor ⁽²⁾	100 t/d	2.0 – 3.0	0.1

⁽¹⁾ There are battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, erection, tie-ins to existing plant and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plant could have a significant impact. In some cases, these factors might be expected to increase the costs by some 50 %.

⁽²⁾ Capacity of the process: 30 000 t/yr of sulphur production. Volume of gas to be treated: 60 million m³/yr. Pollutant initial concentration: 34 000 mg SO₂/m³ (1.2 % molar or 2.3 % weight, the rest considered as air) – 1998 prices

See also Table 4.94 for additional information on costs related to SRUs.

Driving force for implementation

To reduce sulphur emissions.

Example plants

In the market, more than five licensors of this process exist. The Claus process is public and widely applied in the refinery sector. Two stages Claus process is the most common in Europe. More than 35 OxyClaus systems (4 – 270 t/day) are in operation around the world.

Reference literature

[194, Winter 2000], [201, Manduzio 2000], [166, CONCAWE 1999], [151, Sema, Sofres 1991], [181, HP, 1998], [165, Ademe 1999], [25, Pham et al. 2009], [36, CONCAWE n°4/09 2009], [261, Criterion 2006].

4.23.5.2.2 Tail gas treatment units (TGTUs)

Description

Current methods for removing sulphur from the hydrogen sulphide gas streams are typically a combination of two processes: the Claus process (See Section 4.24.5.2.1) followed by a tail gas clean-up or treatment unit (TGTU). Since the Claus process by itself removes only about 94 – 96 % (two stages) or 96 – 98 % (three stages) of the hydrogen sulphide in the gas stream, the TGTU processes must be used to further recover sulphur.

A large number of processes for TGTUs have been developed in order to enhance the recovery of sulphur compounds from natural gas and/or refinery sources. The most frequently operated TGTU processes (see Figure 3.36 in Section 3.23.2) can be broadly divided into the following four categories according to the principles applied:

- direct oxidation to sulphur
- continuation of the Claus reaction
- reduction to H₂S and recovering sulphur from this H₂S
- oxidation to SO₂ and recovering sulphur from SO₂

4.23.5.2.2.1 Direct oxidation to sulphur

In these processes, the main step is achieved on a solid catalyst. In particular:

- **PRO-Claus** stands for Parson RedO_x Claus. It is a dry catalytic process that contains three additional stages (one reduction and two oxidations). In the 1st stage, a highly-selective catalyst developed by the US Lawrence Berkeley National Laboratory is used for the reduction of SO₂ to elemental sulphur. In the 2nd stage, the remaining H₂S is then oxidised to also form elemental sulphur under the presence of another highly specialised catalyst. The remainder is sent to a thermal oxidiser.
- **The SUPERCLAUS** process is by far the most commonly used in this category. It is based on two principles: i) operating the Claus plant with excess H₂S to minimise the SO₂ content in the Claus tail gas, and to simplify and make more flexible the air ratio control, and ii) oxidising selectively the remaining H₂S in the Claus tail gas by means of a specific catalyst, which efficiently converts the remaining H₂S in the presence of water vapour and excess oxygen into elemental sulphur only. This reaction takes place in a specific converter (an oxidation reactor), downstream of two or three reactors in the traditional Claus unit. The catalyst used is an alumina-based catalyst coated with iron oxide and chromium oxide layers.

4.23.5.2.2.2 Continuation of the Claus reaction

These processes operate over a bed of standard Claus catalysts or a non-volatile organic solvent under sub-dew point conditions in the liquid phase. In particular:

- The **CBA** (cold bed absorption) process is very similar to the Sulfreen process except in the fact that the CBA process uses a hot process stream indigenous to the Claus process to accomplish regeneration of the sulphur loaded catalyst bed. The hot process stream is part of the effluent of the first Claus reactor. Several configurations are available depending on the number of Claus converters.
- The **CLAUSPOL** is a process where the tail gas is put into contact with a solvent (polyethylene glycol) and the reaction of H₂S and SO₂ is catalysed by a dissolved catalyst (sodium salt of an inorganic acid, e.g. sodium salicylate), which is a solvent for H₂S and SO₂, but not for liquid sulphur. The Claus reaction can therefore proceed at low temperatures (120 °C) and is shifted further to the right as the produced sulphur is removed from the reaction medium, as it is not soluble and separates.

- The **SULFREEN** process is a dry-bed, sub-dew point absorption process based on the extension of the Claus reaction, i.e. catalytic oxidation of H_2S to S. This basically consists of two (occasionally three for large capacities) Sulfreen reactors in series with the Claus reactors. Activated alumina is used as a catalyst. Regeneration is needed since the sulphur accumulates on the catalyst decreasing its activity. Sulphur from the hot regeneration stream is condensed in a dedicated condenser. Several variations are used.
- The **HydroSulfreen** adds a conversion step upstream of the first sulfreen reactor, to perform the hydrolysis of COS and CS₂ to H₂S with the help of an activated titanium oxide Claus catalyst in order to adjust the H₂S/SO₂ ratio more precisely. The Claus reaction takes place in the HydroSulfreen reactor and sulphur produced is condensed in a dedicated condenser
- The **DoxoSulfreen** concept is based on two ideas: the upstream units are operated to get a slight excess of H₂S, compared to the quantity necessary to maintain the Claus ratio, therefore a nearly total SO₂ conversion takes place on the conventional Sulfreen catalyst; then the remaining H₂S is directly oxidised to elemental sulphur
- The **MAXISULF** is a simplified sulfreen process, including basically a one-stage (one absorber, one regenerator) unit with an open regeneration loop. The regeneration gas is fed to the absorber together with the Claus tail gas.

4.23.5.2.2.3 Reduction to H₂S and recovering sulphur from H₂S

The recovery of sulphur can be carried out with amine scrubbing processes for recycling to the upstream Claus unit. In particular:

- The **FLEXSORB** process has been developed by Exxon Mobil as an alternative to the MDEA amine treatment process. A specific solution is used to remove H₂S from the tail gas after conversion of sulphur compounds to H₂S has been performed. The absorbed H₂S is recycled back to the Claus plant for sulphur recovery.
- The **HCR** (High Claus Ratio) process is directly derived from the SCOT and designed by Siirtec Nigi.
- The **RAR** (Reduction, absorption, recycle) is a MDEA reductive treatment allowing the use of plain MDEA or specifically-formulated MDEA-based solutions. It was originally designed for Claus tail gas treatment, but can also be applied to other, more complex, hydrogen sulphide-containing gas streams which are either too diluted or too contaminated for direct processing through normal Claus units.
- The **SCOT** (H₂S Scrubbing) process is by far the most widely applied in this category. SCOT stands for Shell Claus off-gas treatment. As shown in Figure 4.54, the concepts underlying H₂S scrubbing processes are:
 - hydrogenation and hydrolysis of all sulphur compounds to H₂S passing it through a cobalt-molybdenum catalyst at 300 °C with the addition of a reducing gas;
 - absorption of H₂S by an amine solution (generic amine or specialty amine);
 - regeneration of the amine solution and recycle of the H₂S to the upfront Claus reaction furnace.
- The **BSR** (Beavon Sulphur Removal) process family where, in a first step, sulphur compounds are catalytically (cobalt-molybdate based) converted into H₂S through an hydrogenation/hydrolysis reaction at high temperature (300 – 400°C). In a second step, H₂S is removed by a chemical solution (e.g amines process) or another tail gas process.

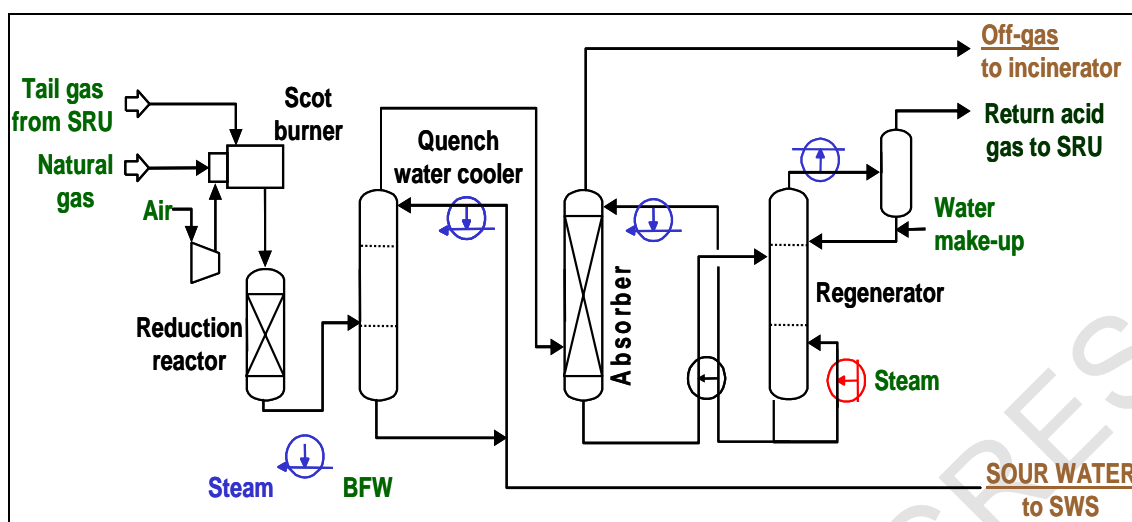


Figure 4.54: Simplified process flow diagram of a tail gas SCOT unit

The recovery of sulphur can be carried out with other recovery process such as the following:

- The **LO-CAT** process is a liquid redox system that uses a chelated iron solution to convert H_2S . Absorption and regeneration are performed in a single vessel divided into two sections: the centerwell and the outer space where aeration with air is performed. The purpose of the centerwell is to separate the sulphite ions from air in order to minimise by-product formation (e.g. thiosulphate). The difference in aeration (and therefore of density) between the centerwell and the outer space give sufficient driving force for solution circulation between the absorption and the regeneration zones without the need for a specific pump. The last type of processing scheme is called the 'aerobic unit' and is used to treat air contaminated with H_2S . All reactions take place in the same vessel, at the expense of increased by-product formation, but with the advantage of a reduced capital cost.
- **MODOP or BSR/SELECTOX** processes use direct oxidation after reduction to H_2S .

4.23.5.2.2.4 Oxidation to SO_2 and recovery of sulphur from SO_2

The processes used one of the following (for more details see also Section 4.23.5.4 on Sulphur dioxide abatement techniques)

- **The WELLMAN LORD** process, where sodium sulphite reacts with SO_2 in the flue-gases forming sodium bisulphite. The concentrated solution is collected and evaporated for regeneration. In the regeneration step, using steam, the sodium bisulphite is broken down, to release the sodium sulphite, to be recycled back to the flue-gases.
- **The CLINTOX** process, where the sulphur species are burnt to be converted to SO_2 , which is then absorbed in a physical solvent, stripped from the solvent and returned to the Claus plant to replace oxygen in the air and contribute to increase the sulphur capacity of the Claus furnace unit.
- **The LABSORB** process, based on a absorption/regeneration cycle including the use of an absorbing solution containing caustic soda and phosphoric acid to capture SO_2 as sodium bisulphite.

Achieved environmental benefits

Tail gas treatment units increase the overall recovery of H₂S and decrease the sulphur emissions from the refinery. For example, if a refinery has a 100 t/d SRU, with a two-stage Claus reactor, this SRU will emit around 5 t/d (1 750 t/yr) of sulphur, and will most likely be one of the major SO₂ emission sources of the site. If a tail gas clean-up process is included in such a refinery, the emissions of sulphur may be reduced to 0.5 t/d, representing a reduction of 90 % of the sulphur emissions from the sulphur recovery units, and saving 1 575 t/yr of SO₂.

Table 4.87 shows the expected overall sulphur recovery yield, the resulting additional recovered sulphur and the dry basis sulphur emission (in the form of SO₂ species) after incineration, of a selection of the tail gas treatments considered in this section.

WORKING DRAFT IN PROGRESS

Table 4.87: Expected performances of SRU for various TGTU processes and configurations

For a generic 100 t/day SRU initially equipped with a two-stage Claus:	Expected sulphur recovery efficiency ⁽¹⁾	Expected additional sulphur recovered ⁽²⁾	Indicative SO ₂ concentration after incineration step (3 % O ₂ content - dry basis) ⁽¹⁰⁾
Added process:	(%)	t/d	mg/Nm ³
Base (two-stage Claus)	95 – 96	-	31 000 – 38 000
+ 3rd stage Claus	96 – 98	1.00 – 2.00	16 000– 31 000
+ 3rd stage Claus and Selectox	97	NA	24 000
I. Direct oxidation to sulphur			
+ PRO-Claus	99.5	4.10	4 000
+ Superclaus	98 – 99.3 ⁽⁷⁾	2.77	5 700 – 16 000
II. Continuation of Claus reaction/Subdewpoint			
+ CBA (cold bed absorption)	99.3–99.4	3.65	5 000– 5 700
+ Clauspol ⁽⁶⁾	99.5 – 99.9		800 – 4 000
+ Clauspol II ⁽⁸⁾	99 – 99.8	3.75	1 600 – 8 100
+ Sulfreen	99 – 99.2	3.56	6 500 – 8 100
+ 3 rd stage Claus + Sulfreen	99.2 – 99.5		4 100 – 6 500
+ DoxoSulfreen ⁽⁴⁾	99.8 – 99.9	4.04	800 – 1 600
+ HydroSulfreen ⁽³⁾	99.5 – 99.7		2 500 – 4 100
+ Maxisulf	98.5		12 500
+ 3 rd stage Claus + Maxisulf	99.0 – 99.5		4 000 – 8 100
III. Reduction to H₂S and S recovery from H₂S			
+ Flexsorb	99.9	4.10	800
+ RAR	99.9	4.10	800
+ SCOT (amine based process)	99.5–99.95	NA	400 – 4 100 ⁽⁹⁾
+ LO-CAT II ⁽⁵⁾	99.99	4.16	90 ⁽⁹⁾
+ Beavon (BSR)	99.5 – 99.9	NA	800 – 4 100 ⁽⁹⁾
IV SO₂ abatement			
Scrubbing techniques	99.9		800 ⁽⁹⁾
Main source for sulphur recovery efficiency: [131, Ballaguet et al. 2006],[76, Hydrocarbon processing 2011]			
⁽¹⁾ For the whole treatment train (SRU + TGTU).			
⁽²⁾ From the TGTU step only.			
⁽³⁾ Sulfreen reactors and hydrolysis section.			
⁽⁴⁾ Sulfreen reactors, hydrolysis section and DoxoSulfreen reactors.			
⁽⁵⁾ As LO-CAT II tail gas cannot be incinerated, sulphur is in the form of H ₂ S species.			
⁽⁶⁾ See present section under applicability information.			
⁽⁷⁾ Values from provider - Upper level is the maximum value guaranteed			
⁽⁸⁾ Upper level requires COS and CS ₂ to be hydrolysed down to 300 ppmv of S through the catalytic stage.			
⁽⁹⁾ Incineration step may not systematically be required for this technique			
⁽¹⁰⁾ Using the calculation described in Annex 9.6 Appendix B – SO ₂ concentration after the incineration step is dependent on the fuel gas/acid gas ratio (FG/AG is specific to SRU configuration and operating parameter). For illustration, the calculation has been made for a FG/AG ratio of 4 %			

Cross-media effects

As already mentioned, the reduction of SO₂ leads to an increase in the CO₂ emissions (see Table 4.83 in Section 4.23.5.2.1). For instance the application of a tail gas treatment would lead to a SO₂ reduction of 96 % (if compared with the three reactor option), however at an increase in CO₂ of 110 %. For example for a 100 t/d sulphur Claus plant with three reactors, the application of a TGTU would reduce emissions of SO₂ to 0.1 t/d, but at a price of increasing the CO₂ emissions to 18 t/d.

Table 4.88: Cross-media effects associated with some of the TGTU

Emissions based on 20 000 t/yr SRU/TGCU				
	Source	Flow	Composition min/max	Comments
Effluents	Sour water from quench column for SRU off-gas	1 m ³ /tonne S produced (2 m ³ /h)	H ₂ S: 50 mg/l; Phenol: 100 mg/l; NH ₃ : 2 000 mg/l	To be treated in the SWS
Waste: SCOT	Spent TGTU catalyst	Regeneration and disposal 20 – 100 t/yr	2 – 8 % Ni/Mo on Al ₂ O ₃ , S: 5 – 15 %; Coke: 10 – 30 %	Spent Claus catalyst is pyrophoric and needs purging with N ₂

Operational data

The actual sulphur recovery yield from the SRU associated with its TGTU depends on the feed composition, the catalyst run time (for catalytic oxidation TGTU), and the progressive fouling during the operation run. Table 4.89 is based on actual sulphur recovery measurements taken in more than 40 European refineries between 2004 and 2008. Measurement campaigns have been carried out during a limited period of time (1 – 2 days) at various given times in the catalyst cycle, thus reflecting a wide range of unit operating conditions and catalyst lifetime situations.

Table 4.89: Expected range of recovery efficiencies for main TGTU categories

TGTU categories	Number of data-sets	% Recovery efficiency (% H ₂ S converted) as daily average for the whole SRU+TGTU		
		Observed range	Median	Typical
Catalytic direct oxidation	26	95.5 – 99.3	98.5	98 – 99
Sub-dew point	16	98.0 – 99.8	99.4	99 – 99.5
Amine-based	19	98.7 – 99.99	99.9	99.5 – 99.95

Source: CONCAWE

Another set of site data recovery efficiencies for 8 SRU from five German refineries and is shown in Table 4.90.

Table 4.90: Range of sulphur recoveries measured after TGTU in 5 German refineries

Refinery/ installation number	TGTU process	Sulphur capacity (t/d)	Operating grade (t/d)	Measured % recovery efficiency (¹)
Ref 2 –Claus 1	Incineration	34.7	18.1	98
Ref 3 –Claus 1	Incineration	16	Na	98
Ref 3 –Claus 2	Incineration	17	Na	98
Ref 1 –Claus 1	Sulfreen	55	26.4	99.6
Ref 4 –Claus	Sulfreen	69.9	55.2	99.5
Ref 1 –Claus 2	SCOT	170	Na	99.9
Ref 5 –Claus	SCOT	128.6	80	99.7
Ref 2 –Claus 2	Clauspol II	33.6	10.2	98.8

(¹) Estimated as efficiency = 1-SER (sulphur emission ratio) - Daily average.

Applicability

TGTUs are applicable to both new and existing plants. Capacities range from two to more than 2 000 tonnes of sulphur per day from the combined Claus/tail gas treatment units. However, the space occupied by such units can be significant. As an example, a new TGT unit (540 t/day gas treatment capacity – 10 t/day sulphur recovery) including a third Claus stage and a Sulfreen Maxisulf TGT was built in 2008 on a French site and occupies an area of 960 m².

Significant difficulties have been reported concerning the poor utilisation factor of 2 Clauspol units (0 – 25 %), due to side reactions favouring the formation of sodium salt precipitates and highly corrosive components (native SO₃ and NH₄HSO₄). Furthermore, shutdowns for cleaning and maintenance generate large quantities of heavily polluted waste waters contaminated with sulphur and PEG (DCO 200 g/l).

Economics

Table 4.91 gives estimates of costs for a new SRU or for the upgrading of an existing SRU, depending on the sulphur recovery yield target and the treatment capacity, while Table 4.92 shows a relative capital cost comparison for the main categories of TGT options reported to a two-stage Claus base case.

Table 4.91: Cost examples for new SRUs and SRU upgrading versus treatment capacity

Recovery yield objective	Plant size range	Approximate capital cost (EUR million installed)	Approximate operating cost (EUR per year)
Additional 3rd stage Claus + TGTU (Maxisulf) to give >98.5 %	540 t/d	31 (2008)	NA
New Sulfreen TGT (Sulfreen) on existing SRU to give 99.5 %	175 t/d	18 (2006)	NA
Additional 3rd stage Claus + TGTU (Superclaus) to give >98.5 %	210 t/d	26 (2005)	600 000 (2005)
New SRU including TGTU to give >99 % S recovery (1998)	50 t/d 100 t/d 250 t/d	12 19 35	NA
Tail gas treatment unit to improve existing SRU recovery to 99 % (1998)	50 t/d 100 t/d 250 t/d	1.6 2.1 2.9	NA
Tail gas treatment unit to improve SRU existing recovery to 99.8 % (1998)	50 t/d 100 t/d 250 t/d	3.5 4.4 6.3	NA

There are battery limit costs including equipment, licencing fees, foundations, erection, tie-ins to existing plant and commissioning. They are an in order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plants could have a significant impact. In some cases these factors might increase the costs by some 50 %.

Table 4.92: Relative capital cost for the upgrading of an existing 100 t/d SRU

SRU upgrading technology option	Relative capital cost in 2009 ⁽¹⁾
Two-stage Claus	100
Two-stage Claus + 3rd stage Claus	109
Two-stage Claus + sub-dewpoint TGT (e.g. CBA)	120
Two-stage Claus + catalytic direct oxidation TGT (e.g. SuperClaus)	130
Two-stage Claus + advanced Sulfreen TGT	140
Two-stage Claus + amine-based TGT	194

⁽¹⁾ Based on a 100 t/d SRU fed with 80 % acid gas feed (95 % H₂S) and 20 % gas from the sour water stripper (56 % H₂S, 43 % NH₃).

The reference to the upstream sulphur unit is indicative and corresponds to the way this kind of comparison is usually presented in the literature. This comparison should be taken with care when comparing with other studies, as the capital cost of a sulphur unit may fluctuate +/- 30 %.

Examples of cost effectiveness for the upgrading of different types of Claus plant with various techniques are shown in Table 4.94.

Operating costs for two Hydrosulfreen units of total maximum capacity 15.2 t/h (44 000 Nm³/h) are estimated in Table 4.93. Costs are given for an utilisation factor of 82 % for each unit.

Table 4.93: Detailed operating costs of a Hydrosulfreen TGT unit

	Consumption	Cost (EUR/h)
Catalyst and utility consumption		
Catalysts and activated carbon	5 year lifetime basis (assumed)	9.13
Fuel gas to incinerator	0.68 t/h	222.4
Combustion air to incinerator	17.32 t/h	10.8
LP Steam	0.70 t/h	11.5
Boiler feed water	8.81 t/h	26.4
Air + nitrogen	50 + 25 m ³ /h	1.7
Electricity	330 kW installed	12.4
	Total:	294.33
Utility production		
MP Steam production	8.39 t/h	-143.7
LLP Steam production	2.90 t/h	-41.8
	Total:	-185.5
	Net cost:	109

Table 4.94 Economics of three SO₂ abatement techniques in sulphur recovery units – Cost effectiveness data from a sample of 7 SRU units

							Direct oxidation to sulphur (e.g. Super Claus process)					Subdewpoint (e.g. Sulfreen process)					
							Efficiency	ACC	Fixed OP	Variable OP	S market value €/t S	Efficiency	ACC	Fixed OP	Variable OP		
Base case in 2006 - Claus process							99 %	7.4 %	4 % TEC/yr	3.9 €/t S	160	99.5 %	7.4 %	4 % TEC/yr	2.8 €/tFF		
Unit	Number parallel trains	Design S	Utilisation	Actual S	Incinerator t/yr	S recovery efficiency	S recovery efficiency	SO ₂ removed (From Base)	Total erected Cost (From Base)	Annualised Cost: Base to SClaus	Cost Effectiveness: Base to SClaus	S recovery efficiency	SO ₂ removed (From Base)	Total erected Cost (From Base)	Annualised Cost: Base to Su;lfreen	Cost Effectiveness: SClaus to Sulfreen	
		t/yr	%	t/yr	t/yr	%	%	t/yr	M€	k€/yr	€/t SO ₂		t/yr	M€	k€/yr	€/t SO ₂	
1	2	150 380	58 %	87 833	1 313	98.5 %	99 %	843	26.1	3 243	346	99.5 %	1 734	65.2	7 539	4 819	
2	1	36 500	43 %	15 604	566	96.5 %	99 %	808	8.4	959	1 185	99.5 %	970	21.1	2 374	8 754	
3	1	36 865	38 %	14 186	233	98.4 %	99 %	176	8.5	1 009	5 715	99.5 %	320	21.2	2 437	9 897	
4	1	87 965	58 %	50 819	513	99.0 %						99.5 %	513	35.8	4 184	8 152	
5	1	26 280	76 %	20 068	140	99.3 %						99.5 %	77	17.3	2 027	26 020	
6	2	151 475	28 %	42 116	420	99.0 %						99.5 %	414	65.5	7 548	18 203	
7	3	237 250	70 %	166 562	599	99.6 %											
Amine based (e.g. SCOT single train)																	
		Efficiency	ACC	Fixed OP	Variable OP												
		99.9 %	7.4 %	4 % TEC/yr	5.1 €/tFF												
Unit	S recovery efficiency	SO ₂ removed (From Base)	Total erected Cost (From Base)	Annualised Cost: Base to Su;lfreen	Cost Effectiveness: Sulfreen to SCOT												
		t/yr	M€	k€/yr	€/t SO ₂												
1	99.9 %	2 448	98.8	11 513	5 573												
2	99.9 %	1 100	42.2	4 807	18 807												
3	99.9 %	436	42.5	4 882	21 198												
4	99.9 %	924	71.6	8 348	10 141												
5	99.9 %	240	34.7	4 037	16 851												
6	99.9 %	755	99.2	11 464	15 186												
7	99.9 %	864	129.9	15 586	18 046												

Source: [139, CONCAWE 6/11 2011]

Driving force for implementation

To reduce sulphur emissions and recover sulphur.

Example plants

These techniques are widely used at refineries in the world.

Table 4.95: Approximate number of commercial installations in the world

Technique	Number of installations all over the world
Beaven	>150 installations
Clauspol	>50 units
Sulfreen/hydrosulfreen	>150 units in operation
Superclaus	>70 commercial plants

Reference literature

[177, WRA 1999], [163, FWE 1999], [224, Kerkhof 2000], [200, Gilbert 2000], [166, CONCAWE 1999], [160, Janson 1999], [181, HP, 1998], [165, Ademe 1999], [151, Sema.Sofres 1991], [244, France 2001], [33, Lurgi 2005], [36, CONCAWE n°4/09 2009], [Questionnaire n°11, 14, 18, 28 (spec.attachments)], [107, Kohl 1997], [131, Ballaguet et al. 2006], [139, CONCAWE 6/11 2011], [76, Hydrocarbon processing 2011].

4.23.5.2.3 Wet gas scrubbing of the SRU off-gas

Other techniques than additional tail gas treatment of the SRU off-gas may be used, such as the SNO_x (a combined NO_x and SO_x abatement technique, see Section 4.23.8) or scrubber techniques, as presented in this section.

Description

As an alternative to an additional TGTU, some refineries have installed non-regenerative or regenerative scrubbers in order to abate sulphur emissions from their SRUs.

- Non regenerative scrubbers used for this application can be of any type such as a jet ejector venturi, high energy venturi, magnesium-based or seawater scrubber. One type of scrubber that has been applied is a two-stage caustic scrubbers (DynaWave) incorporating specific technologies for the enhancement of quenching and frothing effects in order to maximise the turbulent mixing and the gas asorption. These scrubbers are equipped with a droplet removal section and, optionally, brinks mist eliminators.
- A regenerative scrubber based on the Cansolv technology, also used for the desulphurisation of waste gas in sulphuric acid plants and power plant boilers.

Achieved environmental benefits

The sulphur removal efficiency of the DynaWave non-regenerative scrubber is reported to be above 99.99 %. In related refineries, SRU sulphur recovery/removal efficiency reaches a 99.95 % rate.

Cross media effects

Water, reagent and energy consumption.

Economics and operational data

Not available.

Applicability

A DynaWave non-regenerative caustic scrubber has been in operation in two US refineries since 2004, and in another one since 2006.

A regenerative scrubber was installed during four months in 2006, and then it was shut down due to technical problems (independent from the Cansolv section).

Examples plants

Sinclair Oil Corporation-Sinclair, Casper and Tula refineries (US)

BP-Cherry Point refinery (US)

Driving force for implementation

TGTU as described in Section 4.23.5.2.2 produces a concentrated H₂S stream which is recycled to the front end of SRU units for treatment. While this approach typically increases the sulphur-recovery efficiency, it also tends to reduce the amount of fresh acid gas that can be potentially treated by the Claus process. Therefore, non-regenerative scrubbing is preferred for undersized or critical capacity SRUs, in order to avoid the SRU capacity decrease generated by the additional TGTU recovery capacity. With this approach, there is no concentrated H₂S stream recycled to the front end of the SRU.

4.23.5.2.4 Stored sulphur degassing**Description**

In order to reduce the emissions of H₂S from the storage and transport of liquid sulphur, and to improve the product quality, the amount of H₂S and polysulphides in the sulphur can be reduced by oxidation or treatment with a suitable additive.

Achieved environmental benefits

Lowering H₂S concentrations in the gaseous phase of sulphur tanks reduces air releases during handling and improves operator safety. There are a number of techniques for sulphur degassing (SNEA or Aquisulf, Shell, Exxon and Texasgulf). With the Aquisulf degassing process, for example, residual H₂S in liquid sulphur can be reduced down to less than 10 mg/kg.

Cross-media effects

None in particular. Moreover, the reduction of H₂S in the liquid sulphur has a positive effect on the solidity of formed sulphur, and particularly on the sulphur slate strength.

Operational data

Not available.

Applicability

Fully applicable.

Driving force for implementation

To reduce operational hazards (toxicity and explosivity) and environmental nuisances due to H₂S desorbed and accumulated in the gaseous phase of fixed and transportation tanks.

Examples plants

There were more than 50 Aquisulf sulphur degassing units, with capacities of 20 – 3 600 t/day in operation at the end of 2005.

Reference literature

[207, TWG 2001], [33, Lurgi 2005].

4.23.5.3 Hydrogen sulphide and light mercaptan removal

Description

The system works with a fixed-bed or batch-type granular reactant where iron compounds (Fe_3O_4 and Fe_2O_3) react with H_2S to form FeS_2 (pyrite).

Achieved environmental benefits

Processes for odour and low emission control features.

Applicability

Applications to waste water systems, land oil tanker vent, oil storage and transportation, and bitumen plants. Final polishing for odour control may be required to remove higher mercaptans and dimethyl disulphide.

Driving force for implementation

Processes for odour and emission control features.

Example plants

More than 1000 applications worldwide. Processes are licensed under SulfaTreat name.

Reference literature

[181, HP, 1998]

4.23.5.4 Sulphur dioxide abatement techniques

In refinery flue-gases or waste gases, SO_2 may have unabated concentration levels of 1 500 – 7 500 mg/m^3 . Flue-gas desulphurisation (FGD) is a technique by which SO_2 is removed from these gases. FGD processes often involve an alkaline sorbent which captures SO_2 and transforms it into a solid product. Various FGD methods exist with varying SO_2 removal efficiencies. Recent years have shown the development of solvent/catalyst regenerative processes, in which the absorbing/concentrating medium is regenerated and reused. More information can be found in the CWW BREF [6, EC 2003].

Systems either of the regenerative type or the non-regenerative type exist for SO_x removal only, and also for the simultaneous removal of dust and NO_x . They are competitive with systems consisting of separate units for SO_2 elimination (i.e. wet scrubbers) and NO_x removal (i.e. SCR).

Description of the non-regenerative processes

Additive injection (AI) and *spray dry absorber (SD)* are scrubbing processes that remove SO_2 according to the same principle as Wet Limestone Scrubber (WS). They involve a reaction with a Ca-based sorbent however, without the complicating requirements for producing a high-grade gypsum by-product (i.e. prescrubbing and oxidising). The by-product is a mixture of sulphites, sulphates and fly ash, for which there are few or no useful applications. The AI process provides moderate SO_2 removal at relatively low sulphur loads. A dry sorbent is injected into the furnace. The sorbent used is limestone or hydrated lime (for small boilers, more active sodium bicarbonate (NaHCO_3) is injected in the flue-gas duct).

Seawater scrubbing uses the natural alkaline constituents – bicarbonates – of seawater to remove SO_2 . This implies a potential for high removal efficiencies. The discharge will contain sulphate and chlorine ions - which are a natural constituent of seawater.

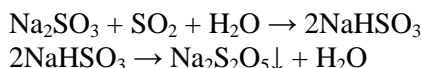
Walther (WA) is a process where SO_2 is absorbed by spray injection of aqueous ammonia, yielding ammonium sulphite. The sulphite is subsequently oxidised to sulphate. The ammonium salt solution from the scrubbing section is concentrated in an evaporation unit and granulated. The end-product is a marketable fertiliser.

Wet limestone scrubber (WS) systems have been very much improved recently and have become less complex than the earlier systems. Generally a limestone/water slurry is used as the sorbent. Gypsum is produced by oxidation (aeration) in the sump of the absorber.

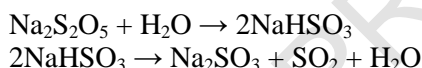
Description of the regenerative processes

Regenerative processes have been widely applied in refineries for SO₂ abatement. The first was the Wellmann-Lord, then the Cansolv and the Labsorb process.

Wellman Lord (WL) is the most widely used regenerative process. The process is based on sodium sulphite/bisulphite equilibrium. The first step is the absorption of SO₂ in a sodium sulphite aqueous solution, forming sodium bisulphite (NaHSO₃). By decreasing the temperature, sodium bisulphite is then converted into sodium pyrosulphite (Na₂S₂O₅) which precipitates, due to its much lower solubility:



By reheating this precipitate with water, the reversed reactions can occur, allowing the regeneration of SO₂, and the recycling of sodium sulphite into the process.



In US, oil refineries where this process is operated for the treatment of SRU tail gases, the regenerated SO₂ is sent back to the sulphur recovery unit.

Cansolv is regenerative technique which uses an aqueous amine solution to achieve selective absorption of sulphur dioxide. The gas to be treated is first saturated in a water prescrubber and is then contacted with the amine solution. The amine solution is regenerated by steam stripping. A slipstream of the amine needs to be purified to prevent the accumulation of salts. The scrubbing by-product is water-saturated SO₂ gas recovered by steam stripping.

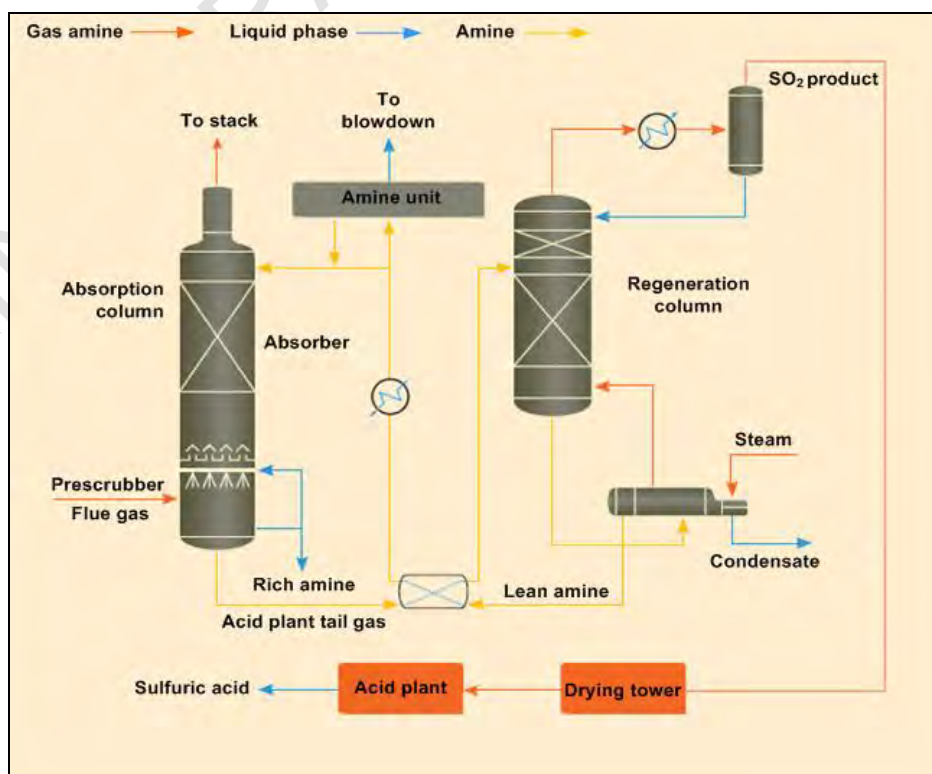


Figure 4.55: Process overview of the Cansolv regenerative scrubbing process

Labsorb is a regenerative scrubbing process which utilises an aqueous solution of sodium phosphate as a scrubbing buffer for the absorption of SO_2 . It generates a $>90\%$ concentrated SO_2 stream that can be used as feed to an SRU or a sulphuric acid plant. The scrubbing solution is regenerated using low-pressure steam, which virtually eliminates the discharge of liquid effluents from the scrubber. Figure 4.56 below shows a simplified flow diagram of the Labsorb process, which consists of a first SO_2 absorption stage, followed by final regeneration stage.

At the absorption stage, the flue-gas is dedusted and quenched in a prescrubber fed with low pH water recirculated from a make-up reservoir, before entering into the absorbing tower itself. The absorbing agent used is a patented solution containing soda (NaOH) and phosphoric acid (H_2PO_4).

The regeneration involves a steam-heated evaporator for the release of the SO_2 absorbed in the reach solvent, followed by a gas/liquid separation, a stripper and a condenser. Concentrated SO_2 saturated in water leaves the condenser as recovered product, while water from the condenser returns to the process after steam stripping. A waste heat boiler before the unit can be used to produce low-pressure steam for buffer generation, further reducing the total operating costs.

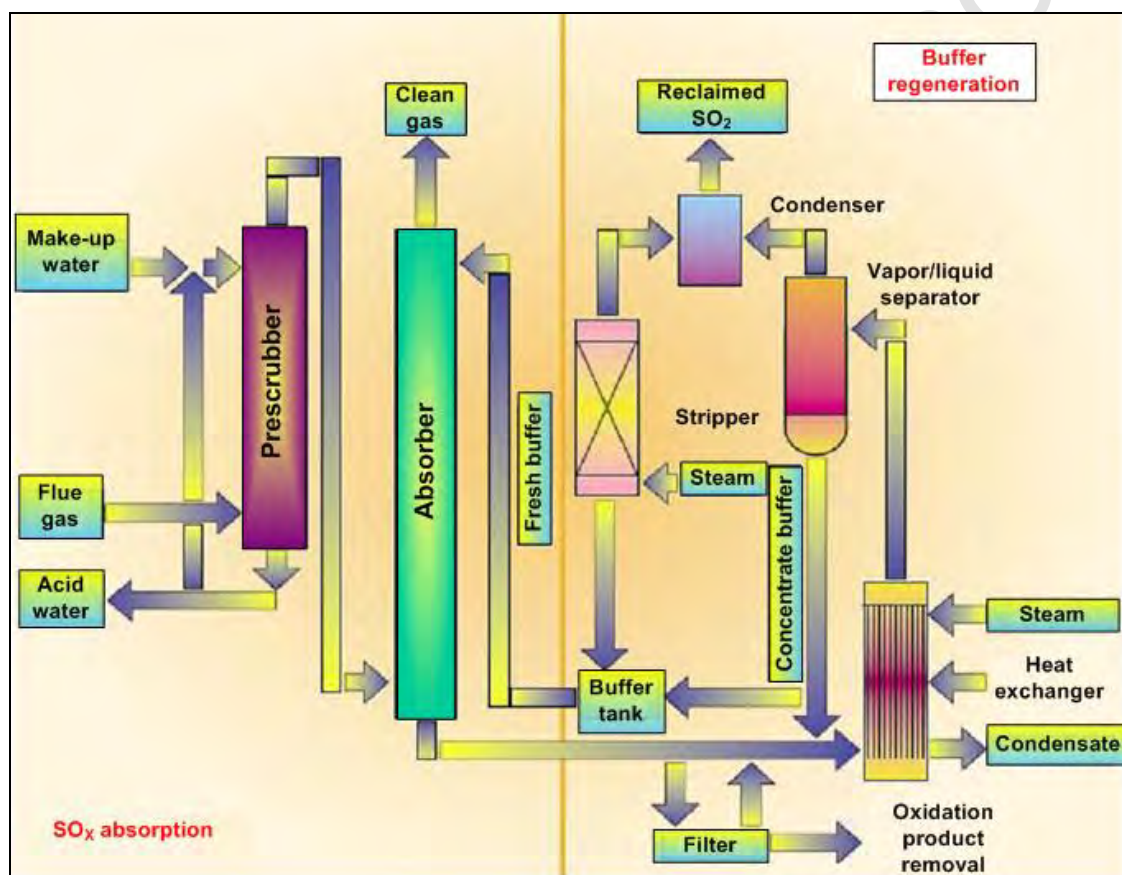


Figure 4.56: Simplified flow scheme of the Labsorb regenerative scrubbing process

SNO_x is a regenerative catalytic process which combines a pre-dedusting stage, followed by a WSA (described immediately below) and an SCR stage, whose purpose is to abate air pollutants in a combined technique. It reaches a high removal of SO_2 , NO_x and particulates. For more information see Section 4.23.8.

Waste gas sulphuric acid (WSA) is a solid-catalytic process allowing the condensation and the recuperation of concentrated sulphuric acid. It is well adapted to wet gases (no pre-drying stage required), but requires a careful pre-dedusting phase (max. 1 mg/Nm^3) in order to maintain the specific potassium-vanadium catalyst performances. The gas temperature should be adjusted to

400 – 420 °C. SO₂ reacts with residual O₂ and forms SO₃ which then combines with residual water vapour and is condensated at concentrations of 93 – 98 %. The adjustment of water and air concentrations is eventually required prior to the catalytic converter.

Achieved environmental benefits

A general overview is shown in the following summary table.

Name of technique	Non regenerative Flue-gas desulphurisation	Regenerative catalytic flue-gas desulphurisation
Efficiency	90 % (500 mg/Nm ³)	95 – 98 % (250 – 100 mg/Nm ³)
Example: Capacity of the process: 5Mt/yr, 120 000 t/yr liquid refinery fuels, 180 000 t/yr refinery fuel gas. Volume of the flue-gas 1.68 x 10 ⁹ Nm ³ /yr. Pollutant: Initial concentration: 5 000 mg/Nm ³ (for liquid refinery fuels with 3 % S). Total quantity 8 400 t/yr.		

Detailed reported percentage reduction by technique are presented in Table 4.96.

Table 4.96: Achieved environmental benefits of various desulphurisation processes

Desulphurisation technique	SO ₂ reduction (%)	Other benefits
Additive injection (AI) alone	50 – 70	
AI and spray dry absorber (SD)	>92	Like with wet scrubbing, the SD system combines an effective removal of SO ₂ , SO ₃ , chlorine and fluorine (>90 % on sulphur compounds, 70 – 90 % for halides)
Seawater scrubbing	85 – 98	The acidic effluent from the absorber flows by gravity to a water treatment plant. Here, air is blown into the water to convert the absorbed SO ₂ into dissolved sulphate and to saturate the seawater with oxygen (COD treating). The pH is adjusted back to neutral partly by added seawater and partly by aeration. The effluent from the treatment plant is discharged directly back to the sea
Walther	>88	Product that can be sold as fertiliser. This product has to meet certain criteria (especially heavy-metal content)
Wet Limestone Scrubber	92 – 98	If the chlorine content is low, this system produces a very low amount of waste water
Wellman Lord	98 (100 mg/Nm ³)	Sulphur can finally be recovered as a product. For the removal of SO ₃ , ammonia is injected, which leads to the formation of ammonium sulphate. Ammonium sulphate may be used as a fertiliser under certain circumstances (especially heavy-metal content)
Cansolv	98	Sulphur by-products have a high purity and can be recovered for chemical
Labsorb	>85	No external flue-gas cooling required upstream of the process. Very low chemical consumption. No residues produced other than limited amounts of sodium sulphate salts, which correspond to less than 1 % of waste mass generated by a wet limestone scrubber. The recovered SO ₂ has a high purity (>90 %) and can be recovered as a chemical or treated for sulphur recovery in existing SRUs
SNO _x	94 – 96.6 %	Up to 96 % for nitrogen oxides. Particulates are essentially completely removed
WSA	99 ⁽¹⁾	NO _x are also reduced when used within the SNO _x process. In combination with an SCR, simultaneous reduction of 95 % NO _x can be achieved

Cross-media effects

Specific data on energy consumption for the various desulphurisation techniques (affecting CO₂ emissions) are not detailed. General information, can be found in the LCP BREF [7, EC 2006].

Table 4.97: Cross-media effects of various desulphurisation processes

Desulphurisation technique	Cross-media effects
Additive injection (AI) and Spray dry absorber (SD)	As the by-product generated by these techniques contains unreacted lime, it requires conditioning before disposal
AI process	The disposal of the by-product requires similar care to SD
Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption	These techniques generally produce a lot of waste
Seawater scrubbing	Some fly-ash with associated heavy metals and organic substances is transferred to the seawater
Walther	The process does not generate solid by-products or liquid waste. If particulates with possible content of metals are present in the flue-gas they appear together with the product
Wet limestone scrubber	Waste water generated by the gypsum dewatering process contains suspended solids and trace elements (metals, chlorides) and is treated by sedimentation, flocculation and filter pressing. The filter cake is disposed of by landfill and the purified water is drained to the sewer
Wellman-Lord	Dust: NH ₃ is injected to prevent the formation of SO ₃ . Therefore, up to 80 % of the ash consists of (NH ₄) ₂ SO ₄ , which can be used as a fertiliser or as a raw material for NH ₃ production. Waste water from the prescrubber has a sour water quality with a pH of around 2 and must be neutralised and stripped. The purified water may still contain up to 100 mg/l ammonia, but most often, values are in the range of 10 to 50 mg/l
Cansolv	No detailed data
Labsorb	No significant side-effect or disadvantage identified so far
SNO _x	See Section 4.23.8
WSA	See Section 4.23.8

Operational data

Table 4.98: Operational data of various desulphurisation processes

Desulphurisation technique	Operation data
Additive injection (AI) and Spray dry absorber (SD)	Being a dry process, corrosion conditions are less severe than is the case with WS. Hence, the scrubber is usually made of (uncoated) carbon steel. Calcium chlorides may yet prompt acid corrosion as they precipitate on the absorber walls and attract moisture. Recycling by-product with wet flue-gas to the sorbent make-up tank may suffer from plugging; regular cleaning is required
AI process	The system is less effective as regards the removal of HCl, hence the fuel should not have a higher Cl content than approximately 0.3 % for corrosion prevention
Seawater scrubbing	The process offers simplicity, thus high availability,
Walther	Chloride aerosols and a visible waste gas plume may occur when fuels are used with a high chlorine content. Aerosol formation can be mitigated by increased liquid to gas ratio in the absorber and the use of multiple tube filters. Deposits of sulphates can be removed by blowing with hot flue-gas or by water washing. NO _x has no influence on the FGD process as it does not react with ammonia
Wet Limestone Scrubber	Through good engineering practice (liberal sizing of spray systems and mixers, applying washing on demisters etc.) deposits and plugging of the various components can largely be avoided. For high-grade gypsum production, forced oxidation and good pH control is required. Furthermore, good quality limestone (>93 % purity in CaCO ₃) must be used and dust and trace elements, in particular chlorine, should be removed by prescrubbing of the raw gas and dewatering and optional washing of the product. Organic buffers (such as adipates and dibasic acid) can be used for pH control, thereby substantially enhancing the SO ₂ removal efficiency – by typically 4 %. Early corrosion problems have been overcome; often rubber lining is used in the absorber, requiring some care in view of abrasion damage.
Wellman-Lord	Operational aspects include problems with respect to fouling, corrosion and erosion. In the prescrubber deposits of ammonium sulphate can occur. The evaporator is susceptible to wear by the abrasive salt slurry, corrosion during shutdowns and mechanical strains related to the high speed centrifuge.
Cansolv	No detailed data
Labsorb	In the refining sector, this process has so far been applied only to FCC units.
SNO _x	See Section 4.23.8
WSA	No detailed data

Applicability

As a general consideration, it is to be noted that the space requirement for scrubbers and ancillary equipment is an important factor for retrofit applications because of their size.

Table 4.99: Applicability of various desulphurisation processes

Desulphurisation technique	Applicability
Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption	Typically used when the amount of SO ₂ to recover are small because they produce waste, for example in small specialised refineries or small natural gas plants
Seawater scrubbing	Because particulates (including their heavy metals content) are transferred to the seawater, an efficient particulate abatement technique is necessary prior to the seawater scrubbing
Walther	Not suitable for fuels with an elevated sulphur content, as these result in increased ammonia slip due to the formation of ammonia sulphates. The sulphates are objectionable because of corrosion and aerosol emissions
Wellman Lord	Despite its excellent emission profile, the process complexity has discouraged wide-spread application
Cansolv	
Labsorb	In the refining sector, successfully applied to FCC units
SNO _x	This system is successfully used for on-site regeneration of H ₂ SO ₄ used in the alkylation unit, and for the treatment of H ₂ S gases (TGTUs) and off-gases from FCC unit regenerators and power plants fed with highly sulphurised fuels and residues

Economics**Table 4.100: Economics of various desulphurisation processes**

Desulphurisation technique	Economics
AI process	35 – 55 EUR/kWth (unit size: 75 – 300 MW). Annual operating cost roughly equal capital cost
Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption	They are typically very cheap compared with other FGD techniques
Seawater scrubbing	Low capital costs and low operating costs (no bulk chemicals required, although sometimes magnesium hydroxide is used to enhance the alkalinity)
Wet limestone scrubber	75 – 180 EUR/kWth (unit size: 75 – 300 MW). Annual operating cost roughly equal capital costs. Capital cost: EUR 10 – 20 million. Operating costs EUR 1.6 – 4 million/yr. Flue-gas flows 200 000 to 650 000 Nm ³ /h. There are battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, construction and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plant could have a significant impact. In some cases, these factors might be expected to increase the costs by some 50 %
Wellman Lord	The investment cost is estimated to be USD 50 million for a unit to handle a flue-gas flowrate of 500 000 Nm ³ /h and a SO ₂ concentration of 0.8 %. The cost includes licensing fees, engineering, equipment delivery, construction, commissioning and start-up services
Cansolv	No information provided
Labsorb	This technique allows significant savings in operating costs compared to non-regenerative wet scrubbing processes, due to the very small consumption of chemicals used in the absorbing buffer make-up, and the intrinsic energy efficiency. See figures for FCC unit applications in Section 4.5.6.
SNO _x - WSA	See Section 4.23.8.

Driving force for implementation

Table 4.101: Overview of the driving forces for the implementation of various desulphurisation processes

Desulphurisation technique	Driving force for implementation
Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption	Abatement of small quantities of SO ₂
WellmanLord	The process characteristics can suit the needs of particular industrial sites using high-sulphur fuels (in refineries in the US, Japan and Austria)
Cansolv	
Labsorb	Generates a by-product ready for conversion into liquid SO ₂ , sulphuric acid or elemental sulphur. Suits the need of industrial processes generating highly sulphurised flue-gases, as SRU tail gases and FCCs, but also fossil-fuel-fired boilers and roaster gases from non-ferrous smelters

Example plants

Table 4.102: Example plants where desulphurisation processes have been implemented

Desulphurisation technique	Example plants
Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption	Applied in some small refineries and natural gas plants
Seawater scrubbing	The process has been applied to some extent (in 1994: 2 500 MW _e /47 units), also used for smelters, refineries and oil-firing (at 3 % S)
Wet limestone scrubber	Operational experience with WS is highly satisfactory, demonstrated by high availability. This system is widely applied in power plants. In Germany, e.g. the TOTAL Mitteldeutschland refinery uses a wet lime desulphurisation process after the three oil-fired heaters of the power plant. The fuels used in this plant are vacuum residues, visbreaker residues and FCC slurry
WellmanLord	More than 40 systems have been applied around the world e.g. on FCCs
Cansolv	Cansolv units are used on Sulphur plants, FCC and cokers
Labsorb	ESSO Norge in Slagentangen (Norway, 1994) - ENI S.p.A in Sannazzaro (Italy, 2000) - VALERO refinery in Paulborough, NJ (US, 2002)
SNO _x - WSA	More than 25 units have been successfully installed worldwide. Applied in particular in AGIP refinery in Gela (Italy, 1997) and in OMV AG refinery in Schwechat (Austria, 2007) for power plants burning high sulphur petcoke and residues

Reference literature

[194, Winter 2000], [200, Gilbert 2000], [181, HP, 1998], [201, Manduzio 2000], [21, ENI SpA 2009], [108, Cansolv 2010], [163, FWE 1999], [151, Sema,Sofres 1991], [218, HMIP UK 2000], [221, Italy 2000].

4.23.5.5 Sulphur recovery units performances and variability

The following Table 4.103 shows the achieved sulphur recovery efficiency (% of S recovered) observed for a number of refinery sulphur recovery units (SRU including TGTU) in Europe.

The sulphur recovery efficiency is calculated from the monitoring data available (emissions values expressed as SO₂ concentration after incineration from the time series) and based on several assumption such as :

- the SRU feed composition;
- the stack gas volume flow;
- the ratio acid gas/fuel gas for the incineration step (a value of 4 % is used for SRU 12).

Table 4.103: Sulphur recovery efficiency reported for a sample of European SRUs

	Sulphur Recovery Units (SRU) reference number							
	1	2	4	6	8	9	11	12
Claus process type	2 Claus Stages	2 Claus Stages	2 Claus Stages	2 Claus Stages	2 Claus Stages	2 Claus Stages	2 Claus Stages	3 Trains
Tail gas treatment unit (TGTU) type	SuperClaus	SuperClaus	ClausPol	SuperClaus	SuperClaus	SuperClaus	Hydro-Sulfreen	Amine based
SWS* gas treated	YES	YES	YES	YES (DSWS**)	YES (DSWS**)	YES	YES	YES
Monthly Min % S recovery	98.2 %	98.0 %	98.2 %	99.2 %	99.4 %	98.8 %	99.2 %	99.91 % - 99.93 %
Monthly Max % S recovery	99.0 %	98.7 %	98.9 %	99.6 %	99.5 %	99.3 %	99.5 %	99.98 % - 99.97 %
*SWS: Sour Water Stripper **DSWS: Double Sour Water Stripper Source: [145, TWG CONCAWE 2012]								

In addition, an illustration of the variability of the sulphur recovery efficiency and the SO₂ concentration at the stack is shown in Figure 4.57 and Figure 4.58.

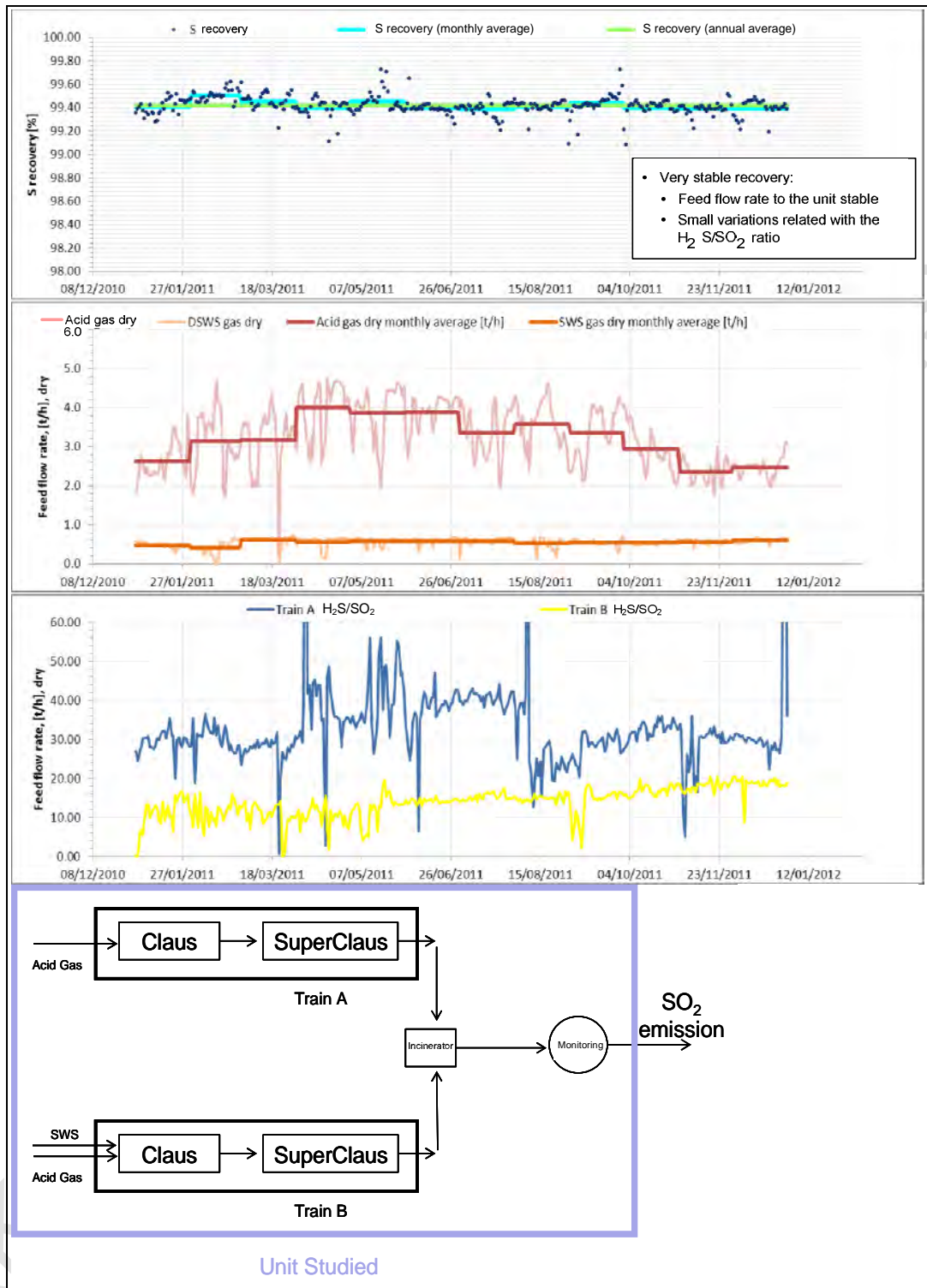


Figure 4.57: Variability of the daily sulphur recovery efficiency for a double train SRU equipped with a Superclaus tail gas treatment unit (data-set 8)

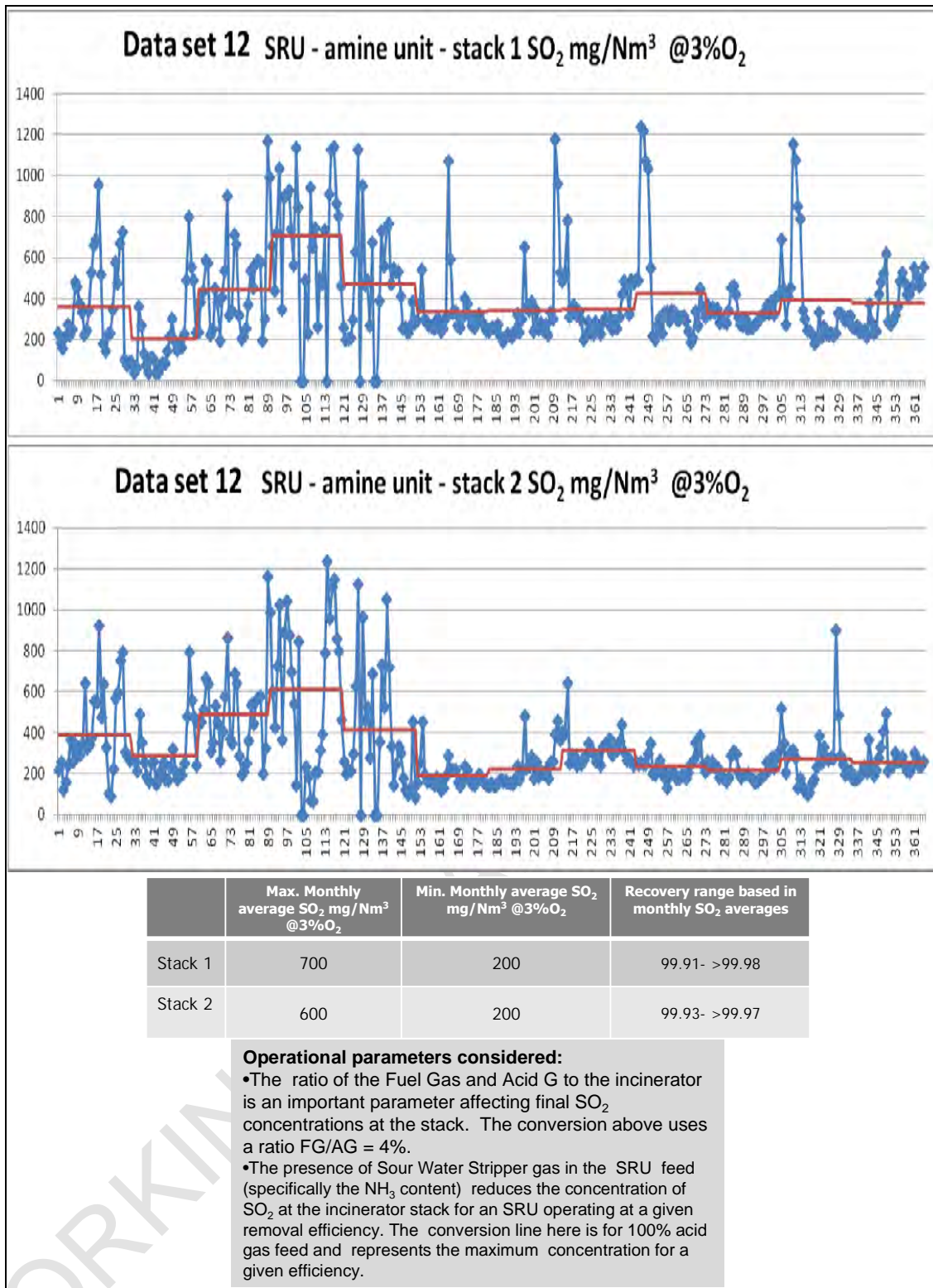


Figure 4.58: Variability of the daily sulphur recovery efficiency and SO₂ concentration at the stack for a 3 trains SRU equipped with two amine-based (SCOT) TGTUs (data-set 12)

4.23.6 VOC abatement techniques

When transferring liquids to vessels at atmospheric pressure, the existing mixture of vapour and gas (often air, but also inerts) in the receiving vessel is often emitted to the atmosphere. Such loading operation is recognised as having an impact on the environment due to the presence of VOC, a precursor of ozone. Directive 94/63/EC (EU Stage 1) requires that Member States prescribe the specific emission reduction measures as laid down in the annexes of the Directive. Also, the application of Vapour recovery units (VRUs) to prevent escape of these vapours to the atmosphere is specified in the Directive. VRUs aim for recovery of hydrocarbons for reuse. In some cases, recovery is not economic, and preference will be given to vapour destruction units (VDU). A more general term covering both options is vapour handling systems (VHS).

4.23.6.1 Techniques for the prevention, detection and control of VOC fugitive emissions

4.23.6.1.1 Techniques to prevent/reduce VOC emissions related to the process and plant design

Description

Techniques to reduce diffuse VOC emissions can be considered during both phases of the design:

- process design
- plant design.

Process design

Process design conditions (e.g. temperature, pressure, vapour pressure of the process fluid) can influence the level of diffuse emissions. However, they are not chosen independently, they also depend on other parameters (e.g. catalyst activity, availability of utilities such as cooling air, water or steam) as well. In some operations with lower operating temperatures and pressures where the fluid vapour pressures are lower, diffuse emissions are relatively lower [121, ESA 2005].

Techniques to reduce diffuse emissions resulting specifically from refinery process design can be:

- to achieve a balance between feed purity, processing steps, product quality and waste generation;
- to treat waste water streams which contain (mixtures of) VOCs by stripping, rectification and extraction or combinations of these techniques in order to remove the substances that could contribute to diffuse emissions (see waste water treatment Section 4.24).

Plant design

The selection of plant components and the manner in which they are configured can both greatly influence the extent of diffuse emissions. For new units, there is a significant opportunity during the initial design phase to incorporate a wide range of techniques to reduce the potential for diffuse emissions. For existing plants, efforts can be made to incorporate many of these techniques over time as part of a process of continuous improvement.

Techniques to reduce diffuse emissions through the selection and configuration of refinery components include:

- limiting the number of potential emission sources, such as by:
 - designing piping layout appropriately by:
 - minimising pipe run length;

- reducing the number of flanges (connectors) valves and screwed pipe fittings;
 - using welded fittings and pipes.
- reducing the number of pumps by using, if possible, other means of fluid transfer e.g. by gravity;
- maximising inherent process containment features, such as by:
 - enclosing (partially or completely) effluent drainage systems and tanks used for effluent storage/treatment;
 - minimising emissions during sampling by using closed sampling systems or in-line analysers;
 - installing a maintenance drain-out system to eliminate open discharges from drains.
 - selecting high integrity equipment, such as:
 - valves with double packing seals or equally efficient equipment;
 - fitting high-integrity gaskets for critical applications ;
 - pumps/compressors/agitators fitted with mechanical seals instead of packing ;
 - magnetically driven pumps/compressors/agitators.
 - selecting appropriate materials for equipment, such as:
 - to ensure that all equipment (e.g. gaskets) is selected appropriately for each process application;
 - to avoid corrosion by appropriate selection of material of construction;
 - to prevent corrosion by lining or coating of equipment, painting pipes to prevent external corrosion and by using corrosion inhibitors of materials in contact with equipment;
 - to apply reactive paints e.g. acid sensitive paints applied on HF alkylation plant flanges.
 - facilitating monitoring and maintenance activities by ensuring good access to components that have the potential to leak;
 - collecting and treating emissions, such as conveying potentially collectable leaks (e.g. compressor seals, vents and purge lines) to flares or to flameless oxidisers.

Achieved environmental benefits

Prevention or reduction of diffuse VOC emissions.

Cross-media effects

The collection and containment of diffuse emissions can lead to explosive limits being reached as a consequence of the build up of VOCs, e.g. where a cover is installed over a waste water treatment facility. This issue is subject to the Explosive Atmospheres Directives 99/92/EC (ATEX 137) and 94/9/EC (ATEX 100).

Environmental performance and operational data

Diffuse emissions can be estimated during process and plant design by using a technique that counts the number of potential emission point sources (flanges, valves, pumps, etc.) and applies standard emissions factors relating to the contained fluid. The reliability of an emission factor in a given application depends on the quality of the factor, the specific pollutants of interest, and the type of source.

Diffuse emissions from tanks can be estimated using the US EPA 'TANKS' software based on algorithms [276, US EPA 2006]. Methods to estimate diffuse emissions for other sources within refineries are provided in [111, CONCAWE 2009].

Technical considerations relevant to applicability

The aforementioned techniques to reduce diffuse emissions related to process and plant design are applicable to all new units that have potential diffuse emissions. For existing units, applicability may be limited by various constraints and efforts should be made to incorporate these techniques over time as part of the process of continuous improvement.

Economics

The cost of techniques to reduce diffuse emissions related to process and plant design depends on the specific installation. The costs are expected to be lower for new plants. In the long run, use of high integrity equipment can reduce maintenance costs and the time dedicated to monitoring.

The reduction of diffuse emissions often provides opportunities for saving raw materials, recycling by-products, or avoiding the loss of final products, which all result in economic benefits.

Driving force for implementation

Reduction of VOC emissions.

The other driving forces for implementation include:

- reduction in material losses;
- safety of employees.

Example plants

All new chemical plants.

Reference literature

[6, EC 2003], [109, IMPEL Network 2000], [62, CONCAWE, 2008], [110, ESA 2005], [111, CONCAWE 2009].

4.23.6.1.2 Techniques to prevent/reduce VOC emissions related to plant installation and commissioning

Description

The manner in which plant components are installed can greatly affect emissions, and this is an obvious issue prior to the first commissioning of a new plant or a new unit. However, the reinstallation of unit components as part of maintenance or project work on units already in operation can also have a significant impact on emissions.

Techniques to reduce diffuse VOC emissions related to the unit installation can include:

- to have in place strict and well-defined procedures for construction and assembly;
- to ensure that gaskets are installed correctly;
- to have robust commissioning and hand-over procedures in place to ensure that the unit is installed in line with the design requirements (e.g. the correct gaskets have been installed, the pipe runs do not include additional flanged connections).

Achieved environmental benefits

Prevention or reduction of diffuse emissions, particularly diffuse VOC emissions.

Cross-media effects

None.

Operational data

Diffuse VOC emissions from some pre-selected individual plant components or equipment types can be monitored as part of the plant commissioning and hand-over process in order to determine whether the plant has been installed correctly, and in accordance with the design.

Applicability

These techniques are applicable to all new and existing units that have potential diffuse emissions.

Economics

The cost of techniques related to the unit installation to reduce diffuse emissions depends on the specific installation.

Reduction of diffuse emissions often provides opportunities for saving raw materials, recycling by-products, or avoiding the loss of final products, which all result in economic benefits.

Driving force for implementation

Reduction of VOC emissions, reduction in material losses and safety of employees.

Example plants

No information.

Reference literature

[109, IMPEL Network 2000], [110, ESA 2005].

4.23.6.1.3 Programme for the prevention, detection and control of VOC fugitive emissions

Description

Fugitive VOC emissions can be reduced by the detection and subsequent repair or replacement of leaking components. This is achieved by adopting a structured approach, commonly known as a leak detection and repair (LDAR) programme. An LDAR programme includes two fundamental steps:

- identification of the leaking components;
- repair of these leaks in order to minimise losses.

Leak detection

Two methods are currently available for the identification of leaks, and each method has its individual strengths and weaknesses. It is therefore necessary to decide upon the purpose behind a measurement exercise when selecting the method. In some circumstances, methods might need to be combined to fully understand the leak levels. Large scale methods (see Section 3.26.1.3) may quickly locate the major emission areas, whereas maintenance may be improved using infrared cameras to locate the leakers.

- **Sniffing method (EN 15446)**

Leak detection using hand-held analysers is called 'sniffing'. This method identifies leaking components by measuring the concentration of hydrocarbon vapours (in ppm) in the immediate vicinity of the leak with a flame ionisation detector (FID), a semi-conductive detector or a photoionisation detector (PID). The selection of the most suitable type of detector depends on the nature of the substance to be detected.

To check each potentially leaking component with hand-held analysers is time and cost intensive. Moreover, some leaking points might be difficult to access with the hand-held detectors to obtain a measurement. Sniffing surveys need careful preparation and are usually executed in campaigns that cover a specified portion of the refinery. Some companies have therefore developed a 'targeted monitoring' approach in which additional emphasis is put on components with a higher frequency of leaks. For more details see Section 3.26.1.3.

- **Optical gas imaging (OGI) method**

The optical gas imaging method involves the detection of leaks with advanced hand-held infrared cameras that are specially developed for this purpose. Both active and passive systems exist: active systems use an adequately tuned laser beam, while passive systems detect infrared radiation reflected by the equipment. Gas imaging based on passive cameras was introduced in the early 2000s, and enables direct visualisation of both leak and the leaking component and the recording of the images. On these recordings, gas clouds are visible as light or dark plumes.

Direct visualisation of leaks is of great value to improve the efficiency of maintenance on equipment as only the leaking equipment is repaired. Another advantage of the camera is the possibility to detect leaks under insulation and to screen from a distance, so that VOC emissions from components not accessible for sniffing can be located and repaired. However, as no reference protocol of use exists for these OGI instruments, detection limits and representativeness might differ from one user to the next (the type of gas and the minimum detected leak rate are generally provided on the supplier website). Furthermore, different commercially available instruments may lead to different sensitivities and detection efficiencies. Moreover, the intensity of the image projected by the camera depends on a number of factors and is not necessarily related to the concentration in the plume.

Infrared cameras therefore need to be employed with full knowledge of their limitations. These cameras can see only a small number of chemicals. For example, unless a BTEX leak is very large the camera will not detect it. In addition to this, they have relatively high detection limits (hundreds of ppm) and do not quantify or speciate the chemicals.

Some refineries are using infrared cameras before start-up to ensure the process is tight. Others are using cameras for safety purposes and for finding large leaks. For more details see Section 3.26.1.3.

Leak repair

A staged approach is often applied to the repair of leaks, involving

- An initial intervention such as tightening bolts to eliminate leaks from valve stems or flanges, installing tight caps on open ends. Such an intervention needs to be performed by skilled operators taking due recognition of necessary safety precautions.
- Repairing equipment with leaks that cannot be stopped by minor interventions. This may involve changing gaskets or packing, and may therefore require the equipment to be taken out of service.
- When no effective repair can be performed, considering the replacement of equipment.

The LDAR programmes based on sniffing typically do not include tanks and difficult to access plant areas. OGI and whole-plant measurements will identify problem areas that are not being monitored and allow them to be addressed. In many instances, they allow for more efficient allocation of maintenance efforts, by targeting the highest emitters first.

Achieved environmental benefits

Prevention and reduction of fugitive VOC emissions which are one of the largest sources of refinery hydrocarbon emissions.

Environmental performance and operational data

One refinery in the US, which has been using the infrared camera for some years, has compared it with their existing LDAR approach using the sniffing method. They have found that the camera does not detect low level leaks and cannot be used as a substitute. They, however, continue using it for safety and large leak detection purposes.

In Sweden, LDAR is done at all the refineries. Sniffing measurements are done twice a year at every potential leaking point that can be reached. If a unit is started up, additional sniffing measurements are carried out. Preem Refinery Lysekil does sniffing measurements on approximately 100 000 potential leaking points twice a year. Leak levels are defined as 100, 500 and 900 ppm (as propane). For medium level leaks (500 ppm), action is taken as soon as possible to reduce the emission. At this refinery, since 1989, the number of leaks in the process area has decreased from 2 % to a level around 0.2 %. OGI is used to complement the sniffing method, although it has not been found that it can replace it. It is especially true for tank roofs which are difficult to monitor with sniffing; OGI has been found to give useful information on such emissions.

Cross-media effects

None.

Technical considerations relevant to applicability

Fully applicable. See descriptions and Section 3.28.1.4 for applicability of each of the detection techniques.

Economics

In a typical US refinery with over 200 000 components, the annual cost for an LDAR programme is reported to exceed EUR 750 000 (actual cost USD 1 000 000, average 2010 USD/EUR exchange rate) with the US EPA Method 21 based on sniffing.

It is reported that full monitoring of a complex refinery can take six months or more to complete and in one example costs were 0.6 million EUR (for 2006 in CONCAWE report 2008).

Driving force for implementation

Reduction of VOC emissions, reduction in material losses, and for the health and safety for employees.

Example plants

LDAR programmes have been used successfully worldwide to reduce VOC releases. See also Preem Refinery Lysekil (SE) under the Environmental performance and operational data paragraph in this section.

Reference literature

[6, EC 2003], [62, CONCAWE 2008], [110, ESA 2005], [113, US EPA 2006], [260, Energy Institute 2010], [111, CONCAWE 2009].

4.23.6.2 Vapour recovery units (VRU)

Description

Vapour recovery units (VRUs) are installations designed for the reduction of volatile organic compounds (VOC) emissions during loading and unloading operations. For a refinery, this is particularly relevant to gasoline and other volatile products, such as naphta, and lighter products. Vapour recovery can also be used to abate emissions from fixed roof tanks storing volatile products which are not fitted with internal floating roofs (see Section 4.21.4). As VOC emission abatement by VRUs is only one aspect of total VOC control in a refinery, this section should be considered in combination with storage, handling and integrated refinery management. In addition to the VRU, a vapour collection system is required, as well as other

equipments: vapour piping, detonation arresters, instrumentation, and possibly booster blowers, and vapour holding tanks.

Detailed information, in particular for refinery product storage, is also provided in the EFS BREF [5, EC 2006]. Additional information is provided in the AEAT report [115, Rudd et al. 2001] on emissions during ship loading and in the ENTEC report on the implementation of Directive 94/63/EC for gasoline emission control [116, ENTEC 2009].

Vapour recovery systems involve two processes:

- separation of the hydrocarbons from air;
- liquefaction of the separated hydrocarbon vapours.

The separation processes that may be used to separate hydrocarbon vapours from the air are:

- pressure swing adsorption on activated carbon;
- absorption by washing in a low volatility absorbent fluid;
- selective membrane separation;
- condensation by cooling or compression (separation and liquefaction are combined in a single process).

The liquefaction processes applicable for separated hydrocarbon vapours are:

- absorption, normally into their own product;
- condensation ;
- compression.

The following VRU systems are used for refined products:

- absorption in a cold lean oil stream;
- adsorption in twin bed pressure swing operation;
- indirect liquid condensation in a refrigerant heat exchanger;
- membrane separation by passage through a hydrocarbon selective surface.
- absorption: the vapour molecules dissolve in a suitable low volatility ('lean') absorbent (glycols or mineral oil fractions such as kerosene or reformate). The absorbent may need to be cooled to reduce its volatility (commonly at -25 to -30 °C for kerosene or reformate). It is then necessary to split the vapour from the absorbent by heating the absorbent/recovered product mix in a heat exchanger and then re-absorbing the rich product vapour in an appropriate stream e.g. of the product being recovered or passing to a condenser, further processing unit or an incinerator. Absorption is not commonly used for gasoline vapour recovery in the EU because the technique is considered less efficient than e.g. adsorption.
- adsorption: the vapour molecules are retained by activate sites on the surface of adsorbent solid materials, like activated carbon (AC) or zeolite. The adsorbent needs periodical regeneration. Continuous processes have two vessels (beds) containing activated carbon, which cycle typically every 15 mn between adsorption and regeneration modes. This regeneration of the carbon activity can be done using steam or, more commonly, vacuum pumps. The resulting desorbate is then absorbed (e.g. in a circulating gasoline component stream) in a downstream wash column (wash stage). The residual gas from the wash column (or separator) is sent to the inlet of the unit for re-adsorption. This technique is the one most commonly used for a gasoline VRU. See an example of a typical adsorption unit in Figure 4.59.

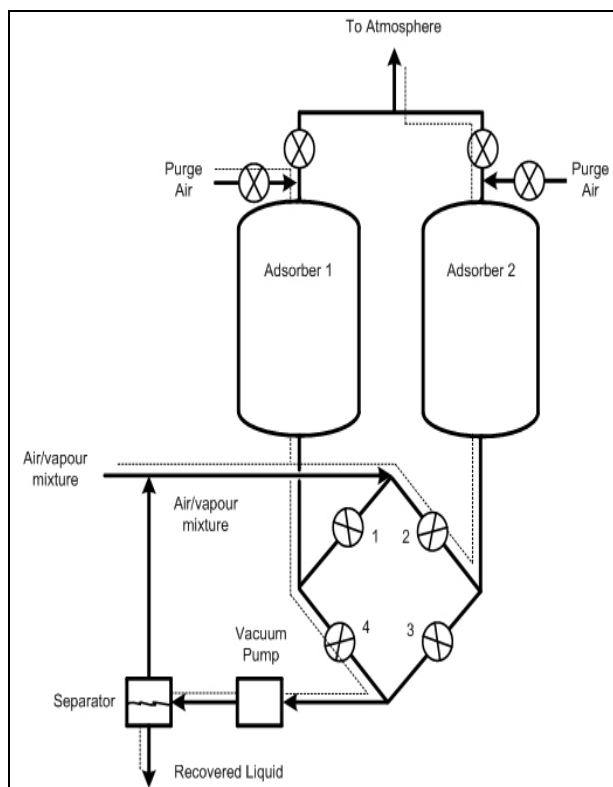


Figure 4.59: VRU-Activated carbon adsorption process

- membrane gas separation: the vapour molecules are processed through selective membranes to separate the vapour/air mixture into a hydrocarbon-enriched phase (permeate), which is subsequently condensed or absorbed, and a hydrocarbon-depleted phase (retentate). The efficiency of the separation process is dependent on the differential pressure across the membrane. For further purification, the membrane process can be combined with other processes. See an example of a typical membrane separation unit in Figure 4.60.

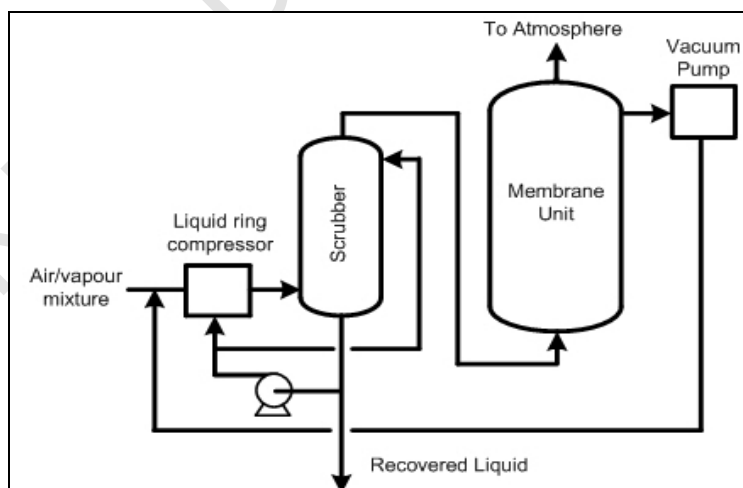


Figure 4.60: VRU-Membrane separation process

- refrigeration/condensation: by cooling the vapour/gas mixture the vapour molecules condense on the surface of a cold heat exchanger and are separated as a liquid. A second stage (e.g. cryogenic condenser using liquid nitrogen) may be required to meet the emission limit. As the humidity leads to the icing-up of the heat exchanger, a two-stage

condensation process providing for alternate operation is required. This method can achieve low exit concentrations if the applied refrigeration temperature is low enough. The vapours are recovered as pure liquids (no waste), which can be returned directly to the storage tank.

- **hybrid systems:** combinations of techniques for the VRUs are commercially available to meet very low emissions standards. An example is a two-stage plant using membrane separation followed by adsorption.

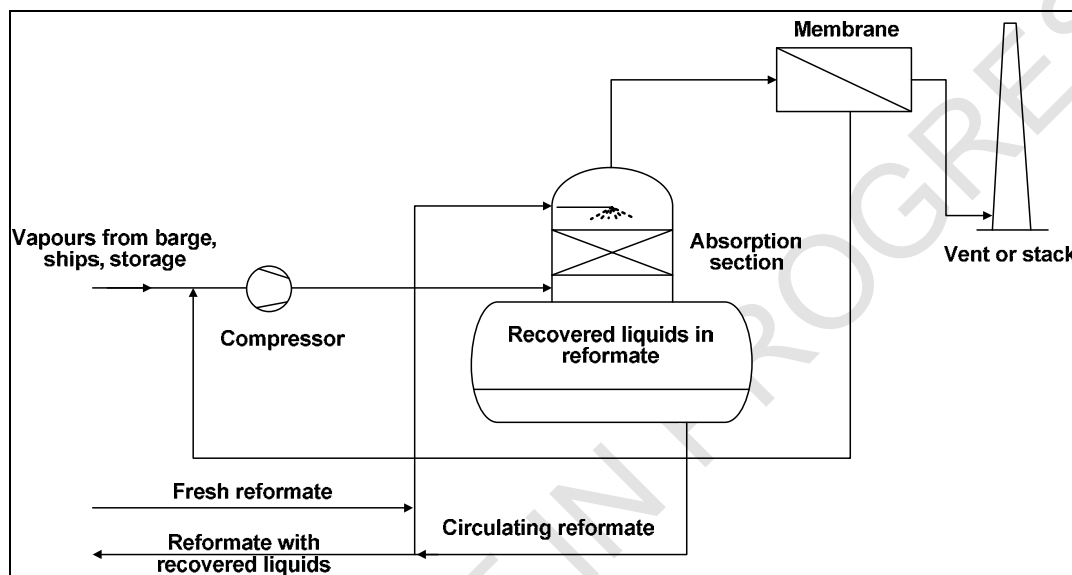


Figure 4.61: Simplified process flow scheme of a vapour recovery unit

Achieved environmental benefits

Emissions of the various systems are directly related to the abatement efficiency and can be as low as 10 mg/Nm^3 (without methane). With an abatement efficiency of 99.9 %, concentrations of 150 mg/Nm^3 (without methane) can be achieved for motor gasoline, as shown in Table 4.104. The emissions reduction achievable will depend upon the techniques used and the composition and concentration of the VOC in the vapour stream being abated. For example, a gasoline vapour stream can have a NMVOC concentration of 1500 g/Nm^3 . Thus, to achieve a vent concentration of 150 mg/Nm^3 requires an abatement efficiency of 99.99 %.

A vapour recovery system for the loading of crude oil vessels can collect about 85 % of the total VOCs, which are condensed and reinjected into the crude feedstock.

Table 4.104 provides some data on the efficiency and environmental performance of vapour recovery units. Non-methane VOC (NMVOC) and benzene measurements can be performed through FID or GC.

Table 4.104: Emissions values for vapour recovery plants during the loading of motor gasolines

Plant type	Recovery ⁽⁴⁾ rates (%)	Average values attainable in continuous operation ⁽⁵⁾ ⁽³⁾	
		NMVOC ⁽¹⁾ (g/Nm ³)	Benzene (mg/Nm ³)
Single-stage condensation plant	80 – 95	50	1
Single-stage absorption plant	90 – 97	35	50
Single-stage, adsorption and membrane separation plants	90 – 99.5	<10 ⁽²⁾	1
Single-stage adsorption plants with supplementary blower	99.98	0.15	1
Compression, absorption and membrane separation ⁽⁶⁾	90 – 95	NA	NA
Two-stage plants	99.98	0.15	1

⁽¹⁾ NMVOC: Non-methane volatile organic compounds. The methane contents in the vapours of the substances to be loaded can vary considerably. Adsorption and adsorption processes cannot notably reduce methane emissions.

⁽²⁾ If single-stage plants are used as a preliminary stage for gas engines, a concentration of approx. 60 g/m³ is necessary for operation of the gas engine.

⁽³⁾ These values are given for an HC concentration in the uncleaned gas of approx. 1 000 g/Nm³.

⁽⁴⁾ As an indicator of performance level.

⁽⁵⁾ Expressed as an hourly average in continuous operation for consistency with 94/63/EC (Annex II).

⁽⁶⁾ Compression followed by a two-stage recovery section: re-absorption of the VOC into a fraction of the condensate being loaded followed by a membrane separation stage.

Source: Updated TWG 2010 (CONCAWE 4/09), TWG- NO

Cross-media effects

The effects are related with energy consumption, especially for two stage units, (for cooling, pumping, heating, vacuum); waste (adsorbent/membrane replacement); and water effluent (i.e. condensates from steam regeneration of adsorbent, defrost water from condensation units). Where explosive mixtures can occur, it is important that safeguards are implemented to limit the risk of ignitions and ignition propagation.

Table 4.105: Cross-media effects associated with VRU techniques

VRU technique	Cross-media effects
Adsorption	The adsorbent will require replacement - carbon life is generally greater than 10 years
Absorption	Waste water can be produced and requires appropriate treatment. Regeneration of the absorbent more than doubles the investment and energy costs. The only waste generated is the exhausted liquid which needs to be replaced once in many years.
Membrane separation	Requires a double set of vapour moving equipment i.e. a compressor and a vacuum pump. Potential for higher energy usage than for adsorption.
Condensation	Generates contaminated water effluent stream from defrost. Cooling systems have the potential for refrigerant losses and high energy usage. For cryogenic units, the production of liquid nitrogen is energy intensive.
Hybrid (two-stage) systems	High energy consumers

Environmental performance and operational data

In Göteborg harbour (SE), three VRUs of the adsorption-type (capacities of 1 500, 2 000 and 2 400 m³/h respectively) serving 4 quays are implemented for the treatment of the vapours generated by the loading of around 1.4 million tonnes/year of gasoline. Calculated emissions have been reduced from 300 to 25 tonne/yr, and the outlet concentration of total VOC in the released stream is below 10 g/Nm³. The investment cost was around EUR 6.4 million (SEK 65 million) in 2001.

One of the biggest VRUs in the world (36 000 Nm³/h) has been in operation since 2008 in the Mongstad refinery (NO) for the treatment of vapours generated from the unloading of crude oil ships (two jetties). The installed power reaches 5.7 MW, and the recovery efficiency of the activated carbon bed filter system is estimated at around 85 % of total VOCs. The investment cost was around EUR 60 million (SEK 630 million) in 2008.

In Germany, recovery rates are reported that enable a minimum VOC emission reduction of 99 %.

In France, since the end of 1990, subsidies to support investment have been provided to companies (15 examples) to achieve more ambitious targets than the regulatory framework for recovery of vapours from loading facilities. One process uses adsorption on activated carbon with vacuum desorption. This process allows reducing the VOC emission level to 2 g/Nm³, below the regulatory target of 35 g/Nm³.

The following Figure 4.62 shows an example of the variability of emissions to air of NMVOC from a VRU (single stage carbon adsorption unit) during the loading of a barge. The measurements are half-hourly averages from continuous monitoring during the loading (each operation taking place on a day). The average over the entire period is 4.4 g/Nm³. The average over each loading operation is less than 10. There are peaks over 10 g/Nm³ for 2 % of the time.

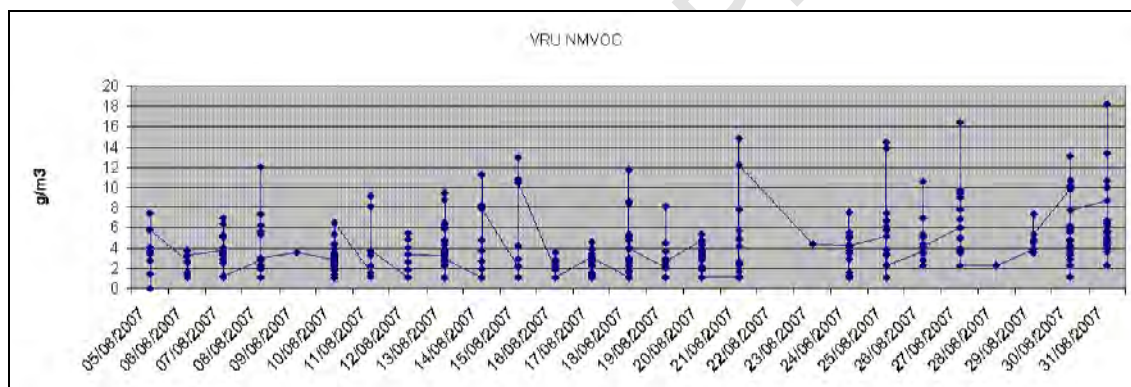


Figure 4.62: Variability of emissions to air from a VRU (data-set 12) over a month

Some of these peaks may be due to the start-up of the VRU, as it seems to be the case for the two data-sets number 8 (average under the 7 hours period: 0.2 g/Nm³) and number 9 (average: 6 g/Nm³), where variations over a day of both inlet and outlet concentrations from continuous monitoring are shown in Figure 4.63. The highest hourly values appear during the starting of the loading operation.

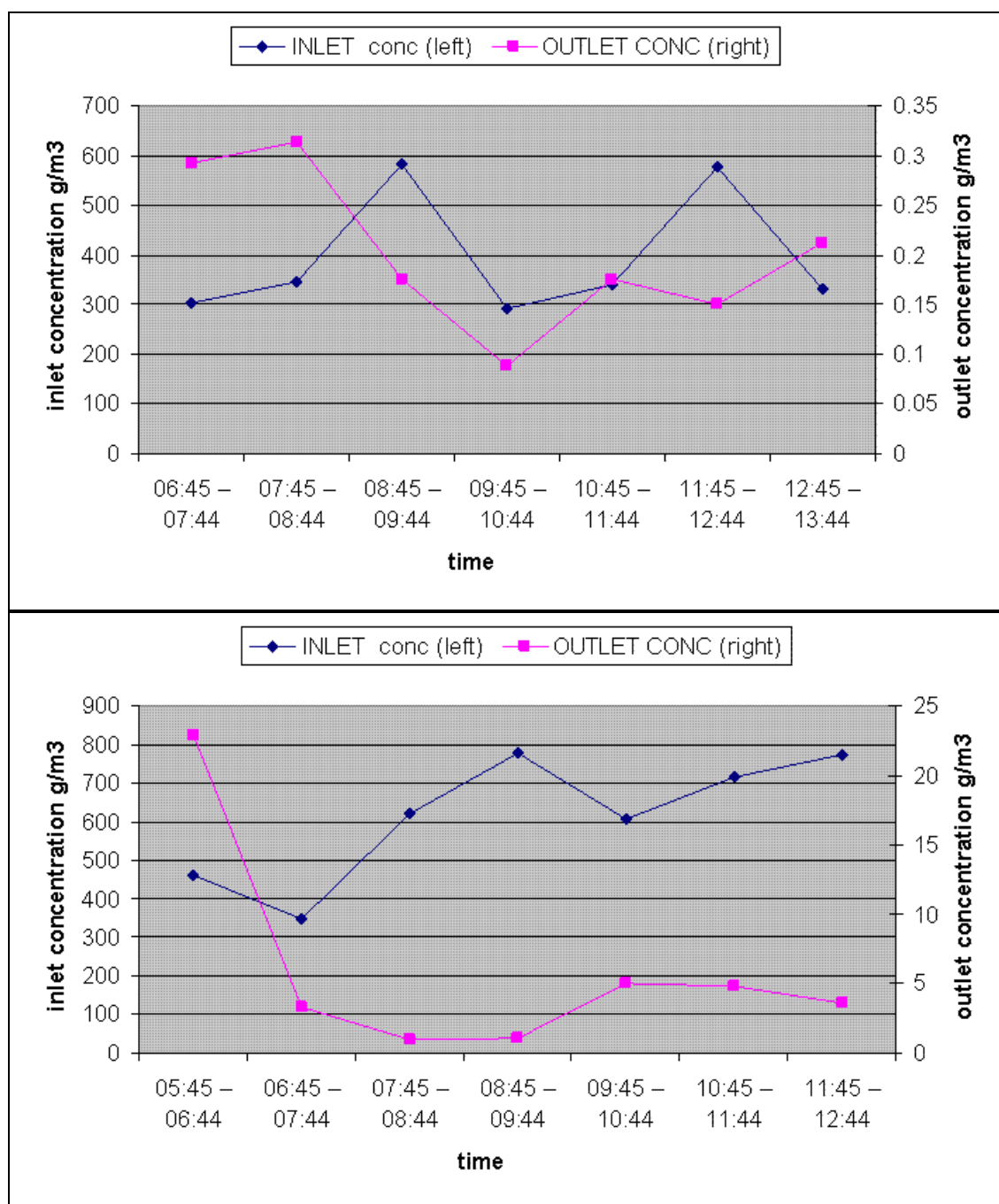


Figure 4.63: Variability of emissions to air from two VRUs (data-sets 8 and 9) over a day

Technical considerations relevant to applicability

Vapour recovery can be applied to crude loading (with the exception of adsorption unless a pretreatment such as sulphur stripper has been used, because of adsorbent fouling), dispatch product stations and in ship loading stations. However, for crude loading, it is less effective than systems for product loading, because the higher levels of methane and ethane in crude oil vapours are recovered with a low efficiency.

These systems are not applicable to unloading processes when the receiving tank is equipped with an external floating roof. Vapour recovery units are generally not considered applicable when the quantity of recovered product is small e.g. for low volatility products.

VRUs occupy limited space. Usually they are preassembled and delivered skid-mounted. Commercial VRU capacities range from 500 – 2 000 Nm³/h. Adsorption systems are commonly used due to simplicity, good operability and high performance.

The main technical restrictions, including safety considerations, are described in Table 4.106. In addition, it is to be noted that one of the major constraints for VRUs is the potential incompatibility of the system with the vapours existing in the vessel due to the previous cargo when cleaning has not been properly done.

Table 4.106: Overview of the applicability of some VRU techniques

VRU technique	Restriction in the applicability of the technique
Adsorption	Handling of non-compatible compounds present in the vapour stream may either poison or destroy active carbon, e.g. H ₂ S in crude oil. Due to the heat of adsorption and the use of supplementary blowers safety systems are required to ensure that auto-ignition does not occur. Appropriate monitoring to prevent it is also required
Membrane separation	Well suited to systems with large vapour volumes (compressor at the inlet to the membrane unit). For very small or variable vapour volume, e.g. road tanker loading, common practice is to install a variable volume vapour holding tank in the inlet vapour piping to the VRU
Condensation	May require double heat exchanger set to enable unit defrosting during continuous operation requirement. Light hydrocarbons form solid hydrates at low temperatures which can cause blockages. Flow variance has to be avoided to ensure efficient condensation. Very low temperature equipments require general safety measures
Hybrid systems	Due to the complexity of operation, a high performance level is difficult to maintain

Economics

Based on the AEAT-report [115, Rudd et al. 2001] on the abatement of ship loading emissions, Table 4.46 shows capital costs for a VRU plant for the various techniques over a range of vapour flows of up to 2 000 m³/h. These costs exclude civil engineering, provision of utility infrastructure and vapour collection systems. The additional corresponding costs are reported to be variable depending on the distance of the VRU to the loading facility (up to five times the cost of the VRU). The operating costs of the techniques consist of a component that is independent of throughput, which is in the range EUR 5 000 to 40 000/yr, plus a variable component which is approximately equal to EUR 0.05/t loaded.

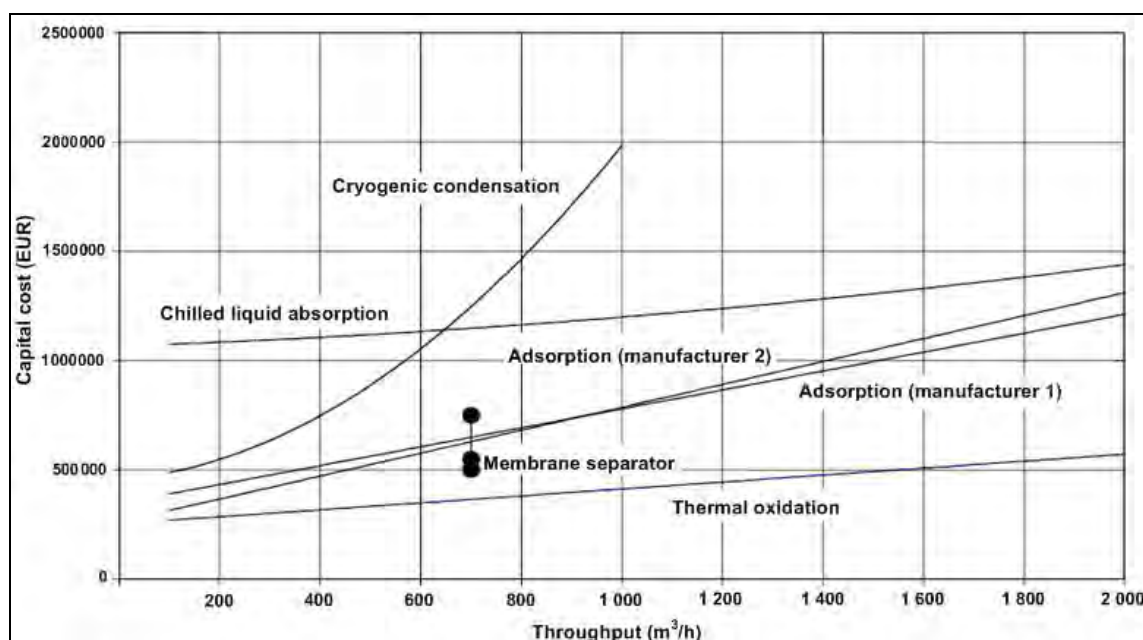


Figure 4.64: Capital costs for some VRU techniques and thermal oxidation (2001)

One report on the implementation of Directive 94/63/EC [116, ENTEC 2009] provides example cost data for a hypothetical single-stage adsorption-type unit operating at a recovery rate of 99.7 % and an inlet concentration of 1 160 g/Nm³, and therefore at an outlet concentration of 3.5 g/Nm³.

Table 4.107: Example cost data (2008) for a single-stage adsorption VRU operating at 3.5 g/Nm³

Sites characteristics	VRU N°1	VRU N°2
Maximum loading rate (m ³ /h)	273	1 090
Capital cost excluding installation (EUR million)	0.345	0.690
Annual electricity usage costs (EUR)	20 000	82 000

In France, the investment cost data (reported from the subsidy programme) given in Table 4.108 are available for the process operating at 2 g/Nm³.

Table 4.108: Examples of costs data for some French VRU sites

Sites	Loading capacity (tonnes/year)	Instantaneous treatment flow (m ³ /h)	Year	Investment cost (EUR million)	Avoided tonnes of COV/year
No 1	1 200 000	3 000	2005	0.580	100
No 2	192 500	800	1999	0.200	106
No 3	1 000 000	NA	1998	0.980	130

VRUs with a capacity of 1 000 Nm³/h can involve a capital cost of EUR 2 million with an installation factor of 1.5 to 5, with marine loading applications being at the top end of the range.

The total capital investment strongly depends on site-specific factors, such as the number of loading vessels connected to the system, the distance between the berth and the emission control facility (cost of piping), the need for blowers and for safety systems (explosion and flame

arresters). The capital costs can range from EUR 4 – 20 million for a VRU of 2 000 Nm³/h capacity. The investment costs can range from EUR 2 – 25 million for an efficiency of 99.2 %, implying an operating cost of EUR 0.02 - 1 million applied to loading operations (road, rail and internal refinery movements).

The investment costs corresponding to Göteborg (SE) and Mongstad (NO) refineries (see previous paragraph on Environmental performance and operational data) were the following:

- at Göteborg, three VRUs of the adsorption-type (capacities of 1 500, 2 000 and 2 400 m³/h respectively) serving four jetties cost around EUR 6.4 million (SEK 65 million) in 2001;
- at Mongstad, a 36 000 Nm³/h crude oil VRU cost around EUR 60 million (SEK 630 million) in 2008.

Quotation costs and power specifications for marine gasoline loading VRUs using different VRU technologies are the following, according CONCAWE (2012):

Table 4.109: Examples of reported capital costs and power specifications for VRUs

Technique	Capacity (m ³ /h)	Emission limit (g/Nm ³)	Cost (EUR million)	Power specifications (installed power)
Single-stage VRU/carbon adsorption	2 500	10	1.05	425 kW
Single-stage VRU/membrane separation	2 500	10	1.37	655 kW
Single-stage membrane separation	3 500	10	2.7	785 kW
Two stage membrane plus carbon adsorption	3 500	0.15	3.5	980 kW
Single-stage carbon adsorption	5 000	10	Unit cost 3.5 Total system cost 23	NA

Source: [259, TWG CONCAWE 2012]

Driving force for implementation

Directive 94/63/EC on the control of VOC emissions resulting from the storage of petrol and its distribution prescribes the installation of vapour balancing lines and vapour recovery units (VRUs) or vapour recovery systems (VRS) during gasoline loading/unloading activities in road and rail tankers and barges at refineries and terminals, to achieve an emission limit of 35 g/Nm³.

The Gothenburg Protocol specifies an emission limit of 10 g/Nm³ for total VOC (in a 24-hour period) for gasoline VRUs, with an exclusion for the loading of seagoing ships. It requires the application of vapour recovery only for motor gasoline loading for road, rail tankers and barges and for throughputs of more than 5 000 m³/yr.

Example plants

Many VRUs at gasoline (un)loading installations for VOC emission reduction have been built in Europe following Stage-1 legislation or for crude unloading e.g., at Göteborg harbour (SE), Mongstad refinery (NO), in Germany or in France (see previous paragraphs on environmental performance and operational data).

Reference literature

[160, Janson 1999], [181, HP, 1998], [182, Ecker 1999], [151, Sema,Sofres 1991], [167, VDI 2000], [228, TWG 2000], [191, UBA Austria 1998], [207, TWG 2001], [201, Manduzio 2000], [5, EC 2006], [115, Rudd et al. 2001], [116, ENTEC 2009], [77, REF TWG 2010], [111, CONCAWE 2009], [117, Germany - VDI 3479 2009], [259, TWG CONCAWE 2012]

4.23.6.3 Vapour destruction (VD)

Description

Apart from the conventional technique of VOC collection and destruction by routing to a flare system, two specific systems are relevant in this respect.

- **Oxidation:** the vapour molecules are converted to CO₂ and H₂O either by thermal oxidation at high temperatures or by catalytic oxidation at lower temperatures.
 - **Thermal oxidation** occurs typically in single chamber, refractory-lined oxidisers equipped with gas burner and a stack. If gasoline is present, the heat exchanger efficiency is limited and preheat temperatures are maintained below 180 °C to reduce ignition risk. Operating temperatures range from 760 to 870 °C and residence times are typically 1 second or less.
 - **Catalytic oxidation** requires a catalyst to accelerate the rate of oxidation by adsorbing the oxygen and the VOC on the the surface. The catalyst enables the oxidation reaction to occur at lower temperature than required by thermal oxidation: typically ranging from 320° to 540 °C. A first preheating step (electrically or with gas) takes place to reach a temperature necessary to initiate the VOCs catalytic oxidation. An oxidation step occurs when the air is passed through a bed of solid catalysts.

Directive 94/63/EC (Stage 1) only allows oxidation in special situations, e.g. when vapour recovery is unsafe or technically impossible because of the volume of return vapour.

- **Biofiltration:** decomposition to CO₂ and H₂O is achieved at temperatures slightly above ambient by micro organisms located in a solid humidified support medium.

Achieved environmental benefits

Respective VOC elimination ratios achievable with such techniques are: thermal oxidation: 99 – 99.9 %, catalytic oxidation 95 – 99 %, and biofilters 95 – 99 %. However, the efficiency of the biofilters is controversial: since high removal efficiencies are only achieved with high inlet loads; emission concentrations well below 50 mg/Nm³ NMVOC are rarely achieved.

Biotreatment units need minimal maintenance and do not produce any noise. No fuel or chemicals are required. Biofilters remove or destroy aliphatic and aromatic hydrocarbons, other VOCs, H₂S and odours in the off-gases from process streams, tank vents, relief valves, soil vapour extraction and waste water treatments, etc.

Cross-media effects

Thermal oxidation can lead to unwanted combustion products such as NO_x, requiring extra treatment. Catalytic oxidation requires less energy to reach combustion temperatures, and can be competitive with thermal oxidation at low inlet concentrations. Thermal oxidation requires good primary and/or secondary safety measures to prevent explosions, while the efficiency of catalytic oxidation may be reduced by catalyst poisoning and ageing. The incineration of VOCs also generates CO₂. Additional fuel is consumed for the combustion of streams with low concentrations and for the preheating of catalysts.

Waste is only generated when biofilters are exhausted. No secondary pollutants or wastes are created.

Operational data

Usually, operating times are longer than two years. For biofilters, input air temperature should be 5 – 55 °C with an appropriate moisture level.

Applicability

Installation for the treatment of flows of 17 m³/h up to 135 000 m³/h are found in the literature.

For biooxidation, the method is highly suited for the treatment of continuous constant-composition air streams with low concentrations of organic pollutants. The method is not suitable for the direct treatment of the vapour/air mixtures often encountered in transshipments, because such mixtures have mostly higher vapour concentrations (>1 % v/v) and appear as sudden peak flows during the rather infrequent unloading operations. Biotreatment facilities are certainly sensitive to poisoning by unexpected compounds in the incoming vapour stream. Consequently, most of these systems need continuous monitoring to prevent the entrance of undesired compounds.

Biofiltration is only suitable for continuous, constant composition, low concentration vapour streams. These conditions are not typical of refining applications.

Economics

The economics of a thermal oxidation system with heat recovery will depend on many factors, including the calorific value of the waste stream. In 1998, a substantial payback was already expected based on the heat recovery from a thermal oxidiser furnished with a gas-to-gas heat exchanger that has an efficiency of 60 % and a gas flow of 4720 l/s. Assuming natural gas was used as supplementary fuel, the costs reached around USD 20/million of kcal and USD 0.08/kWh of electric power. For a system running 24 h/day, 350 d/yr, the payback time for the USD 0.2 million additional capital investment for a plant-type heat exchanger would be less than five months.

Biofiltration costs significantly less than the other air pollution control techniques. Capital costs vary with flowrate and the destruction/removal efficiency. Capital costs start at about USD 15/m³/h. Operation and maintenance costs are extremely low because no fuel or chemicals are required.

Table 4.110: VOC thermal oxidation control technique applied to refinery

Emission source	Refinery process units and equipment (installed and retrofitted)
Control technology	Collection of atmospheric VOCs and relief valves to flare/incineration system
Efficiency	Up to 99.5 % destruction efficiency in incineration
Investment costs	EUR 1.3 million for 5 Mt/yr refinery
Operating costs	EUR 3.0 million
Other impacts	Increase in CO ₂ emissions due to combustion
<i>Source: UN-ECE EC AIR/WG6/1998/5</i>	

See also Figure 4.64 for the costs of thermal oxidation.

Driving force for implementation

Reduction of VOCs.

Example plants

Thermal oxidation: more than 107 units are operating worldwide.

Reference literature

[168, VROM 1999], [181, HP, 1998].

4.23.7 Flares

Description

Flares are used for safety and the environmental control of discharges of undesired or excess combustibles and for surges of gases in emergency situations, upsets, unplanned events or unanticipated equipment failure. The flare is usually required to be smokeless. Flaring is both a source of air emissions and leads to the burning of potential valuable products. Therefore, for environmental and energy efficiency reasons, its use must be limited and the amount of flared gas reduced as much as possible. For routine venting and planned shutdowns, flare gas recovery systems are to be used instead. More information is available in the CWW BREF [6, EC 2003].

Flare systems and designs

Flare systems can normally be divided into two main sections, i.e. the flare collection system with a flare knock-out drum and the flare stack itself. When dealing with large refinery complexes, separate knock-out drums may be installed in different process areas with 'blocking-in' facilities to allow maintenance during shutdowns of these areas.

Figure 4.65 shows a simplified process flow diagram of a flare system.

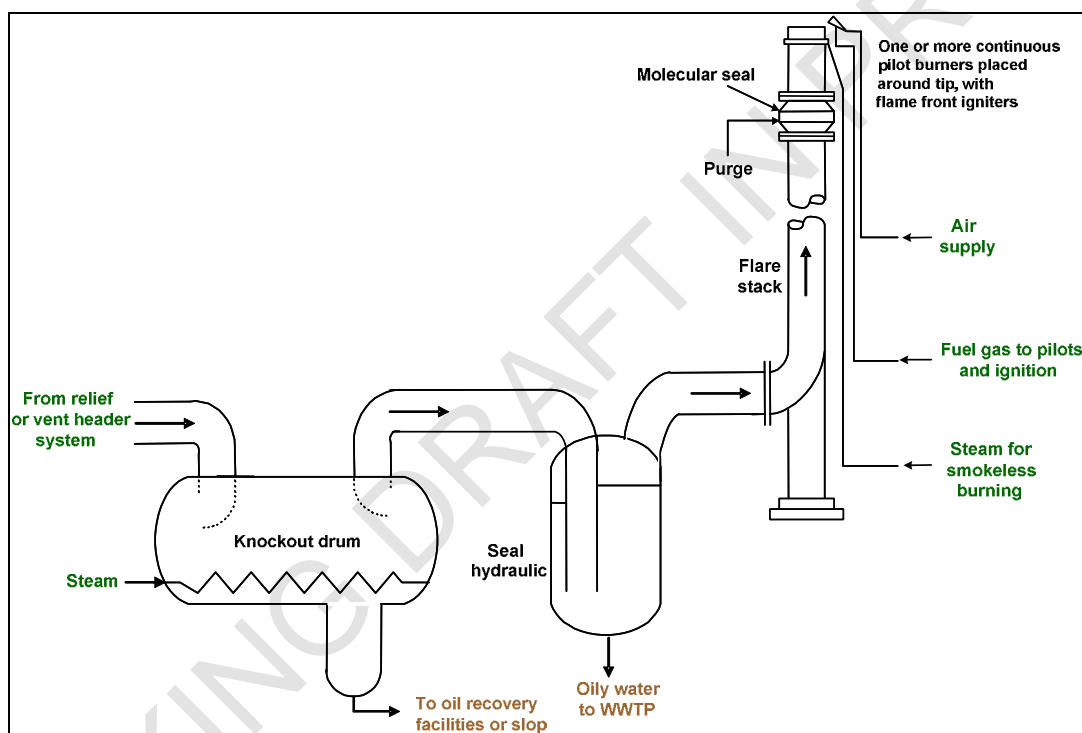


Figure 4.65: Simplified process flow diagram of a flare system

Many flare systems are available today for various purposes. The chosen flare system depends mainly on:

- the flow, pressure, temperature and composition of the gas that is flared;
- the requirements given for combustion efficiency, radiation, soot and noise;
- the availability and the access to steam, air and gas.

Flares can be categorised in several ways and the following distinctions can be made:

- the **type of flares**: elevated or placed on the ground (elevated are the most common flares and have the greatest capacity);
- the **flare system**: non-assisted flares (low or high pressure) or assisted flares (with steam, air, gas or water)
- the **zone in which the oxidation reaction occurs** and includes the following categories: flame flares (open flame flares) or chamber flares (muffle and screen/shielded flares).

Compared to elevated flares, ground flares lead to poorer dispersion, because of the stack being nearer to the ground and therefore possibly resulting in environmental or health concerns (depending on the type of end products).

In chamber flares, combustion occurs inside a cylinder which enables them to operate without smoke formation, noise or radiation. A type of ground flare works as a **premixed surface combustion system** (an enclosed burner), where pre-mixed gas and air burns on a permeable medium. (see [6, EC 2003]).

Table 4.111 shows an overview of the different main groups of flare systems. It also gives a brief description of each flare system, area of application and advantages and disadvantages regarding both environmental and operational consequences.

Extinguished flare systems also exist, where no permanent burning pilot flame is required, but a special mechanism is ignited when the speed of the gas exceeds a defined limit.

Non-assisted flares system:

A flare that only burns natural gas without any supply of air or vapour is called a **non-assisted flare**. It is used when non-smoking combustion can be achieved without external assistance. Depending on the pressure in the process equipment, it could lead to a low or high pressure flare. Pressurised gas provides a good mixing of air and waste gases and so reduces the exposure and smoke formation. On the other hand, it increases the noise level.

Assisted flare

When the pressure in the waste gas to be flared is low, an external medium such as steam, air or gas can be used as the driving force. Depending on their respective availability, the following can be used:

- high pressure steam for steam-assisted flare;
- high pressure gas, for gas-assisted flare;
- air supply, for air-assisted flare;
- water being injected into the flare when low noise and radiation levels are required.

Table 4.111: Various flare system applications

Flare systems		Description	Application	Features
Non-assisted flares	Low-pressure flare	Low-pressure flares are the simplest type of flare. Low-pressure flare tips are designed for a long service life. They are capable of flaring a wide range of waste streams and are primarily used for non-smoking gases	Low-pressure flares can be used when non-smoking combustion can be achieved without external assistance. Low-pressure flares are used for maintenance and lower gas rates.	Cost-effective; Low maintenance costs Stable, reliable combustion
	High-pressure flare	High pressure flares use the energy in the pressurised gas to create turbulent mixing and induce excess quantities of air for more complete combustion	High pressure flares are used onland and offshore in order to achieve non-smoking combustion at large flaring rates. Can handle large quantities of flare gas at high pressure and has large capacity.	Cost-effective Clean, efficient and smokeless combustion Lower radiation
Assisted flare	Steam-assisted flare	Steam assisted flares are designed to dispose of heavier waste gases which have a greater tendency to smoke. Steam is injected into the waste stream as external momentum force for efficient air/waste gas mixing and turbulence. This promotes smokeless flaring of heavy hydrocarbons	Steam assisted flares are employed in low-pressure applications to achieve smokeless flaring where high-pressure steam is available onsite.	Smokeless combustion Low noise; Maximum energy efficiency.
	Air-assisted flare	Air supply is used as an external momentum force for efficient air/waste gas mixing and turbulence. This promotes smokeless flaring of heavy hydrocarbon waste gas	Air assisted flares can be employed for operations that require smokeless, low-pressure flares in areas where steam is not available as smoke suppressant.	Reduce smoke; Lower radiation; Lower noise generation.
	Gas-assisted flare	Gas injection is used as an external momentum force for efficient air/waste gas mixing and turbulence. This promotes smokeless flaring of heavy hydrocarbon waste gas.	Gas-assisted flares can be employed for operations that require smokeless, low-pressure flares in areas where high pressure assisted gas is available.	Maximum combustion; Smokeless performance.
	High-pressure water injection flare	Water is injected into the flare to reduce radiation and flare noise.	For high-pressure applications that requires low noise and radiation, and where water is available.	Significantly reduces radiation and noise; Decreased operational and facility cost.

Sources: [86, SFT 2009]

Techniques for flaring operations

Techniques to be applied to flares that may reduce emissions are given below:

- Use of pilot burners which give more reliable ignition to the vent gases because they are not affected by the wind.

- Steam injection in flaring stacks, which can reduce particulate matter emissions, when appropriately designed.
- Surplus refinery gas has to be flared, not vented. Knock-out pots to remove liquids should be provided, with appropriate seals and liquid disposal systems to prevent the entrainment of liquids into the combustion zone. Water streams from seal drums should be routed to the sour water system.
- Flare-gas recovery systems have been developed where the flare gas is captured and compressed for other uses. Usually recovered flare gas is treated and routed to the refinery fuel gas system. Depending upon the flare gas composition, recovered gas may have other uses. Reductions of flaring to ratios of 0.08 – 0.12 % of production in one natural gas plant in Norway have been reported.
- For minimisation of the soot formation in the flame, flow measurement with automatic steam control is applied in new installations; as well as luminosity measurements with automatic steam control, and remote visual observation using colour TV monitors in plant control rooms, allowing manual steam control and the detection of permanent availability of the pilot flame. The steam injection serves several purposes. Firstly, it improves the mixing of fuel and air by creating turbulence, and thus enhances combustion efficiency. Secondly, it protects the flare tip by keeping the flame away from the metal. Thirdly, the steam reduces soot emissions as it reacts with solid carbon particles to form CO, which is then further oxidised to CO₂. And lastly, the steam injection probably also reduces thermal NO_x formation. When hydrogen or very 'light' hydrocarbons are flared, steam injection is usually not applied as air-fuel mixing is often good and soot formation is unlikely.

Flare monitoring

Flare monitoring is needed in order to keep records of each event as part of the monitoring system of the refinery and to report to local authority.

Flare systems should be equipped with adequate monitoring and control systems necessary to operate smokelessly and evaluate emissions. Flares should be visually monitored under non-emergency conditions. Monitoring and control systems can be either automatic or manual (provided safety for the workers is ensured). They generally include a continuous flow measurement, remote visual observation using colour TV monitors, steam control and pilot flame detection.

Flare combustion efficiency can be monitored through the following operations:

- monitoring the mass flowrate and lower calorific value of the flare gas (e.g. by using automated gas sampling measurements);
- comparing the measured values to the design requirements to guarantee minimum combustion efficiency (e.g. 98 %).

Flare gas flow

Among the various non-intrusive measuring systems that are available and compatible with safety flaring applications, ultrasonic flow measuring has been the preferred choice in most new applications [29, Clearstone 2008]. Ultrasonic flow meters can be used on dry, but also on wet and dirty gas streams, if the liquid content does not exceed ~0.5 % by volume. If greater amounts of liquids are anticipated, a liquids knockout system should be installed directly upstream of the flow meter. They are applicable to a wide volume range, offer high accuracy, do not require frequent calibration, and have no significant flow restriction. However, they need a sufficient length of straight pipe in order to ensure laminar flow measuring conditions, which can raise difficult constraints in the case of retrofitting. They also operate in temperature and pressure ranges which do not always correspond to actual process conditions. The approximate cost for such ultrasonic flow meters is estimated at EUR 0.5 million per measuring device [Questionnaire n°27].

Costs (2004) reported for an ultrasonic flow meter device are in the range of USD 20 000 – 30 000. Additional costs due to state-of-the-art site preparation, installation, calibration, and connection may lead to an overall up-front cost of USD 100 000 (around EUR 79 400) per measuring device [258, Texas Commission on environmental quality 2010].

Like any monitoring device, the gas flow meters require the appropriate specifications (detection limit, measuring range) to deliver an accurate measurement. Alternative methods to estimate the flare gas flow based on operational parameters can be used, provided that a clear correlation is established.

Flare gas composition

Flare gas composition can be analysed by periodical sampling and subsequent laboratory analysis, or by continuous measurement devices. However, on-line gas chromatography for continuous measurement is highly sensitive to fouling and requires strict (and costly) pretreatment and conditioning of the samples, in order to remove water and particles before measurements.

As an example, the gas composition of two flares from a Norwegian refinery determined with online gas chromatography, are provided in Table 4.112.

Table 4.112: Examples of flares gas composition

Components	Main flare (mole %)	Sour gas flare (mole %)
1-Butene	0.1	0.1
C6+	0.7	1.5
C-Butene	0.1	0.1
CO	0.4	1
CO ₂	0.5	0.4
Ethane	12.3	10
Ethene (ethylene)	2.8	5
H ₂	38.9	35
H ₂ S	0.2	0.2 – 1
1-butane	2.9	2
I-butene	0.1	0.1
I-pentane	0.9	0.4
methane	18.4	23
N ₂	5.6	16
n-butane	2.7	1
n-pentane	0.6	1
O ₂	0.3	0.2
propane	10.9	3
propene	1.4	1
t-butene	0.1	0.1
NB: the figures provided are based on normal conditions. H ₂ S concentration will vary with the amount of sour gas sent to the flare		
Source: [86, SFT 2009]		

Flaring activity and emission records

On the above basis, flare gas emissions should be estimated and compiled in daily records of the site flaring activity. For each flaring episode, the record should document the measured or estimated flare gas composition, the measured or estimated flare gas quantity, and the episode duration.

The flare gas emissions can be calculated by using estimated or measured flows and concentrations (e.g. H₂S) that have been measured, together with emissions factors for NO_x and

CO Available literature gives concentration values around 100 – 400 mg/m³ for NO_x formed, and around 30 mg/m³ for CO released [28, Tebert et al. 2009].

For estimating VOC emissions, appropriate combustion efficiency shall be determined. In general, a minimum of 98 % may be assumed under optimised conditions and if guaranteed by the flare provider [6, EC 2003].

Table 4.113: Example of flare gas NO_x emissions factors used at a Norwegian refinery

Component	Source	Emission factor	Base for emission factor
NO _x	Flare gas	3.13 g/kg	Measurements in 2005
	Flare (purge gas)	3.13 g/kg	Measurements in 2005
	Flare (sour gas)	4.0 g/kg	Emission factor from NO _x -tax

Source: [86, SFT 2009]

Achieved environmental benefits

Combustion efficiency, radiation, soot and noise depends on the flare system. Well-operated refinery flares typically achieve a conversion of 98 % to CO₂, 1.5 % are partially combusted products (almost all CO) and 0.5 % are unconverted. Enclosed ground flares have reduced noise and smoke compared to elevated flares. However, the initial cost often makes them undesirable for large releases when compared to elevated systems.

Environmental performance and operational data

In order to achieve a combustion that is as complete as possible, the flare should be operated with a minimum flame temperature of 800 – 850 °C. Flare efficiency is generally maximised through assessment of the heating value of the flared streams and by minimising flame quenching, for example by oversteaming. Since air present in the stack can create a potentially explosive mixture with the incoming flare gas during low-flare gas loads, a continuous stream of purge gas is required. When using nitrogen, a smaller purging rate is required. Very often, a molecular water seal is employed, which allows for using a lower purging rate.

Table 4.114: Example of two flares design conditions in a UK refinery (2007)

Emission Source	Units	1st flare	2nd flare
Height	m	91	137
Type of system		High pressure	Low pressure
Maximum capacity	tonnes/h	397	680
Smokeless capacity	tonnes/h	34	68
Pilot gas consumption	kg/h	1.9	1.9
Purge gas consumption	kg/h	22.7	12.5
Steam consumption ⁽¹⁾	tonnes/h	11.8	21.8
SO ₂ emission ⁽²⁾	kg/h	0.074	0.043

⁽¹⁾ Steam consumption at maximum smokeless capacity.
⁽²⁾ From pilot gas and purge gas.

Cross-media effects

Flare emissions will include, in addition to NO_x, CO from combustion, and a part of uncombusted flared gas compounds (e.g. VOC, H₂S, SO₂), thus causing potential health concerns and odour nuisances (mainly for ground flares).

Flare seal water typically needs treatment before release. Steam injection for combustion enhancement and soot blowing spends thermal energy. The use of ground flares can lead to the potential accumulation of a vapour cloud in the event of a flare malfunction; special safety dispersion systems are therefore usually included in the ground flare system. As a consequence, instrumentation for monitoring and controlling ground flares is typically more stringent than for an elevated system. In addition, flares, especially steam assisted ones, generate noise and light nuisances.

Technical considerations relevant to applicability

The flaring of toxic gases (never via a ground flare) requires special considerations. To ensure safe operation during periods when the flare may not have a flame present, ground level concentration calculations for hazardous components should be performed assuming the flare as a vent only. Other safeguards may be necessary to mitigate ground-level exposure hazards. Reliable continuous pilot monitoring is considered critical when flaring toxic gases.

Due to different burning characteristics of the gases, a separate sour gas flare is usually provided; this flare could be equipped with different burners than the hydrocarbon flare, to allow for more efficient combustion of sour gases (H₂S).

Economics

No detailed data received.

Driving force for implementation

Some local regulations (e.g. South Coast Air Quality Management District-SCAQMD-California – US) require flare minimisation plans. The seven refineries (30 flares) in the SCAQMD area are now required to have continuous flow gas monitors, continuous gas heating value monitors, and semi-continuous total sulphur concentration monitors.

The main other driving force for implementation is health and safety.

Example plants

Flares are common in refineries. Two examples of low flaring ratio refineries in Sweden are provided in Section 3.23.3.

Reference literature

[159, WB 1998], [148, Irish EPA 1993], [167, VDI 2000], [168, VROM 1999], [6, EC 2003], [118, VITO 2009], [86, SFT 2009], [Questionnaire number 43, 27], [258, Texas Commission on environmental quality 2010].

4.23.8 The SNO_x combined technique to abate air pollutants

Description

The SNO_x plant is designed to remove SO₂, NO_x and particulate matter from combustion flue-gases. It is based on a first dust removal stage (by an ESP), followed by catalytic processes. The sulphur compounds are recovered as commercial-grade concentrated sulphuric acid, while NO_x is reduced to N₂.

The only additional material necessary is the ammonia used for the NO_x removal. Furthermore, natural gas and water are needed, besides small quantities of silicone oil for the acid mist control unit.

The process produces 94 – 95 % pure sulphuric acid (H₂SO₄) for sale. The system employs a catalytic converter to oxidise SO₂ to SO₃ at a temperature of 400 – 420 °C. This temperature level allows a DeNO_x, operating at 380 °C, to be well fitted in the process. High NO_x removal at high NH₃ slip is possible with no risk of precipitation of ammonium sulphates, as the reactor temperatures are above the decomposition temperature (350 °C) and any NH₃ slip is destroyed in the SO₂/SO₃ oxidiser.

The process produces no waste water or waste products, nor does it consume any chemical apart from ammonia for NO_x control. The high removal of dust is required by the H₂SO₄ production step. Dedusting with an efficiency consistently at 99.9 % is required so as to avoid frequent clean-up of the SO₂/SO₃ converter and to maintain good product quality.

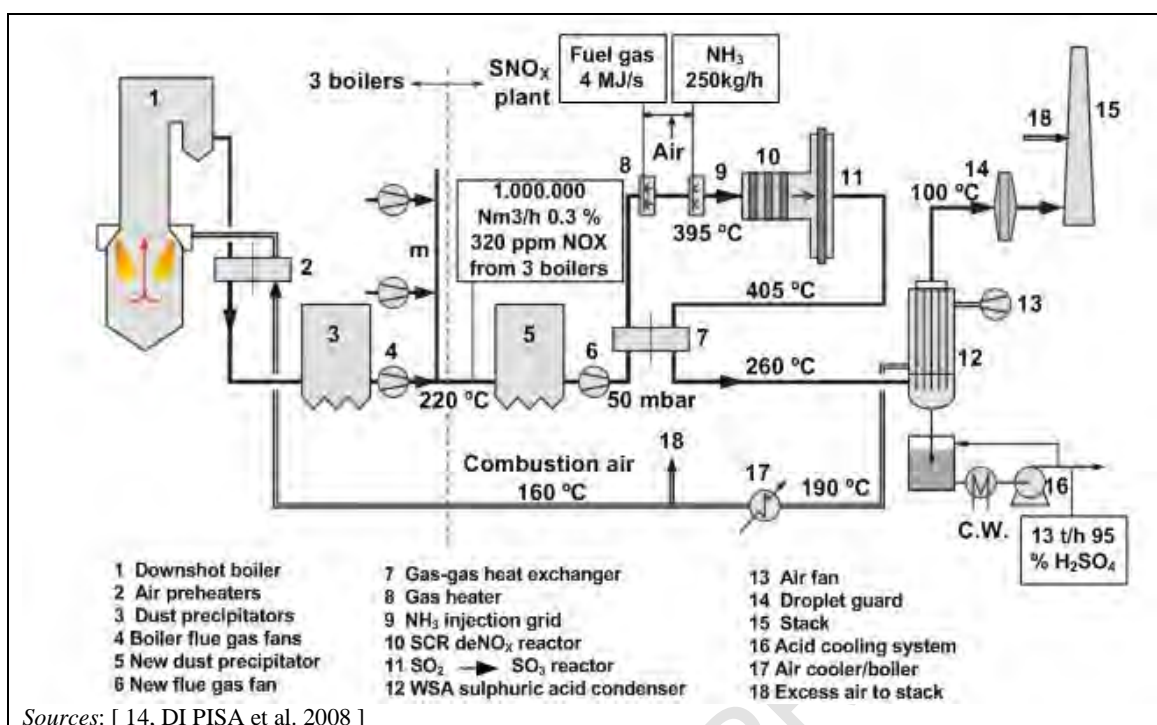


Figure 4.66: SNO_x process scheme in the Gela refinery

As shown in Figure 4.66, the heat from the acid condenser (operating between 240 – 100 °C, hydrating SO₃ and condensing the resulting acid product) is used as the first step in preheating combustion air. The recovered heat, produced by the conversion process, is substantial and makes up for the power demand when the sulphur content in the fuel (oil or coal) is 2 – 3 %. Areas relating to dust that require attention in operation are the HTEP, the SO₂/SO₃ converter and the acid falling-film condenser (made of borosilicate glass tubes). Formation of acid mist (aerosol) in the condenser is avoided by a patented heterogeneous nucleation control, which is essential for the operation of WSA and SNO_x plants.

Achieved environmental benefits

They are summarised as follows:

- removal of up to 98 % of SO₂ and SO₃, up to 96 % of NO_x, and essentially all PM;
- process able to treat high SO₂ concentration flue-gas;
- high removal of SO₂, together with NO_x and particulates removal (see Table 4.115);
- low additional environmental impacts: no raw material required (only ammonia consumption for NO_x control), no waste water or waste production;
- no cooling water consumption;
- production, as by-product of the process, of H₂SO₄ at a commercial grade suitable for sale;
- high heat recovery.

Cross-media effects

The electrical consumption corresponds to an installed power of around 10 MW_e for a 1 million Nm³/h unit.

Operational data

In Gela, the SNO_x unit treats the flue-gas from three pet-coke firing boilers (producing 3 x 380 t/h of HP steam) and is designed for 1 million Nm³/h, with an upstream SO₂ concentration ranging from 6 900 to 13 200 mg/Nm³ (at 6.7 % v/v humidity and 5 % O₂ content) due to the particular refining process based on high sulphur crude. The ammonia injection rate used to

operate the SCR section is about 200 kg/h. The H₂SO₄ production (95 % H₂SO₄ concentration) reaches 13 t/h with a 5.5 % sulphur pet-coke.

Table 4.115: SNO_x performance from a 72 h-test run after 5 months of operation (Gela)

Parameters	Units	Results
Flue-gas flowrate (wet) ⁽¹⁾	Nm ³ /h	971 000
Inlet NO _x (as NO ₂)	mg/Nm ³	451
Outlet NO _x (as NO ₂)	mg/Nm ³	42
NO _x reduction efficiency ⁽²⁾	%	90.5
Inlet SO ₂	mg/Nm ³	8 243
Outlet SO ₂	mg/Nm ³	288
SO ₂ reduction efficiency	%	96.5
Outlet SO ₃ ⁽³⁾	ppm	3
Outlet NH ₃	ppm	NA
H ₂ SO ₄ Concentration	% wt	95
Electricity consumption (Blowers, ESP, pumps)	MWh	132 377
Ammonia consumption	kg/h	238
Methane consumption	Nm ³ /h	456
NB: NA: not available ⁽¹⁾ Maximum flue-gases available from the boilers during the test run. ⁽²⁾ After NH ₃ grid distribution adjustment efficiency raised to 93 - 95 % ⁽³⁾ More accurate measurement shows 2 ppm Source: [14, DI PISA et al. 2008]		

Table 4.117 provides results from a 72 h-test run which was performed in order to check the maximum efficiency after complete renewal of catalyst beds. Additional information based on the Gela site monitoring under average operating conditions from 2003 show the following abatement efficiency in Table 4.117 [257, TWG IT 2012]:

Table 4.116 SNO_x performance under average operating conditions (Gela)

Parameters	Units	Results
Flue-gas flowrate to SNO _x	Nm ³ /h	1 000 000
SO₂ overall abatement efficiency	%	94
SO ₂ concentration.in flue-gas to Snox ⁽¹⁾	mg/Nm ³	9 994
SO ₂ concentration in flue-gas to stack ⁽¹⁾	mg/Nm ³	600
SO ₂ concentration in flue-gas to stack , dry and @ O ₂ 5.4%	mg/Nm ³	627
NO_x overall abatement efficiency	%	90
NO _x concentration in flue-gas to Snox ⁽¹⁾ ⁽²⁾	mg/Nm ³	636
NO _x concentration in flue-gas to stack ⁽¹⁾ ⁽²⁾	mg/Nm ³	64
NO _x in flue-gas to stack, dry and @ O ₂ 5.4 % ⁽²⁾	mg/Nm ³	68
NB: ⁽¹⁾ These values refer to a humidity content of 6.7 v/v% and a oxygen content of 5 % ⁽²⁾ NO _x expressed as NO ₂ Source: [257, TWG IT 2012]		

In Schwechat, the SNO_x unit treats the flue-gas from a central CHP power plant fueled with heavy residues from the thermal cracker, together with the tail gases received from the SRU.

Table 4.117: SNO_x performance (OMV Schwechat)

Parameters	Units	Results
Flue-gas flowrate (wet)	Nm ³ /h	820 000
Inlet NO _x (as NO ₂)	mg/Nm ³	Max 700
Design outlet NO _x (as NO ₂)	mg/Nm ³	<200
NO _x reduction efficiency	%	>87 %
Inlet SO ₂	mg/Nm ³	Max 8 000
Design outlet SO ₂	mg/Nm ³	<200
SO ₂ reduction efficiency	%	>96.6 %
Outlet SO ₃	ppm	NA
Outlet NH ₃	ppm	<1
H ₂ SO ₄ Concentration	% wt	NA
Electricity consumption (Blowers, ESP, pumps)	MW _e installed	NA
Ammonia consumption	kg/h	NA
Methane consumption	Nm ³ /h	NA
NB: NA: not available Source: [54, Gallauner et al. 2009]		

Applicability

The Gela Refinery SNO_x plant was reported in May 2008 to have been operated with 96 % availability on average (including annual planned stops), and no decrease in performance from its start-up in September 1999 (according to measured conversion rates and pressure drops). After a 72500 hour run, the plant had its first general shutdown (1056 hours) for maintenance in June 2006. Only 50 % (12 beds out of 24) of the desulphurisation catalyst were replaced. The SCR catalyst is still the same from the beginning of the plant commissioning.

The Schwechat Refinery SNO_x plant started operation in October 2007 and is designed for a turnaround period of a minimum of 6 years.

Economics

A SNO_x plant designed for a flue-gas load of 1.0 million Nm³/h had a cost of EUR 100 million. For such a unit, reported annual maintenance costs are EUR 4.176 million for a 5-year period between 2003 and 2007, as shown in Table 4.118.

Table 4.118: Maintenance costs (in thousand EUR) of the Gela SNO_x plant for 2003-2007

Year	2003	2004	2005	2006	2007	TOTAL
Routine expenses	211.08	423.71	130.04	177.70	124.79	1 067.32
Extraordinary	112.33	123.21	11.96	128.84	129.79	506.13
Ordinary outage	14.22	83.03	348.11	1 882.41	274.79	2 602.56
TOTAL	337.63	629.95	490.11	2 188.95	529.37	4 176.01
Source: [14, DI PISA et al. 2008]						

Driving force for implementation

Reducing air emissions (SO_x, NO_x and dust) from burning high sulphur fuels (e.g. pet coke), together with recovering a sulphuric acid by-product at commercial specifications.

Example plants

AGIP Refinery in Gela, Italy (1999), OMV Refinery in Schwechat, Austria (2007), NEFO Power Plant in Nordjyllandsvaerket, Denmark (2005). According to TOPSOE Company, 6 more units were contracted in 2008 for a total of over 5 million Nm³/h of flue-gas.

Reference literature

[221, Italy 2000], [13, TOPSOE 2006], [14, DI PISA et al. 2008],
[15, 2008 Refining Process Handbook], [257, TWG IT 2012].

4.23.9 Odour pollution preventing and control techniques

Use of nitrates for odour control

Description

This technique can be used to reduce the odour generated by any equipment (e.g. storage tanks, sewage systems, oil/water separators) where anoxic conditions can lead to the formation of hydrogen sulphide and other odourous mercaptans in contaminated waters from the biodegradation of sulphur organic compounds by bacteria. This technique consists of adding nitrate-based products in septic water areas, in order to replace bacteria feedstock and to favour the development of denitrificative bacteria, which will both reduce added nitrates in nitrogen and existing hydrogen sulphide in sulphates. Nitrate solution can also be injected in bioreactors

Achieved environmental benefits

In favourable conditions of use, hydrogen sulphide and mercaptans can be significantly reduced and even virtually eliminated. For example:

- An addition of a 400 mg/l nitrate solution in a septic ballast water tank with an appropriate decreasing dosing rate can eliminate a pre-existing concentration of 115 mg/l of hydrogen sulphide by >90 % after the first 24 hours. After 36 hours, hydrogen sulphide can be almost eliminated, while the nitrate concentration in the treated water remains below 20 mg/l;
- A 250 m³ biofilm reactor has been installed in 1995 for the treatment of ballast waters which have to be stored for long periods (weeks) before being discharged to the waste water treatment plant of a refinery in Norway. The reactor treats up to 600 m³/h of water and removes up to 60 kg H₂S per hour.

The reduction of hydrogen sulphide and mercaptans concentration in the septic pieces of equipment concerned also has major beneficial effects on occupational safety for the operators intervening on such equipment.

Cross-media effects

Unappropriate dosing can lead to an excessive contamination of nitrates in the treated waters.

Operational data

The available literature reports:

- a consumption of around 90 – 150 t/yr of nitrate-based solution needed for treating the water bottom of a large crude oil tank, avoiding odourous (and dangerous) release of hydrogen sulphide during draining operations;
- a consumption of 100 t/yr for the treatment of a ballast water tank kept at a high level as it doubles as a reserved water source for fire fighting. Nitrate-based solution is injected when pumping additional water into the tank, and further additions are made shortly before any discharges.

Applicability

This technique is fully applicable.

Economics

In 2009, the price of the chemical additives used for implementing this technique was around EUR 350 – 550/tonne, depending on the chemical prices fluctuation, related logistics and

number of injection sites at the refinery. In some cases, there could be additional costs for a storage tank and for pumping system rent.

Driving force for implementation

Elimination of hazardous situations and reduction of odours generated by septic waters

Example plants

This technique is reported to be currently implemented in various refineries operated in the UK and Norway.

Reference literature

[55, Dixon et al. 2009]

WORKING DRAFT IN PROGRESS

4.24 Waste water treatments

This section is complementary to previous sections of Chapter 4 related to individual production processes or units. It gives sector-specific information on key management, reduction and abatement techniques that are or may be implemented for waste waters generated by oil and gas refining.

For a given technique, available data on the way it can be applied and the results it allows on particular processes or units have been given in the related sections. The information provided here aims at completing this information on broader aspects, in particular environmental benefits, cross-media effects, operational data, and applicability issues which will not be repeated in other sections.

The purpose of the waste water treatment plant is to control the amount of substances in waste water that are emitted to the receiving water body. The configurations of waste water treatment plants may differ from one refinery site to another due to site-specific needs and requirements. The techniques applied at a site may include:

- measures directed at managing waste streams at or near their source;
- measures applied downstream of sources to segregate and manage waste streams together that have similar and/or compatible and/or synergistic properties;
- end-of-pipe techniques.

When the techniques applied include a biological treatment step, a pretreatment system of sufficient configuration, capacity, and coupled with best practices is necessary to assure there is no inhibition of the efficiency of the biological step.

Techniques to consider in the determination of BAT include, but are not be limited to:

- techniques that are applied to control routine and non-routine operation and/or maintenance for waste water sources that are characterised to have variable flow and/or substance loads, including:
 - tank water draws;
 - vacuum truck movements;
 - equipment clearing activities for maintenance;
- waste water source control and efficient operation of the waste water treatment systems;
- practices that include utilisation of special procedures and/or temporary equipment to ensure performances are respected when necessary to manage special circumstances such as:
 - spills;
 - loss of containment;
 - misdirected flows;
 - high flowrates;
 - high substance load rates from malfunctions;
 - incidents;
 - routine and/or major maintenance activities.
- practices that assure the cause of deviations in expected treatment performances are identified, and that immediate corrective action is taken to minimise the impact on performance, and corrective actions are implemented to minimise the risk of a repeat occurrence of the deviation.

If needed, further and more in depth information about these techniques, and others can also be found in the CWW BREF [6, EC 2003].

As illustrated in Figure 4.67, a distinction can be made within the global waste water treatment:

- the collection of waste water from units after possible pretreatment;
- the removal of insoluble substances: 1st step recovering oil;
- the removal of insoluble substances 2nd step recovering suspended solid and dispersed oil;
- the removal of soluble substances, including biological treatment (with possible nitrification/denitrification) and clarification;
- additional treatment systems.

Techniques to consider for these treatment steps are described respectively in Sections 4.24.4.1, 4.24.4.2, 4.24.4.3 and 4.24.5.

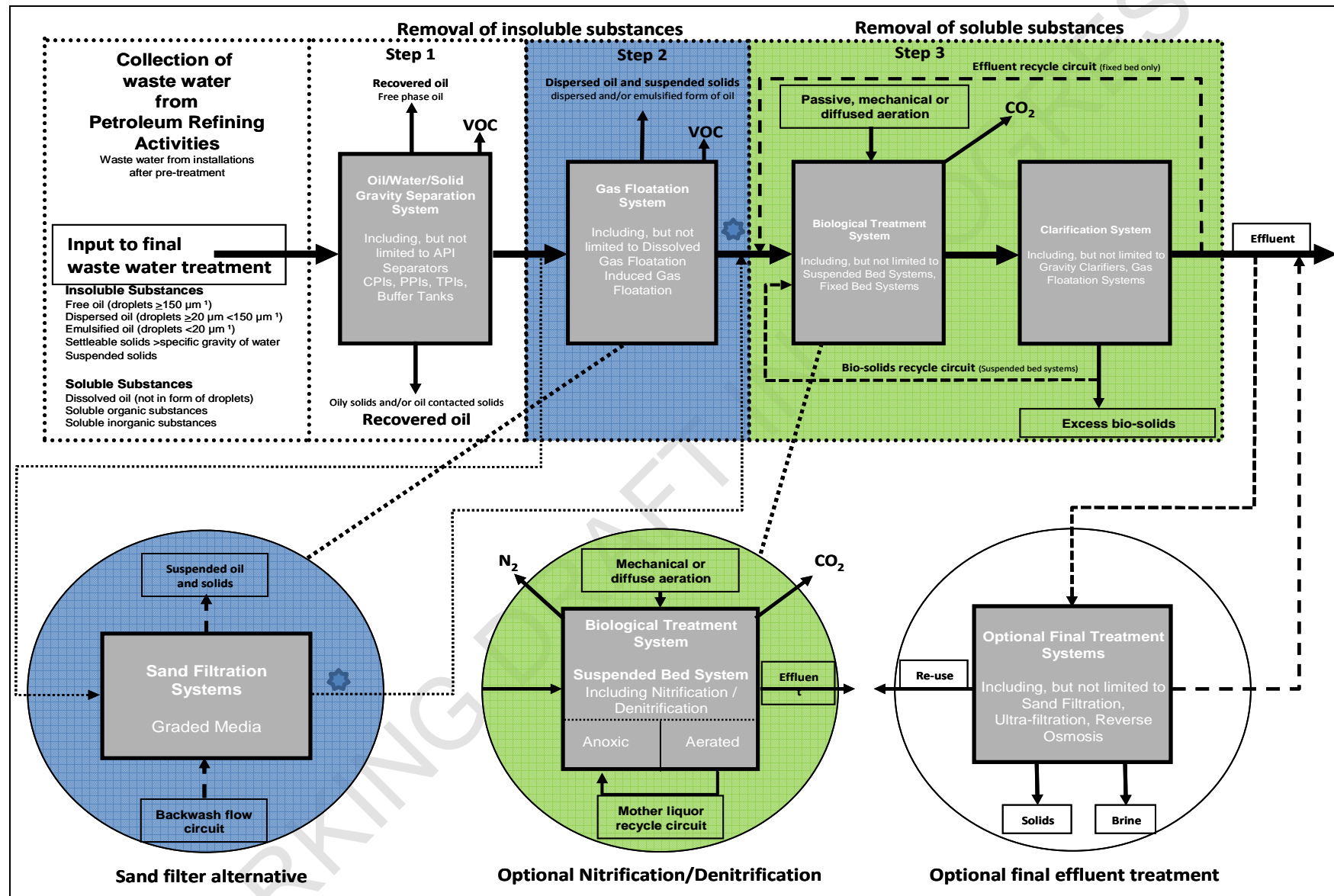


Figure 4.67: Process flow diagram of a typical refinery waste water treatment plant

4.24.1 Management of waste water within a refinery

This section gives some indication on what can be done in a refinery in terms of the management of waste water. In other words, indication will be given as to if it is better to combine waste waters from different processes or if it is better to process them independently in some independent waste water plant. Topics related to the storage of waste water are also included here. This section deals with process waste water, cooling water and sanitary waste water, ballast water, cleaning water, accidentally oil-contaminated water, continuously oil contaminated water, etc.

Description

Some techniques to consider for improving the waste water treatment performance and efficiency are listed below.

- Apply process water integration (see Section 4.15.4.1), e.g. stripped sour water and sour water as desalter wash water (stripped sour water only) or as wash water in overhead FCC main column to reduce the process water flow to the effluent treatment plant.
- Apply water and drainage systems (see Section 4.15.4.2). Rainwater from polluted plant areas (storm water) should be collected and routed to a treatment plant. For collection a 'first flush' scheme may be used that collect the more severely contaminated storm water and discharge subsequent precipitation directly. Non-contaminated water may be discharged directly or reused. It is necessary that the WWTP be able to handle high quantities of rainwater or that a sufficient buffer capacity is installed to prevent overloading. Use of equalising tanks for the storage of waste water.
- The temperature of the waste water is controlled or limited in order to preserve the performance of the biological treatment.
- Control of surfactants in waste water. Surfactants entering the refinery waste water streams will increase the amount of emulsions and sludges generated. They can enter the system from a number of sources, including: washing unit pads with detergents; treating gasolines with an end point over 200 °C. thereby producing spent caustics; cleaning tank truck interiors; and using soaps and cleaners for miscellaneous tasks. In addition, the overuse and mixing of the organic polymers used to separate oil, water and solids in the waste water treatment plant can actually stabilise emulsions. The use of surfactants needs to be minimised by educating operators, routing surfactant sources to a point downstream of the DAF unit and by using dry cleaning, high pressure water or steam to clean oil surfaces of oil and dirt.

Achieved environmental benefits

Water stream integration and other water management techniques (see Section 4.15.4) aim at reducing the total volume of water used prior to discharge and especially saving high quality potable and demineralised water.

Based on Section 3.24, the data of released waste water (2006 to 2008) for 44 European refineries with dedicated waste water treatment plants are the following:

- Annual median (50th percentile) effluent volume: 2.9 million m³/year
- Range: 0.54 – 212 million m³/year
- Specific median (50th percentile) effluent volume: 0.44 m³/tonne throughput
- Range: 0.15 to 11.7 m³/tonne throughput

Driving force for implementation

To reuse water, to reduce the hydrocarbon charge to the waste water treatment, and to reduce VOC emissions.

Reference literature

[168, VROM 1999], [178, HELPE 1999], [160, Janson 1999], [205, Jansson 2000], [207, TWG 2001].

4.24.2 Sour water stripping (SWS)

Sour water from the various refinery units is, for the main part, stripped in a SWS and can normally be reused together with the crude distillation unit overhead wash water as desalter wash water (see Figure 4.68). This is the main process water source in refineries.

Description

One-stage stripping

Most sour water strippers are single stage, requiring one stripping column. Figure 4.68 shows a typical single-stage sour water stripper. The sour water streams from the process units are collected in a sour water collection vessel. This provides both hold-up for feed and acts as a settler, where oil separation takes place. From this vessel, sour water is pumped via a feed/effluent exchanger, to the top of the stripper column. The sour water is counter currently stripped in the column by steam, either injected live or generated in a reboiler. This column is usually refluxed to reduce the water content in the sour gas. Operating pressure in the column varies from 0.5 to 1.2 barg depending on the destination of the off-gas. When necessary pH control is applied to maximise either H₂S or NH₃ removal.

Sour off-gases from a stripper unit can be routed either to a sulphur recovery unit (SRU), to an incinerator, or to the sour flare. Since off-gases directly routed to an incinerator or a flare can contribute very significantly to the overall refinery release of SO₂ (up to 40 %) and NO_x, routing to an SRU unit should be preferred and is now commonly practised with the exception of overhead gases from an air stripped sour water stripper for safety reasons.

Two-stage stripping

The two-stage sour water stripper differs from the single-stage stripper by operating the first column at a lower pH (6) and, eventually, at a higher pressure (9 barg), removing H₂S over the top and NH₃/water via the bottom, and the second stage at a higher pH (10), removing the NH₃ over the top and a stripped water stream at the bottom. A well designed oil/water separation drum instead of a tank, can also achieve the benefits of reduced hydrocarbon entering the sour water stripper. This results in:

- much lower H₂S and NH₃ concentrations in the stripped water;
- the possibility to send to the SRU only sour off-gases generated at the first stripping stage, which do not contain high NH₃ concentrations, known as a source of severe perturbation of the Claus reaction due to ammonium deposits.

Other techniques to consider are:

- Standby stripping facilities or additional storage to be provided for sour water. Duplication of the SWS.
- Sulphide-rich effluents streams should be stripped prior to discharge to effluent treatment. Most commonly, SWSs have a surge drum to remove entrained hydrocarbons that can cause upset in the downstream SRU.

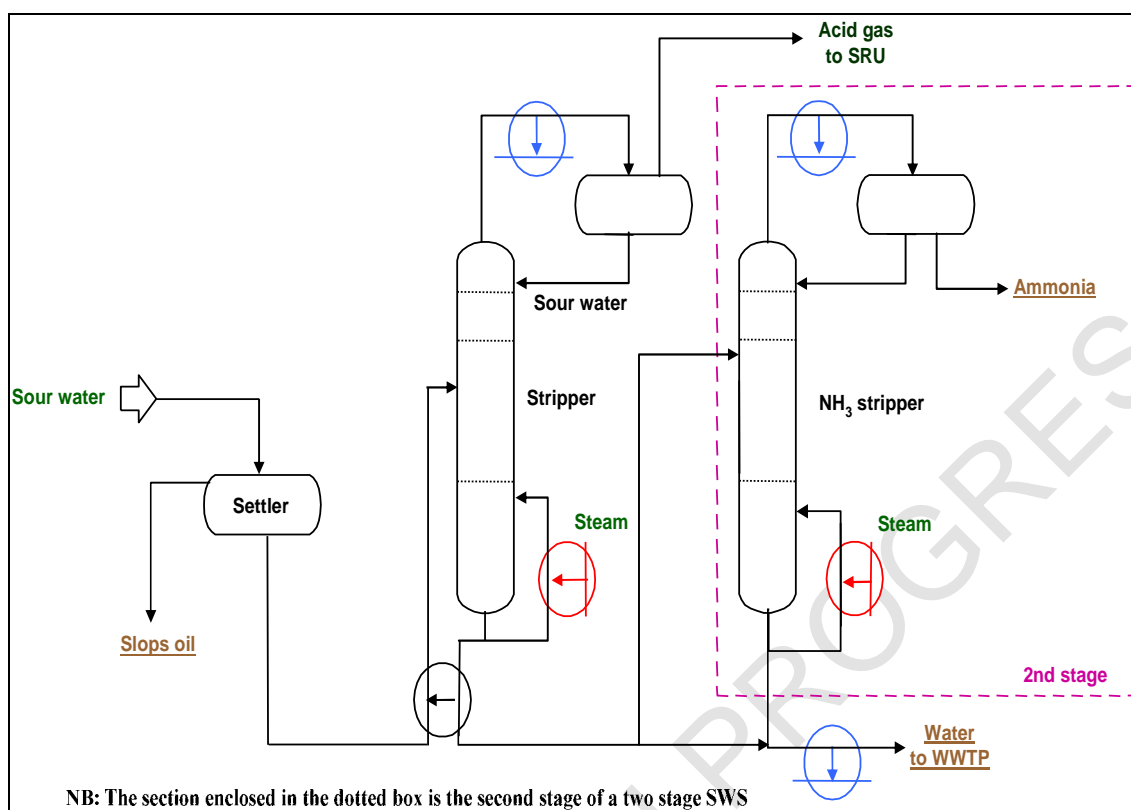


Figure 4.68: Simplified process flow diagram of a sour water stripping unit (SWS)

Achieved environmental benefits

Single-stage stripping

The SWS produces sour off-gas and stripped effluent which are routed to downstream units. The table below shows the achievable levels for a single-stage SWS.

	Source	Flow	Composition min/max	Comments
Emissions: sour gas	SWS off-gas to be routed to SRU	Plant specific	Mainly H ₂ S and NH ₃ . content depends on crude quality and refinery configuration	A 2-stage stripping could allow the separation of sour gas in H ₂ S-rich and NH ₃ -rich streams, which can then be treated much more efficiently
Effluent: stripped sour water (SSW)	SWS effluent to be used as desalter wash water or routed to WWTP	20 – 50 m ³ /h in a 5 Mt/yr refinery	COD: 500mg/l H ₂ S: 10 mg/ Phenol: 30 – 100 mg/l NH ₃ : 75 - 150 mg/l	SSW can be reduced by limiting live steam injection in process units and increasing the use of a reboiler

Stripped sour water can be routed to the waste water treatment plant, or preferably, to the process units for reuse, after appropriate cooling if necessary. Normally stripped sour water can be used as desalter wash water, provided its contaminant levels are adequate (NH₃ less than 150 ppm and H₂S less than 20 ppm). These limits are required to avoid corrosion in downstream units (i.e. CDU overhead system).

Two-stage stripping

In the first stage, H₂S is separated, whereas in the second one NH₃ is removed from water, and concentrated to a solution containing 10 % NH₃ which can be reused to reduce NO_x emissions. Exemple data of a typical two-stage stripping are given in Table 4.119.

Table 4.119: Performance of a two-stage sour water stripping in the Holborn refinery

Parameters	Column 1 supply (mg/l)	Column 2 outlet (mg/l)	Final efflux after treatment by WWTP (mg/l)
COD	14 400	599	37
Hydrocarbons	98	4	1.1
N tot. Inorg.	1 373	6	7
NH ₄ -N	1 372	5	5
Phenols	182	141	0.1
Sulphide	1 323	5	0.5

The two-stage SWS process can achieve an overall H₂S and NH₃ recovery of 98 % and 95 %, respectively associated with residual concentrations in the stripped waters in the respective range 0.1 – 1.0 mg/l and; 1 – 10 mg/l. Sulphide and ammonia loads to be treated in the WWTP are consequently much lower, helping to avoid the need for an additional stage dedicated to treatment (e.g. nitrification/denitrification).

Some level of nitrogen compounds is nevertheless needed in the refinery waste water as an essential nutrient for biological growth in biological Waste Water Treatment.

Ammonia generated in the two-stage SWS process can be used within the refinery after appropriate pretreatment, in particular to reduce NO_x emissions (SNCR – See in particular Sections 4.5.4.2 and 4.23.3.2). For example, at the Holborn refinery (Germany), the reuse of the NH₃-rich effluent from such SWS for a CO boiler achieves a reduction of NO_x of 180 t/yr, NH₄-N of 250 t/yr and solid waste from WWTP of 10 % at Holborn refinery.

Sour water decantation and equilisation

The addition of a sour water tank of sufficient capacity homogenises the different water streams, further removes oil that may cause plugging in the stripper, and helps to produce acid gas of constant composition for the SRU. As less hydrocarbon enters into the SRU, catalysts are better protected against coking phenomenon, with favourable effects on SRU efficiency and reliability.

Cross-media effects

Routing the off-gases from the stripper unit to the SRU, especially in the case of a single-stage SWS, can negatively influence the efficiency and the running conditions of the SRU mainly due to the NH₃ content in the gas. In the case of a 2-stage SWS, the steam consumption increases significantly with the stripping capacity and pressure.

Operational data

Electricity (kWh/t)	Steam consumed (kg/t)	Acid and caustic consumption
2 – 3	100 – 200	NA

Most commonly SWSs have a surge drum to remove entrained hydrocarbons, that could otherwise cause upsets in the downstream SRU. The SWS feed is normally preheated by feed/effluent exchangers to a tower inlet temperature of 100°C to save stripping steam. For a stripper operating at higher pressure, higher temperatures are tolerable. Nevertheless, a feed temperature which results in flashing of the feed in the feed line to the stripper tower is to be avoided.

Decreasing the water content in the off-gas below 30 mol % is not practised, as problems with salt deposition from the vapour phase can occur. This salt deposition particularly occurs when CO₂ is present in the sour gas, and the level of corrosive ammonium bisulphide (NH₄HS) in the

condensate refluxed to the stripper column increases beyond the level acceptable from a materials and corrosion perspective.

The use of a second stripping column consumes extra chemicals for pH control (acid, caustic) and extra energy.

Applicability

Two-stage stripping: in case the SWS bottoms are not reused but are sent to biotreating they may still contain too much NH_3 . In order to solve this in the SWS unit, the SWS column can either be equipped with a larger number of stages or a two-stage stripper can be installed (Section enclosed in dotted box in Figure 4.68). In the case of retrofitting for a two-stage stripper, an existing SWS can be converted to sour water concentrators to reduce its size. The more or less pure ammonia stream from the second stripper top might be sent to the CO boiler of the FCC unit for NO_x reduction purposes or to the hot flue-gas of a furnace.

Economics

In a French refinery, an existing single-stage low-pressure SWS was upgraded in 2010 by adding a new high-pressure stage (9 barg - 180°C - 30 t/h) dedicated to H_2S removal. Expected investment cost is EUR 24.8 million, obviously much higher than the cost range for a low-pressure stage.

Other data for different sour water strippers are shown in Table 4.120.

Table 4.120: Economics and performance of sour water strippers

Year built	Design NH_3 effluent conc. (mg/l)	Actual performance (mg/l NH_3)	Design flow rate (m^3/h)	Capital cost (million EUR)	Operating cost/yr (10^3EUR)
1996	18		22	2.7	–
1996	10		30	4.0	21
1992	Max 150	13	20	0.6	97
1993	50		25	5.4	43
1995	50	35	32	5.3	175
1992	100		50	10.9	–

Driving force for implementation

Nearly all refinery processes have steam injection to enhance the distillation or separation processes. This leads to the production of sour water (containing ammonia and hydrogen sulphide) that will be contaminated with hydrocarbons and/or steam condensate,. Sour water needs stripping prior to further treatment or reuse as wash water. A typical composition of the sour water is 900 mg/l of hydrogen sulphide, 2000 mg/l ammonia, 200 mg/l phenols and 15 mg/l hydrogen cyanide.

Example plants

Two-stage stripping is seldom applied in refineries. In the Holborn refinery in Germany, a two-stage SWS is integrated as an alternative to an effluent denitrification stage in the WWTP. Also in the new TOTAL Mitteldeutschland refinery, a two-stage SWS unit has been installed. The company Total has operated one at Feyzin refinery since 2008 (with a high-pressure single-stage).

Reference literature

[148, Irish EPA 1993], [200, Gilbert 2000], [168, VROM 1999], [182, Ecker 1999], [171, UN/ECE 1998], [222, UBA 2000], [181, HP, 1998], [228, TWG 2000], [166, CONCAWE 1999].

4.24.3 Reduction and recovery of hydrocarbons from waste water at source

Description

Generally Benzene, phenols and hydrocarbons in waste water can often be treated more easily and effectively at the point where they are generated rather than at the waste water treatment plant after mixing. Consequently the identification of hydrocarbon sources is the first measure to consider. The techniques described below as possible options have been identified by a number which is then used throughout this section. More information is available for each technique in the CWW BREF [6, EC 2003].

- Technique 1: Nitrogen or air stripping for benzene recovery from waste water. Nitrogen stripping can be used to strip benzene and other low aromatic compounds from waste water. The mixture is treated by activated carbon beds that capture the organic allowing cleaned nitrogen to recycle to the waste water stripper. Periodically, the carbon bed is in situ regenerated with live steam: desorbed organic vapours are carried by the steam to a condenser and are subsequently decanted into organic and water layers. Organics are returned to the refinery as valuable feed.
- Technique 2: Liquid-liquid extraction from waste waters for phenol extraction from waste water using a countercurrent extraction column. After distillation, the solvent (e.g. butyl acetate) is recycled back to the extraction column.
- Technique 3: High-pressure wet air oxidation (>20 barg). Water is intensively mixed with air and organic compounds are oxidised in the presence of a catalyst at high temperature and high pressure (250 °C, 7 MPa). Sulphur-containing substances are oxidised to sulphates; amines and nitriles are converted to molecular nitrogen; ammonia will require a biological or physical treatment step. More information is available in the CWW BREF [6, EC 2003].
- Technique 4: Low-pressure oxidation (<20 barg). Persistent organic compounds are treated with oxygen and are mineralised in a biological treatment plant (BOC gases).

Achieved environmental benefits

- Technique 1: A refinery uses this system to reduce 1895 l/d of waste water containing 50 ppm of benzene, 100 ppm of toluene/xylenes and 100 ppm of other hydrocarbons liquids. The recovery unit consistently reduced benzene to below 500 ppb. About 35000 kg of hydrocarbon liquid are returned to the refinery feedstock annually. This technique can also be applied to remove MTBE.
- Technique 2: Recoveries greater than 99 % or raffinate concentrations well below 1 ppm can be achieved. With this technique, waste water containing >1 % phenols was treated to get purified water with a phenol content lower than 1 ppm (Efficiencies: higher than 99 %; Koch Process Technology, Inc.). Phenol-containing waste water may also be treated microbiologically.
- Technique 3: Abatement efficiency can be 99 % [6, EC 2003].
- Technique 4: Efficiency can be in the range 60 – 90 % [6, EC 2003].

Operational data

- Technique 1: Nitrogen stripping has several advantages over air: oxygen does not reduce biological fouling of the stripper and nitrogen reduces the risk of refinery upsets creating explosive mixtures in the recovery unit.
- Technique 2: Typical utilities consumption per m³ water feed are:

◦ electricity:	159 kWh
◦ steam (20.7 barg)	15.6 kg
◦ steam (2.07 barg)	103 kgs
◦ water tempered at 45 °C ($\Delta T = 19$ °C)	5.6 m ³
◦ water cooling at 29 °C ($\Delta T = 11$ °C)	2.5 m ³

Applicability

- Technique 1: This technology is used for the treatment of desalting water and waste water from BTEX-plants (Texaco Development Co; AMCEC, Inc.).
- Technique 2: They can be designed to handle waste water streams with phenol levels from several hundred ppm to saturation (approx. 7 %) and above.

Economics

- Technique 1: The design and equipment supply costs of around USD 1 250 000. Annual utility costs are around USD 85 000
- Technique 2: Cost effective for levels of phenols higher than 1 %. A base case example for a waste water stream of 27.2 m³/h containing 6 % phenol was treated with 4.3 m³/h solvent in a four-column system. The overall phenol recovery was 99.3 %.
 - Investment, extractor only: USD 1.32/m³
 - complete system: USD 3.43/m³
 - Recovered value: USD 3.96/m³

Driving force for implementation

Reduction and recovery of hydrocarbon.

Example plants

- Technique 1: More than 15 systems ranging from 800 to 12 000 l/min are now operating in various US refineries. Air stripping for the removal of MTBE has been used successfully in at least one European refinery.
- Technique 2: This system is typically applied when phenol concentrations are high. This type of system treats waste water for a US resin producer.

Reference literature

[4, Hydrocarbon Processing 1998] [182, Ecker 1999], [228, TWG 2000],
[233, L. Helm, C. Spencer, et al. 1998], [6, EC 2003].

4.24.4 Primary treatment - Removal of insoluble substances**Waste water collection**

The collection of waste water from the various units after any specific process treatment can be considered part of the global waste water treatment. Actually, a waste water treatment plant (WWTP), especially with a biological step, operates most effectively under constant conditions (pH, hydraulic load or flowrate) and pollutant load or concentrations.

To buffer the WWTP operation against short-term (e.g. daily) and long-term (e.g. weekly) variations, equalisation facilities are in place, either decentralised at the various production installations or centrally in or near the WWTP. The buffering and retention volumes also allow analysis to check compatibility of the waste water influent with the subsequent treatment. Flow and load/concentration balancing are also referred to as equalisation, buffering or homogenisation. More information on this pretreatment step is available in the CWW BREF [6, EC 2003].

Process water coming from the SWS is one of the main process water sources in refineries. Moreover, some incompatible process effluents and drains from off-sites (flares and tanks) add to the total flow of process water. This effluent has to pass first an oil/water separator (CPI, PPI or API) for free oil and solids removal and an equalisation tank, where sometimes further oil skimming can be accomplished.

4.24.4.1 Step 1 – Oil removal

Description

The purpose of this step is the separation and extraction of insoluble hydrocarbon. These techniques rely on the principle of the difference in gravity between the phases (liquid – liquid or solid – liquid): the phase with the higher density will settle and the one with lower density will float to the surface.

Step 1 may generally include:

- API separators (APIs);
- corrugated plate interceptors (CPIs);
- parallel plate interceptors (PPIs);
- tilted plate interceptors (TPIs);
- buffer and/or equalisation tanks.

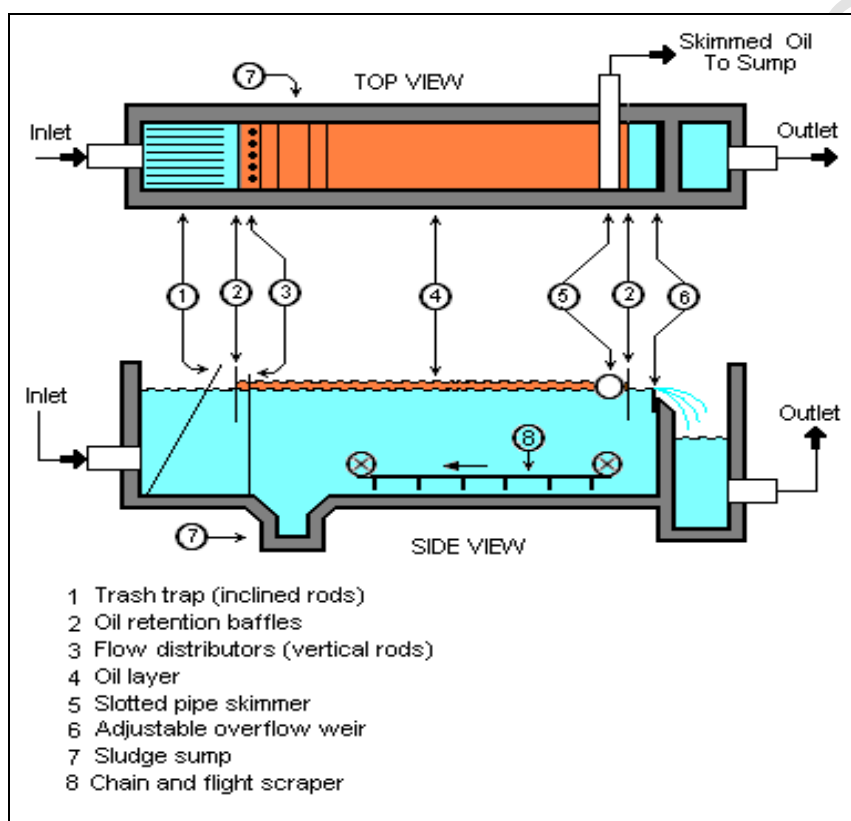


Figure 4.69: API separator general description

Internal corrugated plates used in CPIs, PPIs, and TPIs reduce the residence time required to achieve separation of the insoluble hydrocarbons targeted for removal and, therefore, reduces the required separation system compared to APIs.

These techniques aim at achieving separation and extraction of free oil droplets generally greater than or equal in size to 150 μm .

The water phase exiting these separation systems will generally contain insoluble dispersed oil droplets, emulsified oil droplets, suspended solids, soluble oil not in the form of droplets, soluble inorganic substances, soluble organic substances, and trace amounts of insoluble free phased hydrocarbon and settleable solids.

Accumulations of viscous and/or semi-solid hydrocarbon materials with little fluid characteristics may not be effectively removed by gravity flow using a fixed position overflow skimming pipe. Flexible skimming devices may be applied to improve oil removal. Close operator monitoring and intervention on demand may be necessary to extract viscous and/or semi-solid hydrocarbon material accumulation on the surface using manual measures.

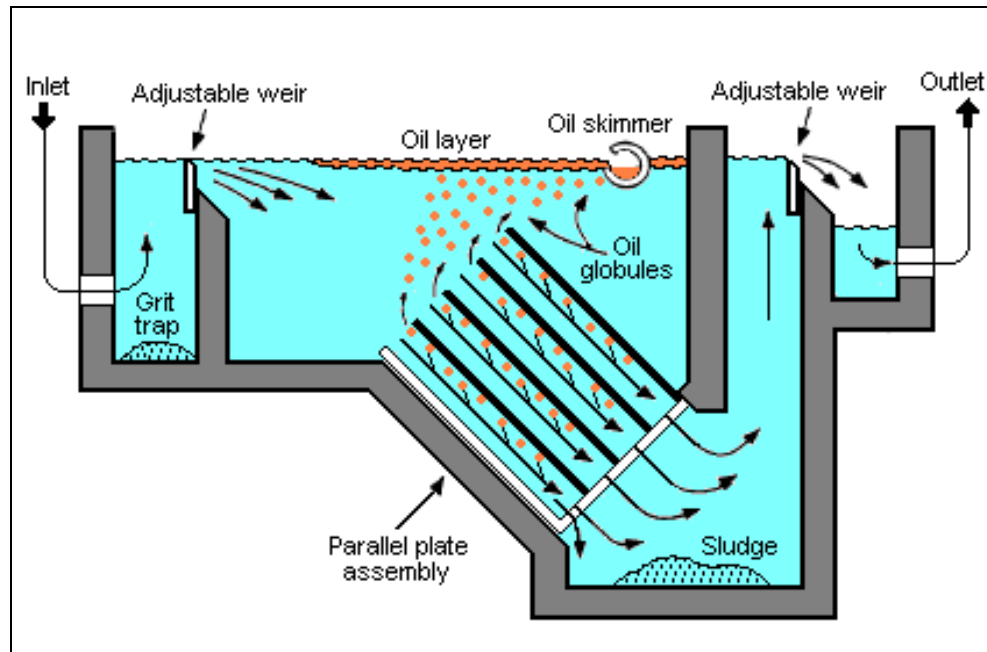


Figure 4.70: Parallel plate separator (PPI) general description

Achieved environmental benefits

The performance of CPIs and APIs, as regards oil removal, suggest 50 – 100 ppm oil in the outlet.

Cross-media effects

Separators operating with internal corrugated plates are susceptible to solids fouling.

These systems may not be equipped with internal mechanical solids extraction systems or internal mechanical oil extraction systems. Systems not equipped with internal mechanical solids extraction systems may be at risk of solids accumulation and eventual plate pack fouling from the bottom up, if accumulated solids cannot be effectively removed through either the gravity drain and/or pump-out techniques.

Systems not equipped with internal mechanical oil extraction systems may be at risk of hydrocarbon accumulation on the surface of the water phase.

When separators are not covered they can lead to VOC emissions.

Operational data

No detailed data

Applicability

These systems are fully applicable. CPIs are easier to cover than APIs. Retrofitting to existing separators may be complicated depending on structural design, type of mechanical oil skimmers and solid scrapper systems used, and position of electrical drivers. Due to VOCs and air inside the covered area, the API may operate above the lower explosive limit, if so, significant modifications may be needed.

Economics

Table 4.121 shows some reported examples of costs for API separators units.

Table 4.121: Examples of costs for API units

Year built	Type	Capacity (m ³ /h)	Capital cost (EUR x 10 ⁶)	Operating cost/yr (EUR x 10 ³)	Comments
2011	API	750	8.825		Replacement of API separator with floating roof tanks
1962		600	-	330	Operating costs for 2010
1966		187	-	148	Operating costs for 2011
2010		300	0.694		
2011		1100	8.500		Estimation for a new API unit

Source: [120, CONCAWE 2012]

Driving force for implementation

Maximising the collection of oil. It has been estimated that between 0.5 and 4 % of the crude oil processed in a refinery can be found in the waste water before any treatment, depending on the complexity of a refinery. Consequently, oil is always recovered from the drainage system before the waste water is passed for final treatment.

Example plants

Well proven technologies of 44 refinery sites in the TWG sample data collection with dedicated WWTPs, 42 reported having one separator, and among them 11 were covered. See detailed figures in Table 4.125. Separators have been progressively covered in a growing number of European refineries.

Reference literature

[160, Janson 1999], [166, CONCAWE 1999], [201, Manduzio 2000], [171, UN/ECE 1998], [191, UBA Austria 1998], [48, TOTAL 2010], [119, CONCAWE 2011].

4.24.4.2 Step 2 - Further oil/water/solid separation**Description**

This further step requires the use of chemicals to improve the solid/liquid or liquid/liquid separation of the remaining hydrocarbons and suspended solids in the waste water stream after the first step treatment. An injection of coagulant or flocculant is necessary to trap the oil droplets and the suspended solids that passed the first treatment. In order to improve the flocculation, a pH adjustment may be required prior to it.

Techniques for this treatment step may include:

- dissolved gas flotation (DGF);
- induced gas flotation (IGF);
- sand filtration.

DGF and IGF are the same techniques as Dissolved Air Flotation (DAF) and Induced Air Flotation (IAF) used in other industrial sectors, where air bubbles enable to float the flocculated solids. But as potentially explosive vapours may accumulate, the pressurization system uses gases instead of air to reduce risks.

DGF and IGF techniques aim at achieving the separation and extraction of free oil droplets generally less than 150 µm in size, emulsified oils and suspended solids. The sludge formed is

brought to the water surface by flotation, whereby tiny gas bubbles are also captured by the sludge flocs. The sludge is skimmed off and the water is routed to the next treatment step. Sand filtration (or dual-media) is an alternative process to flotation. Clarifiers may also be an alternative.

For all these separation techniques, the size of the flocs entering the separation step is crucial. Only flocs over several μm will be stopped. If the flocculation is not efficient, oil and particles will pass through the process. The water phase exiting this step will generally contain soluble oil not in the form of droplets, soluble inorganic substances, soluble organic substances, and trace amounts of free oil droplets, dispersed oil droplets, settleable and suspended solids.

Another technique to consider for this step is the treatment of the DAF float separately, rather than sending it to the slop oil system.

Achieved environmental benefits

Flotation units achieve 10 – 20 ppm of oil and prepare the waste water to improve the biological treatment results.

Cross-media effects

The techniques may lead to VOC and HC emissions. See Section 4.24.7 for odour reduction.

Operational data

Chemicals utilisation includes acid and/or alkali for pH correction, and FeSO_4 or FeCl_3 for coagulant requirements or a polyelectrolyte for the flocculation units. In practice, pH correction and polymer dosing to the flocculation flotation unit need daily attention and fine tuning. The energy requirement for the WWTP is relatively low; the aeration compressor being the largest consumer.

Applicability

Fully applicable.

Economics

Table 4.122 shows some reported examples of costs for flotation units.

Table 4.122: Examples of costs for flotation units

Year built	Type	Design flow rate (m^3/h)	Capital cost ($\text{EUR} \times 10^6$)	Operating cost/yr ($\text{EUR} \times 10^3$)
1995	DAF	80	0.2	18
1994	DAF	300	1.4	20
1989	IAF	400	2.4	47
1993	DAF	350	8.0	683
1996	IAF	818	0.4	112
1996	DAF	50	3.1	–
1996	DAF	800	1.5	–
2009	DAF	500	6.3	250
2010		250	1.5	182 ⁽¹⁾
2009		100	1.7	207

⁽¹⁾ based upon average cost of 12 % per year of capital investments.
Source: Data 2009-2010 CONCAWE

Driving force for implementation

To reduce the hydrocarbon and solids content in the waste water.

Example plants

Well proven technologies of 44 refinery sites from the TWG sample data collection with dedicated WWTP, 40 reported having one flocculation step (mainly DAF type) and two reported the use of a sand filter. See detailed figures in Table 4.125.

Reference literature

[164, Noyes 1993], [166, CONCAWE 1999], [48, TOTAL 2010], [112, CONCAWE 2011].

4.24.4.3 Step 3 – Biological treatment

Description

Step 3 aims at biological assimilation of the soluble hydrocarbons, inorganic substances and organic substances still contained in the water phase after the previous treatment steps. Insoluble substances contained in the water phase exiting Step 2 may also be subject to biological assimilation.

Biological treatment techniques may include:

- fixed bed systems;
- suspended bed systems.

One of the most commonly used suspended bed systems in refinery WWTPs is the activated sludge process. Fixed bed systems may be, for example the biofilter or trickling filter.

By using these techniques, soluble substances are removed from the waste water through the process of adsorptive contact with the biomass, followed by absorption into the biomass and assimilation of the soluble substances. This assimilation results primarily into new biomass growth and carbon dioxide emissions from the biomass respiration process.

The biomass maintained in the bioreactor is typically a mixture of naturally occurring microorganisms, that are acclimated to assimilating the soluble substances in the waste water.

A clarification step may be necessary to separate the biomass solids from the biologically contacted waste water prior to discharge to the environment.

Suspended bed biological treatment systems can be configured for biological nitrification/denitrification.

VOC emissions during aeration can be minimised by replacing shallow aeration turbines with air (or oxygen) dosing devices at the bottom of the aeration basin.

Nitrification/denitrification

In case deep nitrogen removal is required, denitrification in a biotreater is an option. Through this system, biological nitrification occurs with oxygen where ammonia-nitrogen is oxidised to nitrite (with *Nitrosomonas* bacteria) and then to nitrate (*Nitrobacter*). Subsequent biological denitrification of nitrate to nitrogen gas takes place under anoxic conditions and in presence of a carbon source (heterotrophic bacteria).

Other techniques to consider are as follows:

- Heterotrophic denitrification, usually combined with autotrophic sulphide oxidation (the reductive potential of sulphide is used to eliminate nitrogen via denitrification. Simultaneously, sulphide is oxidised, so that sulphide precipitation in subsequent biological treatment units is unnecessary).
- Use of granular activated carbon (GAC). Pollutants are adsorbed and biologically treated in an oxygen rich atmosphere (attainable COD: <100 mg/l)
- Use of powdered activated carbon (PAC, similar to GAC)

- Macro-porous polymer extraction (MPPE) which can be placed upstream of the biological treatment plant. It uses porous polymer beads containing an immobilised extraction liquid. Based on high affinity of the hydrocarbon components for this liquid, phenols, BTEX, PAH, etc. can be removed.
- Covering of the waste water treatment plant. Fixed covers have to be designed taking into account loss prevention purposes (build up of explosive vapours)

In addition, emissions to air of VOC (including benzene) and odorous components (hydrogen sulphides and mercaptans) are not uncommon and cannot always be controlled fully by up-stream measures.

Safety aspects (i.e. the explosiveness of VOC-air mixtures) are also to be attended, however they are less dangerous than in up-stream units.

Achieved environmental benefits

A biotreater can remove 80 – 90 % of dissolved oil and COD, as well as 90 – 98 % of BOD, under normal operating conditions. Natural nitrogen removal is normally about 10 % in an activated sludge unit (ASU), 70 – 80 % in a nitrification/denitrification biotreater (DNB) and up to 90 % in a tertiary (add-on) denitrification unit. For MAH/phenol, >95 % removal can be achieved based on a well-adapted biological system. Oxygen aeration in activated sludge plants can be up to 50 % more efficient than air aeration techniques.

Cross-media effects

Energy consumption, activated carbon wastes when GAC or PAC are applied and methanol consumption (for heterotroph bacteria) when denitrification is applied. Waste water treatment generates sludge. If waste water treatment is not properly operated, the amount of sludge can be increased.

Operational data

If a denitrification biotreater is applied, pumping energy is relatively high. If a tertiary treatment unit is used for ammonia removal by biological nitrification, methanol can be used in a subsequent denitrification stage as an oxygen receptor for denitrifying bacteria. In some refineries, biotreaters powdered activated carbon is dosed for meeting discharge specifications. The sensitivity of a biotreater against shock loads (peak discharges) of toxic compounds (e.g. sulfolane, MTBE, phenol, cyanide, sulphide) is relatively high and should be avoided. Methods to consider include spill prevention measures, appropriate procedures, good housekeeping and the equalisation of influent in a buffer tank.

Applicability

Fully applicable, bearing in mind that toxic or inhibitory streams should not enter a biotreater.

A restriction for nitrification is reported in cases of existing activated sludge systems with a low sludge residence time (average sludge lifetime below 15 to 20 days). A low sludge residence time in existing biological sludge systems is typically caused by a high ratio of organic load to amount of biomass.

For additional information, the CWW BREF [6, EC 2003] provides input concentration thresholds for a list of substances that are toxic to a biological activated sludge process and substances that are likely to inhibit a biological nitrification/denitrification process. Furthermore, other inhibitors to nitrification than these referred to in the CWW BREF should be considered: ammonium and nitrite, sulphides, benzene and phenols.

Ammonium and nitrite

Ammonium and nitrite can slow down nitrification, mainly in their non-dissociated forms (NH_3 and HNO_2). The effects of ammonium and of nitrite on *Nitrosomonas* and *Nitrobacter* bacteria species, which are the ones mostly involved in the biological nitrification activity, are a function of the concentrations and pH values as shown in Figure 4.71.

Nitrosomonas, responsible for the degradation of ammonium into nitrite, are inhibited at concentrations of free ammonia between 10 and 150 mg/l. *Nitrobacter*, in turn, degrade nitrite in nitrate but are inhibited at concentrations of free ammonia between 0.1 and 1 mg/l.

When *Nitrobacter* are inhibited, non-dissociated nitrite can have a retro-effect on *Nitrosomonas* at concentrations between 0.2 and 2.8 mg/l, which causes nitrification to stop almost entirely.

When the active sludge is acclimated, nitrification will take place even if the concentration of ammonia or nitrous acid is higher than the limit values listed above. Concentrations of 10 mg/l $\text{NO}_2\text{-N}$ are not expected to cause problems during nitrification.

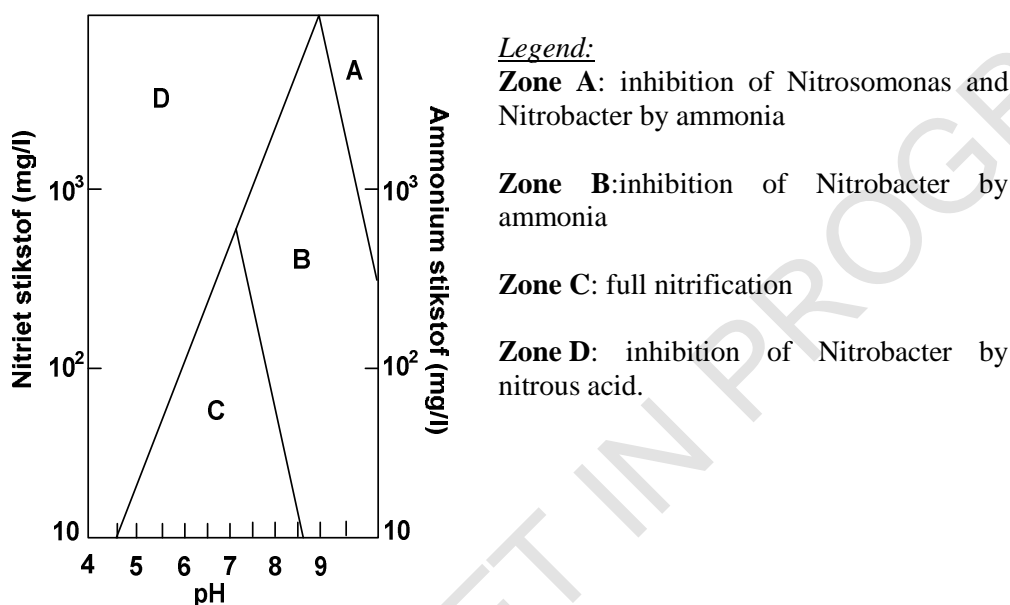


Figure 4.71: Nitrification tolerance of *Nitrosomonas* and *Nitrobacter* species

Sulphides

The biological nitrification processes need very low concentrations of heavy metals in complexed forms. However, sulphurous compounds are strong inhibitors of nitrification, as they have a chelating effect which limits the availability of these heavy metals. Sulphide itself can already inhibit the nitrification at concentrations as low as 0.5 mg/l, leading to a strong reduction of the activity of nitrifying bacteria.

Benzene and phenol

In favourable conditions, an aerobic WWTP is able to cope with concentrations of phenols up to 400 mg/l without any effect on the active sludge. However, high phenol concentrations and phenol peaks are toxic for nitrifying bacteria. Benzene is less toxic for nitrifying bacteria than phenol. However, *Nitrosomonas* have an enzyme which can oxidise benzene into phenol, and consequently increase the substrate toxicity. In Table 4.123, some concentration levels associated with their inhibition effects are reported.

Table 4.123: Inhibition effects of phenol and benzene on the biological nitrification

Concentration	Degree of inhibition (1)	Reference
Phenol		
20 mg/l	IC50 Nitrosomonas	Blum en Speece (1991)
5 – 6 mg/l	IC75 in active sludge	Dyreborg (1995)
4 – 10 mg/l	Minimum inhibition limit value	Eysenbach (1994)
3 mg/l	IC50	Juliastuti (2003)
50 mg/l	Complete inhibition	
100 mg/l	Acclimatisation of sludge by gradually highering the concentration	Stafford (1974)
Benzene		
13 mg/l	IC50 Nitrosomonas	Blum en Speece (1991)
NB: IC = the concentration of an inhibitor that is required for 50 % inhibition of its target.		

According to many sources, mainly peak concentrations are really problematic for nitrification, but can be partially solved by installing enough up-stream buffering capacity.

Economics

Examples of recent cost data for biotreatment

In France, a recently (2009-2010) installed 5 000 m³ aeration tank biotreater, treating 450 m³/h, was built for EUR 18 million (costs including only building and installation of the basin). Two other examples of re-engineered WWTP are provided in Table 4.124.

Table 4.124: Example of cost for waste water treatment plant at a refinery site

Site reference and description	Units	Capacity	Capital cost (million EUR)	Comments
CONCAWE 1 Re-engineering of WWTP system 2003 to 2005	DAF (2 units)	750 m ³ /h	8.860	4.430 per unit
	Bioreactor (Biox design)	1 000 m ³ /h	5.565	
	Sludge management system	-	2.970	
	DAF VOC recovery system	-	0.084	
	Total units costs		17.479	
	Total project costs (Investments, design, labour)			40.000
CONCAWE 2 Re-engineering of WWTP system 2005	Existing DAF upgrading	NA	2.000	2 units
	Bioreactor (Biox) upgrading	NA	2.000	
	Stormwater collection tank		1.000	
	Total units costs		5.000	
	Total project costs			NA

Source: CONCAWE 2011

Driving force for implementation

Removal of dissolve organic compounds by biological treatments.

Denitrification biotreaters are usually applied in environments sensitive to nitrates.

Example plants

Well proven technologies of 44 refineries (2008 TWG data collection), 30 reported using an activated sludge technique, 8 reported using a biofilter or a trickling filter technique. In addition, 12 refineries reported a nitrification or denitrification step technique. See detailed figures in Table 4.125.

Nitrification/denitrification biotreater installations are operational at least at Harburg and Rheinland (DE) and Gothenburg (SE) refineries, and an anoxic reactor is in operation at Antwerp (BE).

An MPPE-unit (Macro Porous Polymer Extraction) is installed at the Kollsnes and Ormen Lange gas plant (NO) for reducing organic components in the process water.

Anqing refinery (China) is to operate in 2012 a 1 000 m³/h powdered activated carbon treatment unit combined with biological treatment in order to reuse 500 m³/h of water from this site.

The current use of waste water techniques in refineries has been investigated in 2008 through a CONCAWE survey [112, CONCAWE 2011] whose results are in the following tables.

Table 4.125: Type of waste water treatment reported by refineries (CONCAWE survey 2008)

Treatment type	Number of sites	Type of biological treatment	Number of sites
Three stage biological	103	Activated sludge	78
		Trickling filter	16
		Aerated lagoon	5
		Non-aerated lagoon	1
		Fixed bed biofilm reactor	1
		Aerated tank	1
		Other	1
Mechanical	2		
Chemical	2		
Physical	4		
API separator	0		
External WWTP	14		
Total	125		

A study made, by a Norwegian refinery, in 2005, to compare the MPPE and the Activated Carbon (AC) adsorption processes applied in a gas refinery showed the following cost.

Table 4.126: Costs of two waste water treatment processes at a gas refinery in Norway

Process	Capital cost (million EUR)	Operating cost/yr (10 ³ EUR)
Macro Porous Polymer Extraction	0.5 – 0.6	130
Activated Carbon	0.26 – 0.39	39
NB: Cost estimated from conversion ratio (2005) of 1 NOK = EUR 0.1289		

Reference literature

[4, Hydrocarbon Processing 1998], [151, Sema, Sofres 1991], [16, Polders 2009], [112, CONCAWE 2011].

4.24.5 Additional treatments

In countries where water is a scarce resource, it is sometimes economically attractive to further improve the quality of the effluent in order to reuse the water as cooling water or even as a source for the preparation of boiler feed water (BFW), provided the pressure level of steam will allow the make-up. In that case, sand filtration (SF) and/or ultrafiltration (UF) followed by activated carbon filtration (AC) and/or reverse osmosis (RO) for salt removal generates sufficiently pure water for entering the demineralisation unit of the BFW preparation unit. Other techniques are ozonation/oxidation, ion exchange, and incineration.

Description

Techniques for the reduction of the salt contents of the waste water include: ion exchange, membrane processes or osmosis. Metals may be separated by precipitation, flotation, extraction, ion exchange or vacuum distillation.

Achieved environmental benefits

See Section 4.24.6.

Cross-media effects

Energy consumption, wastes and concentrates from exhausted activated carbon, membranes and metal sludges.

Operational data

When activated carbon is applied as an adsorbent, it must be re-generated or replaced at set intervals depending on the functioning of the system.

Economics

When the WWTP is extended with SF and AC, the operating costs of the resulting WWTP is doubled compared with a WWTP without these systems (base case). With UF and RO, both the investment costs and the operating costs will approximately triple the base case.

Driving force for implementation

Applied in refineries where shortages of water supply may occur.

Example plants

Sandfilters, ultrafiltration, activated carbon and reverse osmosis are proven technologies in many industrial sectors. For the refinery sector, dealing with large volumes of effluent, sand filtration is possible. From the 2008 TWG data collection, among the 44 refineries sampled the following breakdown treatment steps were reported.

Table 4.127: Techniques reported for WWTPs within the 2008 TWG data collection

Treatment type	Number of sites reporting	Techniques reported as used at this step	Number of sites ⁽¹⁾	% use of the technique
First step	44	API	37	84 %
		CPI	7	16 %
		Buffering-Equalisation	21	48 %
Second step	44	DAF	30	68 %
		IAF	4	9 %
		Flocculation/Flotation	5	11 %
		Sand filtration	4	9 %
		<i>None or not identified</i>	3	7 %
Third step (biological)	44	Activated sludge	27	61 %
		Trickling filter	1	2 %
		Biofilter	11	25 %
		<i>None or not identified</i>	4	9 %
Additional step	44	Sand filtration	9	20 %
		Lagoon	4	9 %
		Miscellaneous ⁽²⁾	9	20 %
		<i>No final treatment</i>	22	50 %

⁽¹⁾ Various techniques may be reported for same site
⁽²⁾ For the additional step, miscellaneous includes e.g. oxidation pond, clarification, decantation and DAF or IAF
Source: [TWG data collection questionnaires]

Reference literature

[4, Hydrocarbon Processing 1998]

4.24.6 Global refinery waste water treatments performance

Description

This section deals with emission values that can be achieved, individually or in combination, by today's waste water treatment in refineries. The waste water system considered contains the various treatment steps, including the optional final one as shown in Figure 4.67 and as reported in

Table 4.127 through the details of the 2008 TWG data collection.

Achieved environmental benefits and environmental performance

Ranges of release levels expressed in concentration on a yearly average basis are displayed in Table 4.128 and are considered to be achievable for the key water parameters typically used to characterise a refinery release to water which is using a good combination of techniques as described in this section. Specific load values are shown here as indicative parameters, as they are strongly dependent on the complexity or the type of refinery. These ranges suppose, in particular, that the treatment capacity of each treatment step is well adapted to the actual effluent load (average and peak regimes) received at the WWTP. Depending on the nitrogen intake, the lowest range limits for nitrogen compounds would require the use of a specific denitrification/nitrification stage.

Table 4.128: Reported ranges of emissions to water (50th percentiles) in dedicated WWTPs - 2008 TWG data collection

Parameter	Reported concentration (mg/l) (yearly average)	Indicative corresponding load (g/tonne crude oil or feedstocks processed) (yearly average)
Maximum temperature	30 – 35 °C	1 – 5
pH	6.5 - 8.5	
Total suspended solids (TSS) (dried @ 105 °C)	<5 – 15	1 – 5
Total organic carbon (TOC)	5 – 15	1 – 5
Total hydrocarbon oil content THC (EN 9977-1 or EN 9977-2)	<0.1 – 1	<0.1 – 0.5
Biological oxygen demand BOD (5 day ΔTU @ 20 °C)	2 – 10	0.5 – 3
Chemical oxygen demand COD (2 hour)	<30 – 60	<10 – 25
Ammoniacal nitrogen (as N)	0.25 – 2.5	0.1 - 1
Nitrites (as N)	<0.05 – 0.2	0.05 – 0.1
Nitrates (as N)	<0.5 – 2	0.2 – 1
Kjeldahl nitrogen (as N)	<2 – 5	1 – 2.5
Total nitrogen (as N)	2 – 10	0.5 – 3
Cyanides	0.003 – 0.01	0.001 – 0.005
Fluor (refineries using HF alkylation)	<0.2 – 2	<0.25 – 1
Phosphates (as P)	0.1 – 0.5	0.05 – 0.15
Total P (as P)	0.05 – 0.5	0.05 – 0.15
Sulphides	0.005 – 0.05	0.002 – 0.02
Sulphite	<2	
AOX (as Cl)	<0.1 – 0.2	<0.01 – 0.06
Benzene	<0.001 – 0.005	<0.001 – 0.002
Polycyclic aromatic hydrocarbons (PAH-16)	<0.0001 – 0.001	<0.0001 – 0.0003
BTEX	<0.001 – 0.005	0.001 – 0.005
MTBE (lower levels for refineries not producing MTBE)	<0.001 – 0.01	0.001 – 0.005
Phenols	0.01 – 0.1	0.001 – 0.02
Tensioactives (ionic and anionic)	<0.5	
Heavy metals (Cd+ Cr+ Cu+ Hg+ Mn+ Ni+ Pb+ Se+ Sn+ V+ Zn)	0.05 – 0.2	0.02 – 0.1
As	<0.001 – 0.003	<0.0001 – 0.001
Cd	<0.001 – 0.005	<0.0001 – 0.001
Total Cr	<0.001 – 0.003	<0.0001 – 0.001
Cr (VI) as Cr	<0.001 – 0.002	<0.0001 – 0.001
Co	<0.001 – 0.003	<0.0001 – 0.001
Zn	<0.005 – 0.05	<0.001 – 0.02
Pb	<0.0001 – 0.001	<0.0001 – 0.005
Fe	0.15 – 0.5	0.01 – 0.2
Cu	0.003 – 0.05	<0.001 – 0.02
Ni	0.002 – 0.05	<0.001 – 0.02
Hg	<0.0001 – 0.0005	<0.0001 – 0.001
V	<0.005 – 0.02	<0.001 – 0.005

NB: Levels given within this table are indicative ranges derived from the TWG 2008 data collection (38 sites with dedicated WWTPs - yearly averages data and main graphs are provided in Section 3.1.3) and based on a 50 % percentile calculation applied independently to each pollutant. Source: [207, TWG 2001]
Updated with TWG data collection questionnaires (2008).

Table 4.129 : Reported emissions to water observed in 98 EU refineries (2010 survey)

Parameter	Concentration weighted annual average per refinery (mg/l)			Relative load (g/tonne throughput)		
	5 %-tile	95 %-tile	Average	5 %-tile	95 %-tile	Average
Biological Oxygen Demand - BOD (5d)	0.17	26.68	8.62	0.49	36.61	11.83
Chemical Oxygen Demand - COD (2h)	2.67	149.00	59.00	6.81	270.00	106.35
Total Organic Carbon - TOC	0.06	38.30	13.62	0.03	38.82	15.94
Total Suspended solids	0.46	117.35	63.09	1.09	315.53	180.54
Oil in Water (OiW) or Total Petroleum Hydrocarbons index (TPH)	0.04	6.24	1.83	0.02	10.78	2.68
Benzene	0.00	0.11	0.02	0.00	0.07	0.02
Toluene	0.00	0.09	0.02	0.00	0.07	0.02
Ethylbenzene	0.00	0.01	0.01	0.00	0.01	0.01
Xylenes	0.00	0.22	0.03	0.00	0.18	0.02
Phenol index	3.50 10 ⁻⁴	0.36	0.08	1.71 10 ⁻⁴	0.38	0.08
MTBE	1.00 10 ⁻⁵	0.20	0.05	2.06 10 ⁻⁶	0.21	0.08
Naphthalene	0.00	1.71 10 ⁻³	9.50 10 ⁻⁴	0.00	2.94 10 ⁻³	1.17 10 ⁻³
Anthracene	0.00	2.68 10 ⁻⁴	6.33 10 ⁻⁵	0.00	2.42 10 ⁻⁴	7.49 10 ⁻⁵
Fluoranthrene	0.00	4.44 10 ⁻⁴	8.13 10 ⁻⁵	0.00	3.53 10 ⁻⁴	8.92 10 ⁻⁵
Benzo(a)pyrene	0.00	1.46 10 ⁻⁴	3.34 10 ⁻⁵	0.00	1.73 10 ⁻⁴	4.70 10 ⁻⁵
benzo(b)fluoranthrene	0.00	1.00 10 ⁻⁴	4.49 10 ⁻⁵	0.00	7.75 10 ⁻⁴	1.33 10 ⁻⁴
benzo(k)fluoranthrene	0.00	2.03 10 ⁻⁵	4.45 10 ⁻⁶	0.00	1.93 10 ⁻⁵	5.94 10 ⁻⁶
benzo(g,h,i)perylene	0.00	2.40 10 ⁻⁴	9.96 10 ⁻⁵	0.00	6.81 10 ⁻⁴	2.09 10 ⁻⁴
Indeno(1,2,3 ^{cd})pyrene	0.00	9.82 10 ⁻⁵	2.69 10 ⁻⁵	0.00	1.18 10 ⁻⁴	3.74 10 ⁻⁵
Dichloromethane	0.00	3.51 10 ⁻³	2.47 10 ⁻³	0.00	2.03 10 ⁻⁰²	0.01
Trichloromethane	0.00	8.69 10 ⁻³	1.22 10 ⁻³	0.00	4.23 10 ⁻³	1.22 10 ⁻³
Pentachlorobenzene	0.00	5.20 10 ⁻³	1.51 10 ⁻³	0.00	5.38 10 ⁻³	1.57 10 ⁻³
Ammonia	0.00	10.39	2.71	0.00	12.97	3.14
Ammoniacal Nitrogen	0.01	13.82	3.12	0.04	12.31	3.04
Chlorides	0.35	2 628.31	548.25	0.10	4119.30	641.41
Fluorides	0.00	5.07	1.23	0.00	3.38	0.93
Free cyanides	0.00	0.08	0.02	0.00	0.06	0.02
Kjeldahl Nitrogen	0.02	22.44	6.36	0.02	9.85	3.79
Nitrates	6.23 10 ⁻⁴	34.56	8.15	0.00	28.99	7.08
Nitrites	0.02	3.56	0.77	0.00	3.23	1.33
Sulphides	0.00	0.23	0.08	0.00	0.33	0.08
Sulphites	0.00	32.73	7.31	0.00	155.51	34.56
Total Nitrogen	0.10	30.32	8.92	0.49	20.71	9.02
Total Phosphorus	0.01	1.81	0.55	0.03	1.51	0.48
Arsenic	0.00	0.02	0.01	0.00	0.03	0.01
Cadmium	0.00	0.01	1.83 10 ⁻³	0.00	0.01	3.04 10 ⁻⁴
Chromium	0.00	0.02	0.01	0.00	0.03	0.01
Chromium (VI)	0.00	0.05	0.02	0.00	0.08	0.02

Parameter	Concentration weighted annual average per refinery (mg/l)			Relative load (g/tonne throughput)		
	5 %-tile	95 %-tile	Average	5 %-tile	95 %-tile	Average
Cobalt	0.00	0.01	$2.55 \cdot 10^{-3}$	0.00	0.02	$3.05 \cdot 10^{-3}$
Copper	0.00	0.04	0.01	0.00	0.03	0.01
Iron	0.01	1.49	0.42	0.00635966	2.70	0.56
Lead	0.00	0.03	0.01	0.00	0.03	0.01
Mercury	0.00	0.00	$4.38 \cdot 10^{-4}$	0.00	$1.31 \cdot 10^{-3}$	$4.60 \cdot 10^{-4}$
Nickel	$6.17 \cdot 10^{-5}$	0.09	0.02	$2.1579 \cdot 10^{-5}$	0.08	0.02
Selenium	0.00	0.05	0.02	0.00	0.05	0.02
Vanadium	0.00	0.15	0.04	0.00	0.13	0.03
Zinc	$1.35 \cdot 10^{-3}$	0.21	0.06	$1.08 \cdot 10^{-3}$	0.22	0.06

Source: CONCAWE 2010 Effluent Survey in [254, CONCAWE 2012]

In addition, another data-set on water emissions has been made available by CONCAWE (Report 10/3) for a *spot sample campaign* measurements (ESP survey 2008-2009), including 105 refineries in Europe. From direct discharging sites (90 % of the entire refineries sample), the following ranges are reported for a number of parameters (Table 4.130.).

Table 4.130: Reported emissions from a spot sample campaign measurements with direct discharge (ESP survey 2008-2009)

Parameter	Concentration range (mg/l)	5th percentile (mg/l)	Median 50 th percentile	Average (mg/l) ⁽²⁾	75th percentile (mg/l)	95th percentile (mg/l)	Limit of quantification (LoQ) mg/l
Total hydrocarbon content (Oil in Water) ⁽¹⁾	0.05 – 24	0.05	0.18	1.55	1.40	11	0.05
COD	16 – 391	23	48	61	78	135	10
BOD	1 – 130	1	4	8	9	23	3
Kjeldahl-N	1 – 83	1	3.4	7	10	26	1
Cadmium (Cd)	$2 \cdot 10^{-3}$ – $40 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$	$21 \cdot 10^{-3}$	$21 \cdot 10^{-3}$	$30 \cdot 10^{-3}$	$38 \cdot 10^{-3}$	$1 \cdot 10^{-3}$
Lead (Pb)	$7 \cdot 10^{-3}$ – $12 \cdot 10^{-3}$	$7 \cdot 10^{-3}$	$9 \cdot 10^{-3}$	$9 \cdot 10^{-3}$	$11 \cdot 10^{-3}$	$12 \cdot 10^{-3}$	$4 \cdot 10^{-3}$
Mercury (Hg)	$0.02 \cdot 10^{-3}$ – $2 \cdot 10^{-3}$	$0.039 \cdot 10^{-3}$	$0.095 \cdot 10^{-3}$	$0.3 \cdot 10^{-3}$	$0.4 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$0.02 \cdot 10^{-3}$
Nickel (Ni)	$5 \cdot 10^{-3}$ – $460 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	$12 \cdot 10^{-3}$	$35 \cdot 10^{-3}$	$24 \cdot 10^{-3}$	$106 \cdot 10^{-3}$	$5 \cdot 10^{-3}$
Vanadium	$3 \cdot 10^{-3}$ – 1.7	$6 \cdot 10^{-3}$	$13 \cdot 10^{-3}$	$60 \cdot 10^{-3}$	$28 \cdot 10^{-3}$	$104 \cdot 10^{-3}$	$5 \cdot 10^{-3}$
Benzene	$0.2 \cdot 10^{-3}$ – 0.630	$2.4 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$51 \cdot 10^{-3}$	$11 \cdot 10^{-3}$	$238 \cdot 10^{-3}$	$0.2 \cdot 10^{-3}$

⁽¹⁾ Oil in Water: measurements made by GC-FID method compatible with EN9377-2 – LoQ 0.05 mg/l.
⁽²⁾ For average calculation, <LoQ has been replaced by LoQ.
⁽³⁾ May include several streams for a same site - Source [122, CONCAWE 2010]

Operational data

Effluent treatment units are designed so that the most important key parameters (suspended solids, TOC, COD and BOD) of the final discharge stream can be appropriately monitored in order to ensure efficient treatment. The specific constrains of each parameter analysis are to be taken into account, e.g. TOC and COD may be monitored continuously whereas BOD needs several days for the analysis.

Examples of two data-sets based on short-term averaging period (daily or monthly) for COD emissions for one entire year appear in Figure 4.72 and Figure 4.73. Additional data from a CONCAWE survey including 50 data-sets from 30 refineries (some data-sets for the same site and different years) with short-term (mainly daily) and long-term values have been gathered and their results are presented in Table 4.132 and Figure 4.74 to Figure 4.84.

From these data, it is possible to observe the variation of the daily or monthly averages against the reported yearly averages.

Table 4.131: Examples of emissions to water values variation

Site	Parameter (Unit)	Yearly average	Daily average variation	Monthly average variation	Observations
FR-01	COD (mg/l)	Avg. = 82 (Med. = 84)	[56 % -156 %] ⁽¹⁾	[66 % - 123 %] ⁽³⁾	Based on daily data
FR-02	COD (mg/l)	Avg. = 50	[50 % - 240 %] ⁽²⁾	[79 % - 137 %] ⁽³⁾	Based on monthly aggregated data
FR-01	TSS (mg/l)	Avg = 8	[25 % - 215 %] ⁽¹⁾	[51 % - 190 %] ⁽³⁾	Based on daily data
FR-02	TSS (mg/l)	Avg = 11	[17 % - 235 %] ⁽²⁾	[52 % - 87 %] ⁽³⁾	Based on monthly aggregated data

(¹) Expressed as a range: [Percentile 5 %/Yearly Average -Percentile 95 %/yearly average].
(²) Expressed as a range: [Minimum data/yearly Average -Maximum data/yearly average].
(³) Expressed as a range: [Min. monthly average/Yearly Average-Max. monthly average/yearly average].

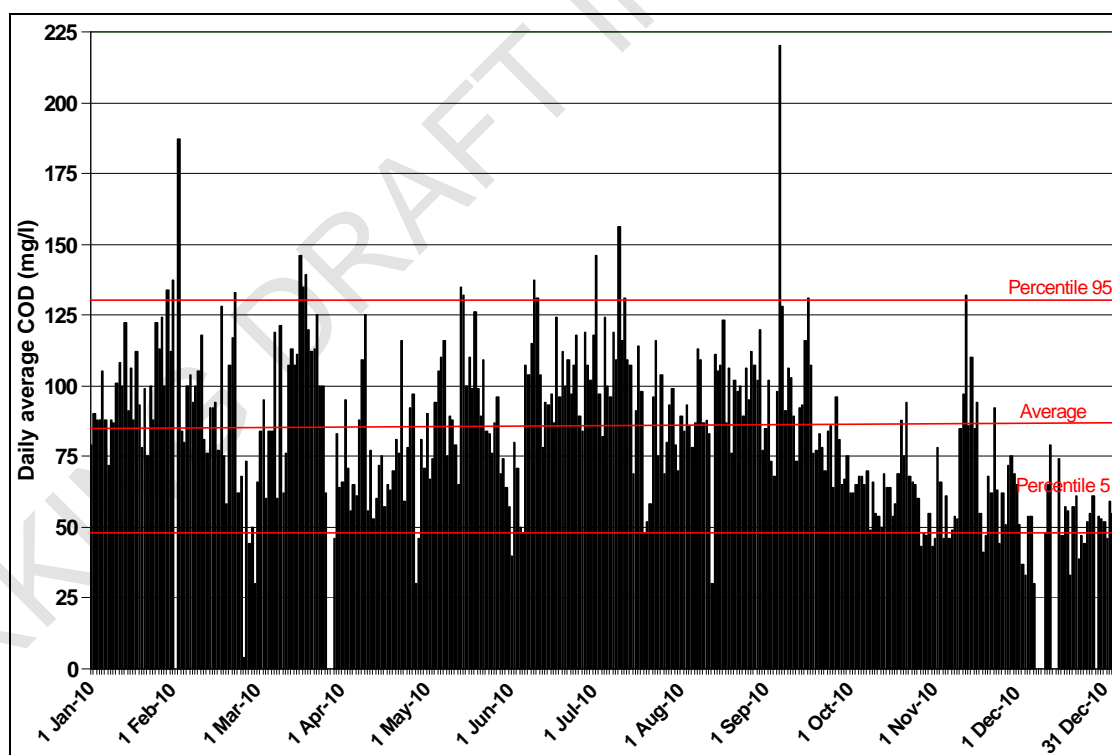


Figure 4.72: Daily COD concentration variations from one refinery site (FR-01)

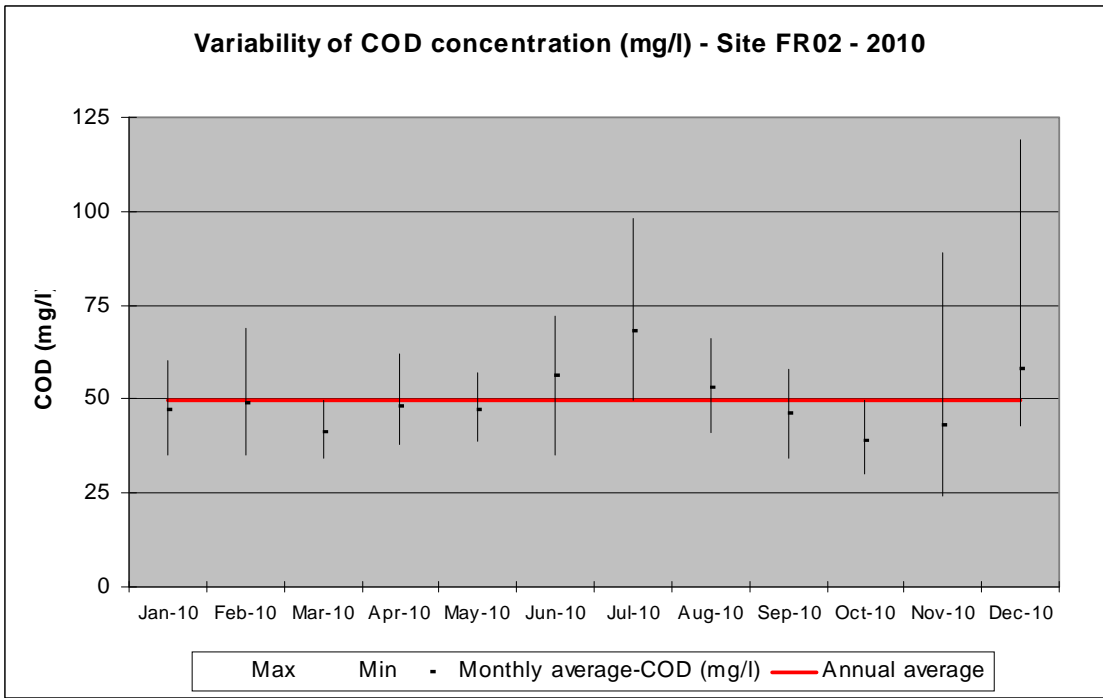


Figure 4.73: Monthly COD concentration variations from one refinery site (FR-02)

Table 4.132: Results from 50 data-sets from 30 refinery sites for COD, TSS and TPH

Parameter	COD			TSS			TPH		
	Yearly Average	Max/average Ratio	P95/average Ratio	Yearly Average	Max/average Ratio	P95/average Ratio	Yearly Average	Max/average Ratio	P95/average Ratio
Site 1-2010	49.61	2.40	1.43	7.87	8.64	2.16	1.26	9.30	1.43
Site 2-2010	84.44	2.61	1.52	11.84	2.87	1.82	1.50	3.90	1.00
Site 3-2009	67.75	3.69	1.67	14.19	8.74	2.47	3.243	15.42	2.78
Site 3-2010	48.40	4.59	1.94	7.86	5.34	2.16	1.525	7.15	1.97
Site 3-2011	50.84	13.26	2.20	7.47	8.04	2.68	1.117	19.69	2.40
Site 4-2009	189.96	3.81	1.86	45.81	2.05	1.64	11.31	2.74	1.87
Site 4-2010	157.55	3.22	1.86	37.51	4.19	2.01	4.38	4.11	2.81
Site 4-2011	175.82	3.56	2.24	37.20	2.63	2.01	1.29	10.07	1.01
Site 5-2009	42.52	2.82	1.41	10.56	3.88	2.00	1.17	7.70	1.71
Site 5-2010	49.23	5.36	1.45	11.20	8.84	2.05	1.19	4.22	2.53
Site 5-2011	48.34	2.88	1.65	12.13	5.36	2.47	1.34	39.16	2.83
Site 6-2009	90.74	3.06	1.64	27.77	2.88	2.26	5.40	5.19	1.48
Site 6-2010	95.64	2.31	1.56	23.98	3.71	2.72	5.23	2.87	1.34
Site 6-2011	84.42	2.19	1.47	20.52	3.22	1.93	5.34	3.37	1.31
Site 7-2009	55.82	1.79	1.42	16.60	5.96	2.00	NA	NA	NA
Site 7-2010	48.82	4.04	1.47	15.74	8.83	2.22	NA	NA	NA
Site 7-2011	52.48	6.02	1.56	16.10	10.56	2.17	NA	NA	NA
Site 8-2011	29.24	2.02	1.40	NA	NA	NA	0.60	3.16	2.33
Site 9-2010	100.52	5.19	1.63	23.90	9.08	2.21	1.34	39.16	2.83
Site 10-2010	86.12	4.41	1.51	13.29	5.57	2.46	3.00	1.98	1.00
Site 11-2010	34.16	5.39	2.01	8.04	11.19	2.24	0.21	25.27	3.12
Site 12-2011	93.39	5.25	2.13	45.70	6.47	2.30	0.74	15.43	2.85
Site 13-2011	106.42	8.53	2.44	46.88	14.84	2.86	2.73	8.10	2.13
Site 14-2011	93.17	2.63	2.25	25.28	2.85	1.99	NA	NA	NA
Site 15-2011	45.51	2.99	1.49	4.17	10.41	2.41	0.21	8.13	2.39
Site 17-2009	NA	NA	NA	29.40	3.98	1.83	NA	NA	NA
Site 17-2010	NA	NA	NA	41.18	7.77	1.96	NA	NA	NA
Site 17-2011	NA	NA	NA	36.75	4.43	2.07	NA	NA	NA
Site 18-2009	67.92	4.53	2.51	19.43	6.48	2.82	NA	NA	NA
Site 18-2010	52.57	16.74	2.49	26.95	6.68	2.15	NA	NA	NA
Site 18-2011	47.03	5.70	2.51	19.03	4.36	2.30	NA	NA	NA
Site 19-2009	70.28	2.06	2.02	9.67	3.93	3.81	1.58	6.15	5.39
Site 19-2010	78.20	1.89	1.85	11.99	3.25	2.87	1.54	6.17	3.37
Site 19-2011	90.98	1.63	1.62	14.03	2.71	2.42	2.94	3.30	3.09
Site 20-2010	47.08	2.70	1.33	0.06	16.72	0.84	0.14	8.29	2.07
Site 21-2010 A	NA	NA	NA	7.41	4.68	2.47	NA	NA	NA
Site 21-2010 B	59.60	1.73	1.32	15.12	1.79	1.78	0.38	18.57	2.51
Site 22-2010 A	34.14	2.90	1.64	14.91	17.44	2.55	0.16	8.71	2.64
Site 22-2010 B	64.65	2.00	1.53	NA	NA	NA	0.92	3.26	2.44
Site 23-2011	43.87	1.82	1.41	NA	NA	NA	0.16	3.14	2.25
Site 25-2011	46.47	1.72	1.44	8.58	7.57	3.26	0.33	5.99	2.89
Site26-2010	153.85	3.25	1.95	27.54	2.76	2.13	0.44	1.59	1.59
Site26-2011	146.53	3.82	1.50	26.24	2.06	1.84	0.40	1.94	1.90
Site 27-2011	44.31	5.55	1.69	17.13	2.63	1.98	1.54	5.40	2.27
Site 28-2010	31.88	2.07	1.83	NA	NA	NA	0.77	2.02	1.69
Site 29-2010	61.14	3.11	1.60	13.04	3.30	1.98	0.55	11.19	2.93
Site 30-2010	NA	NA	NA	NA	NA	NA	0.58	5.69	2.07
Site 32-2010-1	39.56	1.87	1.24	NA	NA	NA	0.17	9.24	2.31
Site 32-2010-2	65.57	1.89	1.48	21.56	3.94	1.67	0.13	1.60	1.60
Site 33-2011	41.63	1.44	1.25	NA	NA	NA	NA	NA	NA
Nb values	45	45	45	43	43	43	38	38	38
Median	59.60	2.99	1.62	16.10	4.68	2.16	1.18	6.07	2.29
Average	72.63	3.83	1.72	19.81	6.11	2.23	1.76	8.90	2.27
Range	29 – 190	1.4 – 16.7	1.2 – 2.5	0 – 47	1.8 – 17.4	0.8 – 3.8	0.1 – 11	1.6 – 39.2	1 – 5.4
Standard deviation	38.97	16.74	0.35	11.95	17.44	0.48	2.18	9.04	0.82
Coefficient of variation (°)	54 %	75 %	21 %	60 %	63 %	21 %	124 %	101 %	36 %

NB: Data are daily measurements reported from sites monitoring (except for both COD, TSS weekly at sites 19,20,21, 27,28,33- for TSS weekly at sites 6, 25,26 - for TPH weekly at sites 4,15,20,21,22,23,25, 32 – TPH monthly at site 26.
All refineries operating a 3 steps waste water treatment plant on site.
(°)Coefficient of variation is the standard deviation/average expressed as %
Source: [255, CONCAWE 2012]

Assessment of daily variability and use of P95/AA ratio

It is reported that daily variability is strongly dependent on local factors, such as unexpected crude changes, periodic activities upstream of the treatment (e.g. purges, cleaning, operational unit changes), or weather conditions, that may interfere with the WWTP performance [255, CONCAWE 2012].

The daily variability may be due to:

- normal variations of WWTP efficiency;
- normal variations of input streams to the WWTP;
- other than normal operating conditions (OTNOC) of the entire system (production units and WWTP).

In order to assess these daily average fluctuations (from the data presented in Table 4.132 for COD, TSS and TPH) and to compare them to the annual average the following ratios can be used:

- *the maximum/annual average ratio (MAX/AA)*: this is in a wide range (1.5 – 17) for both COD and TSS or even 1.5 – 39 for TPH;
- *the 95th percentile/annual average ratio (P95/AA)*: this is in a more narrow range (1.2 – 2.5) for COD, (0.8 – 3.8) for TSS, and (1 – 5.4) for TPH. For COD, TSS and TPH, the average is close to 2, with a limited coefficient of variation (21 % for both COD and TSS, 36 % for TPH).

These observations point to the use of the P95/AA ratio as an appropriate tool to assess the daily variability of a determinate data-set.

Based on the observed the data provided (see Table 4.132) and examples of analysis of possible causes for variations of the emissions concentration after WWTP, it appears that in more than half of the reported cases, the value of P95/AA ratio is less than 2 for both COD and TSS. For TPH, in more than half of the cases, the value of the P95/AA is less than 2.5 (see Figure 4.74, Figure 4.75 and Figure 4.76)

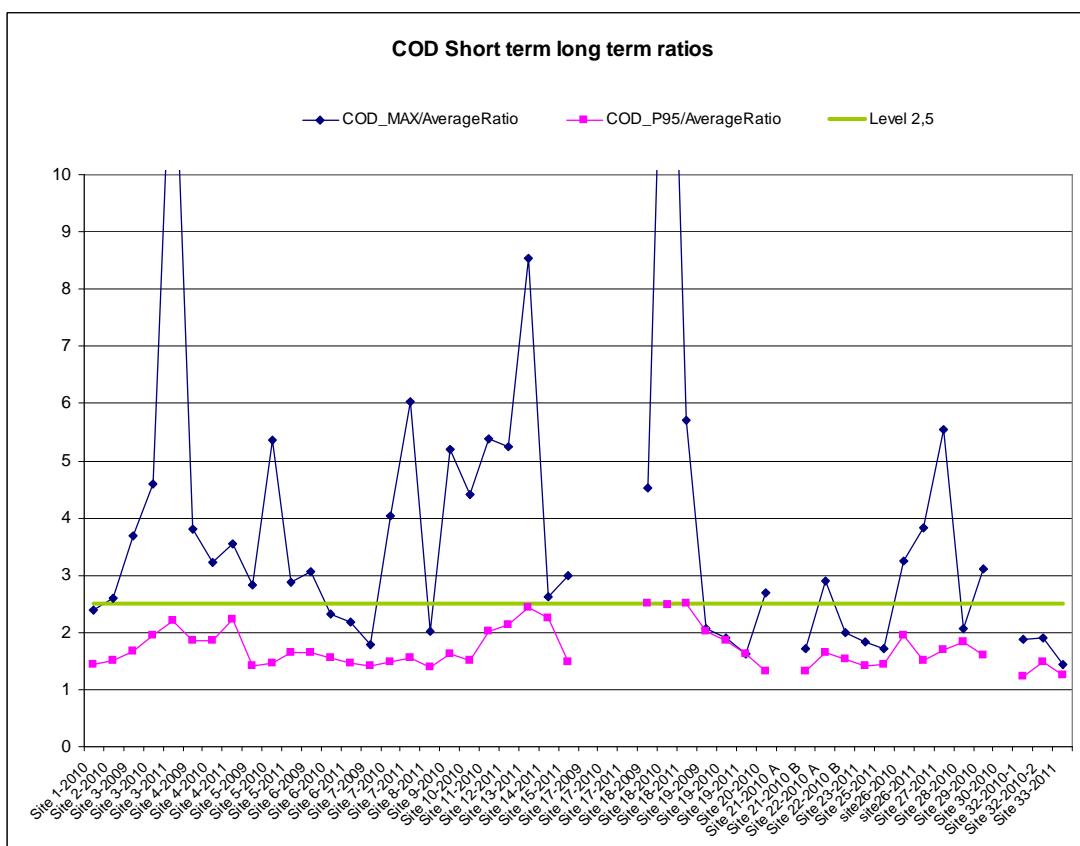


Figure 4.74: Assessment of daily variability of COD concentrations

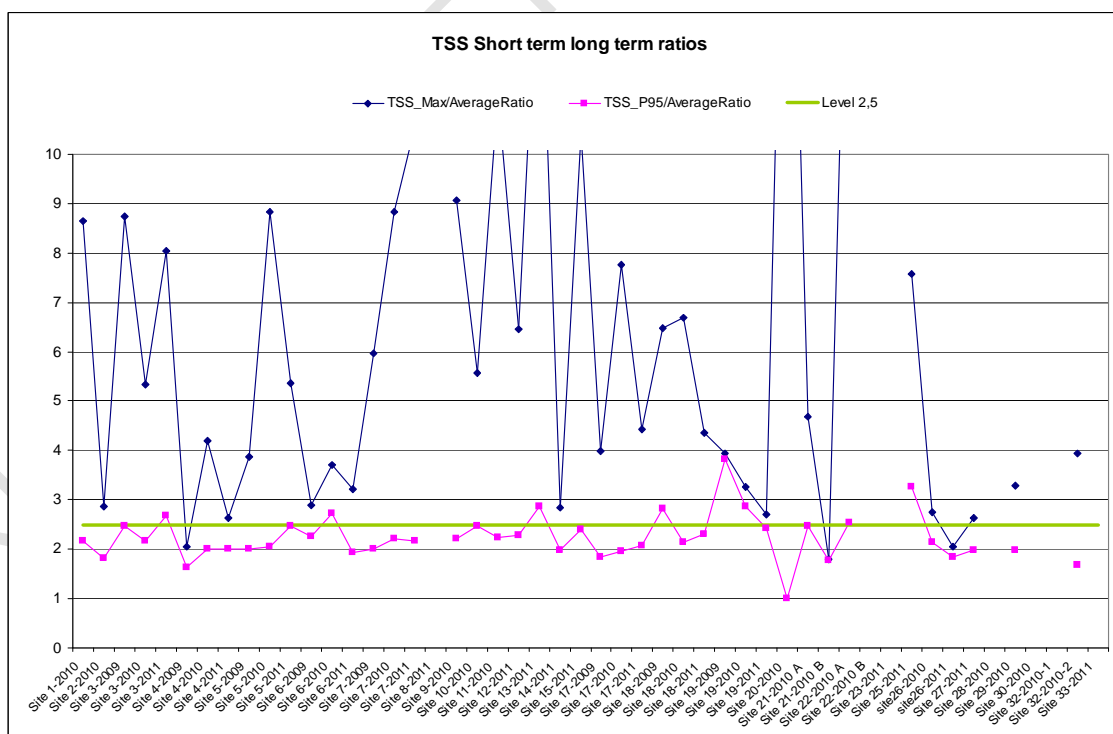


Figure 4.75: Assessment of daily variability of TSS concentrations

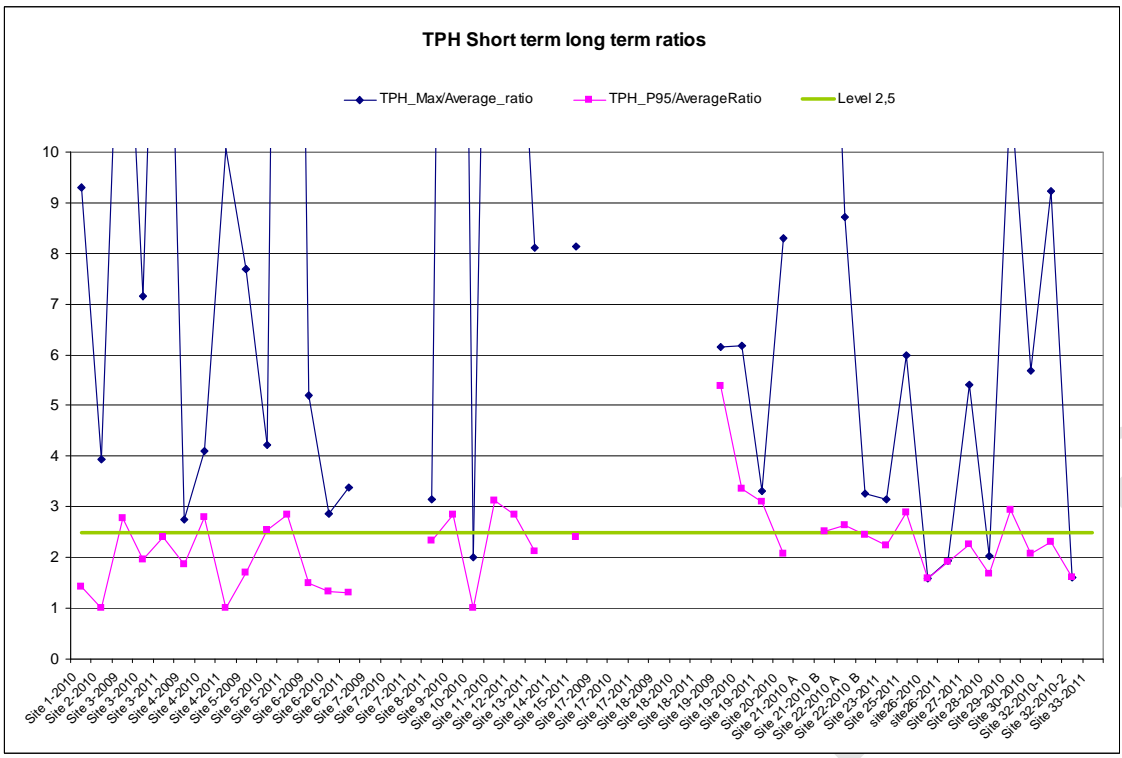


Figure 4.76: Assessment of daily variability of TPH concentrations

Influence of other than normal operating conditions on daily fluctuations of COD and TSS

The following graphs (see Figure 4.77 and Figure 4.78) show an example of a long time span (three years) data-set for COD and TSS, where some particular events are reported e.g. unit start-up, incident, acclimatisation of biology treatment step.

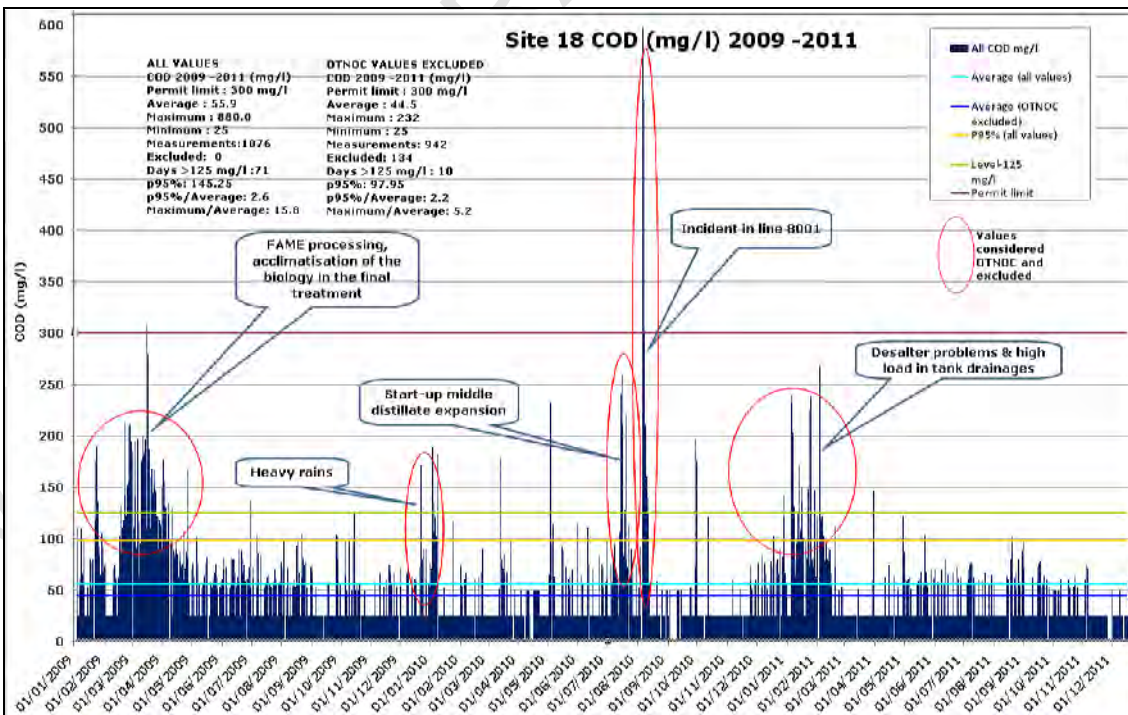


Figure 4.77: Example of a three years data-set of COD concentrations (Site 18)

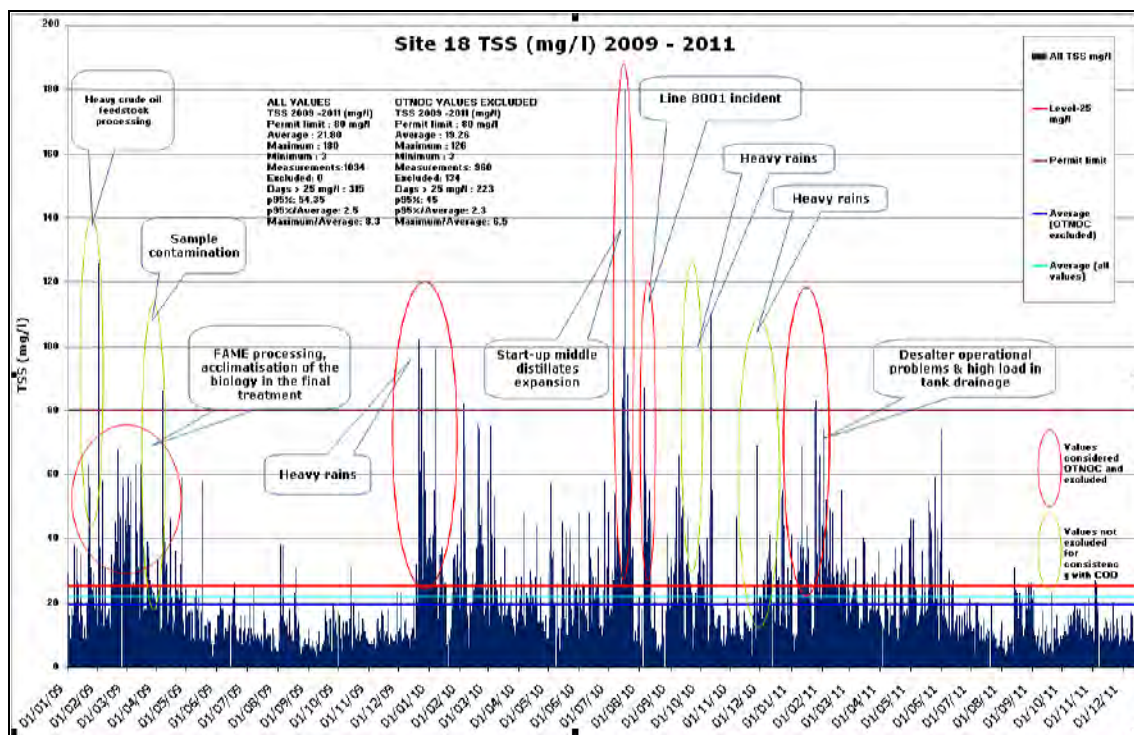


Figure 4.78: Example of a three years data-set of TSS concentrations (Site 18)

Variance and achieved values for COD, TSS and TPH in the data-set

The following figures show, for each parameter (COD, TSS and TPH), on the first graph:

- the distribution of the annual average within the data-set;
- the minimum and maximum reported values;
- the outliers and the reasons for considering them as such.

For each parameter, the second associated graph shows the ordered values and the variability of the P95/AA ratio.

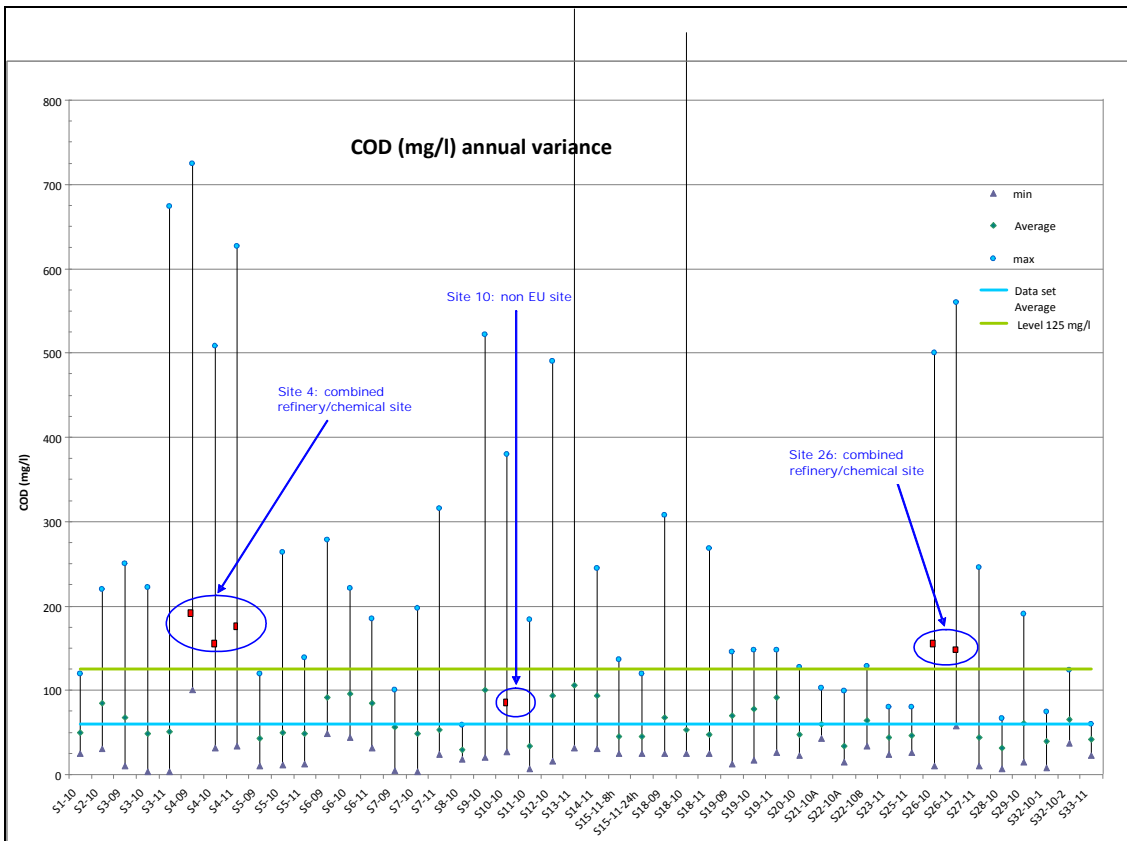


Figure 4.79: Annual variance for COD concentrations

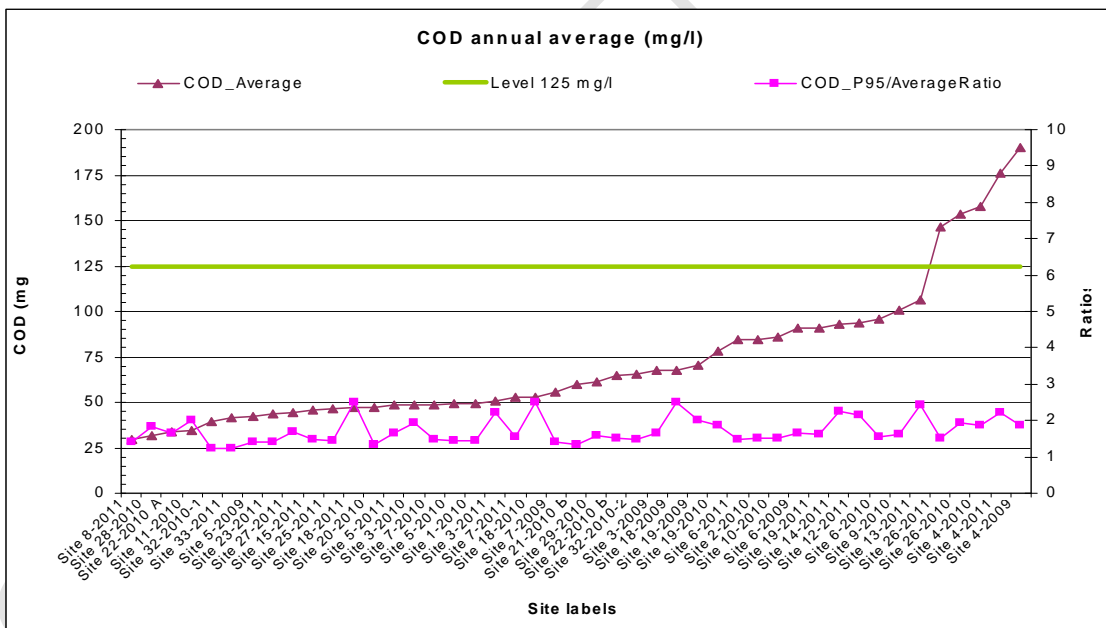


Figure 4.80: Achieved annual values and daily variations of COD concentrations

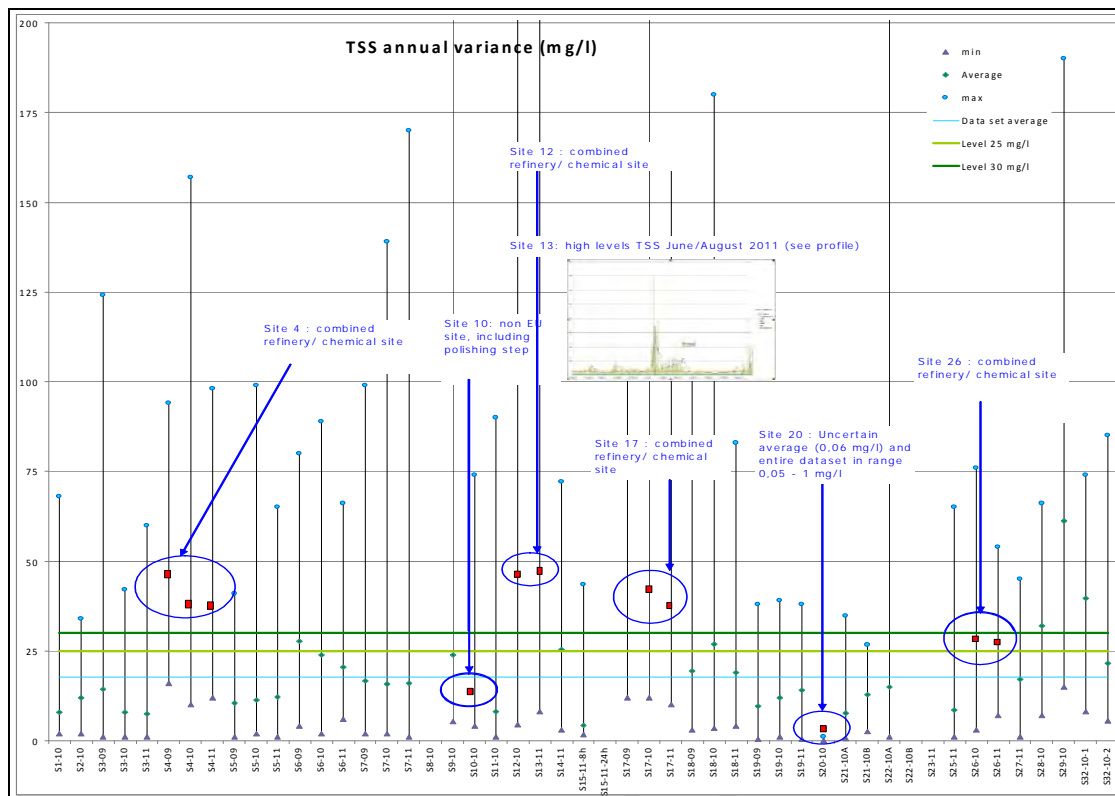


Figure 4.81: Annual variance of TSS concentrations

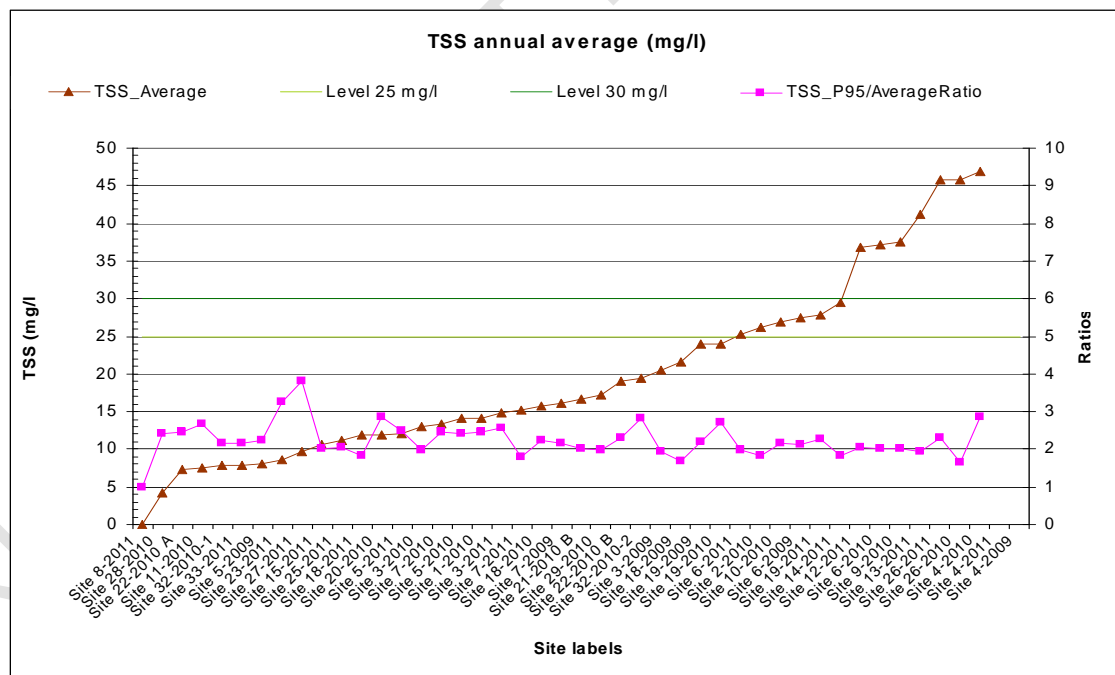


Figure 4.82: Achieved annual values and daily variations of TSS concentrations

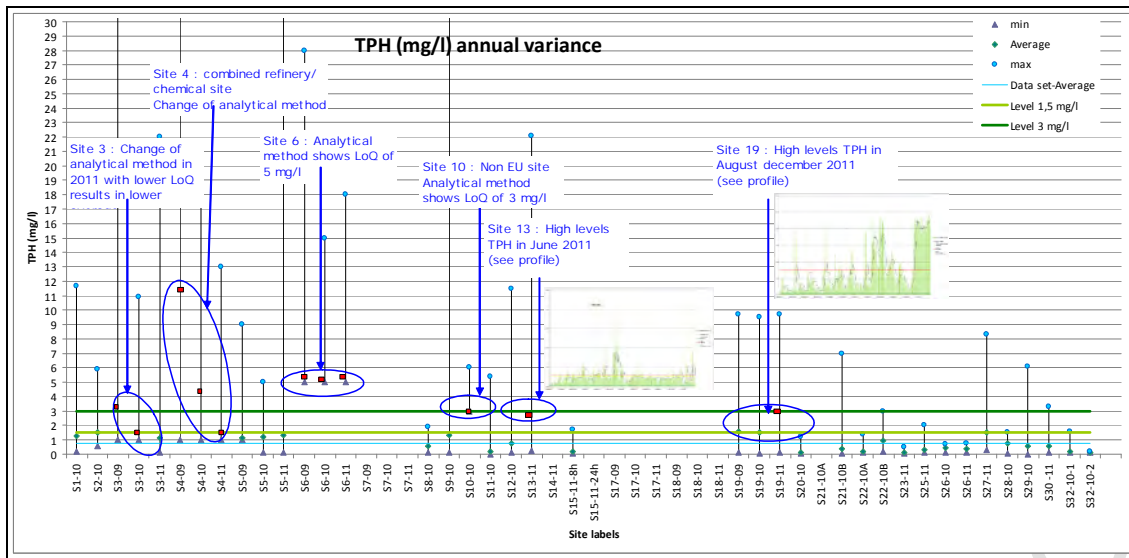


Figure 4.83: Annual variance of TPH concentrations

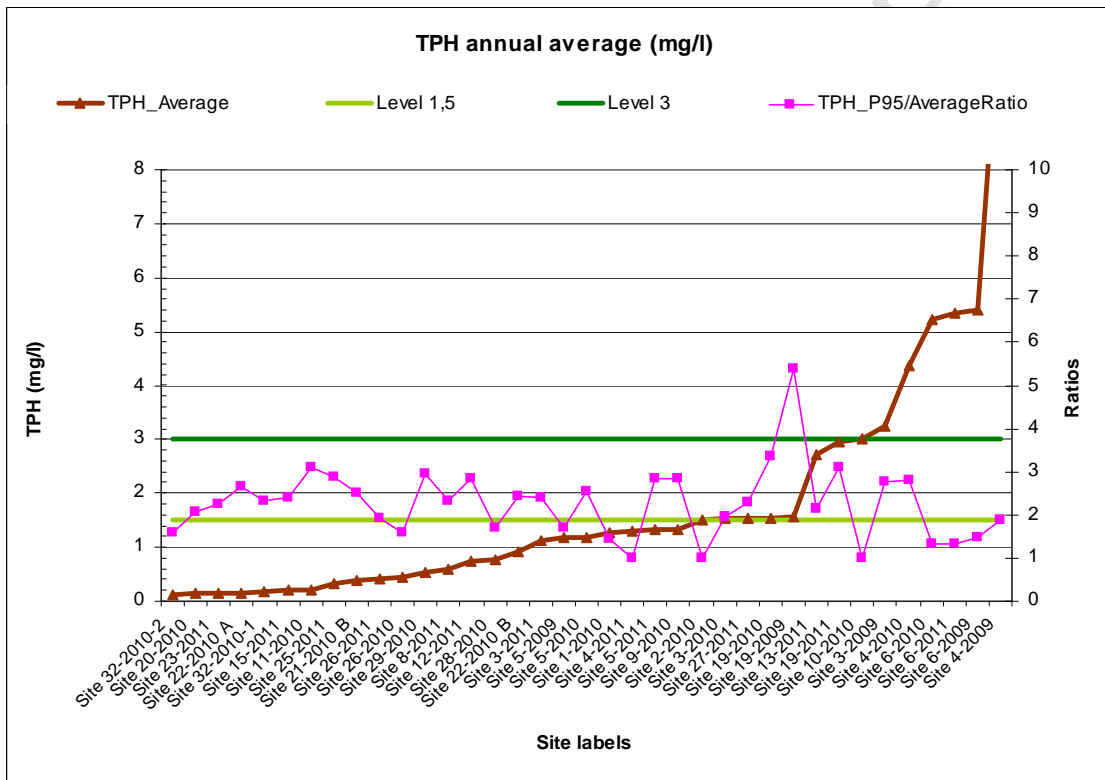


Figure 4.84: Achieved annual values and daily variations of TPH concentrations

Applicability

The WWTP system as described previously is applicable to all refineries to treat the discharge streams that require control and treatment. It may be advisable to install an observation basin between the final treatment step and the discharge to prevent any waste water that is not treated adequately to be directly discharged. In this case, the collected water can be re-routed for additional treatment. Such basins do require sufficient additional space to be available.

Reference literature

[77, REF TWG 2010 2010], [121, CONCAWE 2012], [122, CONCAWE 2010], [255, CONCAWE 2012]

4.24.7 Reduction of odours

4.24.7.1 Reduction of odours from WWTP

Description

For both various steps of WWT, emissions to air of VOCs (including benzene) and odorous components (hydrogen sulphides and mercaptans) are directly related to the surface area of the open separation and collection compartments. The release of dissolved gases in the dissolved gas (DGF) flotation unit increases the effective water area exchanging with air and produced a continuous gas flow through the water column into the gas space above the liquid surface. The substances volatilised by diffusion into the gas bubbles and above the water column are then subject to ambient air convection. The generation of VOC and odours, can be further reduced by covering these units with closed and tightly sealed covers. However, due to eventual fluctuations of the internal pressure, such covers cannot be 100 % tight and have to be mechanically protected by an atmospheric vent. To be considered acceptable in order to protect covers together with minimising convective losses, the usual dimensions of such vents are around 0.90 m minimum height and 10.2 cm maximum diameter. An additional pressure relief/vacuum breaker valve can also be installed, in order to accommodate an exceptional gas exchange rate beyond the vent capacity.

Cover vents can be collected and treated, with an appropriate off-gas treatment system (e.g. biofilter, activated carbon absorber, incinerator, thermal oxidiser - see Section 4.23.6.3) or can be reinjected into the aeration basin.

Achieved environmental benefits

VOC emissions from oil separators can be reduced to 3 g/m³ by covering the CPI and API. The HC emissions from the waste water systems can be determined by calculation from the exposed surface area of the oil-contaminated untreated water tank (API separator) and an empirical oil evaporation factor of [167, VDI 2000]:

- 20 g/m² per hour for open oil separator
- 2 g/m² per hour for covered oil separator

Cross-media effects

When separators are covered, the flammability/explosion limits and the toxicity concentration thresholds for some gaseous sulphur compounds may easily be reached. Consequently, occupational safety and environmental protection should be carefully considered at equipment design stage, and appropriate procedures should be set up for ensuring safe operating conditions. Safety should be addressed in the case of a fixed roof tank at any step of the WWT.

Applicability

Significant modifications may be needed before accepting a cover. Retrofitting to existing units may be complicated depending, on the structural design, the type of mechanical float skimmers and solid scrapper systems used, as well as the position of electrical drivers.

Economics

For covering the 1st step separator units, the investment for the installation of two 200 m³ floating slab-covers is about EUR 75 000 and the total annual operating costs about EUR 42 800 per year.

Table 4.133: VOC controls in oily water operations (installed and retrofitted)

Emission Source	Oily water sewers/sumps/separations and drainage operations			
	Automatic drainage facilities	Fixed/floating covers on APIs/sump	Incineration	'Dry' oil collection systems
Control technique	Automatic drainage facilities	Fixed/floating covers on APIs/sump	Incineration	'Dry' oil collection systems
Efficiency	80 %	80 – 90 %	98 %	90 %
Investment costs	0.002 – 0.03 EUR million/tank ⁽¹⁾	0.001 EUR million/m ² ⁽¹⁾	1 EUR million ⁽¹⁾	NA
Operating costs	Small	Moderate	0.1 EUR million/yr ⁽¹⁾	NA
Other impacts comments	May not be suitable for all tank stocks	Limitation on access to APIs. Fixed covers may require purging systems	Assumes API is covered	NA

⁽¹⁾ Source: Industry propriety information.

A floating cover (assuming a 800 m³/h process capacity of oily water, with VOCs emissions up to 1 000 t/yr) will result in a 90 % VOC recovery efficiency for the following costs:

- Investment costs: EUR 0.6 million
- Operating costs: EUR 0.03 million per year

Example plants

Separators have been progressively covered in a growing number of European refineries

4.24.7.2 Reduction of odours from water buffer tanks

Description

Water buffer tanks are used upstream and/or downstream of API/CPI/PPI separation systems to receive variable rate transfers of waste water containing insoluble floating oils, insoluble suspended oils and solids, and soluble substances. This section also includes process area storm water surge tanks.

As for any other treatment step, the generation of odours from open top water buffer tanks will be directly related to the surface area of oil and water that will come in contact with air. Substances will be volatilised by diffusion into the air and be subjected to the convective forces of airflow. The generation of odours can be reduced by maintaining the smallest possible surface area of oil and water in contact with air. For such a purpose, the tank should be routinely checked and maintained free of oil by the operator, and the following actions can be taken:

- Operate the water buffer tank with a fixed roof equipped with a pressure relief/vacuum breaker valve to prevent convective losses when the tank level is static.
- Use an internal floating roof or an external floating roof equipped with at least a primary seal or, more efficiently, a primary and secondary seal between the floating roof and the tank shell, for further reducing the diffusive and convective losses.
- Instead of gravity draining to an open collection system, install an internal oil skimming system to extract oil from the tank through closed piping using a pump station or vacuum truck to minimise the possible loss of volatile substances. For safety reasons, in the case of using a vacuum truck, special care should be paid towards the flash point or H₂S concentrations in the liquid phase. The addition of carbonate neutraliser on the vapour phase of the truck can be considered.

Achieved environmental benefits

By using a fixed roof tank or a floating roof tank, the emission of VOC and other odorous compounds can be reduced by 80 – 90 % compared to an open system. This ratio can be even higher and reaches 99 – >99.9 % if vented emissions from the fixed roof tank are collected and

routed to an appropriate off-gas treatment system (e.g. biofilter, activated carbon absorber, incinerator, thermal oxidiser - see Section 4.23.6.3).

Cross-media effects

Safety should be addressed in the case of a fixed roof tank (same as for a DAF or a CPI unit).

Applicability

All new installations can be originally constructed with dual-sealing floating roofs or other systems with equivalent efficiency. Many existing water buffer tanks can be retrofitted with floating roofs, and existing floating roof tanks originally designed for crude or fuel storage can also be reused as water buffer tanks.

Economics

No data received for revamping and reuse of existing crude tanks as water buffer tanks.

Driving force for implementation

To reduce VOC emissions and odour pollution.

Example plants

Several examples in Europe.

Reference literature

[48, TOTAL 2010]

4.25 Waste management

This section is complementary to previous sections of Chapter 4 related to individual production processes or units. It gives sector-specific information on key management, reduction and abatement techniques that are, or may be implemented for waste generated by oil and gas refining. European legislation for waste is fully applicable to the refinery sector and especially the waste hierarchy which is described in 2008/98/EC Directive, as a priority order in waste prevention and management, namely:

- prevention;
- preparing for reuse;
- recycling;
- other recovery, e.g. energy recovery;
- disposal.

For a given technique, available data on the way it can be applied and the results it enables achieving for particular processes or units have been given in the related sections. The information provided here aims at completing this information on the broader aspects, in particular environmental benefits, cross-media effects, operational data, and applicability issues which will not be repeated in other sections.

Residual refinery wastes are typically in the form of sludges, spent process catalysts, filter clay, and incinerator ash. Other waste fractions are waste from flue-gas desulphurisation, fly ash, bottom ash, spent activated carbon, filter dust, inorganic salts as ammonium sulphate and lime from water pretreatment, oil-contaminated soil, bitumen, sweepings, spent acid and caustic solutions, and chemicals, among others. The treatment of these wastes includes incineration, land treating off-site, landfilling on-site, landfilling off-site, chemical fixation, neutralisation, and other treatment methods.

4.25.1 Establishment of a waste management programme

Description

The establishment of an Environmental Management System (Section 4.15.1) contains elements to prevent waste generation. Some techniques that may be included are:

- implementation of a sludge master plan with the aim to reduce the sludge generated;
- provide enclosed sampling loops;
- cleaning and assembly preferably in specially constructed and dedicated areas;
- providing dedicated drainage systems;
- correct conditioning of a catalyst during a run, to extend catalytic life;
- control of sodium content in visbreaker feedstock, to reduce coke formation;
- process optimisation, to reduce off-specification products and hence recycling;
- recycling caustic sufficiently, to ensure it is completely spent;
- Sorting waste mixes e.g. concrete and scrap metal, as a cost-effective option (cheaper disposal routes for some components) and to eliminate the risk of unwanted components;
- asbestos lagging: special equipment for compaction and packing;
- where still relevant, apply permanganate treatment to eliminate traces of tetraethyl lead and tetramethyl lead (TEL/TML) in sludges;
- for oiled solids (soil): de-oiling in an oil extractor, neutralisation: mixing polymerisation catalyst (H_3PO_4) with lime;
- applying process treatment by steaming, flushing or regeneration prior to disposal: clay and sand filters; catalysts;

Additionally:

- Solids released to the waste water sewer system can account for a large portion of a refinery's oily sludges. Solids entering the sewer system (primarily soil particles) become coated with oil and are deposited as oily sludges in the API oil/water separator. Because a typical sludge has a solids content of 5 to 30 % by weight, preventing one kg of solids from entering the sewer system can eliminate 3 to 20 kg of oily sludge. The Amoco/US EPA study estimated that at the Yorktown facility, 1 000 tonnes of solids per year enter the refinery sewer system. Methods used to control solids include: using a street sweeper on paved areas, paving unpaved areas, planting ground cover on unpaved areas, re-lining sewers, cleaning solids from ditches and catch basins, and reducing heat exchanger bundle cleaning solids by using antifoulants in cooling water.
- A significant portion of refinery waste arises from oily sludges found in combined process/storm sewers. When possible, segregation of the relatively clean rainwater run-off from the process streams can reduce the quantity of oily sludges generated. Furthermore, there is a much higher potential for the recovery of oil from smaller, more concentrated process streams.

Achieved environmental benefits

The aim of a waste management programme is to prevent the generation of waste and to reduce its final disposal.

Reference literature

[177, WRA 1999], [228, TWG 2000], [166, CONCAWE 1999]

4.25.2 Sludge management and treatment

Description

Sludges are defined as semi-liquid residue from industrial processes and waste water treatment.

In refineries, a number of different types of sludges are generated at the following sources: crude and product tanks (bottoms), API separation units, flocculation and flotation units, DAF. Biological sludges represent a significant category of sludges in terms of oil content and dewaterability. Land filling and land farming of sludges are severely restricted.

Pretreatment and treatment of sludge

The purpose of sludge treatment by dewatering, drying and/or incineration is to reduce the volume and the residual hydrocarbon content, in order to save the subsequent processing or disposal costs. The principle of mechanical dewatering by decanters is based on centrifugal forces and on the density difference between water, oil and solids. The principle of the thermal treatment steps is based on a combination of evaporation by indirect heating and/or the destruction of the organic constituents by thermal oxidation (incineration).

Decanter centrifuges are the most widely used for dewatering biosludges. Steam dryers are almost exclusively applied for biosludge and often as a pretreatment step for incineration.

Decanter centrifuges are widely used in sludge dewatering and deoiling applications throughout the (refining) industry, either as fixed facilities or as a mobile service rendered by contractors. Dewatered biological and oily sludges can be further processed using drying and/or incineration techniques resulting in virtually oil-free residues for which useful applications are available.

Oily sludge dewatering is only applied at refineries that dispose of sludge cakes outside their premises in order to reduce the volume and associated disposal cost. Disposal to cement kilns, coal-fired power plants, dedicated sludge incinerators, municipal and hazardous waste incinerators are all used. Drying is hardly employed by refineries due to safety risks. De-oiling/dewatering of sludges gives a small volume of solid, low solvent waste, (centrifuging or filtration). An option for refineries with cokers is to reuse oily sludges in the coking process, as already mentioned in Section 4.7.5.

Figure 4.85 shows a simplified process flow diagram of a decanter combined with a fluidised-bed incinerator (FBI) being considered as BAT for sludge incineration in the WI BREF [82, COM 2006]. The feeding of sludge cake into the sand bed of the FBI can be accomplished with a positive displacement pump.

It should be mentioned that the emissions of SO₂, NO_x, CO, organic compound, PAH and heavy metals generated by these systems should be properly controlled by suitable abatement techniques as addressed in the WI BREF.

In addition, other techniques for the management of sludges (including biological treatment) are described in the Waste Treatment BREF 2006 [87, EC 2006].

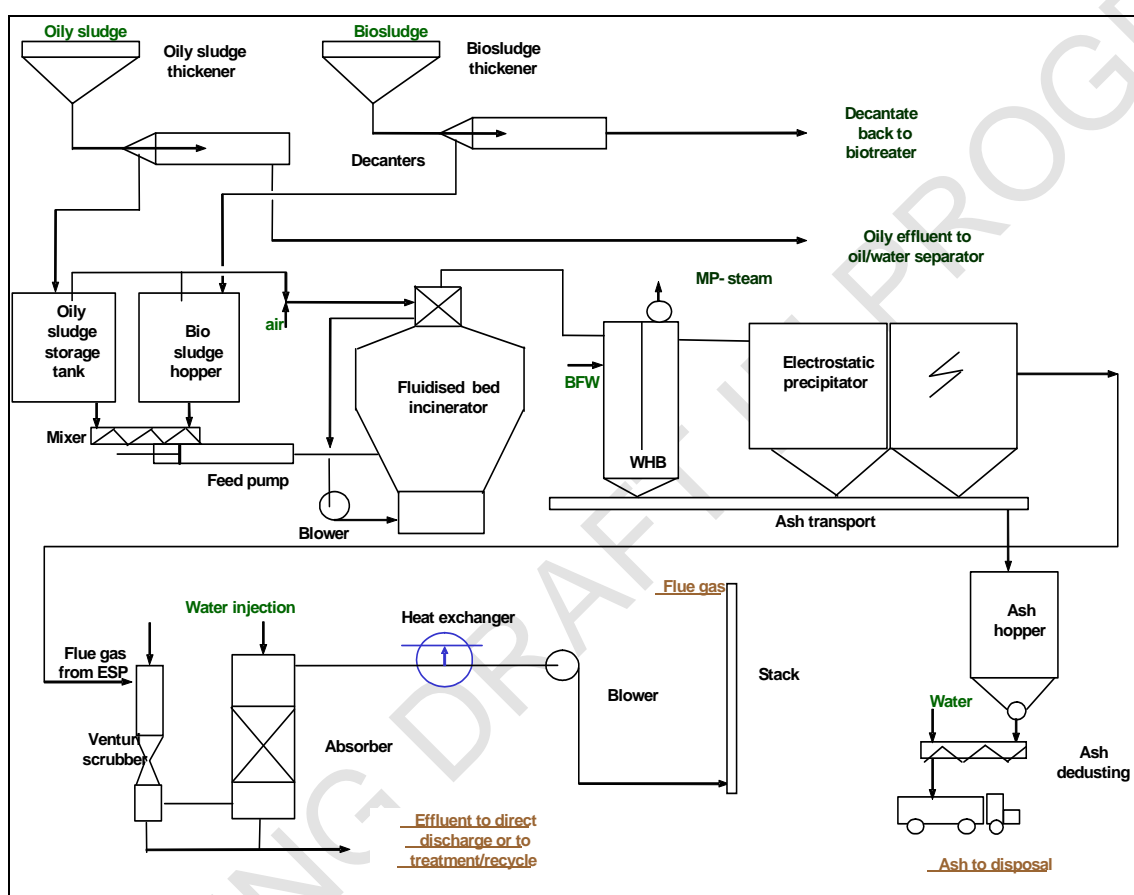


Figure 4.85: Simplified process flow diagram of sludge handling and incineration

Achieved environmental benefits

Generation of sludges can be reduced to values between 0.1 to 0.5 kg per tonne of feedstock processed within the refinery.

Cross-media effects

The cross media effects of sludge incineration are addressed in the WI BREF.

Operational data

Safety issues are associated with start-up and (planned or emergency) shutdown, for which a flame control interlock and a nitrogen purging system is required. Anaerobic and pyrophoric sludges (tank bottoms) can cause safety problems during storage and drying. The energy requirements of sludge drying and incineration depend strongly on the sludge cake characteristics (water and residual oil contents). Energy integration with FBI is two fold: air

preheating of the primary fluidisation air is standard, and steam generation can be economically accomplished with systems able to generate more than 8 tonnes of MP steam/hour. An intrinsic disadvantage of FBI is the relatively large excess of air utilised in order to keep the bed fluidised.

Applicability

Reuse of oily sludges in the coking process is dependent on the availability of this unit and the specifications of the final product. Dewatering units are fully applicable and are mainly used for waste minimisation before waste incineration. A fluidised-bed incinerators (FBI) is a proven technology already fully applicable in the waste treatment industry.

Operational data and economics

For an FBI with a capacity of 4 t/h sludge cake (20 % dry solids), a footprint of about 50x100 m is required including tankage and complete flue-gas and ash handling. The installation is normally 12 - 15 m high (tanks, incinerator, WHB, ESP, ash hopper) and the stack height is usually at least 40 m, depending on ancillary installations. The above-described system would be suitable for a large 20 Mt/yr refinery and requires a capital investment of about EUR 37.5 million (including installation). The operational costs could amount to EUR 500 - 700/tonne dry solids. If large scale domestic sludge incinerators are available, which are authorised to take industrial sludges, the installation of a dedicated sludge incineration system is not economically justifiable.

A combination of decanters with an advanced drying system for oily sludge occupies only 10 - 15 % of the above indicated space, and would involve a capital investment of EUR 5 million, since expensive flue-gas treatment is avoided.

Driving force for implementation

Oil recovery. Operating cost reduction. Waste legislation.

Example plants

Decanter centrifuges are reliable, advanced and proven techniques with minimum emissions. At refinery locations, permanent decanter centrifuges have for example been installed at refineries in Godorf, Gothenburg and Stanlow. A few times per year, contractors are hired in either for on-site sludge processing or for collection and off-site processing (decanting, drying, incineration in cement kilns, power plants or in industrial/domestic waste or dedicated sludge incinerators).

Sludge incineration plants using the fluidised-bed system are considered state-of-the-art but require advanced design and process control. At several refineries, such as Mobil, Wilhelmshafen, Shell Pernis and Godorf, Esso Botlek these systems were already built in the 1970s. Some of them have been dismantled due to the current availability of more economic options compared with the necessary investment and operation of additional flue-gas cleaning equipment for today's operation. For oily sludges, mixing with other wastes and use as secondary fuel in cement kilns and/or power plants is an attractive disposal route if these plants use appropriate abatement techniques. International sludge contractors employ either mobile decanter and drying systems for oil recovery (Impex, EPMS, Soil Recovery A/S) or fixed oily sludge treatment systems (ATM).

4.25.3 Spent solid catalyst management

The techniques used for the recovery of metals from secondary materials, such as the catalysts used in the oil and gas refining industry, are described in the NFM BREF [123, EC 2001].

The use of catalytic processes in refineries has increased significantly. This increase is mainly due to the introduction of catalytic residue conversion processes, such as heavy oil residue cracking, hydrocracking and residue hydroconversion, hydrodemetallisation and hydrofinishing and also hydrogen production. Since 1980, a significant expansion has taken place of the hydrotreating and hydrodesulphurisation capacity, as well as of sulphur recovery units and

associated tail gas treatment, whose processes also utilise catalysts. Traditional catalytic processes such as fluid catalytic cracking, catalytic reforming and isomerisation are also generators of spent catalysts.

The purpose of spent catalyst management is to minimise environmental and health impacts. To achieve this goal, spent catalysts are carefully handled, safely removed, carefully packed and sent for reactivation or metal reclamation. When the finally-spent catalyst is no longer regenerable, it is sent to metal reclamation or to other waste treatments. Metal recovery aims at the conversion of spent catalysts into useful products, which can be recycled and reused with minimum impact on the environment.

The principle of spent catalyst management is a scheduled, strictly regulated and safe handling of the materials involved, usually executed by specialised contractors during plant turn-arounds. Arrangements with the supplier of fresh catalyst can sometimes be made for them to take back the spent catalyst.

The regeneration of hydroprocessing catalysts is usually possible for 3 or 4 times. The finally-spent catalysts are almost exclusively reworked by third parties into commercial metal oxides or metal salt solutions. Although a regeneration process has been developed for spent FCC catalysts, this process is hardly used due to the availability of cheaper alternatives. The catalyst carrier (alumina and/or silica) can sometimes be converted into products or otherwise disposed of. Some refineries store spent catalysts at the refinery site in appropriate environmental conditions with permission of the authorities. Spent catalysts are distinguished by type, process, composition and recyclability. A summary is given in Table 3.94 and below:

- Co/Mo catalysts from hydrodesulphurisation, hydrocracking, hydrotreating. Extensive regeneration and reclamation options are available.
- Ni/Mo catalysts are typically used in hydrotreaters and hydrocracking units. Regeneration and reclamation capacity is available.
- Ni/W catalysts are used in lube oil hydrofinishing. This category experiences limitations to dispose off in view of the high Tungsten content (24 % w/w).
- FCC spent catalysts, also including heavy oil and residue cracking spent catalysts (RCC), are the largest catalyst waste category in refineries. Outlets in road building are becoming available.
- Reformer and Isomerisation catalysts are exclusively reprocessed by the suppliers of the fresh catalysts. Replacement contracts have been concluded since the introduction of these processes due to the very expensive noble Pt metal involved.
- Hydrodemetallisation catalysts typically have high vanadium contents (10 - 20 %) and are currently alumina based (used to be silica). Direct disposal to the steel industry is possibly the most cost-effective option.
- Zn containing beds from H₂ plants are typically recycled to the Zn-industry where ZnS ores are processed. Amounts are some 50 t/yr.

The applied regeneration processes are based on pyrometallurgical techniques (roasting, calcination, smelting, sintering and reduction furnaces) for the thermal destruction of the inorganic matrix and on hydrometallurgical methods (aqueous/acid extraction, crystallisation, precipitation, separation and drying) for the recovery/purification of metal salts, either in dry form or as liquid metal concentrates.

The reclamation plants (more information can be found in the NFM BREF [123, EC 2001]) are typically operated in batch mode and contain many different unit operations. From the total spent catalysts, only some 5 % pure products are produced. The remainder is either ferro-alloy feed or ceramic raw material. The plant usually processes relatively small batches. Spent hydroprocessing catalysts can vary considerably in composition. Hence the plants have limited process automation.

4.25.3.1 Control and reuse of the catalyst fines

Description

Significant quantities of catalyst fines are often present around the catalyst hoppers, reactors and regeneration vessels of the FCC unit, as well as those collected by the abatement techniques mentioned above. The fines can be collected and recycled before being washed to the sewers or migrating off-site via the wind. These techniques may be considered housekeeping measures, and are thus included in Section 4.15. Some techniques to consider are:

- dry sweeping the catalyst fines and sending the solids to be recycled or disposed of as non-hazardous waste;
- using of vacuum ducts in dusty areas (and vacuum hoses for manual collection), which run to a small baghouse for collection;
- reusing the fines (cement production);
- returning FCC spent catalysts back to the manufacturer.

Achieved environmental benefits

Reduced the emission of particulates.

Cross-media effects

None worth being mentioned.

Operational data

No data available.

Applicability

Fully applicable especially during catalyst loading/unloading processes.

Economics

No data available.

Driving force for implementation

Reduction of soil contamination by particulates.

Example plants

Techniques already in use in US refineries.

Reference literature

[156, MCG 1991].

4.25.3.2 Removal of catalyst from slurry decant oil

Description

Three types of techniques are applied to improve the separation of catalysts from the slurry decant oil used in catalytic crackers. One system incorporates high-voltage electric fields to polarise and capture catalyst particles from decant oil; here, catalyst fines suspended in the separator underflow are recycled back to the reactor. In another system, the amount of catalyst fines reaching the decant oil can be minimised by installing high-efficiency cyclones in the reactor, to shift the catalyst fines losses of the decant oil to the regenerator, where they can be collected by any particulate abatement technique. A third method is to use a mechanical filter with backwash.

Achieved environmental benefits

Decant oil sludge from an FCC can contain significant concentrations of catalyst fines. These fines often do not allow use of the decant oil as a feedstock and require treatment which

generates an oily catalyst sludge. Catalysts in the decant oil can be minimised by using a decant oil catalyst removal system.

Cross-media effects

These techniques have their own energy consumption.

Operational data

No data available.

Economics

No data available.

Applicability

Hydrocyclones are applied in many FCC units.

Driving force for implementation

Reduction of consumption of catalyst and reduction of the decant oil sludge.

Example plants

Hydrocyclones, for removal of catalyst fines, are successfully applied in many FCCs.

Reference literature

[228, TWG 2000]

4.25.4 Recycling and re-using waste

Recycling and reuse of unintended by-products in different refinery processes or outside the refinery reduces the quantity of waste for disposal.

4.25.4.1 Treatment of heavy residues

Heavy residues generated by refineries are the heaviest fractions from the different units (distillation, conversion). These residues may be mixed with bitumen or other residues fractions if meeting the specifications of a product. They may not have application for products and are typically reused within the refinery where their calorific value can be exploited. Below is a list of treatments that may be applied to reduce the amount of these residues. All these techniques are already analysed in other sections but are put together here to help the reader to understand what refineries may do with their heavy residues.

Methods to increase the hydrogen content (hydrogenation):

- Catalytic hydrogenation (included within Section 4.13) such as Resid Fining, RCD UNIBON, Unicracking, HYVAHL-ASVAHL hydrotreatment, AUROBAN, H-Oil, LC-Fining, HYCON;
- Non catalytic hydrogenation (included within Section 4.22) as Hydrovisbreaking, Dynacracking, Donor Solvent Visbreaking.

Methods to increase the C-content:

- Catalytic cracking (included within Section 4.5) such as residue catalytic cracking (RCC), Heavy oil Cracking, VEBA combi cracking (VCC), Deep catalytic cracking (DCC);
- Non catalytic cracking (included within Section 4.7 and 4.22) as delayed coking, fluid coking, flexicoking, LR-Coking, deasphalting: DEMEX, Rose-Technology, visbreaking, thermal cracking, and partial oxidation.

4.25.4.2 Improving the recovery of oils from oily sludges

Because oily sludges make up a large portion of refinery solid wastes, any improvement in the recovery of oil from the sludges can significantly reduce the volume of waste. There are a number of technologies currently in use to mechanically separate oil, water and solids, including: belt filter presses, recessed chamber pressure filters, rotary vacuum filters, scroll centrifuges, disc centrifuges, shakers, thermal dryers and centrifuge-dryer combinations.

4.25.4.3 Regenerate or eliminate filtration clay

Clay from refinery filters must periodically be replaced. Spent clay often contains significant amounts of entrained hydrocarbons and, therefore, must be designated as hazardous waste. Techniques that may be applied are:

- Back washing spent clay with water or steam to reduce the hydrocarbon content to levels so that it can be reused or handled as a non-hazardous waste.
- Washing the clay with naphtha, drying it by steam heating and then feeding it to a burning kiln for regeneration.
- In some cases, clay filtration can be entirely replaced with hydrotreating (See Section 4.20.4).

4.25.4.4 Reprocessing off-specification products

It is customary in refineries to have dedicated tankage (or 'slops') for the collection of hydrocarbon streams/intermediate products that cannot be blended into final products for the market. These slops are generally reprocessed, often by injection into the crude oil feedstock to the crude distilling unit or to the coker. Often, segregation is practised between wet and dry slops (as a general rule the wet slop contains significant amounts of dissolved and emulsified water and is unsuitable for direct reprocessing – the dry slop is sufficiently dehydrated to be ready for reprocessing). The wet slops tank is equipped with facilities to separate (drain) water from oil (to prevent slugs of water from coming into the crude distiller). In some refineries, separate slops processing (distillation) facilities are installed [202, Dekkers 2000].

Streams from water treatment units (e.g. oil/water mixtures from interceptors) can be routed to the wet slops tank. Oil from sludge thickeners (centrifuges/decanter) can be routed to the slops tanks. The oil in sludges (e.g. from DAF units) can be recovered in this way also [202, Dekkers 2000].

4.25.4.5 Recycle/Reuse outside the installation

Some options to reduce the waste generation is to recycle or reuse them. Bellow are some examples of good environmental practices:

- Treat catalysts for metal recovery (reforming, desulphurisation) (See Section 4.20.2).
- Waste lubes: re-refining or reuse (See Section 4.25.4.6).
- Drums/containers: reconditioning .
- Spent caustic can be used: (See Section 4.20.2).
- Alkylation process: CaF₂ can be used.
 - for HF production,
 - as a fluxing agent (steel industry).
- Resale of polymerisation plant catalyst as a fertiliser (See 4.18.2).

- Sale of gypsum or sulphuric acid from flue-gas desulphurisation units
- For dust: in the regenerative flue-gas desulphurisation process according to Welmann Lord NH_3 is injected to prevent the formation of SO_3 . Therefore up to 80 % of the ash consists of $(\text{NH}_4)_2\text{SO}_4$, which can be used as a fertiliser or as a basic material for NH_3 production [194, Winter 2000]
- Paper, wood, glass, scrap metal according to selective collection and recycling schemes and circuits which may be implemented at national or regional levels.
- Construction/demolition debris:
 - concrete to a crusher, for use in road building, etc.
 - asphalt scrapings reused, e.g. in road building.

It has to be mentioned, that reuse of waste fractions/residues outside the company is only an option but needs to comply with the requirements of waste framework directive (2008/98/EC), if these waste fractions meet certain criteria (such as concentration of pollutants in a fertiliser) and do not alter the original product characteristics (e.g. when using gypsum in the cement industry).

4.25.4.6 Reuse of waste lubes

Description

Waste lubes can be reused within the refinery as a fuel component or as feedstock for re-refining. Controlled incineration of waste lube oils is another alternative.

Achieved environmental benefits

Reduction in the amount of waste lubes produced within the refinery.

Cross-media effects

Waste lubricating oils may contain additives that need to be disposed of properly.

Applicability

Some applicability problems have been detected. For example, waste lubricating oil from garages may contain organic chlorides used as degreasers; in hydrotreaters they will be converted into HCl and can cause severe corrosion in this high pressure unit filled with hydrogen. Only by application of well-controlled pretreatment techniques, can the treated waste oil be upgraded to a fuel component. Such a pretreatment activity is normally not compatible with refinery operations and is done outside the refinery by specialised companies, which also do the collection of the waste oils. The only exception to the use of waste lubes as fuel component is for waste lube oil that is generated in the refinery itself and of which its composition is beyond any doubt.

Driving force for implementation

To reduce the amount of waste lubes.

Reference literature

[202, Dekkers 2000].

4.25.4.7 Recycle lab samples

Lab samples can be recycled to the oil recovery system.

4.25.5 Biodegradation of wastes

This section contains methods for the biodegradation of refinery wastes that may be used specifically within refineries on-site. This section does not contain methods for the remediation

of contaminated soils. As it was stated in the scope of this document, soil remediation techniques are considered out of the scope of this document.

Description

Many hazardous chemicals present in refinery waste can be converted by microbiological methods to harmless compounds such as water and carbon dioxide. In general, the microbiological degradation of contaminants in soil is very slow in nature, because process conditions for such degradation are seldom favourable. To accelerate degradation a number of conditions have to be fulfilled.

Current techniques for biological decontamination are based on optimisation of the process conditions for microbiological degradation. The appropriate microorganisms for microbiological degradation may already be present in the waste to be treated or may have to be added. The latter is necessary if special microorganisms are required. These special microorganisms can be achieved by selection and adaptation.

Operational data

The most important factors are the availability of temperature control, sufficient oxygen, nutrients, and the appropriate microorganisms. Also important are the concentration level of the contaminants and the variation in concentration. The presence of toxic compounds can disturb the degradation process. Sometimes the presence of natural organic compounds has a positive influence on the biodegradation process.

In summary the following conditions have to be met in order to optimise the degradation rate of a waste generated by a refinery:

- sufficient number of microorganisms of the right strains;
- non-toxic concentrations of contaminants or other compounds;
- adjustment of an accurate water content;
- presence of sufficient nutrients (mainly P and N in ratio 1: 10);
- presence of sufficient oxygen for aerobic processes and a full depletion of oxygen for anaerobic processes;
- favourable temperature (20 - 30°C);
- pH 6 – 8;
- temperature control;
- measures have to be applied to prevent emissions into air by volatile contaminants or degradation products (by covering the area and by treating the exhaust air) and to prevent emissions into water and soil (by sealing the floor and reuse of excess water);
- sufficient availability of contaminants (preferably without high peak concentrations) to the microorganisms including good mixing of nutrients, waste, inert (e.g. soil) and contaminants.

Reference literature

[166, CONCAWE 1999]

4.25.6 Waste storage

Wastes awaiting disposal should be stored in an environmentally acceptable manner, as approved by the local control authority. Storage should not give rise to secondary environmental problems, such as odour or pollution of groundwater due to rainwater percolation through or run-off from the site. Storage should be in closed vessels, containers or bags, on a site surrounded by a bund wall or toe wall, with drainage to a prepared system. Special precautions are of course required for pyrophoric materials to eliminate the risk of fires; they must be kept wet, sealed or blanketed with inert gas.

WORKING DRAFT IN PROGRESS

5 BEST AVAILABLE TECHNIQUES (BAT) CONCLUSIONS

SCOPE

These BAT conclusions concern the following activities specified in Section 1.2 of Annex I to Directive 2010/75/EU, namely:

- 1.2 Energy industries: Refining of mineral oil and gas.

This document addresses the activities and processes set out in the following table.

Activity	Subactivities or processes included in activity
Alkylation	All alkylation processes: hydrofluoric acid (HF), sulphuric acid (H ₂ SO ₄) and solid-acid
Base oil production	Deasphalting, aromatic extraction, wax processing and lubricant oil hydrofinishing
Bitumen production	All techniques from storage to final product additives
Catalytic cracking	All types of catalytic cracking units such as fluid catalytic cracking
Catalytic reforming	Continuous, cyclic and semi-regenerative catalytic reforming
Coking	Delayed and fluid coking processes. Coke calcination
Cooling	Cooling techniques applied in refineries
Desalting	Desalting of crude oil
Combustion for energy production	Refinery power plants, including all types of techniques applied within EU refineries and burning refinery fuels. Energy production techniques using only conventional or commercial fuels are not covered.
Etherification	Production of chemicals (e.g. alcohols and ethers such as MTBE, ETBE and TAME) used as motor fuels additives
Gas separation	Separation of light fractions of the crude oil e.g. refinery fuel gas (RFG), liquefied petroleum gas (LPG)
Hydrogen consuming processes	Hydrocracking, hydrorefining, hydrotreatments, hydroconversion, hydroprocessing and hydrogenation processes
Hydrogen production	Partial oxidation, steam reforming, gas heated reforming and hydrogen purification
Integrated refinery management	Environmental activities, utility and overall refinery management
Isomerisation	Isomerisation of hydrocarbons compounds C ₄ , C ₅ and C ₆
Natural gas plants	Natural gas (NG) processing including liquefaction of NG
Polymerisation	Polymerisation, dimerisation and condensation
Primary distillation	Atmospheric and vacuum distillation
Product treatments	Sweetening and final product treatments
Storage and handling of refinery materials	Storage, blending, loading and unloading of refinery materials
Visbreaking and other thermal conversions	Thermal treatments such as visbreaking or thermal gas oil
Waste gas treatment	All techniques to reduce or abate emissions to air
Waste water treatment	Techniques to reduce or treat waste water prior to release
Waste management	Techniques to prevent and reduce the generation of waste

These BAT conclusions **do not address** the following activities:

- the exploration and production of crude oil and natural gas;
- the transportation of crude oil and natural gas;
- the marketing and distribution of products.

Other reference documents which may be of relevance for the activities covered by these BAT conclusions are the following.

Reference document	Subject
Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW)	Waste water management and treatment techniques
Industrial Cooling Systems (ICS)	Cooling processes
Economics and Cross-media Effects (ECM)	Economics and cross-media effects of techniques
Emissions from Storage (EFS)	Storage, blending, loading and unloading of refinery materials
Energy Efficiency (ENE)	Energy efficiency and integrated refinery management
Large Combustion Plants (LCP)	Combustion of commercial fuels
Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers Industries (LVIC-AAF)	Steam reforming and hydrogen purification
Large Volume Organic Chemical Industry (LVOC)	Etherification process (MTBE, ETBE and TAME production)
General Principles of Monitoring (MON)	Monitoring of emissions to air and water
Waste Incineration (WI)	Waste and waste water management
Waste Treatments Industries (WT)	Waste and waste water management

The techniques listed and described in these BAT conclusions are neither prescriptive nor exhaustive. Other techniques may be used that ensure at least an equivalent level of environmental protection.

Definitions

For the purpose of these BAT conclusions, the following definitions apply:

Term used	Definition
Unit	A segment/subpart of the installation in which a specific processing operation is conducted
New unit	A unit first permitted on the site of the installation following the publication of these BAT conclusions or a complete replacement of a unit on the existing foundations of the installation following the publication of these BAT conclusions
Existing unit	A unit which is not a new unit
Process off-gas	The collected gas generated by a process which must be treated e.g. in an acid gas removal unit and a sulphur recovery unit (SRU)
Flue-gas	The exhaust gas exiting a unit after an oxidation step, generally combustion (e.g. regenerator, Claus unit)
Tail gas	Common name of the exhaust gas from an SRU (generally Claus process)
VOC	Volatile organic compounds as defined under Directive 2010/75/EU
Diffuse VOC emission	Non-channelled VOC emissions that are not released via specific emission points such as stacks. They can result from 'area' sources (e.g. tanks) or 'point' sources (e.g. pipe flanges)
Fugitive VOC emission	Diffuse VOC emissions from 'point' sources
NO _x expressed as NO ₂	The sum of nitrogen oxide (NO) and nitrogen dioxide (NO ₂) expressed as NO ₂

Term used	Definition
SO _x expressed as SO ₂	The sum of sulphur dioxide (SO ₂) and sulphur trioxide (SO ₃) expressed as SO ₂
H ₂ S	Hydrogen sulphides. Carbonyl sulphide and mercaptan are not included
Hydrogen chloride expressed as HCl	All gaseous chlorides expressed as HCl
Hydrogen fluoride expressed as HF	All gaseous fluorides expressed as HF
FCC unit	Fluid catalytic cracking (FCC) is the common process name. The catalytic cracking is a conversion process for upgrading heavy hydrocarbons. It uses heat and a catalyst to break larger hydrocarbon molecules into lighter molecules
SR Unit	Sulphur recovery unit. See technique definition in Glossary Section 5.19.3
Refinery fuel	Solid, liquid or gaseous combustible material from the distillation and conversion steps of the refining of crude oil. Examples of commonly used refinery fuels are refinery fuel gas (off-gases from distillation or conversion), syngas and refinery oils. Pet coke may also be used
Combustion unit	Liquid, gas, solid or multi-fuel fired unit burning refinery fuels alone or with other fuels for the production of energy at the refinery site. Combustion units include e.g. boilers (except CO boilers), furnaces, and gas turbines. NB: Combustion plants running exclusively on commercial fuels (e.g. natural gas) are not covered by the REF BREF, but may be covered by the LCP BREF
Continuous measurement	Measurement using an 'automated measuring system' (AMS) or a 'continuous emission monitoring system' (CEMS) permanently installed on site
Periodic measurement	Determination of a measurand (particular quantity subject to measurement) at specified time intervals using manual or automated reference methods
Indirect Monitoring of emissions to air	Estimation of the emissions concentration in the flue-gas of a pollutant obtained through an appropriate combination of measurements of surrogate parameters (such as O ₂ content, sulphur or nitrogen content in the feed/fuel), calculations and periodic stack measurements. The use of emission ratios based on S content in the fuel is one example of indirect monitoring. Another example of indirect monitoring is the use of PEMS
Predictive Emissions monitoring systems (PEMS)	System to determine the emissions concentration of a pollutant based on its relationship with a number of characteristic continuously monitored process parameters (e.g. fuel gas consumption, air/fuel ratio) and fuel or feed quality data (e.g. the Sulphur content) of an emission source
Volatile liquid hydrocarbon compounds	Petroleum derivatives with a Reid vapour pressure (RVP) of more than 4 kPa. This is particularly meant for e.g. naphtha, crudes and aromatics
NM VOC	Non methane volatile organic compounds (VOC)
Recovery rate	Percentage of non-methane volatile organic compounds (NMVOC) recovered from the streams conveyed into a vapour recovery unit (VRU)

NOTE: Whilst cross-references are provided to other parts of this BREF in this draft document in order to aid the work of the TWG, they will not be included in the final BAT conclusions themselves. Such cross references are consequently displayed in *[square brackets and italic.]*

General considerations

Averaging periods and reference conditions for emissions to air

Unless stated otherwise, emission levels associated with the best available techniques (BAT-AELs) for emissions to air given in these BAT conclusions refer to monthly average values of concentrations, expressed as mass of emitted substance per volume of waste gas under the following standard conditions: dry gas, temperature 273.15 K, pressure 101.3 kPa.

For continuous measurements	Unless stated otherwise, BAT-AELs refer to monthly average values
	Monthly average: average over a period of one month based on valid hourly averages measured by continuous measurements
	Daily average: average over a period of one day based on valid hourly averages measured by continuous measurements
For periodic measurements	BAT-AELs refer to the average value of three spot samples of at least 30 minutes each

For combustion, catalytic cracking processes and sulphur recovery units, reference conditions for oxygen are shown in Table 5.1.

Table 5.1: Reference conditions for BAT-AELs concerning emissions to air

Activities	Unit	Oxygen reference conditions
Combustion process using liquid or gaseous fuels with the exception of gas turbines and engines	mg/Nm ³	3 % oxygen by volume
Combustion process using solid fuels	mg/Nm ³	6 % oxygen by volume
Catalytic cracking (regeneration of catalyst)	mg/Nm ³	3 % oxygen by volume
Gas turbines (including combined cycle gas turbines – CCGT) and engines	mg/Nm ³	15 % oxygen by volume
Sulphur recovery unit (SRU)	mg/Nm ³	3 % oxygen by volume

Conversion of emissions concentration to reference oxygen level

The formula for calculating the emissions concentration at a reference oxygen level (see Table 5.1 is shown below.

$$E_R = \frac{21 - O_R}{21 - O_M} \times E_M$$

Where:

- E_R (mg/Nm³): emissions concentration corrected to the reference oxygen level O_R
 O_R (vol %): reference oxygen level
 E_M (mg/Nm³): emissions concentration referred to the measured oxygen level O_M
 O_M (vol %): measured oxygen level.

Reference conditions for emissions to water

Unless stated otherwise, emission levels associated with the best available techniques (BAT-AELs) for emissions to water given in these BAT conclusions refer to values of concentration (mass of emitted substances per volume of water) expressed in mg/l.

Averaging periods for emissions to water

Unless stated otherwise, the averaging periods associated with the BAT-AELs are defined as follows:

Daily average	Average over a sampling period of 24 hours taken as a flow-proportional composite sample. Time-proportional sampling can be used provided that sufficient flow stability is demonstrated.
Yearly/Monthly average	Average (weighted according to the daily flows) of the daily average values taken with the minimum frequency set for the relevant parameter within a year/month

5.1 General BAT conclusions for the refining of mineral oil and gas

Unless otherwise stated, the BAT conclusions presented in this section are generally applicable.

The process specific BAT conclusions included in Sections 5.2 to 5.18 apply in addition to the general BAT conclusions mentioned in this section.

5.1.1 Environmental management systems

1. BAT is to implement and adhere to an environmental management system (EMS) that incorporates all of the following features:

- i. commitment of the management, including senior management;
- ii. definition of an environmental policy that includes the continuous improvement for the installation by the management;
- iii. planning and establishing the necessary procedures, objectives and targets, in conjunction with financial planning and investment;
- iv. implementation of the procedures paying particular attention to:
 - (a) structure and responsibility
 - (b) training, awareness and competence
 - (c) communication
 - (d) employee involvement
 - (e) documentation
 - (f) efficient process control
 - (g) maintenance programmes
 - (h) emergency preparedness and response
 - (i) safeguarding compliance with environmental legislation.
- v. checking performance and taking corrective action, paying particular attention to:
 - (a) monitoring and measurement (see also the reference document on the General Principles of Monitoring)
 - (b) corrective and preventive action
 - (c) maintenance of records
 - (d) independent (where practicable) internal and external auditing in order to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained;
- vi. review of the EMS and its continuing suitability, adequacy and effectiveness by senior management;
- vii. following the development of cleaner technologies;
- viii. consideration for the environmental impacts from the eventual decommissioning of the installation at the stage of designing a new plant, and throughout its operating life;
- ix. application of sectoral benchmarking on a regular basis.

Applicability

The scope (e.g. level of details) and nature of the EMS (e.g. standardised or non-standardised) will generally be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

5.1.2 Energy efficiency

2. In order to use energy efficiently, BAT is to use an appropriate combination of the techniques given below:

Technique	Description
i. Design techniques	
a. Pinch analysis	Methodology based on a systematic calculation of thermodynamic targets for minimising energy consumption of processes. Used as a tool for the evaluation of total systems designs
b. Heat integration	Heat integration of process systems ensures that a substantial proportion of the heat required in various processes is provided by exchanging heat between streams to be heated and streams to be cooled
c. Heat and power recovery	Use of energy recovery devices e.g.: <ul style="list-style-type: none"> • waste heat boilers • expanders/power recovery in the FCC unit • use of waste heat in district heating
ii. Process control and maintenance techniques	
a. Process optimisation	Automated controlled combustion in order to lower the fuel consumption per tonne of feed processed, often combined with heat integration for improving furnace efficiency
b. Management and reduction of steam consumption	Systematic mapping of drain valve systems in order to reduce steam consumption and optimise its use
c. Use of energy benchmark	Participation in ranking and benchmarking activities in order to pursue a continuous improvement by learning from best practice
iii. Energy efficient production techniques	
a. Use of combined heat and power	System designed for the co-production (or the cogeneration) of heat (e.g. steam) and electric power from the same fuel
b. Integrated gasification combined cycle (IGCC)	Technique whose purpose is to produce steam, hydrogen (optional) and electric power from a variety of fuel types (e.g. heavy fuel oil or coke) with a high conversion efficiency

[This BAT conclusion is based on information given in Section 4.10.1]

5.1.3 Solid materials storage and handling

3. In order to prevent, or where that is not practicable, to reduce dust emissions from the storage and handling of dusty materials, BAT is to use one or a combination of the techniques given below:

- i. store bulk powder materials in enclosed silos equipped with a dust abatement system (e.g. fabric filter)
- ii. store fine materials in enclosed containers or sealed bags
- iii. keep stockpiles of coarse dusty material wetted, stabilise the surface with crusting agents, or store under cover in stockpiles
- iv. use road cleaning vehicles.

5.1.4 Monitoring of emissions to air and key process parameters

4. BAT is to monitor emissions to air by using the monitoring techniques with at least the minimum frequency given below and in accordance with EN standards. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality.

Description	Process unit	Minimum frequency	Monitoring technique
Monitoring of emissions to air			
i. Monitoring of SO _x , NO _x , and dust emissions	Catalytic cracking	Continuous ^(2,4)	Direct measurement
	Combustion units ≥ 100 MW and calcining units	Continuous ^(2,4)	Direct measurement ⁽⁵⁾
	Other combustion units of 50 up to 100 MW ⁽⁶⁾	Continuous ^(2,4)	Direct measurement or indirect monitoring
	Other combustion units	Once a year and after significant fuel changes ⁽¹⁾	Direct measurement or indirect monitoring
	Sulphur recovery units (SRU)	Continuous for SO ₂ only ⁽⁴⁾	Direct measurement or indirect monitoring ⁽³⁾
ii. Monitoring of emissions of NH ₃	All units equipped with SCR or SNCR	Continuous	Direct measurement
iii. Monitoring of emissions of CO	Catalytic cracking and combustion units ≥ 100 MW	Continuous	Direct measurement
	Other combustion units	Once every 6 months ⁽¹⁾	Direct measurement
iv. Monitoring of metals emissions (Ni, Sb ⁽⁷⁾ , V)	Catalytic cracking	Once every 6 months and after significant changes to the unit ⁽¹⁾	Direct measurement or analysis based on metals content in the catalyst fines and in the fuel
	Combustion units ⁽⁸⁾		
v. Monitoring of emissions of PCDD/F	Catalytic reformer	Once a year or once a regeneration, whichever is longer	Direct measurement
⁽¹⁾ Monitoring frequencies may be adapted if, after a period of one year, the data series clearly demonstrate a sufficient stability ⁽²⁾ Continuous measurement of SO ₂ emissions may be replaced by calculations based on measurements of the sulphur content of the fuel or the feed; where it can be demonstrated that this leads to an equivalent level of accuracy. ⁽³⁾ SO ₂ emissions measurements from SRU may be replaced by a continuous material balance or other relevant process parameter monitoring, provided appropriate measurements of SRU efficiency are based on periodic (e.g. once every 2 years) plant performance tests. ⁽⁴⁾ Only SO ₂ is continuously measured, SO ₃ is only periodically measured (e.g. during calibration of the SO ₂ monitoring system). ⁽⁵⁾ Or indirect monitoring of SO _x . ⁽⁶⁾ Refers to the capacity connected to the stack where emissions occur. ⁽⁷⁾ Sb to be monitored only in catalytic cracking units when Sb injection is used in the process (e.g. for metals passivation). ⁽⁸⁾ With the exception of combustion units firing only refinery fuel gas.			

- 5. BAT is to monitor the relevant process parameters by using the monitoring techniques and the minimum frequency given below:**

Description	Process unit	Minimum frequency	Monitoring technique
Monitoring of parameters linked to pollutant emissions, e.g. O ₂ content in flue-gas, N and S content in fuel or feed ⁽¹⁾	Catalytic cracking and combustion units	Continuous for O ₂ content. For N and S content, periodic at a frequency based on significant fuel/feed changes	Specific to each relevant parameter
⁽¹⁾ N and S monitoring in fuel or feed is not applicable when continuous measurements of NO _x and SO ₂ are carried out at the stack.			

- 6. BAT is to monitor diffuse VOC emissions to air from the entire site by using all of the following techniques :**

- i. sniffing methods associated with correlation curves for key equipment;
- ii. optical gas imaging techniques;
- iii. calculations of chronic emissions based on emissions factors periodically (e.g. once every 2 years) validated by measurements.

The screening and quantification of site emissions by periodic campaigns with optical absorption based techniques, such as differential absorption light detection and ranging (DIAL) or solar occultation flux (SOF) is a useful complementary technique.

Description: See Section 5.19.6.

[This BAT conclusion is based on information given in Section 3.26.1.3]

5.1.5 Operation of waste gas treatment systems

- 7. In order to prevent or reduce emissions to air, BAT is to operate the acid gas removal units, sulphur recovery units and all other waste gas treatment systems with a high availability and at optimal capacity.**

Applicability

Special procedures can be defined for specific operating conditions, in particular:

- i. during start-up and shutdown operations;
 - ii. during other special operations which could affect the proper functioning of the systems (e.g. regular and extraordinary maintenance work and cleaning operations of the units and/or of the waste gas treatment system);
 - iii. in case of insufficient waste gas flow or temperature which prevents the use of the system at full capacity.
- 8. In order to prevent and reduce ammonia (NH₃) emissions to air when applying selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) techniques, BAT is to maintain suitable operating conditions of the SCR or SNCR waste gas treatment systems, with the aim of limiting emissions of unreacted NH₃**

BAT-associated emission levels: See Table 5.2.

Table 5.2: BAT-AEL for ammonia (NH₃) emissions to air when using SCR or SNCR techniques

Parameter	BAT-AEL ⁽¹⁾ (monthly average) mg/Nm ³
Ammonia expressed as NH ₃	<5 – 15 ⁽²⁾
⁽¹⁾ The higher levels are associated with higher inlet NO _x concentrations, higher NO _x reduction rates and the ageing of the catalyst ⁽²⁾ The lower end of the range is associated with the use of the SCR technique	

[This BAT conclusion is based on information given in Section 4.23.3.2]

- 9. In order to prevent and reduce emissions to air when using a sour water steam stripping unit, BAT is to route the acid off-gases from this unit to an SRU or any equivalent gas treatment process. It is not BAT to directly incinerate the untreated sour water stripping gases.**

[This BAT conclusion is based on information given in Section 4.24.2]

5.1.6 Monitoring of emissions to water

- 10. BAT is to monitor emissions to water Table 5.3 by using the monitoring techniques with at least the minimum frequency given below (see Table 5.3) and in accordance with EN standards. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality.**

5.1.7 Emissions to water

11. In order to reduce water consumption and the volume of contaminated water, BAT is to use all of the techniques given below:

Technique	Description	Applicability
i. Water stream integration	Reduction of process water produced at unit level prior to discharge by internal reuse of water stream from e.g. cooling, condensates, especially for use in crude desalting	Generally applicable for new units. For existing units, applicability may require a complete rebuilding of the unit or the installation
ii. Water and drainage system for segregation of contaminated water streams	Design of an industrial site aiming at an optimised water management where each stream is treated as appropriate, by e.g. routing generated sour water (from distillation, cracking, coking units, etc.) to appropriate pre-treatment, such as a stripping unit	Generally applicable for new units. For existing units, applicability may require a complete rebuilding of the unit or the installation
iii. Segregation of non-contaminated water streams (e.g. once-through cooling, rain water)	Design of a site in order to avoid sending non-contaminated water to general waste water treatment and to have a separate release after possible reuse for this type of stream.	Generally applicable. For existing units, applicability may require a complete rebuilding of the unit or the installation
iv. Prevention of spillages and leaks	Practices that include utilisation of special procedures and/or temporary equipment to maintain performances when necessary to manage special circumstances such as spills, loss of containment, etc	Generally applicable

[This BAT conclusion is based on information given in Sections 4.15.5.1, 4.15.5.2, and 4.24]

12. In order to reduce the emission load of pollutants in the waste water discharge to the receiving water body, BAT is to remove insoluble and soluble polluting substances by using all of the techniques given below:

Technique	Description	Applicability
i. Removal of insoluble substances by recovering oil	See Section 5.20.2	Generally applicable
ii. Removal of insoluble substances by recovering suspended solids and dispersed oil	See Section 5.20.2	Generally applicable
iii. Removal of soluble substances including biological treatment and clarification	See Section 5.20.2	Generally applicable

[This BAT conclusion is based on information given in Section 4.24.]

BAT-associated emission levels: See Table 5.3.

13. When further removal of organic substances or nitrogen is needed, BAT is to use an additional treatment step as described in Section 5.22.2.

Table 5.3: BAT-associated emission levels for direct waste water discharges from the refining of mineral oil and gas and monitoring frequencies associated with BAT ⁽⁵⁾

Parameter	Unit	BAT-AEL (yearly average)	Monitoring ⁽¹⁾ frequency
Hydrocarbon oil index (HOI)	mg/l	0.1 – 2.5	Daily with EN 9377- 2 analytical method ⁽⁴⁾
Total suspended solids (TSS)	mg/l	5 – 25	Daily
Chemical oxygen demand (COD) ⁽²⁾	mg/l	30 – 125	Daily
BOD ₅	mg/l	No BAT-AEL	Weekly
Total nitrogen ⁽³⁾ (expressed as N)	mg/l	1 – 25 ⁽⁶⁾	Daily
Lead, expressed as Pb	mg/l	0.005– 0.030	Quarterly
Cadmium, expressed as Cd	mg/l	0.002 – 0.008	Quarterly
Nickel, expressed as Ni	mg/l	0.005 – 0.100	Quarterly
Mercury expressed as Hg	mg/l	0.000 1 – 0.001	Quarterly
Vanadium	mg/l	No BAT-AEL	Quarterly
Phenol Index ⁽⁵⁾	mg/l	No BAT-AEL	Monthly with EN 14402 analytical method
Benzene, toluene Ethyl benzene, Xylene (BTEX)	mg/l	Benzene: 0.001 – 0.050 No AEL for T, E, X reporting only	Monthly

⁽¹⁾ Refers to a flow-proportional composite sample taken over a period of 24 hours. Time-proportional sampling can be used provided sufficient flow stability is demonstrated.

⁽²⁾ Where on-site correlation is available, COD may be replaced by TOC. The correlation between COD and TOC should be elaborated on a case by case basis.

⁽³⁾ Where Total-nitrogen is the amount of Total Kjeldahl Nitrogen (TKN), Nitrates and Nitrites

⁽⁴⁾ Moving from the current method to EN 9377-2 may require an adaptation period.

⁽⁵⁾ Not all parameters and sampling frequencies are applicable to effluent from gas refining sites.

⁽⁶⁾ When nitrification/denitrification is used, levels below 15 mg/l can be achieved.

5.1.8 Waste generation and management

14. In order to prevent, or where it is not practicable, to reduce waste generation, BAT is to adopt and implement a waste management plan that, in order of priority, ensures that waste is prepared for reuse, recycling, recovery or disposal.

[This BAT conclusion is based on information given in Section 4.27.1]

15. In order to reduce the amount of sludge to be treated or disposed of, BAT is to use one or a combination of the techniques given below:

Technique	Description	Applicability
i. Sludge pre-treatment	Prior to final treatment (e.g. in a fluidised bed incinerator), the sludges are dewatered and/or de-oiled (by e.g. centrifugal decanters or steam dryers) to reduce their volume and to recover oil from slop equipment	Generally applicable
ii. Reuse of sludge in process units	Certain types of sludge (e.g. oily sludge) can be processed in units (e.g. coking) as part of the feed due to their oil content	Applicability is restricted to sludges that can fulfil the requirements to be processed in units with appropriate treatment

[This BAT conclusion is based on information given in Section 4.25.2]

16. In order to reduce the generation of spent solid catalyst waste, BAT is to use one or a combination of the techniques given below:

Technique	Description
i. Spent solid catalyst management	See Section 5.21
ii. Removal of catalyst from slurry decant oil	See Section 5.21

[This BAT conclusion is based on information given in Section 4.25.3]

5.1.9 Noise

17. In order to prevent or reduce noise, BAT is to use one or a combination of the techniques given below:

- i. make an environmental noise assessment and formulate a noise management plan as appropriate to the local environment;
- ii. enclose noisy equipment/operation in a separate structure/unit;
- iii. use embankments to screen the source of noise;
- iv. use noise protection walls.

[Note: No specific information for noise reduction management from REF BREF]

5.1.10 BAT conclusions for integrated refinery management

18. In order to prevent or reduce diffuse VOC emissions, BAT is to apply the techniques given below:

Technique	Description	Applicability
I. Techniques related to plant design	<ul style="list-style-type: none"> i. limiting the number of potential emission sources ii. maximising inherent process containment features iii. selecting high integrity equipment iv. facilitating monitoring and maintenance activities by ensuring access to potentially leaking components 	Applicability of the techniques may be limited for existing units
II. Techniques related to plant installation and commissioning	<ul style="list-style-type: none"> i. well-defined procedures for construction and assembly ii. robust commissioning and hand-over procedures to ensure that the plant is installed in line with the design requirements. 	Applicability of the techniques may be limited for existing units
III. Techniques related to plant operation	use of a risk-based leak detection and repair (LDAR) programme in order to identify leaking components, and to repair these leaks. See Section 5.19.6	Generally applicable

[This BAT conclusion is based on information given in Sections 4.23.6. and 3.26.1.3]

5.2 BAT conclusions for alkylation process

5.2.1 Hydrofluoric acid alkylation process

19. In order to prevent hydrofluoric acid (HF) emissions to air from the hydrofluoric acid alkylation process, BAT is to use a wet scrubbing technique with alkaline solution to treat incondensable gas streams prior to venting to flare.

Description

See Section 5.19.3.

Applicability:

The technique is generally applicable. Safety requirements, due to the hazardous nature of hydrofluoric acid, are to be considered

20. In order to reduce emissions to water from the hydrofluoric acid alkylation process, BAT is to use a combination of the techniques given below:

Technique	Description	Applicability
i. Precipitation/Neutralisation step	Precipitation (with, e.g. calcium or aluminium-based additives) or system neutralisation (where the effluent is indirectly neutralised with KOH)	Generally applicable. Safety requirements due to the hazardous nature of HF are to be considered
ii. Separation step	The insoluble compounds produced at the first step (e.g. CaF ₂ or AlF ₃) are separated in, e.g. a settlement basin	Generally applicable

[This BAT conclusion is based on information given in Section 4.2.1]

5.2.2 Sulphuric acid alkylation process

21. In order to reduce the emissions to water from the sulphuric acid alkylation process, BAT is to reduce the use of sulphuric acid by regenerating the spent acid and to neutralise waste water generated by this process before routing to waste water treatment.

[This BAT conclusion is based on information given in Section 4.2.2]

5.3 BAT conclusions for base oil production process

22. In order to prevent and reduce the emissions of hazardous substances to air and water from base oil production processes, BAT is to use one or a combination of the techniques given below:

Technique	Description	Applicability
i. Closed process with a solvent recovery	Process where solvent, after being used during base oil manufacturing (e.g in extraction, dewaxing units), is recovered through distillation and stripping steps. (See Section 5.19.7)	Generally applicable
ii. Multi-effect extraction solvent based process	Solvent extraction process including several stages of evaporation (e.g. double or triple effect) for a lower loss of containment	Generally applicable to new units. The use of a triple effect process may be restricted to non-fouling feed stocks
iii. Extraction unit processes using less hazardous substances	Design (new plants) or implement changes (into existing) so that the plant operates a solvent extraction process with the use of a less hazardous solvent: e.g. converting Furfural or Phenol extraction into the n-methylpyrrolidone (NMP) process	Generally applicable to new units. Converting existing units to another solvent based process with different physico-chemical properties may require substantial modifications
iv. Catalytic processes based on hydrogenation	Processes based on conversion of undesired compounds via catalytic hydrogenation similar to hydrotreatment (see Section 5.19.3)	Generally applicable to new units

[This BAT conclusion is based on information given in Sections 4.3.2, 4.3.3, 4.3.9, 4.3.10]

5.4 BAT conclusions for the bitumen production process

23. In order to prevent and reduce emissions to air from the bitumen production process, BAT is to treat the gaseous overhead by using one of the techniques given below:

Technique	Description	Applicability
i. Thermal oxidation of gaseous overhead over 800 °C	See Section 5.19.6	Generally applicable for the bitumen blowing unit
ii. Wet scrubbing of gaseous overhead	See Section 5.19.3	Generally applicable for the bitumen blowing unit

[This BAT conclusion is based on information given in Sections 4.4.1, 4.4.2, 4.4.3 and 4.4.4]

5.5 BAT conclusions for the fluid catalytic cracking process

24. In order to prevent or reduce NO_x emissions to air from the regeneration of the catalyst, BAT is to use one or a combination of the techniques given below:

I. Primary or process related techniques, such as:

Technique	Description	Applicability
Process optimisation and use of promoters or additives		
(a) Process optimisation	Combination of operating conditions or practices aimed at reducing NO _x formation, e.g. lowering the excess oxygen in the flue-gas in full combustion mode, air staging of the CO boiler in partial combustion mode, provided that the CO boiler is appropriately designed.	Generally applicable
(b) Low-NO _x CO oxidation promoters	Use of a substance which selectively promotes the combustion of CO only and prevents the oxidation of the nitrogen which contains intermediates to NO _x : e.g. non-platinum promoters	Applicable only in full combustion mode for the substitution of platinum-based CO promoters. Appropriate distribution of air in the regenerator may be required to obtain the maximum benefit
(c) Specific additives for NO _x reduction	Use of specific catalytic additives for enhancing the reduction of NO by CO	Applicable only in full combustion mode in an appropriate design and with achievable oxygen excess. The applicability of copper-based NO _x reduction additives may be limited by the gas compressor capacity

II. Secondary or end-of-pipe techniques, such as:

Technique	Description	Applicability
i. Selective catalytic reduction (SCR)	See Section 5.19.2	To avoid potential fouling downstream, additional filtering might be required upstream of the SCR. Applying the technique in existing units may require significant space availability
ii. Selective non-catalytic reduction (SNCR)	See Section 5.19.2	For partial combustion FCCs with CO boilers, a sufficient residence time at the appropriate temperature is required. For full combustion FCCs without auxiliary boilers, additional fuel injection (e.g. hydrogen) may be required to match a lower temperature window
iii. Low temperature oxidation	See Section 5.19.2	Need for additional scrubbing capacity. Ozone generation and the associated risk management need to be properly addressed. The applicability may be limited by the need for additional waste water treatment and related cross-media effects (e.g. nitrate emissions) and by an insufficient supply of liquid oxygen (for ozone generation). The applicability of the technique may require significant space availability

BAT-associated emission levels: See Table 5.4.

Table 5.4: BAT-AELs for NO_x emissions from catalytic cracking process (regenerator)

Parameter	Type of units/combustion mode	BAT-AEL (monthly average) (mg/Nm ³)
NO _x expressed as NO ₂	New units/all combustion mode	<30 – 100
	Existing units/full combustion mode	<100 – 300 ⁽¹⁾
	Existing units/partial combustion mode	100 – 400 ⁽¹⁾

⁽¹⁾ When Sb injection is used for metal passivation, NO_x levels up to 700 mg/Nm³ may occur. The lower end of the range can be achieved by using SCR.

The associated monitoring is in BAT 4.

[This BAT conclusion is based on information given in Section 4.5.4.]

25. In order to reduce dust and metals emissions to air from the catalytic cracking process (regenerator), BAT is to use one or a combination of the techniques given below:

I. Primary or process related techniques, such as:

Technique	Description	Applicability
i. Use of an attrition-resistant catalyst	Selection of catalyst substance which is able to resist abrasion and fragmentation in order to reduce dust emissions	Generally applicable provided the activity and selectivity of the catalyst are sufficient
ii. Use of low sulphur feedstock (e.g. by feedstock selection or by hydrotreatment of feed)	Feedstock selection favours low sulphur feedstocks among the possible sources to be processed at the unit. Hydrotreatment aims at reducing thr sulphur, nitrogen and metal contents of the feed. See Section 5.19.3	Requires sufficient availability of low sulphur feedstocks, hydrogen production and hydrogen sulphide (H ₂ S) treatment capacity (e.g. amine and Claus units)

II. Secondary or end-of-pipe techniques, such as:

Technique	Description	Applicability
i. Electrostatic precipitator (ESP)	See Section 5.19.1	For existing units, the applicability may be limited by space availability
ii. Multistage cyclone separators	See Section 5.19.1	Generally applicable
iii. Third stage blowback filter	See Section 5.19.1	Applicability may be restricted due to limited full-scale examples
iv. Wet scrubbing	See Section 5.19.3	The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with high level of salts) cannot be reused or appropriately disposed of. The applicability of the technique may require significant space availability

BAT-associated emission levels: See Table 5.5.

Table 5.5: BAT-associated emission levels for dust emissions from the catalytic cracking process (regenerator)

Parameter	Type of units	BAT-AEL (mg/Nm ³) (monthly average) ⁽¹⁾
Dust	New units	10 – 25
	Existing units	10 – 50 ⁽²⁾

⁽¹⁾ Soot blowing in CO boiler and through the gas cooler is excluded.

⁽²⁾ The lower end of the range can be achieved with a 4-fields ESP.

The associated monitoring is in BAT 4.

[This BAT conclusion is based on information given in Sections 4.5.3. and 4.5.5]

26. In order to prevent or reduce SO_x emissions to air from the catalytic cracking process (regenerator), BAT is to use one or a combination of the techniques given below:

I. Primary or process related techniques, such as:

Technique	Description	Applicability
i. SO _x reducing catalysts additives	Use of a substance which transfers sulphur associated to coke from the regenerator back to the reactor. See description in 5.19.3	Applicability may be restricted by regenerator conditions design. Requires appropriate hydrogen sulphide abatement capacity (e.g. SRU)
ii. Use of low sulphur feedstock (e.g. by feedstock selection or by hydrotreatment of the feed)	Feedstock selection favours low sulphur feedstocks among the possible sources to be processed at the unit. Hydrotreatment aims at reducing the sulphur, nitrogen and metal contents of the feed. See description in 5.19.3	Requires sufficient availability of low sulphur feedstocks, hydrogen production and hydrogen sulphide (H ₂ S) treatment capacity (e.g. amine and Claus units)

II. Secondary or end-of-pipe techniques, such as:

Techniques	Description	Applicability
i. Non-regenerative scrubbing	Wet scrubbing or seawater scrubbing See Section 5.19.3	The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with high level of salts) cannot be reused or appropriately disposed of. The applicability of the technique may require significant space availability
ii. Regenerative scrubbing	Use of specific SO _x absorbing reagent (e.g. absorbing solution) which generally enables the recovery of sulphur as a by-product during a regenerating cycle where the reagent is reused. See Section 5.19.3	The applicability is limited to the case where regenerated by-products can be sold. Retrofitting existing units may be limited by the existing sulphur recovery capacity. The applicability of the technique may require significant space availability

BAT-associated emission levels: See Table 5.6.

Table 5.6: BAT-associated emission levels for SO₂ emissions from catalytic cracking (regenerator)

Parameter	Type of units/mode	BAT-AEL (monthly average) mg/Nm ³
SO ₂	New units	≤ 300
	Existing units/full combustion	<100 – 800 (*)
	Existing units/partial combustion	100 – 1 200(*)

(*) Where selection of low sulphur (e.g. < 0.5 % w/w) feed (or hydrotreatment) and/or scrubbing is applicable, for all combustion modes: ≤ 600 mg/Nm³ can be achieved.

The associated monitoring is in BAT 4.

[This BAT conclusion is based on information given in Sections 3.5.2.1, 4.5.6 and 4.23.5.]

27. In order to reduce carbon monoxide (CO) emissions to air from the regeneration of the catalyst, BAT is to use one or a combination of the techniques given below:

Technique	Description	Applicability
i. Combustion operation control	See Section 5.19.4	Generally applicable
ii. Catalysts with carbon monoxide (CO) oxidation promoters	See Section 5.19.4	Generally applicable only for full combustion mode
iii. Carbon monoxide (CO) boiler	See Section 5.19.4	Generally applicable only for partial combustion mode

BAT-associated emission levels: See Table 5.7.

Table 5.7: BAT-associated emission levels for carbon monoxide emissions from partial combustion mode catalytic cracking (regenerator stack)

Parameter	Combustion mode	BAT-AEL monthly mg/Nm ³
Carbon monoxide, expressed as CO	Partial combustion mode	≤ 100 (*)
(*) May not be achievable when not operating the CO boiler at full load.		

The associated monitoring is in BAT 4.

[This BAT conclusion is based on information given in Section 3.5.2.1 and 4.5]

5.6 BAT conclusions for the catalytic reforming process

28. In order to reduce emissions of PCDD/F to air from the catalytic reforming unit, BAT is to use one or a combination of the techniques given below:

Technique	Description	Applicability
i. Choice of the catalyst promoter	Use of catalyst promoter in order to minimise PCDD/F substances formation during regeneration-See Section 5.19.7	Generally applicable
ii. Treatment of the regeneration flue-gas		
a. Regeneration gas recycling loop with adsorption bed	Waste gas from the regeneration step is treated to remove chlorinated compounds (e.g. dioxins)	Generally applicable to new units. Retrofitting existing units may depend on the current regeneration unit design
b. Wet scrubbing	See Section 5.19.3	Not applicable to semi regenerative reformers
c. Electrostatic precipitator (ESP)	See Section 5.19.1	Not applicable to semi regenerative reformers

[This BAT conclusion is based on information given in Section 4.6.and 3.6]

5.7 BAT conclusions for the coking process

29. In order to reduce emissions to air from coking production processes, BAT is to use one or a combination of the techniques given below:

Primary or process related techniques, such as:

Technique	Description	Applicability
i. Collection and recycling of coke fines	Systematic collection and recycling of coke fines generated during the whole process coking (drilling, handling, crushing, cooling, etc.)	Generally applicable
ii. Handling and storage of coke according to BAT 3	See BAT 3	Generally applicable
iii. Use of a closed blowdown system	Arrestment system for pressure relief from the coke drums	Generally applicable
iv. Recovery of gas (including the final venting) as a component of refinery fuel gas (RFG)	Carrying final venting from the coke drum to the gas compressor to recover as RFG, rather than flaring. For the flexicoking process, a conversion step (to convert the carbonyl sulphide (COS) into H ₂ S) is needed prior to treating the gas from the coking unit	For existing units, the applicability of the techniques may be limited by space availability

30. In order to reduce NO_x emissions to air from the calcining of green coke process, BAT is to use selective non-catalytic reduction (SNCR).

Description: See Section 5.19.2.

Specific applicability for calcining process:

The applicability of the technique may be restricted due to the specificity of the calcining process (e.g. residence time, temperature window).

31. In order to reduce SO_x emissions to air from the calcining of green coke process, BAT is to use one or a combination of the techniques given below:

Technique	Description	Applicability
i. Non-regenerative scrubbing	Wet scrubbing or seawater scrubbing. See Section 5.19.3	The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with high level of salts) cannot be reused or appropriately disposed of. The applicability of the technique may require significant space availability
ii. Regenerative scrubbing	Use of a specific SO _x absorbing reagent (e.g. absorbing solution) which generally enables the recovery of sulphur as a by-product during a regenerating cycle where the reagent is reused. See Section 5.19.3	The applicability is limited to the case where regenerated by-products can be sold. Retrofitting to existing units may be limited by the existing sulphur recovery capacity The applicability of the technique may require significant space availability

32. In order to reduce dust emissions to air from the calcining of green coke process, BAT is to use a combination of the techniques given below:

Technique	Description	Applicability
i. Electrostatic precipitator (ESP)	See Section 5.19.1	For existing units, the applicability may be limited by space availability. For graphite and anode coke calcining production, the applicability may be restricted due to the high resistivity of the coke particles
ii. Multistage cyclone separators	See Section 5.19.1	Generally applicable

BAT-associated emission levels: See Table 5.8

Table 5.8 BAT-associated emission levels for dust from the calcining of green coke process

Parameter	BAT-AEL (monthly average) mg/Nm ³
Dust	10 – 50 ^(1,2,3)
⁽¹⁾ For existing units equipped with a 3-fields ESP, the upper end of the range is 50 mg/Nm ³ ⁽²⁾ The lower end of the range can be achieved with a 4-fields ESP. ⁽³⁾ When an ESP is not applicable, values of up to 150 mg/Nm ³ may occur.	

The associated monitoring is in BAT 4.

5.8 BAT conclusions for the desalting process

33. In order to reduce water consumption and emissions to water from the desalting process, BAT is to use one or a combination of the techniques given below:

Technique	Description	Applicability
i. Recycling water and optimisation of the desalting process	An ensemble of good desalting practices aiming at increasing the efficiency of the desalter and reducing wash water usage e.g. using low shear mixing devices, low water pressure. It includes the management of key parameters for washing (e.g. good mixing) and separation (e.g. pH, density, viscosity, electric field potential for coalescence) steps	Generally applicable
ii. Multistage desalter	Multistage desalters operate with water addition and dehydration, repeated through two stages or more for achieving a better efficiency in the separation and therefore less corrosion in further processes	Applicable for new units
iii. Additional separation step	An additional enhanced oil/water and solid/water separation designed for reducing the charge of oil to the waste water treatment plant and recycling it to the process. This includes, e.g. settling drum, the use of optimum interface level controllers.	Generally applicable

5.9 BAT conclusions for the combustion units

34. In order to prevent or reduce NO_x emissions to air from the combustion units, BAT is to use one or a combination of the techniques given below:

I. Primary or process related techniques, such as:

Technique	Description	Applicability
i. Selection or treatment of fuel		
(a) Use of gas to replace liquid fuel	Gas generally contains less nitrogen than liquid and its combustion leads to a lower level of NO _x emissions. See Section 5.19.3.	The applicability may be limited by the constraints associated with the availability of low sulphur gas fuels, which may be impacted by the energy policy of the Member State
(b) Use of low nitrogen refinery fuel oil (RFO) e.g. by RFO selection or by hydrotreatment of RFO	Refinery fuel oil selection favours low nitrogen liquid fuels among the possible sources to be used at the unit. Hydrotreatment aims at reducing the sulphur, nitrogen and metal contents of the fuel. See Section 5.19.3.	Applicability is limited by the availability of low nitrogen liquid fuels, hydrogen production and hydrogen sulphide (H ₂ S) treatment capacity (e.g. amine and Claus units)
ii. Combustion modifications		
(a) Staged combustion: • air staging • fuel staging	See Section 5.19.2	Fuel staging for mixed or liquid firing may require a specific burner design
(b) Optimisation of combustion	See Section 5.19.2	Generally applicable
(c) Flue-gas recirculation	See Section 5.19.2	Applicable through the use of specific burners with internal recirculation of the flue-gas. The applicability may be restricted to retrofitting external flue-gas recirculation to units with a forced/induced draught mode of operation
(d) Diluent injection	See Section 5.19.2	Generally applicable for gas turbines where appropriate inert diluents are available
(e) Use of low-NO _x burners (LNB)	See Section 5.19.2	Generally applicable for new units taking into account, for LNB, the fuel specific limitation (e.g. for heavy oil). Applicability may be restricted for retrofitting existing units where complexity depends on site specific conditions e.g. furnaces design, surrounding devices. In very specific cases, heavy modifications may be required. The applicability of low-NO _x burners may be restricted for furnaces in the delayed coking process, due to possible coke generation in the furnaces. In gas turbines, the applicability of dry low-NO _x burners is restricted to low hydrogen content fuels (generally < 10 %)

II. Secondary or end-of-pipe techniques, such as:

Technique	Description	Applicability
vi. Selective catalytic reduction (SCR)	See Section 5.19.2	Generally applicable for a new unit The applicability for retrofitting to existing units may be constrained by a significant space availability and the requirements for optimal reactant injection
vii. Selective non-catalytic reduction (SNCR)	See Section 5.19.2	Generally applicable for a new unit The applicability for retrofitting an existing unit may be constrained by the requirement for the temperature window and the residence time to be reached by reactant injection
viii. Low temperature oxidation	See Section 5.19.2	Need for additional scrubbing capacity Ozone generation and the associated risk management need to be properly addressed. The applicability may be limited by the need for additional waste water treatment and related cross-media effects (e.g. nitrate emissions) and by an insufficient supply of liquid oxygen (for ozone generation). The applicability of the technique may require significant space availability
ix. SNO _x combined technique	See Section 5.19.5	Applicable only for high flue-gas flow and when combined NO _x and SO _x abatement is needed

BAT-associated emission levels: See Table 5.9, Table 5.10 and Table 5.11.

Table 5.9 BAT-associated emission levels for NO_x emissions from combustion gas turbines

Parameter	Type of equipment	BAT-AEL ⁽¹⁾ (monthly average) mg/Nm ³ at 15 % O ₂
NO _x expressed as NO ₂	Gas turbine (including combined cycle gas turbines – CCGT) and integrated gasification gas cycle (IGCC)	40 – 120 (existing turbines)
		20 – 50 (new turbines) ⁽²⁾
⁽¹⁾ BAT-AEL refers to emissions from the common stack for the gas turbine and, if present, for the supplementary firing recovery boiler.		
⁽²⁾ For high H ₂ content fuel (i.e. above 10 %), the upper end of the range is 75 mg/Nm ³ .		

The associated monitoring is in BAT 4.

Table 5.10 BAT-associated emission levels for NO_x emissions from gas-firing combustion units, with the exception of gas turbines

Parameter	Type of combustion	BAT-AEL (monthly average) mg/Nm ³
NO _x expressed as NO ₂	Gas firing	30 – 150 for existing units ⁽¹⁾
		30 – 100 for new units
⁽¹⁾ For existing units using high air pre-heat (i.e. > 200 °C) or with H ₂ content in the fuel gas higher than 50 %, the upper end of the BAT-AEL range is 200 mg/Nm ³ .		

The associated monitoring is in BAT 4.

Table 5.11: BAT-associated emission levels for NO_x emissions from multi-fuel firing combustion units with the exception of gas turbines

Parameter	Type of combustion	BAT-AEL (monthly average) mg/Nm ³
NO _x expressed as NO ₂	Multi-fuel firing	30 – 300 for existing units ⁽¹⁾ ⁽²⁾
⁽¹⁾ For existing units < 100 MW with fuel oil nitrogen content higher than 0.5 % (w/w) or with percentage liquid firing > 50 % or using air preheating, values up to 450 mg/Nm ³ may occur. ⁽²⁾ The lower end of the range is achieved when using SCR.		

The associated monitoring is in BAT 4.

[This BAT conclusion is based on information given in Section 4.10.4 and 4.23.3]

35. In order to prevent or reduce dust and metal emissions to air from the combustion units, BAT is to use one or a combination of the techniques given below:

- I. Primary or process related techniques, such as:

Technique	Description	Applicability
i. Selection or treatment of fuel		
(a) Use of gas to replace liquid fuel	Gas instead of liquid combustion leads to lower level of dust emissions See Section 5.19.3	The applicability may be limited by the constraints associated with the availability of low sulphur fuels such as natural gas, which may be impacted by the energy policy of the Member State
(b) Use of low sulphur refinery fuel oil (RFO) e.g. by RFO selection or by hydrotreatment of RFO	Refinery fuel oil selection favours low sulphur liquid fuels among the possible sources to be used at the unit. Hydrotreatment aims at reducing the sulphur, nitrogen and metal contents of the fuel. See Section 5.19.3	The applicability is limited by the availability of low sulphur liquid fuels, hydrogen production and the hydrogen sulphide (H ₂ S) treatment capacity (e.g. amine and Claus units)
ii. Combustion modifications		
(a) Optimisation of combustion	See Section 5.19.2	Generally applicable to all types of combustion
(b) Atomisation of liquid fuel	Use of high pressure to reduce the droplet size of liquid fuel. Recent optimal burner designs generally include steam atomisation	Generally applicable to liquid fuel firing

II. Secondary or end-of-pipe techniques, such as:

Technique	Description	Applicability
i. Electrostatic precipitator (ESP)	See Section 5.19.1	For existing unit, the applicability may be limited by space availability
ii. Third stage blowback filter	See Section 5.19.1	Generally applicable
iii. Wet scrubbing	See Section 5.19.3	The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with a high level of salt) cannot be reused or appropriately disposed of. The applicability of the technique may require significant space availability.
iv. Centrifugal washers	See Section 5.19.1	Generally applicable

BAT-associated emission levels: See Table 5.12.

Table 5.12: BAT-associated emission levels for dust emissions from the combustion units with the exception of gas turbines

Parameter	Type of combustion	BAT-AEL (monthly average) mg/Nm ³
Dust	Multi-fuel firing	5 – 50 for existing units ⁽¹⁾ ⁽²⁾
		5 – 25 for new unit < 50 MW

The associated monitoring is in BAT 4.

[This BAT conclusion is based on information given in Sections 4.10.5, 4.23.4 and 4.5.5.]

36. In order to prevent or reduce SO_x emissions to air from the combustion units, BAT is to use one or a combination of the techniques given below:

- I. Primary or process related techniques based on a selection or a treatment of the fuel, such as:

Technique	Description	Applicability
i. Use of gas to replace liquid fuel	See Section 5.19.3	The applicability may be limited by the constraints associated with the availability of low sulphur fuels such as natural gas, which may be impacted by the energy policy of the Member State
ii. Treatment of refinery fuel gas (RFG)	See Section 5.19.3. Residual H ₂ S concentration in RFG depends on the treatment process parameter, e.g. the amine-scrubbing pressure	For low calorific gas containing carbonyl sulphide (COS) e.g. from coking units, a converter may be required prior to H ₂ S removal
iii. Use of low sulphur refinery fuel oil (RFO) e.g. by RFO selection or by hydrotreatment of RFO	Refinery fuel oil selection favours low sulphur liquid fuels among the possible sources to be used at the unit. Hydrotreatment aims at reducing the sulphur, nitrogen and metal contents of the fuel. See Section 5.19.3	The applicability is limited by the availability of low sulphur liquid fuels, hydrogen production and the hydrogen sulphide (H ₂ S) treatment capacity (e.g. amine and Claus units).

- II. Secondary or end-of-pipe techniques:

Technique	Description	Applicability
i. Non-regenerative scrubbing	Wet scrubbing or seawater scrubbing. See Section 5.19.3	The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with high level of salts) cannot be reused or appropriately disposed of. The applicability of the technique may require significant space availability
ii. Regenerative scrubbing	Use of a specific SO _x absorbing reagent (e.g. absorbing solution) which generally enables the recovery of sulphur as a by-product during a regenerating cycle where the reagent is reused. See Section 5.19.3	The applicability is limited to the case where regenerated by-products can be sold. Retrofitting to existing units may be limited by the existing sulphur recovery capacity. The applicability of the technique may require significant space availability
iii. SNO _x combined technique	See Section 5.19.5	Applicable for high flue-gas (e.g. > 800 000 Nm ³ /h) flow and when combined NO _x and SO _x abatement is required.

BAT-associated emission levels: See Tables Table 5.13 and Table 5.14.

Table 5.13: BAT-associated emission levels for SO₂ emissions from RFG gas firing in combustion units, with the exception of gas turbines

Parameter	BAT-AEL (monthly average) mg/Nm ³
SO ₂	5 – 35 (*)
(*) In the specific configuration of RFG treatment with a low scrubber operative pressure and with a refinery fuel gas with an H/C ratio above 5, the upper end of the range can be as high as 45 mg/Nm ³ .	

The associated monitoring is in BAT 4.

Table 5.14: BAT-associated emission levels for SO₂ emissions from multi-fuel firing in combustion units, with the exception of gas turbines and stationary gas engines

Parameter	BAT-AEL monthly average) mg/Nm ³
SO ₂	35 – 600 (*) for existing units
(*) Refers to the weighted average emissions from multi-fuel firing in combustion units, with the exception of gas turbines and stationary gas engines.	

The associated monitoring is in BAT 4.

[This BAT conclusion is based on information given in Sections 4.10.2, 4.10.3, 4.23.5.4 and 4.5.6.]

37. In order to reduce carbon monoxide (CO) emissions to air, BAT is to use combustion operation control (See Section 5.19.4).

BAT-associated emission levels: See Table 5.15.

Table 5.15: BAT-associated emission levels for carbon monoxide emissions from combustion units

Parameter	BAT-AEL (monthly average) mg/Nm ³
Carbon monoxide, expressed as CO	≤ 100

The associated monitoring is in BAT 4.

[This BAT conclusion is based on information given in Sections 4.10.3]

5.10 BAT conclusions for the etherification process

38. In order to reduce emissions to air from the etherification process, BAT is to ensure the appropriate treatment of process off-gases by routing them to the refinery fuel gas system.
39. In order to prevent upset of the biotreatment, BAT is to use a storage tank and an appropriate unit production plan management to control the toxic components dissolved content (e.g. methanol, formic acid, ethers) of the waste water stream prior to final treatment.

[This BAT conclusion is based on information given in Sections 4.11]

5.11 BAT conclusions for the isomerisation process

40. In order to reduce emissions to air of chlorinated compounds, BAT is to optimise the use of chlorinated organic compounds used to maintain catalyst activity when such a process is in place or to use non chlorinated catalytic systems.

[This BAT conclusion is based on information given in Section 4.16.]

5.12 BAT conclusions for the natural gas refinery

41. In order to reduce sulphur emission to air from the natural gas plant, BAT is to apply BAT 54.
42. In order to reduce nitrogen oxides (NO_x) emission to air from the natural gas plant, BAT is to apply BAT 34
43. In order to prevent emissions of mercury when present in raw natural gas, BAT is to remove it and recover the mercury-containing sludge for waste disposal.

[This BAT conclusion is based on information given in Section 4.17]

5.13 BAT conclusions for the distillation process

- 44. In order to prevent or reduce waste water flow generation from the distillation process, BAT is to use liquid ring vacuum pumps or surface condensers.**

Applicability

May not be applicable in some retrofit cases. For new units, vacuum pumps, either in or not in combination with steam ejectors, may be needed to achieve a high vacuum (10 mm Hg). Also, a spare should be available in case the vacuum pump fails.

- 45. In order to prevent or reduce water pollution from the distillation process, BAT is to route sour water to the stripping unit.**

- 46. In order to prevent or reduce emissions to air from distillation units, BAT is to ensure the appropriate treatment of process off-gases, especially incondensable off-gases, by acid gas removal prior to further use.**

Applicability

Generally applicable for crude and vacuum distillation units. May not be applicable for stand-alone lubricant and bitumen refineries with emissions of less than 1 t/d of sulphur compounds. In specific refinery configurations, applicability may be restricted, due to the need of e.g. large piping, compressors or additional amine treating capacity.

[This BAT conclusion is based on information given in Section 4.19]

5.14 BAT conclusions for the products treatment process

- 47. In order to reduce emissions to air from the products treatment process, BAT is to ensure the appropriate disposal of off-gases, especially odorous spent air from sweetening units, by routing them to destruction by e.g. incineration.**

Applicability

Generally applicable to products treatment processes where the gas streams can be safely processed to the destruction units. May not be applicable to sweetening units, due to safety reasons.

- 48. In order to reduce waste and waste water generation when a products treatment process using caustic is in place, BAT is to use cascading caustic solution and global management of spent caustic, including recycling after appropriate treatment e.g. by stripping.**

[This BAT conclusion is based on information given in Section 4.20]

5.15 BAT conclusions for storage and handling processes

49. In order to reduce VOC emissions to air from the storage of volatile liquid hydrocarbon compounds, BAT is to use floating roof storage tanks equipped with high efficiency seals or a fixed roof tank connected to a vapour recovery system.

Description

High efficiency seals are specific devices for limiting losses of vapour e.g. improved primary seals, additional multiple (secondary or tertiary) seals (according to quantity emitted).

Applicability

The applicability of high efficiency seals may be restricted for retrofitting tertiary seals in existing tanks.

50. In order to reduce VOC emissions to air from the storage of volatile liquid hydrocarbon compounds, BAT is to use one or a combination of the techniques given below:

Technique	Description	Applicability
i. Manual crude oil tank cleaning	Oil tank cleaning is performed by workers entering the tank and removing sludge manually	Generally applicable
ii. Use of a closed-loop system	For internal inspections, tanks have to be periodically emptied, cleaned and rendered gas-free. This cleaning includes dissolving the tank bottom. Closed-loop systems which can be combined with end-of-pipe mobile abatement techniques prevent or reduce VOC emissions	The applicability may be limited by e.g. the type of residues, tank roof construction or tank materials

[This BAT conclusion is based on information given in Section 4.21.11]

51. In order to prevent or reduce emissions to soil and groundwater from the storage of liquid hydrocarbon compounds, BAT is to use one or a combination of the techniques given below:

Technique	Description	Applicability
i. Maintenance programme including corrosion monitoring, prevention and control	A management system including leak detection and operational controls to prevent overfilling, inventory control and risk-based inspection procedures on tanks at intervals to prove their integrity, and maintenance to improve tank containment. It also includes a system response to spill consequences to act before spills can reach the groundwater. To be especially reinforced during maintenance periods	Generally applicable
ii. Double bottomed tanks	A second impervious bottom that provides a measure of protection against releases from the first material	Generally applicable for new tanks and after overhaul of existing tanks ⁽¹⁾
iii. Impervious membrane liners	A continuous leak barrier under the entire bottom surface of the tank	Generally applicable for new tanks and after an overhaul of existing tanks ⁽¹⁾

Technique	Description	Applicability
iv. Sufficient tank farm bund containment	A tank farm bund is designed to contain large spills potentially caused by a shell rupture or overfilling (for both environmental and safety reasons). Size and associated building rules are generally defined by local regulations	Generally applicable.
(1) Techniques ii and iii may not be fully applicable where tanks are dedicated to products that require heat for liquid handling (e.g. bitumen), and where no leak is likely because of solidification.		

[This BAT conclusion is based on information given in Section 4.21.8, 4.21.9]

52. In order to prevent or reduce VOC emissions to air from loading and unloading operations of volatile liquid hydrocarbon compounds, BAT is to use one or a combination of the techniques given below to reach a recovery rate of at least 95 %:

Techniques	Description	Applicability (1)
I. Vapour recovery i. Condensation ii. Absorption iii. Adsorption iv. Membrane separation v. Hybrid systems	See Section 5.19.6	Generally applicable to loading/unloading operations where annual throughput is > 5 000 m ³ /yr. Not applicable to loading/unloading operations for sea-going vessels with an annual throughput < 1 million m ³ /yr
(1) A vapour incineration unit may be substituted for a vapour recovery unit if vapour recovery is unsafe or technically impossible because of the volume of return vapour.		

BAT-associated emission levels: See Table 5.16.

Table 5.16: BAT-associated emission levels for non-methane VOC and benzene emissions to air

Parameter	BAT-AEL (hourly values concentration)(1)
Non-methane volatile organic compounds (NMVOC)	0.15 – 10 g/Nm ³ (2) (3)
Benzene (3)	<1 mg/Nm ³
(1) Hourly values in continuous operation expressed and measured according to Directive 94/63/EC.	
(2) Lower value achievable with two-stage hybrid systems. Upper value achievable with single-stage adsorption or membrane system.	
(3) Benzene monitoring may not be necessary where emissions of NMVOC are in the lower end of the range.	

[This BAT conclusion is based on information given in Section 4.23.6.2]

5.16 BAT conclusions for visbreaking and other thermal processes

53. In order to reduce emissions to water from visbreaking and other thermal processes, BAT is to ensure the appropriate treatment of waste water streams by applying the techniques of BAT 11.

5.17 BAT conclusions for waste gas sulphur treatment

54. In order to reduce sulphur emissions to air from off-gases containing hydrogen sulphides (H₂S), BAT is to use all of the techniques given below:

Technique	Description	Applicability ⁽¹⁾
i. Acid gas removal e.g. by amine treating	See Section 5.19.3	
ii. Sulphur recovery units (SRU) e.g. by Claus process	See Section 5.19.3	
iii. Tail gas treatment unit (TGTU)	See Section 5.19.3	For retrofitting existing SRU, the applicability of the technique may be limited by the SRU size and configuration of the units and the type of sulphur recovery process already in place.
⁽¹⁾ May not be applicable for stand-alone lubricant or bitumen refineries with a release of sulphur compounds of less than 1 t/d		

BAT associated environmental performance levels: see Table 5.17.

Table 5.17: BAT-associated sulphur recovery efficiency for waste gas sulphur (H₂S) removal techniques

Parameter	BAT-associated environmental performance level (monthly average)
Acid gas removal	Achieve hydrogen sulphides (H ₂ S) removal in the treated RFG in order to meet gas firing BAT-AEL for BAT 36
Sulphur recovery efficiency ⁽¹⁾	New units: 99.5 – >99.9 %
	Existing units: ≥ 98.5 %
⁽¹⁾ Sulphur recovery efficiency of the whole treatment chain (e.g. including SRU and TGTU) is calculated as the fraction of sulphur in the feed which is recovered in the sulphur stream routed to the collection pits. When the applied technique does not include a recovery of sulphur (e.g. seawater scrubber), it refers to the sulphur removal efficiency, as the % of sulphur removed by the whole treatment chain.	

The associated monitoring is described in BAT 4.

[This BAT conclusion is based on information given in Sections 4.23.5.1 and 4.23.5.2]

5.18 BAT conclusions for flares

- 55.** In order to prevent emissions to air from flares, BAT is to use flaring only for safety reasons or non-routine operational conditions (e.g. start-ups, shutdown).
- 56.** In order to reduce emissions to air from flares when flaring is unavoidable, BAT is to use the techniques given below:

Technique	Description	Applicability
i. Correct plant design	See Section 5.19.7	Applicable to new units. Flare gas recovery system may be retrofitted in existing units
ii. Plant management	See Section 5.19.7	Generally applicable
iii. Correct flaring devices design	See Section 5.19.7	Applicable to new units
iv. Monitoring and reporting	See Section 5.19.7	Generally applicable

[This BAT conclusion is based on information given in Section 4.23.7]

GLOSSARY

5.19 Description of techniques for the prevention and control of emissions to air

5.19.1 Dust

Technique	Description
Electrostatic precipitator (ESP)	Electrostatic precipitators operate such that particles are charged and separated under the influence of an electrical field. Electrostatic precipitators are capable of operating over a wide range of conditions. Abatement efficiency may depend on the number of fields, residence time (size), catalyst properties and upstream particles removal devices. At FCC units, 3-fields ESPs and 4-fields ESPs are commonly used. ESPs may be used on a dry mode or with ammonia injection to improve the particle collection. For the calcining of green coke, the ESP capture efficiency may be reduced due to the difficulty for coke particles to be electrically charged
Bag filter	Bag filters are constructed from porous woven or felted fabric through which gases are flowed to remove particles. The use of a bag filter requires a fabric material selection adequate to the characteristics of the waste gases and the maximum operating temperature
Multistage cyclone separators	Cyclonic collection device or system installed following the two stages of cyclones. Generally known as a third stage separator, common configuration consists of a single vessel containing many conventional cyclones or improved swirl-tube technology. Performance mainly depends on the particle concentration and size distribution of the catalyst fines downstream of the regenerator internal cyclones
Centrifugal washers	Centrifugal washers combine the cyclone principle and an intensive contact with water e.g. Venturi washer
Third stage blowback filter	Reverse flow (blowback) ceramic or sintered metal filters are devices where after retaining the solids elements at the surface as a cake, it is dislodged by initiating a reverse flow. The dislodged solids are then purged from the filter system

5.19.2 Nitrogen oxides (NO_x)

Technique	Description
Combustion modifications	
Reduction of air/fuel ratio	The technique is mainly based on the following features: <ul style="list-style-type: none"> • minimisation of air leakages into the furnace • careful control of air used for combustion • modified design of the furnace combustion chamber
Staged combustion	<ul style="list-style-type: none"> • Air staging – involves substoichiometric firing and the addition of the remaining air or oxygen into the furnace to complete combustion. • Fuel staging – a low impulse primary flame is developed in the port neck; a secondary flame covers the root of the primary flame reducing its core temperature
Flue-gas recirculation	Implies the reinjection of waste gas from the furnace into the flame to reduce the oxygen content and therefore the temperature of the flame. The use of special burners is based on the internal recirculation of combustion gases which cool the root of the flames and reduce the oxygen content in the hottest part of the flames
Low-NO _x burners	The technique (including ultra-low-NO _x burners) is based on the principles of reducing peak flame temperatures, delaying but completing the combustion and increasing the heat transfer (increased emissivity of the flame). It may be associated with a modified design of the furnace combustion chamber. The design of ultra-low-NO _x burners (ULNB) includes combustion staging (air/fuel) and flue-gas recirculation. Dry low-NO _x - burners (DLNB) are used for gas turbines
Optimisation of combustion	Based on permanent monitoring of appropriate combustion parameters (e.g. O ₂ , CO content, fuel/air (or oxygen) ratio, unburnt components), the technique uses control technology for achieving the best combustion conditions
Diluent injection	Inert diluents, e.g. flue-gas, steam, water, nitrogen added to combustion equipment reduce the flame temperature and consequently the concentration of NO _x in the flue-gases
Selective catalytic reduction (SCR)	The technique is based on the reduction of NO _x to nitrogen in a catalytic bed by reaction with ammonia (in general aqueous solution) at an optimum operating temperature of around 300 – 450 °C. One or two layers of catalyst may be applied. A higher NO _x reduction is achieved with the use of higher amounts of catalyst (two layers)
Selective non-catalytic reduction (SNCR)	The technique is based on the reduction of NO _x to nitrogen by reaction with ammonia or urea at a high temperature. The operating temperature window must be maintained between 900 and 1050 °C for optimal reaction
Low temperature NO _x oxidation	The low temperature oxidation process injects ozone into a flue-gas stream at optimal temperatures below 150 °C, to oxidise insoluble NO and NO ₂ to highly soluble N ₂ O ₅ . The N ₂ O ₅ is removed in a wet scrubber by forming dilute nitric acid waste water that can be used in plant processes or neutralised for release and may need additional nitrogen removal

5.19.3 Sulphur oxides (SO_x)

Technique	Description
Treatment of refinery fuel gas (RFG)	Some refinery fuel gases may be sulphur-free at source (e.g. from catalytic reforming and isomerisation processes) but most other processes produce sulphur-containing gases (e.g. off-gases from the visbreaker, hydrotreater or catalytic cracking units). These gas streams require an appropriate treatment for gas desulphurisation (e.g. by acid gas removal –see infra – to remove H ₂ S) before being released to the refinery fuel gas system
Liquid fuel desulphurisation	In addition to low sulphur crude selection, fuel desulphurisation is made by hydrotreatment process (see infra) where hydrogenation reactions take place and lead to reducing sulphur content
Use of gas to replace liquid fuel	Decrease the use of liquid refinery fuel (generally heavy fuel oil containing sulphur, nitrogen, metals,...) by replacing it with on-site Liquefied Petroleum Gas (LPG) or refinery fuel gas (RFG) or by externally supplied gaseous fuel (e.g. natural gas) with a low level of sulphur and other undesirable substances. At the individual combustion unit level, under multi-fuel firing, a minimum of liquid firing is necessary to ensure flame stability
Use of SO _x reducing catalysts additives	Use of a substance (e.g. metallic oxides catalyst) which transfers sulphur associated with coke from the regenerator back to the reactor. It operates most efficiently in full combustion mode rather than in deep partial-combustion mode. Note: SO _x reducing catalysts additives might have a detrimental effect on dust emissions by increasing catalyst losses due to attrition, and on NO _x emissions by participating in CO promotion, together with the oxidation of SO ₂ to SO ₃
Hydrotreatment	Based on hydrogenation reactions, hydrotreatment aims mainly at producing low-sulphur fuels (e.g. 10 ppm gasoline and diesel) and optimising the process configuration (heavy residue conversion and middle distillate production). It reduces sulphur, nitrogen and metal content of the feed. As hydrogen is required, sufficient production capacity is needed. As the technique transfer sulphur from the feed to hydrogen sulphide (H ₂ S) in the process gas, treatment capacity (e.g. amine and Claus units) is also a possible bottleneck.
Acid gas removal e.g. by amine treating	Separation of acid gas (mainly hydrogen sulphide H ₂ S) from the fuel gases by dissolving it in a chemical solvent (absorption). The commonly used solvents are amines. It is generally the first step treatment needed before elemental sulphur can be recovered in the SRU.
Sulphur recovery unit (SRU)	Specific unit which most often consists of a Claus process for sulphur removal of hydrogen sulphide (H ₂ S)-rich gas streams from amine treating units and sour water strippers. SRU is generally followed by a tail gas treatment unit (TGTU) for remaining H ₂ S removal.
Tail gas treatment unit (TGTU)	A family of techniques, additional to SRU in order to enhance the removal of sulphur compounds. They can be divided into four categories according to the principles applied: <ul style="list-style-type: none"> • direct oxidation to sulphur • continuation of the Claus reaction (sub-dewpoint conditions) • oxidation to SO₂ and recovering sulphur from SO₂ • reduction to H₂S and recovering sulphur from this H₂S (e.g. amine process)
Flue-gas desulphurisation (FGD)	Technique or ensemble of scrubbing techniques where sulphur is removed from flue-gases through various processes generally involving an alkaline sorbent for capturing SO ₂ and transforming it into solid sulphur.

Technique	Description
Wet scrubbing	<p>In the wet scrubbing process, gaseous compounds are dissolved in a suitable liquid (water or alkaline solution). Simultaneous removal of solid and gaseous compounds may be achieved. Downstream of the wet scrubber, the flue-gases are saturated with water and a separation of the droplets is required before discharging the flue-gases. The resulting liquid has to be treated by a waste water process and the insoluble matter is collected by sedimentation or filtration</p> <p>According to the type of scrubbing solution, it can be:</p> <ul style="list-style-type: none"> • a non regenerative technique (e.g. sodium or magnesium based) • a regenerative technique (e.g. amine or soda solution) <p>According to the contact method, the various techniques may require e.g. :</p> <ul style="list-style-type: none"> • Venturi using the energy from inlet gas by spraying it with the liquid; • packed towers, plate towers, spray chambers. <p>Where scrubbers mainly aim at SO_x removal, a suitable design is needed to also efficiently remove dust.</p> <p>The SO_x removal efficiency is in the range 85 – 98 %</p>
Non-regenerative scrubbing	<p>Sodium or magnesium based solution is used as alkaline reagent to absorb SO_x generally as sulphates. Techniques are based on e.g</p> <ul style="list-style-type: none"> • wet limestone • aqueous ammonia • seawater (see infra)
Seawater scrubbing	<p>A specific non regenerative type of scrubbing using alkalinity of the seawater as solvent where large amount of seawater is available. Requires generally an upstream abatement of dust.</p>
Regenerative scrubbing	<p>Use of specific SO_x absorbing reagent (e.g. absorbing solution) which generally enables the recovery of sulphur as a by-product during a regenerating cycle where the reagent is reused.</p>
Dry or semi-dry scrubbing, in combination with a filtration system	<p>Dry powder or a suspension/solution of alkaline reagent are introduced and dispersed in the waste gas stream. The material reacts with the sulphur gaseous species to form a solid which has to be removed by filtration (bag filter or electrostatic precipitator). In general, the use of a reaction tower improves the removal efficiency of the scrubbing system</p>

5.19.4 Carbene monoxide (CO)

Technique	Description
Combustion operation control	<p>The increase in CO emissions due to the application of combustion modifications (primary techniques) for the reduction of NO_x emissions can be limited by a careful control of the operational parameters.</p>
Catalysts with carbon monoxide (CO) oxidation promoters	<p>Use of a substance which selectively promotes the oxidation of CO into CO₂ (combustion).</p>
Carbon monoxide (CO) boiler	<p>Specific post combustion device where CO present in the flue-gas is consumed downstream of the catalyst regenerator to recover the energy. It is usually used only with partial-combustion FCC units</p>

5.19.5 Combined air pollutants emissions prevention and control

Wet scrubbing	See Section 5.19.3
SNO _x combined technique	<p>Combined technique to remove SO_x, NO_x and dust where a first dust-removal stage (ESP) takes place followed by some specific catalytic processes. The sulphur compounds are recovered as commercial-grade concentrated sulphuric acid, while NO_x is reduced to N₂.</p> <p>Overall SO_x removal is in the range: 94 - 96.6 %.</p> <p>Overall NO_x removal is in the range: 87- 90 %</p>

5.19.6 Volatile organic compound (VOC) emissions prevention and control

Vapour balancing	<p>Technique in which, to prevent emissions to atmosphere from loading operations, the expelled mixture is returned to the liquid supply tank and replaces the pumped-out volume. Can be used where loading takes place from tanks, vessels or barges. Vapour can be stored prior to vapour recovery or destruction.</p>
Vapour recovery	<p>Volatile organic compounds which are emitted during loading and unloading operations of most volatile products, especially crude oil and lighter products can be abated by various techniques e.g.:</p> <ul style="list-style-type: none"> • absorption: the vapour molecules dissolve in a suitable absorption liquid (e.g. glycols or mineral oil fractions such as kerosene or reformat). The loaded scrubbing solution is desorbed by reheating in a further step. The desorbed gases must either be condensed, further processed, incinerated or re-absorbed in an appropriate stream (e.g. of the product being recovered) • adsorption: the vapour molecules are retained by activate sites on the surface of adsorbent solid materials, e.g. activated carbon (AC) or zeolite. The adsorbent is periodically regenerated. The resulting desorbate is then absorbed in a circulating stream of the product being recovered in a downstream wash column. Residual gas from wash column is sent to further treatment • membrane gas separation: the vapour molecules are processed through selective membranes to separate the vapour/air mixture into a hydrocarbon-enriched phase (permeate), which is subsequently condensed or absorbed, and a hydrocarbon-depleted phase (retentate). • two stage refrigeration/condensation: by cooling of the vapour/gas mixture the vapour molecules condense and are separated as a liquid. As the humidity leads to the icing-up of the heat exchanger, a two stage condensation process providing for alternate operation is required. • hybrid systems: combinations of available VRUs techniques <p><i>Note: The achievable concentration is expressed for non-methane VOC (NMVOC) as absorption and adsorption processes cannot notably reduce methane emissions.</i></p>

Vapour destruction	<p>Destruction of VOCs can be achieved through e.g. thermal oxidation (incineration) or catalytic oxidation when recovery is not easily feasible. Safety requirements (e.g. flame arrestors) are needed to prevent explosion. Thermal oxidation occurs typically in single chamber, refractory-lined oxidisers equipped with gas burner and a stack. If gasoline is present, heat exchanger efficiency is limited and preheat temperatures are maintained below 180 °C to reduce ignition risk. Operating temperatures range from 760 to 870 °C and residence times are typically 1 second. When a specific incinerator is not available for this purpose, an existing furnace may be used to provided the required temperature and residence times.</p> <p>Catalytic oxidation requires a catalyst to accelerate the rate of oxidation by adsorbing the oxygen and the VOCs on its surface. The catalyst enables the oxidation reaction to occur at lower temperature than required by thermal oxidation: typically ranging from 320° C to 540° C. A first preheating step (electrically or with gas) takes place to reach a temperature necessary to initiate the VOCs catalytic oxidation. An oxidation step occurs when the air is passed through a bed of solid catalysts</p>
LDAR programme	<p>An LDAR programme is a structured approach to reduce fugitive VOC emissions by detection and subsequent repair or replacement of leaking components. Currently, sniffing (described by EN 15446) and optical gas imaging methods are available for the identification of the leaks.</p> <p><i>Sniffing method:</i> The first step is the detection using hand-held VOC analysers measuring the concentration adjacent to the equipment (e.g. by using flame ionisation or photo-ionisation). The second step consists of bagging the component to carry out a direct measurement at the source of emission. This second step is sometimes replaced by mathematical correlation curves derived from statistical results obtained from a large number of previous measurements made on similar components.</p> <p><i>Optical gas imaging methods:</i> Optical imaging uses small lightweight hand-held cameras which enable the visualisation of gas leaks in real time, so that they appear as ‘smoke’ on a video recorder together with the normal image of the component concerned to easily and rapidly locate significant VOC leaks. Active systems produce an image with a back-scattered infra red laser light reflected on the component and its surroundings. Passive systems are based on the natural infra red radiation of the equipment and its surroundings.</p>
VOC diffuse emissions monitoring	<p>Full screening and quantification of site emissions can be undertaken with an appropriate combination of complementary methods, e.g. Solar occultation flux (SOF) or differential absorption lidar (DIAL) campaigns. These results can be used for trend evaluation in time, cross checking and updating/validation of the ongoing LDAR programme.</p> <p><i>Solar occultation flux (SOF):</i> The technique is based on the recording and spectrometric Fourier Transform analysis of a broadband infra red or ultra violet/visible sunlight spectra along a given geographical itinerary, crossing the wind direction and cutting through VOC plumes.</p> <p><i>Differential absorption lidar (DIAL):</i> DIAL is a laser-based technique using differential adsorption LIDAR (light detection and ranging) which is the optical analogue of sonic radio wave based RADAR. The technique relies on the back-scattering of laser beam pulses by atmospheric aerosols, and the analysis of spectral properties of the returned light collected with a telescope.</p>
High integrity equipment	<p>High integrity equipment include e.g.:</p> <ul style="list-style-type: none"> • valves with double packing seals • magnetically driven pumps/compressors/agitators • pumps/compressors/agitators fitted with mechanical seals instead of packing • high-integrity gaskets (such as spiral wound, ring joints) for critical applications.

5.19.7 Other air emissions prevention and control

Techniques to prevent or reduce emissions from flaring	<p>Correct plant design: includes sufficient flare gas recovery system capacity, the use of high integrity relief valves and other measures to use flaring only as a safety system for other than normal operations (start-up, shut down, emergency).</p> <p>Plant management: includes organizational and control measures to reduce the case of flaring by e.g. balancing RFG system, using advanced process control.</p> <p>Flares design includes height, pressure, assistance by steam, air or gas, type of flare tips, etc. It aims at enabling smokeless and reliable operations and ensuring an efficient combustion of excess gases when flaring from non routine operations.</p> <p>Monitoring and reporting: Continuous monitoring (measurements of gas flow and estimations of other parameters) of gas sent to flaring and associated parameters of combustion (e.g. mixture flow gas and heat content, ratio of assistance, velocity, purge gas flowrate, pollutant emissions). Reporting of flaring events makes possible to use flaring ratio as a requirement included in the EMS and to prevent the future ones.</p> <p>Visual remote monitoring of the flare can also be carried out by using colour TV monitors during flare events</p>
Choice of the catalyst promoter to avoid dioxins formation	<p>During the regeneration of the reformer catalyst, organic chloride is generally needed for effective reforming catalyst performance (to re-establish the proper chloride balance in the catalyst and to assure the correct dispersion of the metals). The choice of the appropriate chlorinated compound will have an influence on the possibility of emissions of dioxins and furans</p>
Solvent recovery for base oil production processes	<p>The <i>solvent recovery</i> unit consists in a distillation step where the solvents are recovered from the oil stream and a stripping step (with steam or an inert gas) in a fractionator.</p> <p>The solvents used may be a mixture (DiMe) of 1,2-Dichloroethane (DCE) and Dichloromethane (DCM).</p> <p>In wax-processing units, solvent recovery (e.g. for DCE) is carried out using two systems: one for the deoiled wax and another one for the soft wax. Both consist of heat integrated flashdrums and a vacuum stripper. Streams from the dewaxed oil and waxes product are stripped for removal of traces of solvents.</p>

5.20 Description of techniques for prevention and control of emissions to water

5.20.1 Waste water pre-treatment

Pretreatment of sour water streams before reuse or treatment	Send generated sour water (e.g. from distillation, cracking, coking units) to appropriate pretreatment (e.g. stripper unit)
Pretreatment of other waste water streams prior to treatment	To preserve treatment performance, appropriate pretreatment may be required

5.20.2 Waste water treatment

Removal of insoluble substances by recovering oil.	<p>These techniques include generally</p> <ul style="list-style-type: none"> • API Separators (APIs); • Corrugated Plate Interceptors (CPIs); • Parallel Plate Interceptors (PPIs); • Tilted Plate Interceptors (TPIs); • Buffer and/or equalisation tanks.
Removal of insoluble substances by recovering suspended solid and dispersed oil	<p>These techniques include generally</p> <ul style="list-style-type: none"> • Dissolved Gas Flotation (DGF); • Induced Gas Flotation (IGF); • Sand Filtration.
Removal of soluble substances including biological treatment and clarification	<p>Biological treatment techniques may include:</p> <ul style="list-style-type: none"> • Fixed bed systems; • Suspended bed systems. <p>One of the most commonly used suspended bed system in refineries WWTP is the activated sludge process. Fixed bed systems may be e.g. biofilter or trickling filter.</p>
Additional treatment step	A specific waste water treatment aiming at complementing the previous treatment steps for e.g. further reducing nitrogen or carbon compounds. Generally used where specific requirements for water preservation are locally needed
External waste water treatment	A waste water treatment which is performed by a plant outside the installation

5.21 Description of techniques for the prevention of waste generation and the management of waste

Sludge pretreatment	Prior to final treatment (e.g. in a fluidised bed incinerator), the sludge are dewatered and/or de-oiled (by e.g. centrifugal decanters or steam dryers) to reduce their volume
Reuse of sludge in process units	Certain types of sludge (e.g. oily sludge) can be processed in units (e.g. coking) as part of the feed due to their oil content
Spent solid catalyst management	Scheduled and handling of the materials used as catalyst (e.g. by contractors) in order to recover or reuse them in off site facilities. These operations depend on the type of catalyst and process
Removal of catalyst from slurry decant oil	Decant oil sludge from process units (e.g. FCC unit) can contain significant concentrations of catalyst fines. These fines need to be separated prior to the reuse of decant oil as a feedstock.

6 EMERGING TECHNIQUES

Emerging technique is understood in this document as a novel technique that has not yet been applied in any industrial sector on a commercial basis. This chapter contains these techniques that may appear in the near future and that may be applicable to the refinery sector.

6.1 Refinery activities overview

Throughout its history the refining industry has continuously developed new and improved processes in response to changes in feed quality, product specifications, product slates, new product outlets and economic and environmental requirements. These developments have slowed down in recent years for the following reasons:

- Large oil companies are cutting down on their R&D budgets, and are increasingly relying on third parties for new developments in refinery technology and catalytic processes. These third parties develop techniques for licensing income or for income from catalyst sales. Developments are reported in the technical literature (Hydrocarbon Processing, Chemical Engineering Progress, Oil and Gas Journal, Erdöl, Gas und Kohle, Petroleum Technology Review) and during seminars and conferences (World Petroleum Congress, WEFA, Hart's Fuel Conference, European Refining Technology Conference, NPRA and API specialist meetings) for the dissemination of these techniques.
- Technological developments are concentrating on optimising current systems for higher yields (e.g. more selective catalysts and solvents), higher energy efficiency (e.g. improved reactor design and better heat integration) and shorter downtimes (e.g. scavenging of impurities, automatic cleaning systems), rather than on novel processes.
- The current tool box of conversion, separation, treatment and environmental technologies seems adequate and sufficient to meet any desired product slate and product specifications for the coming decade, as well as meeting stringent regulatory requirements.

Meanwhile, the upgrading process of the refinery sector to implement existing techniques for meeting new product specifications will continue. The rationalisation process in the refining industry also continues and low margins are forcing refineries to look for cost savings.

6.2 Alkylation

6.2.1 Alkylation of parafines

As described in Chapter 2, there are four routes being pursued for development of alkylation:

- Sulphuric acid;
- Hydrofluoric acid;
- Soli-acid;
- Ionic liquids.

6.2.1.1 Sulphuric acid process

This is the most commonly use alkylation process but it has not seen dramatic improvements in recent years.

6.2.1.2 Hydrofluric acid (HF) process

The HF route suffered upgrades aiming to reduce hazardous problems (see Chapter 2)

6.2.1.3 Solid-acid technology

There have been substantial achievements in the following options during recent years and these processes have now become commercially available:

- In the Alkyclean process, simultaneous reactor carries out a mild liquid phase regeneration and periodically a reactor undergoes a higher temperature vapour phase H₂ strip. No generation of acid soluble oils occurs.
- UOP Alkylene is based on increasing the density of catalyst acid sites and achieving high reactivation degree. Impurities in the feedstock do not need treatment. One contract has been awarded in Azerbaijan.
- Exelus Exsact is based on keeping the catalyst stable for up to 24 hours, with periodic catalyst reactivation
- Other initiatives are ongoing and some have reached commercialization (e.g. Fixed Bed of super acid catalyst in solid support by Haldor Topsoe; acid Chevron Isoalky, Eurofuel from Lurgi.).

In the AlkyClean solid-acid process, the reactors operate in the liquid phase at 50 – 90°C at about 21 barg. No chilling is required in this process. The general process scheme (see Figure 6.1 and Figure 6.2) is similar to that used in the case of HF and H₂SO₄ liquid acid alkylation processes. The main difference is the use of a solid-acid catalyst, which does not contain any volatile components. Isobutane is recycled through a set of reactors that contain a fixed-bed catalyst. Olefins are injected in such a way that the olefin is well dispersed in order to keep the olefin concentration low. No corrosive and poisonous liquid acid catalysts are used. The fixed-bed catalyst has a lifetime of several years and therefore catalyst consumption is low, compared to liquid technologies. Furthermore no acid soluble oil waste is formed and no downstream treatment is required to remove traces of liquid acids or halogen compounds from the product. The products contain no nitrogen, sulphur (H₂SO₄ process) or halogens (HF process).

Overall olefin conversion is almost 100 % and yield and quality of the product are similar to that found with the liquid acid processes. Regeneration of the catalyst is carried out continuously by cyclic switching from olefins addition to the addition of a small amount of dissolved hydrogen without changing the reactor conditions.

Depending on the severity of operation, the overall conversion of olefins will drop slowly below 99 – 99.5 %, after some time. Moderate temperature (about 250 °C) regeneration with hydrogen gas is carried out for the complete catalyst activity and selectivity.

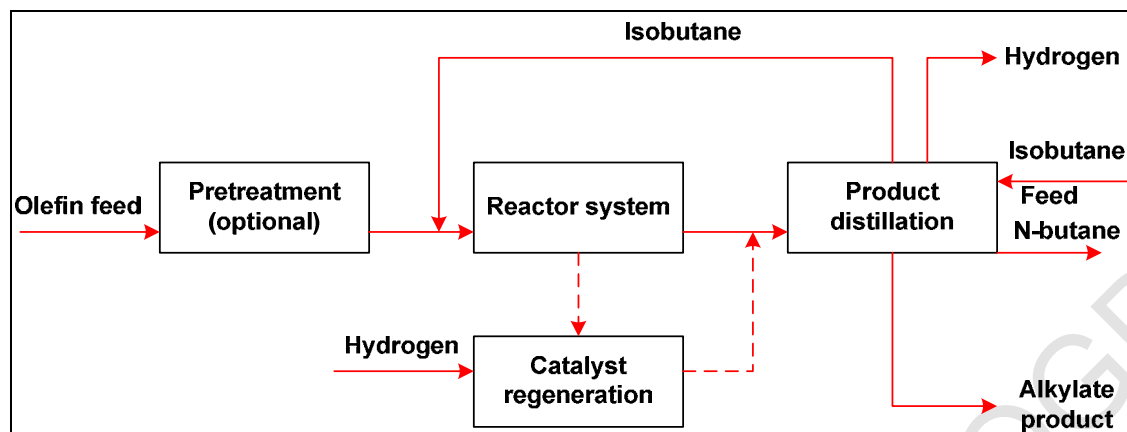


Figure 6.1: Simplified block diagram of the AlkyClean solid-acid alkylation process

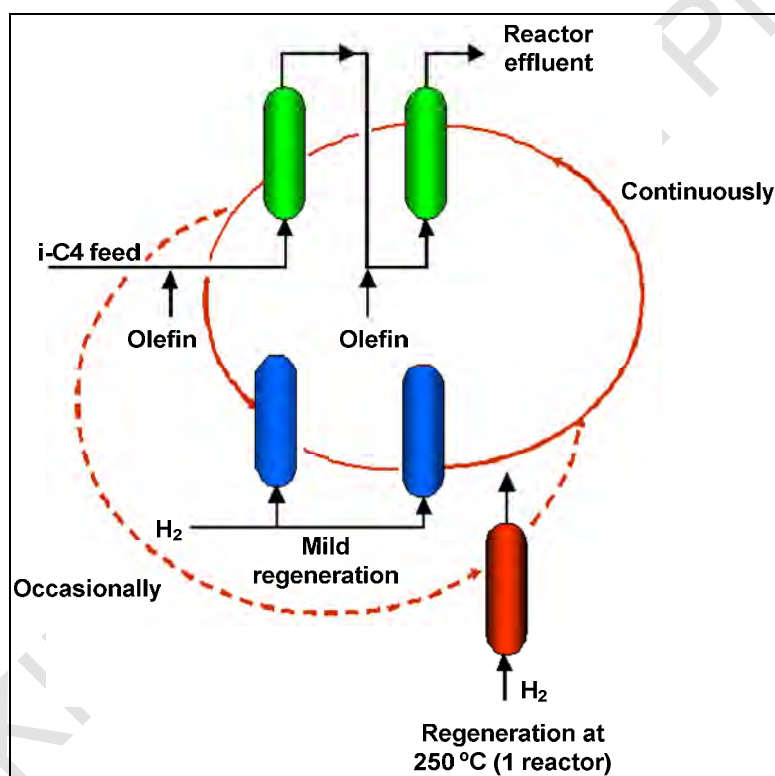


Figure 6.2: Simplified reaction/regeneration scheme of the AlkyClean solid-acid alkylation process

Achieved environmental benefits

The main advantage of the solid-acid alkylation process is the fact that no liquid acids are needed. As a consequence catalyst consumption is the lowest of all the processes. The *in situ* regeneration of the catalyst with hydrogen creates a product gas that can be reused in other applications of the refinery, since it contains no acids or halogens. No routine flaring of gas is required. Also, no waste water nor sludge are produced from the acid neutralisation units. Furthermore, the absence of liquid acids or any halogens will mean that no product treatment or disposal of acids is needed. There will be no acid soluble oil produced in a solid-acid alkylation unit.

No corrosive nor erosive environment is expected in this alkylation process, so on stream reliability is expected to be high and maintenance low compared to HF and sulphuric processes. This reduces the chance of accidental emissions of hydrocarbons (and acids in the case of HF and H₂SO₄).

Cross-media effects

Effluent gas emissions

Gas effluent from regeneration can be used as a diluted hydrogen source or in the refinery fuel gas system. Fugitive emissions contain only hydrocarbons and no acids or acid components. Furthermore, since no corrosive environment is created in the case of solid-acid alkylation, maintenance and repairs are expected to be lower. This will reduce the overall fugitive emission levels of hydrocarbons considerably, compared to liquid acid technologies.

Effluent liquid discharges

None.

Waste elimination

No tars are produced. Only spent catalyst will, after many years of operation, be a solid waste. The catalyst is a fixed-bed catalyst that contains zeolite, alumina and a very low concentration of noble metal. Consequently, it is relatively harmless and can easily be transported for the off-site reclaiming of noble metal. The noble metal is reutilised, while the solids can be reused in the building industry. The amount of spent catalyst produced by the solid-acid alkylation process AlkyClean is about a factor 100 lower than HF alkylation, and a factor 1000 lower than sulphuric alkylation.

Operational data

There are no liquid acids or halogens so there are no corrosion issues. Based on a demonstration plant, the maintenance costs for equipment are expected to be much lower than in the case of the liquid acid processes.

No special safety precautions are required, other than those for any refinery unit processing hydrocarbons.

There is no need for expensive mitigation (acid dump and water spray systems) and vapor pressure suppression facilities, such as that are required for HF units. Compared to H₂SO₄ units, catalyst consumption is lower and does not require large daily transports of spent and regenerated acid to external regeneration facilities.

Applicability

The retrofit of conventional HF or H₂SO₄ units with a solid-acid process is impossible. AlkyClean utilises a swing reactor system, which makes an on-stream catalyst change out of the catalyst possible and thus turnarounds can be tailored to fit the refinery's schedule. In the case of repairs involving one of the reactors, the unit can remain on-stream using the remaining reactors. In addition, it is to be noted that cycling the reactors frequently between reaction and regeneration may lead to additional cost, operating complexity and reliability challenges.

Economics

For solid-acid alkylation, utility and chemical costs will be somewhat higher than reported in the case of hydrofluoric alkylation, but lower than those of the H₂SO₄ process, since the AlkyClean process has much lower catalyst consumption. Table 6.1 shows the data resulting from a US project evaluation in 2008. See also Section 4.2.1 and 4.2.2.

Table 6.1: Utility and chemical costs of the three alkylation processes

Values per tonne of alkylate produced	Sulphuric acid	Hydrofluoric	Solid acid
Utilities			
Electricity (USD 0.06/kWh)	7.7	1.20 – 3.90	8.02
Fuel (USD 0.006/MJ)	No	5.7 – 17.06	No
Steam (USD0.014/kg)	11.71	1.41 – 14.11	14.50
Cooling water (USD 0.026/m ³)	1.90	1.64	0.02
Industrial water	negligible	negligible	negligible
Chemicals			
Fresh acid (kg)	25.74 – 39.6 ⁽²⁾	1.64	13.48 ⁽¹⁾
Caustic (USD 0.55/kg)	0.23	0.31	No
Total	47.28 – 61.14	24.6 – 25.96	36.02
⁽¹⁾ Based on 2008 Pt price and used Pt lease rate 5 %.			
⁽²⁾ Based on sulphuric acid price of USD 330/tonne.			

The overall investment and operational costs for a new alkylation unit are projected to be significantly lower if choosing the solid-acid process instead of an HF unit, due to substantial savings on the safety devices required (e.g. leak detection, water spray systems, acid dump facilities) and safety management procedures and equipment to be implemented for HF Units operation.

Driving force for implementation

Production of an excellent gasoline blending component with a high octane number and low sulphur, nitrogen, benzene and aromatics contents, by using a clean solid-acid catalyst technology that replaces corrosive and poisonous liquid acid technologies. This technique has the potential to provide a dramatic reduction of the environmental impact and risk to refinery employees and nearby communities. This technique was given the ‘Affordable Green Chemistry Award’ in 2010 from the American Chemical Society.

Example plants

No full-size commercial unit is in operation yet. However, the technology has been developed over a 10-year intensive research and development period, on a laboratory and pilot plant scale. During this period Albemarle started a project in cooperation with the engineering company Lummus Technology to check and improve the technology from an engineering point of view.

After the R&D period the catalyst was produced on a full-size commercial plant scale to demonstrate that commercial production of the catalyst is possible. This resulted in a high performance catalyst that was used to operate a demonstration AlkyClean alkylation plant at Neste Oil’s refinery in Porvoo (Finland).

Reference Literature

[52, Broekoven et al. 2008] [53, Van Rooijen et al. 2009].

6.2.1.4 Ionic liquids (IL)

Ionikylation is an isobutane alkylation process. The process uses a composite-Ionic liquid (IL) as homogeneous catalyst for alkylation reactions at ambient temperatures and moderate pressures. ILs are ionic, salt-like materials that are liquid at less than 100° C. ILs have been historically used as solvents and homogeneous catalysts due to their negligible vapour pressure, good solubility to a wide range of organic and inorganic compounds, and ability to be recycled for reuse. Acidic chloroaluminate (III) IL has been used as a homogeneous catalyst for isobutane alkylation. Its use eliminates the diffusion limitation present with solid-acid catalyst systems, and alkylated gasoline is more easily separated from the ionic liquid.

Active components in alkylate gasoline are iso-octane or trimethylpentanes (TMPs). Nevertheless, TMP yield and selectivity, are low with conventional-IL-with and without adjusting the IL's acidity by varying either the molar fraction of aluminum chloride (AlCl₃) of the IL or adding hydrochloric acid (HCl). A study showed that adding aromatic hydrocarbons and metal chlorides to aluminum chloride-dialkyl ether complex enhanced the TMP selectivity.

A pilot plant exists in China (retrofitted into an existing 65 000 t/yr sulphuric acid plant).

Source: O&G Journal, 2006

6.2.2 Alkylation aiming to reduce benzene content in gasoline.

See further Section 6.14 on products treatment.

6.3 Base oil production

A new technology is the application of membranes for solvent recovery in solvent extraction/dewaxing processes. The driving force is the reduction in energy consumption. [202, Dekkers 2000]

6.4 Catalytic cracking

Some promising lines of investigation for the improvement of the environmental performance of catalytic cracking units are:

- The capability to process heavier feedstocks, containing more contaminants (catalyst deactivators) such as vanadium and nickel and having a higher Conradson Carbon Residue (CCR) content. Responses that are being developed are: to continue the development of more active catalysts and more effective (e.g. two-stage) catalyst regeneration. Driving forces are the reduction of residue (i.e. enhanced upgrading) and higher overall refinery efficiency (e.g. the elimination of high vacuum unit operation) [202, Dekkers 2000].
- Improvement of the catalyst separation by use of a magnet (Kellogg Tech company). [191, UBA Austria 1998]

6.5 Catalytic reforming

The current practice of applying continuously improved catalysts (supplied by catalyst manufacturers) is expected to continue. [202, Dekkers 2000]

6.6 Coking

Total coke gasification is regarded as the key future technology for deep desulphurisation and hydrogen production. In this process, crude oil can be refined without the co-production of heavy oil residues.

The interest (research papers and other publications) and investment on the potential refinery use of coke for energy purposes is growing. IGCC and CFB Boiler technologies are being further developed, optimised and applied with the use of coke feedstock.

6.7 Energy system

Some promising lines of investigation for the improvement of the environmental performance of the energy systems are CO₂ abatement techniques (more information in Section 6.15 on Waste gas treatments). Others are the heat integration. The search for further energy improvements is continuing, with the current focus on attractive cogeneration opportunities and more complex heat integration.

6.8 Etherification

Methanol to gasoline (MTG) reactions de-hydrate methanol and convert the available carbon and hydrogen into various hydrocarbons.

The 'Shape-Selective' MTG catalyst limits the synthesis reactions to 10 carbons, which results in a sulphur free gasoline with a typical 92 Research Octane Number (RON)

The first MTG plant (14 500 barrels per day capacity) was operated at Plymouth (New Zealand) from 1985 to 1997, converting natural gas to gasoline.

A second generation MTG plant has started in China (Shanxi province)

Source: Exxon Mobil Research and Engineering

6.9 Hydrogen production

Some promising lines of investigation in hydrogen production technologies are:

- The hydrocarb process, in which the residual oil is essentially cracked to carbon and hydrogen. This process can be seen as an internal source of natural gas for a refinery. The process produces carbon, hydrogen and methanol. It has been calculated in a refinery of 4.98 Mt/yr, that this process can increase by 40 % the total gasoline production, i.e. to 1150 m³/d of methanol and 795 m³/d of C/H₂O slurry [32, Steinberg et al. 1992].
- Methane pyrolysis, which takes advantage of the thermal decomposition of natural gas and the direct production of hydrogen while sequestering the carbon or using the carbon for other commodity purposes. Consequently, the CO₂ generation is completely eliminated [32, Steinberg et al. 1992], [213, Steinberg 2000].

Some hydrogen purification process developments enable lower costs by using new techniques such as structured adsorbent beds and integrated rotary valves. The rapid cycle pressure swing adsorption (RCPSA) process claims to enable:

- cheaper construction costs (30 to 50 %) compared to PSA and low operating costs;
- smaller plot space requirement - as little as one quarter of PSA.

Source: Exxon Mobil Research and Engineering

6.10 Hydrogen-consuming processes

Some promising lines of investigation for the improvement of the environmental performance of energy systems are:

- Residue hydrotreating and hydroconversion processes (e.g. slurry bed technology). These processes have only been demonstrated at a semi-commercial scale and no commercial plants are yet in operation.
- Gasoline deep desulphurisation techniques with a lower hydrogen consumption are currently under development. Parameters are not yet available.

Also, it is to be noted that, bunker fuel oil desulphurisation is one of the next technical challenges ahead that could possibly lead to new techniques or significant improvements in the current ones.

Deep gasoline and gas oil desulphurisation

These process have gained importance during recent years. Many of the new design improvements, optimisation or new grass root processes are now reaching the commercialisation stage.

- In the standard HDS process now operated under more severe conditions, there are a large amount of new generation catalysts that are more active and more selective. These lead to a direct impact on the overall process efficiency.
- New process developments use less H₂ consuming technologies. Reactive adsorption at high temperature using metal oxide sorbent or alumina based adsorption are delivering

promising results. Selective extraction or polar adsorption (Irvad process) are also emerging techniques to consider.

Non H₂ desulphurisation techniques

Oxidative desulphuration may be one of the most promising in this group (see Section 2.13), but there are still some design challenges to overcome.

Below is a list of some other emerging techniques:

- Olefin alkylation of thiophenic sulphur (OATS process by BP);
- Polymer membrane (S-Brane technique by Grace);
- Caustic extraction (Exomer process by Exxon);
- Biochemical desulphurisation (Energy biosystems);
- Selective adsorption (Penn State SARS).

Source: 'Recent advances in the science and technology of ultra low sulphur diesel (ULSD) production'. [80, Stanislaus et al. 2010]

Selective desulphurisation of the main unit feedstock

Treating the primary distillation outlet stream is becoming more common.

Feedstock purification before further use in a refining process includes for example:

- C3 or C4 olefinic cut from FCC: alkynes and diolefins selective hydrogenation before further use in an alkylation or oligomerisation process; naphtha from visbreaking, coking: diolefins and olefins selective hydrogenation before further use in the catalytic reforming process;
- Feedstock purification to obtain on-spec products, for example steam-cracked gasoline: selective hydrogenation of dienes is mandatory in order to stabilise the gasoline without octane loss;
- Feedstock purification to produce petrochemical intermediates, for example a C2 olefinic cut from steam cracking: selective acetylene hydrogenation in order to produce on-spec ethylene without ethylene yield loss.

6.11 Hydrocracking

The treatment of heavier feedstocks require optimal technical solutions that include catalyst and flow scheme considerations. Hydrotreatment is done before the cracking step.

- Once through (85-90 %) conversion is done with minimal investment. Delivers middle distillates and high residue value.
- Single stage full conversion requires medium investment but a higher product quality is achieved. Higher middle distillates selectivity is also achieved.
- Two stag full conversion requires the highest investment costs. This schemes delivers highest quality and best diesel/kerosene ratio (IFP and UOP developments).

6.12 Isomerisation

Catalytic hydroisomerisation of long paraffins to produce biofuels

This technique uses the selectivity of the zeolites to improve the conversion of n-paraffins.

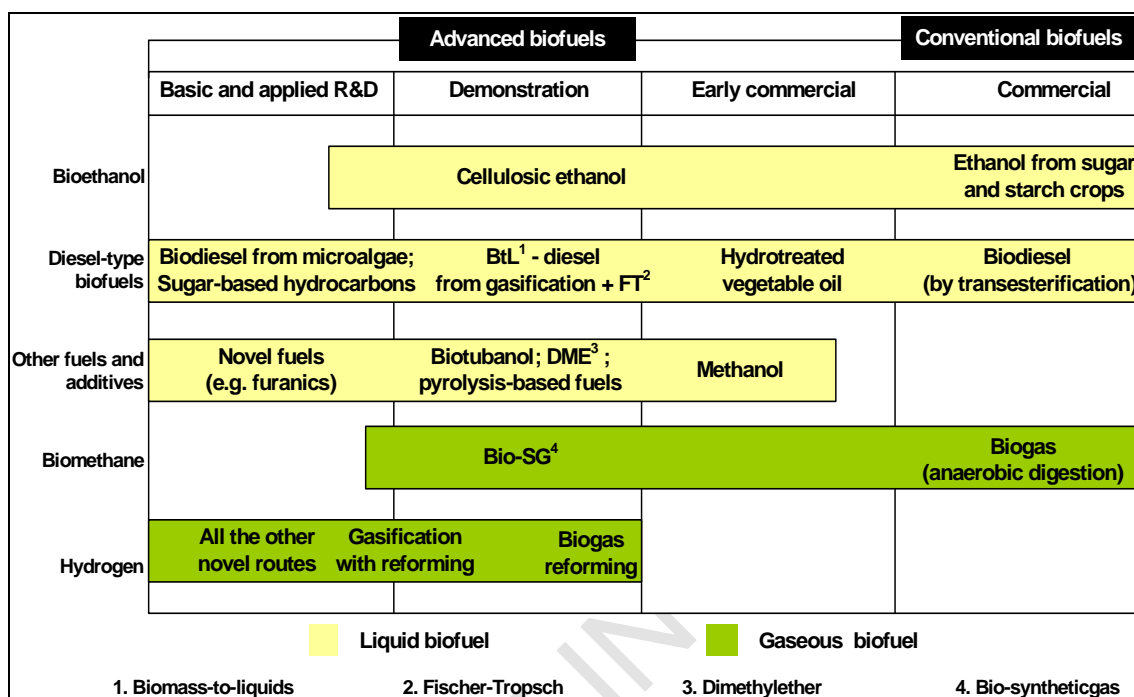


Figure 6.3: Status of main biofuels technologie (Source: International Energy Agency)

The bio gas oils are produced from mainly triglyceride containing feedstocks (vegetable oils, used frying oils, animal fats, etc.) by heterogenic catalytic hydrogenation in one or more stages. They contain mainly normal paraffins which are undesirable due to e.g. freezing points of the C16–C18 normal paraffins being between +18°C and +28°C. For this reason, it is needed to convert the chemical structure of the n-paraffins into isoparaffins having lower freezing points and still high cetane number.

Isomerisation dewaxing (Mobil MIDW) is applied to various streams (renewable diesel dewaxing) and is based on catalyst shape selectivity, including a zeolite and a metal for dehydrogenation/hydrogenation. Selectively converts long chain paraffins to isoparaffins.

This enables fuels to flow at low temperatures. This technique is currently in operation in 8 units.

6.13 Primary distillation

Among developments to reduce the energy consumption by primary distillation in refineries, the divided wall column technique is to be distinguished.

Divided wall column

A DWC is a distillation column that has a vertical partition wall in the central section.

- The column may contain either trays or packing.
- The feed side of the two compartments acts as the prefractionator and the product side as the main column.
- In the case of a sharp split, a DWC can be used to produce three pure products from a single tower.
- A DWC can handle more than three components.

A DWC typically can cut capital and energy costs by approximately 30 % compared to a traditional two-columns system.

6.14 Product treatments

Biodesulphurisation of gas oil and even crude oil: still under development
[202, Dekkers 2000]

Reforming gasoline accounts for 70–85 % of the benzene presented in the gasoline pool (US-EPA).

Pretreatment technologies that withdraw benzene precursors from the reforming feedstock actually are facing some difficulties: e.g. octane and hydrogen forming reduction, and difficulties for complying with benzene specifications. Removing benzene precursors from the reformer feed nearly eliminates (0.3 %w) benzene in the reformat. By using a dehexaniser with a side column, the top composition remains unchanged.

Post-treatment technologies:

- Benzene saturation, converts benzene to cyclohexane, sometimes coupled with isomerization to increase octane. Some of the saturation technology drawbacks are: hydrogen consumption, loss of octane number and benzene conversions that may not be sufficient to achieve the required level.
- Benzene extraction. Gasoline volume reductions, need of proprietary solvents that require a high level of heat, storage facilities and an available market for the extracted benzene are disadvantages of the extraction technology. Expensive.
- Benzene alkylation, offers increments in octane number and gasoline volume, although the technology is considered pioneer. It is the only benzene reduction option that increases the volume for gasoline and does not lead to the consumption of H₂.

6.15 Waste gas treatments

Some developments to be mentioned are:

- biological H₂S removal [4, Hydrocarbon Processing 1998];
- particulate abatement techniques by new developments including ceramic filters (e.g. NGK, Japan) and a rotating particulate separator (Lebon and Gimbrair, the Netherlands);
- CO₂ abatement techniques.

Emerging techniques to enable carbon dioxide capture and storage (CCS)

The production of power and other use of fossil energy are the largest source of greenhouse gas emissions. For many years, there has been considerable international interest in the development of technology for the capture and storage of CO₂, particularly from coal-fired power plants. The IPCC report points out that the technology for capture and storage of CO₂ is not yet mature.

With CCS, a power plant could reduce its CO₂ emissions to the atmosphere by approximately 80–90 % compared to a plant without CCS. At the same time, CCS leads to a loss in overall efficiency of power plants or industrial processes due to the additional energy required for capture, transport and storage. The additional energy required for CCS depends on intrinsic performances of the capture system and on the energy management in the global installation.

A power plant equipped with a CCS system would need roughly 10–40 % more energy than a plant of equivalent output without CCS, of which most is for capture and compression.

As an example, the range reflects three types of power plants: for Natural Gas Combined Cycle plants, the range is 11–22 %, for Pulverized Coal plants, 24–40 % and for Integrated Gasification Combined Cycle plants, 14–25 % (*Source: IPCC report*).

Technique for capturing CO₂

These techniques are still in the early stages of development. The available technology is highly expensive, and there are many uncertainties linked to the costs and operation of a CO₂ chain. They can be divided into three main categories:

- post-combustion;
- pre-combustion;
- oxy-fuel.

Post-combustion entails separating CO₂ from the exhaust gas from the power plant using chemical absorption. Because CO₂ is separated from the exhaust gas, this technology can, in principle, be utilised in existing power plants without major modifications of the plant itself. Post-combustion is considered to be the most mature technology, although there is still significant uncertainty surrounding its use.

With the aid of ***pre-combustion*** technology, CO₂ is captured before combustion. This is accomplished by converting the natural gas to a hydrogen-rich gas mixture. This gas mixture is treated so that CO₂ is captured, and the new fuel is thus 'decarbonised' (exhaust gas contains very little CO₂). Although pre-combustion capture requires modification of the gas turbines to burn hydrogen rich gas streams, the preceding steps are technically proven in the form of ammonia production plants worldwide.

With ***oxy-fuel***, combustion takes place in the gas turbine with pure oxygen instead of air. This means that the exhaust contains water vapour and CO₂, and the CO₂ can be separated out by cooling the exhaust. Today's gas turbines suffer from low performance with oxygen combustion, and to date there has been little effort to develop new types of turbines that are better suited to oxygen combustion. In addition, production of oxygen is energy-intensive, and the corresponding technology is quite costly. Of the three categories of capture technologies, oxy-fuel is the least mature.

The costs associated with capturing CO₂ from a power plant amount to approximately two-thirds of the costs for the entire CO₂ chain, while transport and storage amount to approximately one-third.

Transport of CO₂

CO₂ must be transported from the CO₂ source to the geological structure where the CO₂ will be stored. This transport can be accomplished by pipeline or by ship. Transport is the least complicated element in the CO₂ chain, both as regards technology and the possibility of

evaluating realistic costs. Anyhow, the transport of CO₂ requires substantial resources in terms of energy and costs. As CO₂ behaves very differently under various pressures and temperatures, transport must take place in a controlled manner to avoid the solid state and subsequent clogging of pipes or equipment. The choice of the means of transport will depend on the specific requirements, including the number of emission sources, the volume of emissions from each source, the distance from the source to the storage place and the volume of CO₂ to be transported. With existing technology, pipeline transport is believed to be the simplest and most cost-effective alternative.

Storage of CO₂

There is significant technical potential for storing CO₂ in geological formations around the world. Producing oil and gas fields, abandoned oil and gas fields, and other formations are all candidates for such storage. Storage in reservoirs that are no longer in operation is a good solution in terms of geology; because these structures are likely to be impermeable after having held oil and gas for million of years. Other formations are also considered to be secure storage alternatives for CO₂.

Full-scale test in Norwegian refinery

At the Mongstad refinery, a new combined heat and power (CHP) is to be built to produce 280 MW of electricity and 350 MW of heat. In the agreement with the Norway government, a full-scale carbon capture facility is to be built at the Mongstad refinery. At the time of writing this document, it has been reported that this project will experience an additional delay (2016).

6.16 Waste water treatment

Emerging techniques on this issue are addressed in the CWW BREF [[6, EC 2003](#)].

7 CONCLUDING REMARKS AND RECOMMENDATIONS FOR FUTURE WORK

Timing of the review process

The key milestones of the review process are summarised in the following Table 7.1.

Table 7.1: Key milestones in the review of the BREF for the refining of mineral oil and gas

Key milestone	Date
Reactivation of the TWG	29 January 2008
Call for wishes	7 March 2008
Kick-off meeting	22 – 24 September 2008
Subgroup discussions for elaborating the questionnaire	End of 2008
Collection of information	April 2008 – January 2010
First TWG subgroup meeting on the 'bubble approach'	May 2010
First draft of revised REF BREF (D1)	23 July 2010
Second TWG subgroup meeting on the 'bubble approach'	April 2011
Second draft of revised REF BREF (D2)	16 March 2012
Final TWG meeting	11 – 15 March 2013

During the review process, a total of 19 refinery site visits were carried out, in 9 countries comprising mainly oil refineries of various sizes, configurations and levels of complexity, and also some gas refineries.

Sources of information and information gaps

A large number of documents were shared by the TWG to assist the review of the BREF for the Refining of Mineral Oil and Gas (REF BREF), principally via the Commission's BAT Information System (BATIS), thereby ensuring a high level of transparency.

Major contributions

Contributions included information on general aspects of the refining sector and also more specific information on refining units and particularly data emissions and techniques

The data collection exercise provided a large basis for emissions data and techniques in use at the refinery site level: a total of 62 filled-in site specific questionnaires were received by the European IPPC Bureau. In addition, during the commenting periods on the first and second draft of the revised REF BREF, complementary information, generally focusing on specific issues or process units was provided. In particular, detailed information on emissions data was provided by CONCAWE (Industrial NGO) after the second draft. This information was shared via BATIS.

Information on specific issues discussed at the final TWG meeting

Emissions to water of nitrogen compounds:

Based on the data from the refinery effluents, it was agreed that there is no need to monitor ammoniacal nitrogen, since the pH values are low enough and therefore will not lead to the formation of toxic compounds.

Emissions to water of phenols:

It was agreed that the current data on phenols were misleading (data showing both phenol and phenol index results in the same table in Chapters 3 and 4) and that for the next review it is recommended to collect and use the data from monitoring of the phenol index instead of phenol.

Degree of consensus reached during the information exchange

A high degree of consensus was reached on the BAT conclusions. Nevertheless, some dissenting views were raised, as described in the following table.

References

Table 7.2: Split views

Split view number	TWG member	Expression of the split view
1	AT, DE,EEB SE	A dissenting view was expressed by Austria, Germany and the European Environmental Bureau (EEB) who consider that, BAT-associated emission levels (BAT-AELs) for emissions to water should refer, in general, to a short-term averaging period i.e. daily average. A dissenting view was also expressed by Sweden proposing to express BAT-AELs for emissions to water as specific loads with the following levels: <ul style="list-style-type: none"> • COD: 10 – 50 g/t crude (yearly average); • Total Nitrogen: 2 – 15 g/t crude (yearly average).
2	AT, DE, NL and EEB	A dissenting view was expressed by Austria, Germany, the Netherlands and the European Environmental Bureau who considered that, BAT-associated emission levels (BAT-AELs) for emissions to air should, in general, refer to a short-term averaging period i.e. daily averages
4	CONCAWE	A dissenting view was expressed by CONCAWE. This TWG member considers that, the applicability restrictions should include economic considerations e.g. by referring to 'high investments and operational costs' to clarify that the applicability of some specific BATs (e.g. ESP, wet gas scrubber, COS converter) may be restricted for existing units
5	CZ, EL, ES and CONCAWE	A dissenting view was expressed by CONCAWE, the Czech Republic, Greece and Spain who consider, that the BAT-associated emission level (BAT-AEL) ranges for emissions to air of SO ₂ from the catalytic cracking units should be the following: <ul style="list-style-type: none"> • 100–1 000 mg/Nm³ for existing units in full combustion mode, • 100–1 700 mg/Nm³ for existing units in partial combustion mode.
6	CZ, EL, FI, PT, and CONCAWE	A dissenting view was expressed by CONCAWE, the Czech Republic, Greece, Finland and Portugal who consider that the BAT-associated emission level (BAT-AEL) ranges for emissions to air of NO _x from the catalytic cracking units in full combustion mode should be complemented by the following footnote (²): (²) In some FCC designs, all secondary techniques include applicability restrictions and in case the NO _x additive reduction efficiency is limited to less than 50 %, NO _x levels up to 400 mg/Nm ³ may occur
7	NL and EEB BE and SE	A dissenting view was expressed by the Netherlands and the EEB, who consider that, the BAT-associated environmental performance level (BAT-AEPL) range for the sulphur recovery efficiency of sulphur recovery units should be 99.5 – 99.9 % for both new and existing units. A dissenting view was expressed by Belgium and Sweden, who consider that the BAT-associated environmental performance level (BAT-AEPL) range for the sulphur recovery efficiency of sulphur recovery units should be ≥ 99 % for existing units
8	CZ, EL, IT and CONCAWE	A dissenting view was expressed by CONCAWE, the Czech Republic, Greece and Italy who consider that, the BAT-AEL range for gas-fired existing combustion units of less than 50 MW should be the following: <ul style="list-style-type: none"> • NO_x: 30 – 300 mg/Nm³

In addition, during the final TWG meeting, it was acknowledged that: *'The links between the 'bubble approach' and the implementation of the IED need further legal consideration. The Commission Services will consider the most appropriate way to take into account the outcome of the TWG meeting and to continue the work on this issue over the next months'*.

{Pending this further work, the dissenting view expressed by CONCAWE, the Czech Republic, Greece, Spain, Finland, France, Italy, Poland, Portugal, Sweden and Slovakia who consider that the BAT conclusions should make reference to the bubble approach, has been recorded in the conclusions of the TWG meeting, but is not reported in the previous table.}

Consultation of the Forum and subsequent formal adoption procedure of the BAT Conclusions

{At a later stage, the opinion of the Forum and any other information concerning the formal adoption of the BAT conclusions will be added here.}

Recommendations for future work

The information exchange revealed a number of issues where further information should be collected during the next review of the REF BREF. These recommendations include:

- Emissions to water:
 - To collect short term emissions data, expressed both in loads and in concentrations linked to the use of the techniques;
 - To collect and use the data from monitoring of the phenol index instead of phenol.
- Emissions to air:
 - emissions to air of dioxins and furans (PCDD/F) from catalytic reformer units should be further assessed;
 - emissions of metals from FCC units and combustion units should be further assessed (including from gas-firing combustion units);
 - the impact of the use of low N feedstock on NO_x emissions from FCC units should be further studied;
 - specific data should be collected in order to assess the potential detrimental effect of the use of additives for sulphur reduction on dust emissions and the related abatement systems;
 - to reconsider the issue of new combustion units (both gas and multi-fuel firing) as, due to lack of data, no BAT conclusions and BAT-AELs for SO₂ and NO_x have been set for new units;
 - to consider collecting robust data on NO_x emissions from coking processes;
 - to consider the ongoing work in the EU regarding an EN standardisation for diffuse VOC emissions monitoring methods.

Suggested topics for future R&D work

The Commission is launching and supporting, through its Research and Technological Development programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially, these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the European IPPC Bureau of any research results which are relevant to the scope of this document.

WORKING DRAFT IN PROGRESS

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WORKING DRAFT IN PROGRESS

GLOSSARY

This glossary is meant to facilitate the understanding of the information contained in this document. The definitions of terms in this glossary are not legal definitions (even if some of them may coincide with definitions given in European legislation), they are meant to help the reader understand some key terms in the context of their use in the specific sector covered by this document.

This glossary is divided up into the following sections:

1. ISO country codes
2. Monetary units
3. Unit prefixes
4. Units
5. Chemical elements
6. Chemical formulae commonly used in this document
7. Acronyms and technical definitions

8.1 ISO country codes

ISO code	Country
<i>Member States</i> (°)	
AT	Austria
BE	Belgium
BG	Bulgaria
CZ	Czech Republic
CY	Cyprus
DE	Germany
DK	Denmark
EE	Estonia
EL	Greece
ES	Spain
FI	Finland
FR	France
HU	Hungary
HR	Croatia
IE	Ireland
IT	Italy
LT	Lithuania
LU	Luxembourg
LV	Latvia
MT	Malta
NL	Netherlands
PL	Poland
PT	Portugal
RO	Romania
SE	Sweden
SI	Slovenia
SK	Slovakia
UK	United Kingdom
<i>Non-member countries</i>	
CH	Switzerland
MK	Former Yugoslav Republic of Macedonia
NO	Norway
TR	Turkey
US	United States
(°) The protocol order of the Member States is based on the alphabetical order of their geographical names in the original language(s).	

8.2 Monetary units

Code ⁽¹⁾	Country/territory	Currency
<i>Member State currencies</i>		
EUR	Euro area ⁽²⁾	euro (pl. euros)
BGN	Bulgaria	lev (pl. leva)
CZK	Czech Republic	Czech koruna (pl. koruny)
DKK	Denmark	Danish krone (pl. kroner)
GBP	United Kingdom	pound sterling (inv.)
HUF	Hungary	forint (inv.)
LTL	Lithuania	litas (pl. litai)
PLN	Poland	zloty (pl. zlotys)
RON	Romania	Romanian leu (pl. lei)
SEK	Sweden	krona (pl. kronor)
<i>Other currencies</i>		
CHF	Switzerland	Swiss franc
JPY	Japan	yen
NOK	Norway	Norwegian krone
USD	United States	US dollar

⁽¹⁾ ISO 4217 codes.
⁽²⁾ Includes Austria, Belgium, Cyprus, Estonia, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, Malta, the Netherlands, Portugal, Slovakia, Slovenia and Spain.

8.3 Unit prefixes

Symbol	Prefix	10 ⁿ	Word	Decimal Number
T	tera	10 ¹²	Trillion	1 000 000 000 000
G	giga	10 ⁹	Billion	1 000 000 000
M	mega	10 ⁶	Million	1 000 000
k	kilo	10 ³	Thousand	1 000
-----	-----	1	One	1
c	centi	10 ⁻²	Hundredth	0.01
m	milli	10 ⁻³	Thousandth	0.001
μ	micro	10 ⁻⁶	Millionth	0.000 001
n	nano	10 ⁻⁹	Billionth	0.000 000 001

8.4 Units

Unit	Unit Name	Measure name (Symbol)	Conversion
A	ampere	Electric current	
atm	normal atmosphere	Pressure	1 atm = 101 325 Pa
bar	bar	Pressure	1.013 bar = 100 kPa = 1 atm
barg	bar of gauge pressure.	Pressure relative to current atmospheric pressure	
bbl	US barrel	Volume	US barrel = 159 litres
bpcd	barrels per calendar day	Average flowrates based on operating 365 d/yr	
bpsd	barrels per stream day	Flowrates based on actual on-stream time of a unit	
Btu	British thermal unit	Energy	1 Btu ~ 1 054 J 1 TBtu ~ 1.054 million GJ
°C	degree Celsius	Temperature	
°API	degree API	Density	Specific density = 141.5/(°API+131.5)
d	day	Time	
dB(A)	decibel	Noise unit A-weighting sound pressure level	
FOE	fuel oil equivalent	Energy	1 tonne FOE = 4.25•10 ¹⁰ J
g	gram	Weight	
h	hour	Time	
ha	hectare	Area	1 ha = 10 ⁴ m ²
Hz	hertz	Frequency	
J	joule	Energy	
K	Kelvin	Temperature	0 °C = 273.15 K
kcal	kilocalorie	Energy	1 kcal = 4.1868 kJ
kg	kilogram	Weight	
kWh	kilowatt-hour	Energy	1 kWh = 3 600 kJ
l	litre	Volume	
m	metre	Length	
m ²	square metre	Area	
m ³	cubic metre	Volume	
min	minute	Time	
MW	megawatts	Energy	
Mt/yr	Million of tonnes per year	Throughput annual amount	
N	Newton	Force	1 N= 1 kg m/s ²
Nm ³	normal cubic metre	Volume at 101.325 kPa, 273 K	
Pa	pascal	Pressure	1 Pa = 1 N/m ²
ppb	parts per billion	Composition of mixtures	
ppm	parts per million	Composition of mixtures	
ppmw	parts per million (by weight)	Composition of mixtures	
psi	pounds per inch	Pressure	1 bar = 14.5 psi
ppmv	parts per million (by volume)	Composition of mixtures	
s	second	Time	
sq ft	square foot	Area	1 sq ft = 0.092 m ²
St	stokes	Kinematic viscosity	1 St = 10 ⁻⁴ m ² /s
t	metric tonne	Weight	1 t = 1 000 kg or 10 ⁶ g
t/d	tonnes per day	Materials consumption	
t/yr	tonnes per year	Materials consumption	
V	volt	Voltage - Electric potential	
% v/v	percentage by volume	Composition of mixtures	
% w/w	percentage by weight	Composition of mixtures	
W	watt	Power	
yr	year	Time	
Ω	ohm	Electrical resistance	

8.5 Chemical elements

Symbol	Name	Symbol	Name
Ac	Actinium	Mn	Manganese
Ag	Silver	Mo	Molybdenum
Al	Aluminium	N	Nitrogen
Am	Americium	Na	Sodium
Ar	Argon	Nb	Niobium
As	Arsenic	Nd	Neodymium
At	Astatine	Ne	Neon
Au	Gold	Ni	Nickel
B	Boron	No	Nobelium
Ba	Barium	Np	Neptunium
Be	Beryllium	O	Oxygen
Bi	Bismuth	Os	Osmium
Bk	Berkelium	P	Phosphorus
Br	Bromine	Pa	Protactinium
C	Carbon	Pb	Lead
Ca	Calcium	Pd	Palladium
Cd	Cadmium	Pm	Promethium
Ce	Cerium	Po	Polonium
Cf	Californium	Pr	Praseodymium
Cl	Chlorine	Pt	Platinum
Cm	Curium	Pu	Plutonium
Co	Cobalt	Ra	Radium
Cr	Chromium	Rb	Rubidium
Cs	Caesium	Re	Rhenium
Cu	Copper	Rf	Rutherfordium
Dy	Dysprosium	Rh	Rhodium
Er	Erbium	Rn	Radon
Es	Einsteinium	Ru	Ruthenium
Eu	Europium	S	Sulphur
F	Fluorine	Sb	Antimony
Fe	Iron	Sc	Scandium
Fm	Fermium	Se	Selenium
Fr	Francium	Si	Silicon
Ga	Gallium	Sm	Samarium
Gd	Gadolinium	Sn	Tin
Ge	Germanium	Sr	Strontium
H	Hydrogen	Ta	Tantalum
He	Helium	Tb	Terbium
Hf	Hafnium	Tc	Technetium
Hg	Mercury	Te	Tellurium
Ho	Holmium	Th	Thorium
I	Iodine	Ti	Titanium
In	Indium	Tl	Thallium
Ir	Iridium	Tm	Thulium
K	Potassium	U	Uranium
Kr	Krypton	V	Vanadium
La	Lanthanum	W	Tungsten
Li	Lithium	Xe	Xenon
Lr	Lawrencium	Y	Yttrium
Lu	Lutetium	Yb	Ytterbium
Md	Mendelevium	Zn	Zinc
Mg	Magnesium	Zr	Zirconium

8.6 Chemical formulae commonly used in this document

Chemical formula	Name
HF	Hydrofluoric acid
KOH	Potassium hydroxide. Also called caustic potash
H ₂ O ₂	Hydrogen peroxide
H ₂ SO ₄	Sulphuric acid
HCl	Hydrochloric acid
MEK	Methyl ethyl ketone
MIBK	Methyl isobutyl ketone
NaOH	Sodium hydroxide. Also called caustic soda
NH ₄ -N	Ammonium (calculated as N)
NO ₂ -N	Nitrite (calculated as N)
NO ₃ -N	Nitrate (calculated as N)
NO _x	The sum of nitric or nitrogen(II) oxide (NO) and nitrogen dioxide (NO ₂) expressed as NO ₂
SO _x	The sum of sulphur dioxide (SO ₂) and sulphur trioxide (SO ₃) expressed as SO ₂

8.7 Acronyms and technical definitions

A

Absorption	A volume process in which one substance permeates another (soaking up)
AC	Alternating Current
AC	Activated Carbon
ACC	Annualised capital charge
Adsorption	A surface process. The adhesion of molecules of a gas, liquid or dissolved substance to a solid surface resulting in the formation of a thin film on the surface of the solid (surface assimilation)
Amylenes	Pentenes
AOC	Accidentaly Oil Contaminated
API	American Petroleum Institute
API separator	Oil/water/sludge separator (developed by the American Petroleum Institute)
ASU	Activated Sludge Unit
Auto-Oil	Co-operative programmes between the EU and the oil and motor industries to find the most cost-effective way to improve air quality in Europe. These have led to Directives on fuel properties and vehicle emissions.

B

BAT-AEL	Emission level associated with the best available techniques
BBU	Bitumen Blowing Unit
BFO	Bunker Fuel Oil
BFW	Boiler Feed Water to produce steam or hot water
Biofuel	Liquid or gaseous fuel for transport produced from biomass
BOD	Biochemical Oxygen Demand
BREF	Best Available Techniques reference document
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
BTX	Benzene, Toluene, Xylene

C

CAGR	Compound Annual Gross Rate
CAS	Cemical abstracts service (registry number)
cat cracker	Catalytic cracker (typically refers to fluid catalytic cracker)
CCGT	Combined Cycle Gas Turbine
CCR	Conradson Carbon Residue (See under Concarbon more information)
CDD/CDF	Chlorodibenzoparadiioxins/furans
CDU	Atmospheric Crude Distillation Unit
CEMS	Continuous emissions monitoring system.
CHP	Combined Heat and Power (co-generation)
CMR	Carcinogenic, mutagenic, reprotoxic
COC	Continuously Oil Contaminated
COD	Chemical Oxygen Demand
Concarbon	Conradson carbon = measurement of carbon residue (expressed in % w/w). Measurement of the tendency of a hydrocarbon to form coke.
CONCAWE	European Refinery Association for Environment, Health and Safety
CORINAIR	European Air Emissions inventory
CPI	Corrugated Plated Interceptor
C _x	Hydrocarbons with x number of carbons
CW	Cooling Water

D

DAF	Dissolved Air Flotation
DGF	Dissolved Gas Flotation
DC	Direct Current
DCU	Delayed Coker Unit
DENOX	Process/technique for reducing nitrogen oxides from waste gases

DESOX	Process/technique for reducing sulphur oxides from waste gases
DEA	Diethanol Amine
DGA	Diglycolamine
DIAL	Differential absorption light detection and ranging
DIPA	Di-isopropanol amine
DNB	Nitrification/denitrification biotreater
DS	Dissolved Solids
E	
EEA	European Environment Agency
EEB	European Environmental Bureau
EFRT	External Floating Roof Tanks
EFTA	European Free Trade Association (established on 3 May 1960)
EIA	Environmental Impact Assessment
EII	Energy intensity index (Solomon index. See Section 3.10.1)
EIPPCB	European IPPC Bureau
EMAS	European Community Eco-Management and Audit Scheme (EC 1221/2009).
EMS	Environmental Management System (see Section 4.15.1)
Emissions factor	The estimated average emissions rate of a given pollutant for a given source, relative to units of activity
EN	European Norming standard
EOP	End-of-pipe
EPA	(United States) Environmental Protection Agency (also USEPA)
ETBE	Ethyl tert-butyl ether
EU	European Union.
EU-27	Member States of the European Union from 1 January 2007
EU+	EU-27 plus Croatia, the Former Yugoslav Republic of Macedonia, Norway, Switzerland and Turkey
F	
FAME	Fatty acid methyl ester (reference: EN 14214)
FBI	Fluidised-bed Incinerator
FC	Flue Control
FCC	Fluidised-bed Catalytic Cracking or Fluid Catalytic Cracker
FCCU	Fluidised-bed Catalytic Cracking Unit or Fluid Catalytic Cracker Unit
FF	Fresh feed (used for operating cost e.g. EUR/tonnes FF)
FFU	Flocculation/flotation unit
FGD	Flue-gas Desulphurisation
FGR	Flue-gas Recirculation
FID	Flame ionisation detector
FOE	Fuel oil equivalent
FRT	Fixed roof tank
G	
GAC	Granular activated carbon
GC	Gas Chromatography
GCV	Gross calorific value (see also NCV)
GO	Gas oil
GT	Gas turbine
GTCC	Gas turbine combined cycle.
H	
HC (1)	Hydrocarbon
HC (2)	Hydrocracking
HCU	Hydrocracker Unit
HDM	Hydrodemetallisation
HDS	Hydrodesulphurisation

HFO	Heavy Fuel Oil
HGO	Heavy Gas oil
HHV	Higher Heating value (see also LHV)
HORC	Heavy Oil and Residue Catalytic cracking
HP	High Pressure
HSE	Health, Safety and Environment
HT	High Temperature
HVU	High Vacuum Unit
Hydrofiner	Selective hydrocracking
I	
I-TEQ _{DF}	International toxic equivalent of dioxins/furans
IAF	Induced Air Flotation
IED	Industrial Emissions Directive (2010/75/EU)
IFRT	Internal Floating Roof Tank
IGF	Induced Gas Flotation
IGCC	Integrated Gasification Combined Cycle
IMO	International Maritime Organisation
IMPEL	European Union Network for the Implementation and Enforcement of Environmental Law
IPPC	Integrated pollution prevention and control
ISO	International Organisation for Standardization
I-TEQ	International toxicity equivalence (used for PCDD/F)
K	
kero	kerosene
L	
LCO	Light Coking Oil
LCP	Large Combustion Plant
LDAR	Leakage Detection and Repair Programme
LGO	Light Gas oil
LHV	Lower Heating Value (see also HHV)
LP	Low Pressure
LPG	Liquefied Petroleum Gas
LT	Low Temperature
LVGO	Light Vacuum Gas oil
LVOC	Large Volume Organic Chemicals
M	
MAH	Mono Aromatic Hydrocarbon
MAH (2)	Major accident and hazard
MDEA	Mono diethanolamine
MEA	Mono ethanolamine
MP	Medium Pressure
MS	EU Member State
MTBE	Methyl Tert-butyl Ether
N	
n-	normal, linear organic compound
N-	Normal (refers to volume of gases under normal conditions: temperature 0 °C and pressure of 1 atmosphere (101.3 kPa)
NA	Not available (typically for data not available within the document)
Naphthenic	The naphthenes contain one or more saturated rings of 5 or 6 carbon atoms in their molecules to which paraffinic-type branches are attached.
NCV	Net calorific value or lower heat value (LHV) (see also: GCV)
NG	Natural gas

NGO	Non governmental organisation
NMVO	Non-methane volatile organic compounds
NOC	Non-oil contaminated
NO _x	Nitrogen Oxides (NO + NO ₂ , normally expressed as NO ₂)
O	
OP	Operational costs (fixed or variable)
P	
PAC	Powdered activated carbon
PAH	Polycyclic Aromatic Hydrocarbons
PC	Pressure Control
PCDD/F	Polychlorodibenzoparadioxins/furans
Platformer	Type of catalytic reformer
PM	Particulate Matter
PM ₁₀	Particulate matter of size less than 10 µm
PM _{2.5}	Particulate matter of size less than 2.5 µm
Poly-unit	Polymerisation unit
PPI	Parallel Plate Interceptor
PPS	Pressurised cross flow plate separation of the desalting unit
PSA	Pressure-swing adsorption used for purification of hydrogen
Pt-based	Used for catalists containing platinum
PUF	Pick-up factors- kg SO ₂ removed per kg additive introduced
R	
RCC	Residue Catalytic Cracker
Residue	The heaviest fractions of the distillation and conversion units. These fractions are used as feedstock in other processes or as liquid refinery fuel.
RFG	Refinery Fuel Gas
RO	Reversed Osmosis
RON	Research Octane Number
RSH	Mercaptan
RVP	Reid Vapour Pressure
S	
S	Sulphur
SCR	Selective Catalytic Reduction –
SF	Sand Filter
SNCR	Selective Non-Catalytic Reduction
SO _x	Sulphur oxides (SO ₂ and SO ₃)
SRA	Sulphur reduction additives
SRU	Sulphur Recovery Unit
SS	Suspended Solids
SW	Sour Water
SWS	Sour Water Stripper
T	
TAME	Tertiary Amyl Methyl Ether
TCDD/F	Tetrachlorodibenzoparadioxins/furans (toxicity reference for dioxins)
TEC	Total erected cost
TEL	Tetra ethyl lead
TKN	Total Kjeldahl nitrogen - the sum of organic nitrogen, ammonia (NH ₃) and ammonium (NH ₄ ⁺) in the chemical analysis of soil, water, or waste water.
TGT	Tail Gas Treatment of the sulphur recovery unit
TML	Tetra methyl lead
TN	Total nitrogen – the sum of total kjeldahl nitrogen and nitrate and nitrite
TOC	Total Organic Carbon

Annexes

TSS	Total Suspended Solids (water)
TSS (2)	Third-stage separator (air)
TWG	European Technical Working Group on refineries
U	
U	Unit (used together with names of process)
UF	Ultrafiltration
Ultraformer	Type of reformer
USEPA	Environmental Protection Agency of the United States
V	
V.I.	Viscosity Index
VBU	Visbreaking Unit
VGO	Vacuum gas oil
VOC	Volatile Organic Compound
VR	Vacuum Residue
VRO	Vacuum residue oil
VRU	Vapour Recovery Unit
VSBGO	Visbreaking Gas oil
W	
WGS	Wet gas scrubber
WHB	Waste Heat Boiler
WWTP	Waste Water Treatment Plant
Z	
Zeolites	Microporous, aluminosilicate minerals commonly used as molecular sieves.

9 ANNEXES

9.1 Refinery configurations

Worldwide there are in total approximately 650 refineries. Every year on average between four and six brand-new refineries come on-stream, mainly outside Europe (China, India). On the other hand the origin of some of the oldest refineries still in operation dates back to the end of last century. Many of these refineries have been extended and modernised since. Basically there are about 25 typical refinery processes (excluding treatment) used in the refinery industry. The simplest type, the so-called hydroskimming refinery, comprises a minimum of five processing units. Some large and complex refineries can comprise up to fifteen different processing units or more.

In this section four of the most common refinery schemes or configurations will be discussed in detail. The classification of refineries into these configurations is slightly arbitrary. Other approaches do exist, but the main purpose is to illustrate the great diversity of refinery types in existence.

Configuration	Units included
1	Hydroskimming (Base Scheme) + Isomerisation Unit
2	Base Scheme + High Vacuum Unit + Fluid Cracking Unit + MTBE Unit + Alkylation Unit + Visbreaker
3	Base Scheme + High Vacuum Unit + Hydrocracker Unit + Isomerisation Unit (+ Delayed Coker Unit)
4	Large complex refinery comprising Scheme 2 + Hydrocracker (+ Hydrogen Residue Cracking unit + IGCC + Petrochemical feedstock production + Flexicoker)

The overall block flow diagrams of the above four configurations are shown in Figure 9.1 to Figure 9.4

The first diagram is the aforementioned 'Hydroskimming' refinery including an Isomerisation Unit. Such a refinery merely produces fuels such as gasoline, kerosene (jet fuel), middle distillates (diesel and light heating oil) and fuel oil, in a ratio determined by the crude oil composition. By adding a Vacuum Distillation Unit and conversion units the atmospheric residue from the Crude Distillation Unit can be converted to lower boiling fuels with higher product values. Two schemes will be discussed, to cover the most commonly used conversion processes, i.e. Fluid Catalytic Cracking and Hydrocracking. The Fluid Catalytic cracker (FCC) configuration (N°2) may include an MTBE unit and an Alkylation unit to increase the production and to improve the quality of the gasoline. A Thermal Cracker or Visbreaker unit is often also included in this scheme to reduce the quantity of the heavy fuel oil. The Hydrocracker configuration (N°3) may include a Delayed Coker unit to reduce heavy fuel production and to maximise light fuels production. The last configuration included in this overview is a large, very complex refinery. Besides a Hydrocracker and an FCC unit, this refinery scheme includes units for the conversion of the vacuum residue, a Residue Hydroconversion unit and an Integrated Gasification Combined Cycle Unit.

The complexity of the above 4 configurations (Simple, Complex catalytic cracking, Complex hydrocracking, and Very Complex) can be quantified and various approaches prevail in the Industry. One approach is to express each processing unit in its so-called 'equivalent distillation capacity' (EDC), and calculate the sum of these EDCs as a total refinery EDC (the crude distillation unit has an EDC of 1 by definition). The complexity is then the sum of EDCs.

Another approach is to express the conversion (of residual material into distillates) of each conversion unit into its 'catalytic cracking equivalency', and then to define the refinery complexity as the sum of all the catalytic cracking equivalencies. In comparing refineries, both

the configuration (which units are in) and the complexity (what is the capacity of these units) are important to consider.

Energy requirements will generally increase from configuration 1 to 4 and with complexity. Similar generalisations can be made regarding e.g. process water requirements, sulphur production (at same sulphur intake) etc., but qualifications often need to be made. In the schemes that represent the configurations in the following pages, processing units are abbreviated; for more details on these process units, see the Glossary.

9.1.1 Configuration 1: hydroskimming + isomerisation unit

This is the simplest type of refinery, producing fuels by straightforward operations (see Figure 9.1). This type of refinery has a very rigid product distribution pattern; the produced fuels are almost entirely fixed by the type of crude being processed. The production cannot be greatly influenced by changing the operating modes of the various processing units.

Many of the Hydroskimming refineries were built in the fifties and sixties when the demand for all fuels increased significantly, the cost of crude was relatively low and the demand for heavy fuel oil was relatively high. In the seventies and eighties the majority of the Hydroskimming refineries were expanded to include a cracking complex, but quite a lot of Hydroskimming refineries dating from that period are still in operation. In the Crude Oil Distillation Unit the crude oil is fractionated into straight-run naphtha overhead product, kerosene, gas oil side-stream products and atmospheric residue product from the bottom of the column. The straight-run unstabilised naphtha is passed to the Naphtha Hydrotreating Unit to make it suitable for Catalytic Reforming. The hydrotreated naphtha stream is split into a light and a heavy naphtha fraction.

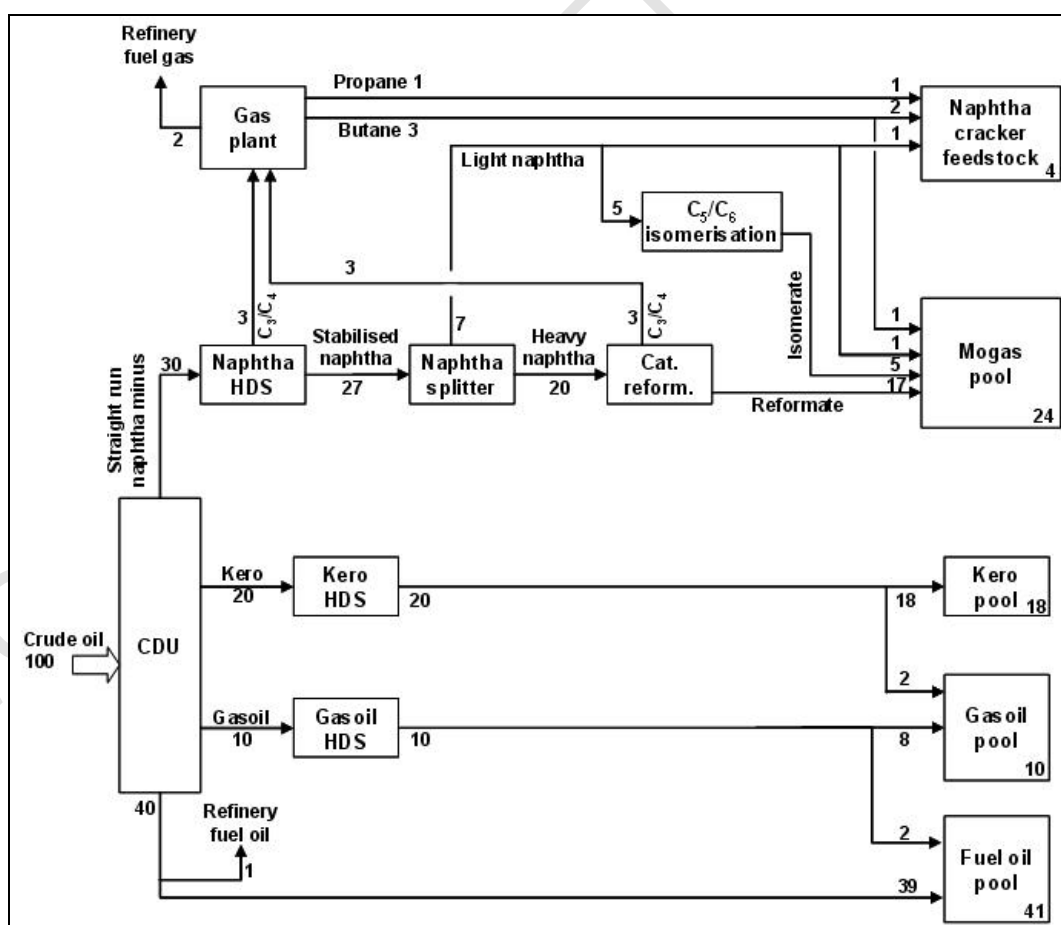


Figure 9.1: Scheme 1: Hydroskimming and isomerisation unit

In the past part of the light naphtha fraction was used as mogas (motor gasoline) blend component, and the balance was sold as feedstock to Naphtha Crackers. More recently, as a result of the lead (TEL) phase-out programme, many Isomerisation Units are included in the Hydroskimming refineries to isomerise the light naphtha stream. The isomerate produced has a roughly 20 - 25 higher octane number than its feed and compensates for the loss of octane resulting from the lead phase-out. This avoids the complete light naphtha stream being sold as low value feedstock to Naphtha Crackers. The heavy naphtha fraction from the Naphtha Hydrotreater is upgraded in the Catalytic Reformer to a high-octane gasoline-blending component. The hydrogen from the Catalytic Reformer is used to desulphurise the gas oil and naphtha. Normally two grades of gasoline are produced in a refinery, regular and premium gasoline. These grades of gasoline are produced by blending different ratios of isomerate, reformat and butane. Saturated light hydrocarbons from the CDU Naphtha Hydrotreater, Isomerisation Unit and Catalytic Reformer Unit are sent to the Gas Plant. Propane from the Gas Plant is either sold directly as propane product or blended with butane to be sold as LPG. A proportion of the butanes produced in the Gas Plant is used as blend stock for the mogas pool, the remainder of the butanes are either blended with propane to be sold as LPG or directly sold as butane product. The components lighter than propane are sent to the refinery fuel gas system. Straight-run kerosene is often hydrotreated in the Kero Hydrotreating Unit (or kero HDS) and run down as jet fuel. Normally a portion of the hydrotreated kerosene is used as blending component for the automotive diesel oil pool.

Straight-run gas oil is hydrotreated in the Gas Oil Hydrotreating Unit to reduce its sulphur content. Automotive diesel oil is produced by blending desulphurised kerosene with desulphurised gas oil. Heating oil and marine diesel oil (MDO) are produced by blending desulphurised gas oil with straight-run gas oil. Both products have higher maximum allowable sulphur contents than diesel oil. Heavy fuel oil is produced from atmospheric residue with adjustment for viscosity and sulphur content by addition of desulphurised gas oil. In some cases the atmospheric residue is thermally cracked. This is not indicated in the configuration scheme. The sour off-gases from the Naphtha Hydrotreater, the Kerosene and Gas Oil Hydrotreating units (or Gas oil HDS) are treated in the Amine Treating Unit to remove H₂S and other sour components present, prior to being sent to the refinery fuel gas system. The sour LPG stream from the Naphtha Hydrotreater is also treated in the Amine Unit to reduce its sulphur content before combining with the sweet LPG stream from the Catalytic Reformers. Sour waste water from all process units is stripped, prior to utilisation as wash water in the Desalter and final purification in Effluent Water Treating facilities. The sour off-gas from the Sour Water Stripper is combined with the H₂S rich-off-gas from the Amine Unit and sent to a Sulphur Recovery Unit (SRU), where the H₂S is converted to elemental sulphur, and a nearly sulphur-free off-gas is vented to the atmosphere.

9.1.2 Configuration 2: catalytic cracker configuration

Scheme 2 is a configuration whereby the Hydroskimming refinery is extended with a High Vacuum Unit (HVU), a Fluid Catalytic Cracking Unit (FCC unit) and a Visbreaker Unit (VBU). In this refinery configuration, a considerable part of the atmospheric residue is converted into lighter fuel components (see Figure 9.2.). As a result, the production of residual fuel oil and/or the export of atmospheric residue is considerably reduced. FCC units are specifically designed to increase the production of gasoline. Depending on the refinery market and strategy, a significant quantity of kerosene can also be produced, when the heavier fraction of the catcracked naphtha is separated and hydrotreated along with the straight-run kerosene product. The overall yield of middle distillates is also increased due to the production of 'light cycle oil'.

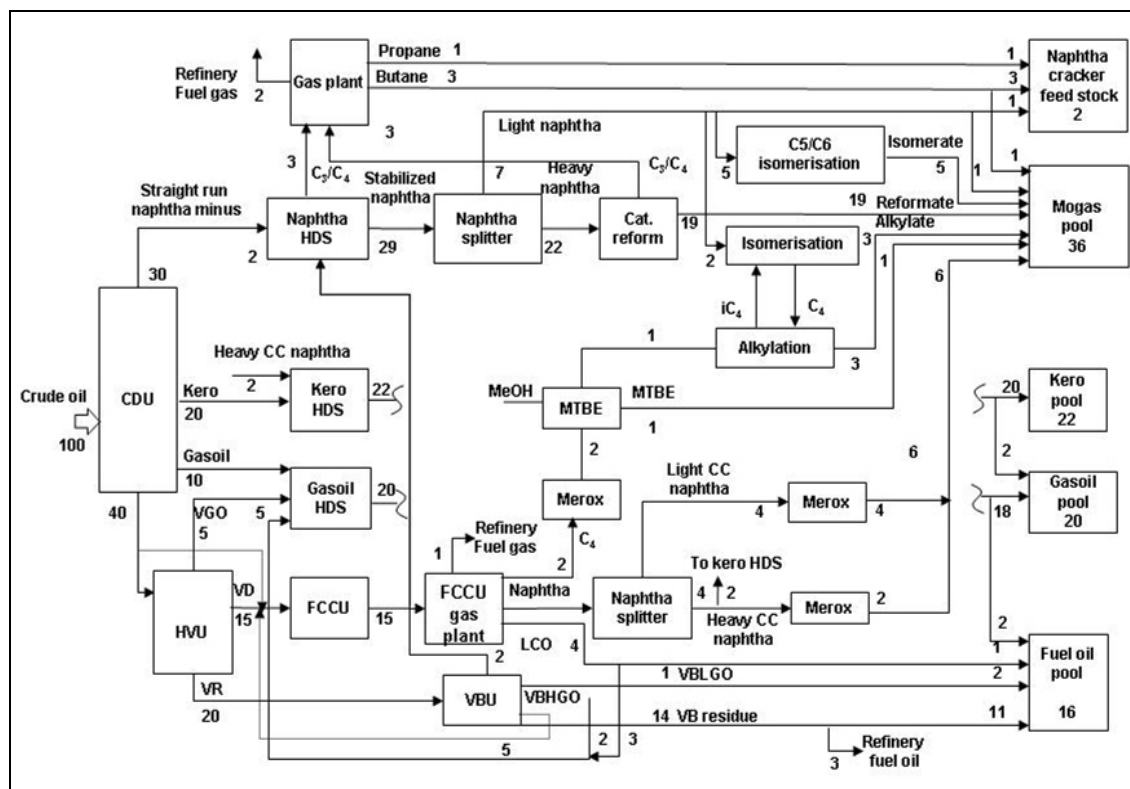


Figure 9.2: Scheme 2: Catalytic cracker configuration

Many Catalytic cracker refineries in Europe include a Visbreaker Unit to reduce the heavy fuel oil production. If no VBU is applied, significant quantities of high value gas oil components will have to be blended to the vacuum residue product, mainly to meet the viscosity specifications of heavy fuel oil. The VBU converts the vacuum residue into a residue which has a much lower viscosity and also produces some naphtha and gas. This type of refinery has a flexible product distribution pattern. The fuel slate can be significantly influenced by changing the operating modes of the various processing units and by the blending of products. This type of refinery configuration is predominant in Europe. Most of these FCC refineries were built in the fifties and sixties as a simple Hydroskimming refinery. In the seventies and eighties, a Catalytic cracker complex was added to these refineries.

9.1.3 Configuration 3: hydrocracker configuration

Scheme 3 is a Hydroskimming refinery expanded with an HVU, Hydrocracker Unit (HCU) and e.g. a Delayed Coker Unit (DCU, see Figure 9.3.). In this configuration, an even larger part of the atmospheric residue is converted into lighter fuel components together with reduced production of residual fuel oil. The addition of a Coker allows this refinery to eliminate the production of residual fuel oil completely. HCU units are specifically used to maximise the production of gasoline and middle distillates. A limited number of Hydrocracker refineries in Europe include a Delayed Coker Unit (DCU) to reduce heavy fuel production and maximise light fuels production. The DCU converts heavy residues in lighter hydrocarbon fractions and petroleum coke. Dependent on the quality, coke is used in the cement and steel or in the aluminium industry. The hydrogen necessary for the HCU is supplied by a Hydrogen Plant. A Catalytic Reformer does not normally produce enough hydrogen for the HCU. Alternatively, the supplemental hydrogen requirement can be provided via partial oxidation of heavy hydrocarbons followed by hydrogen separation.

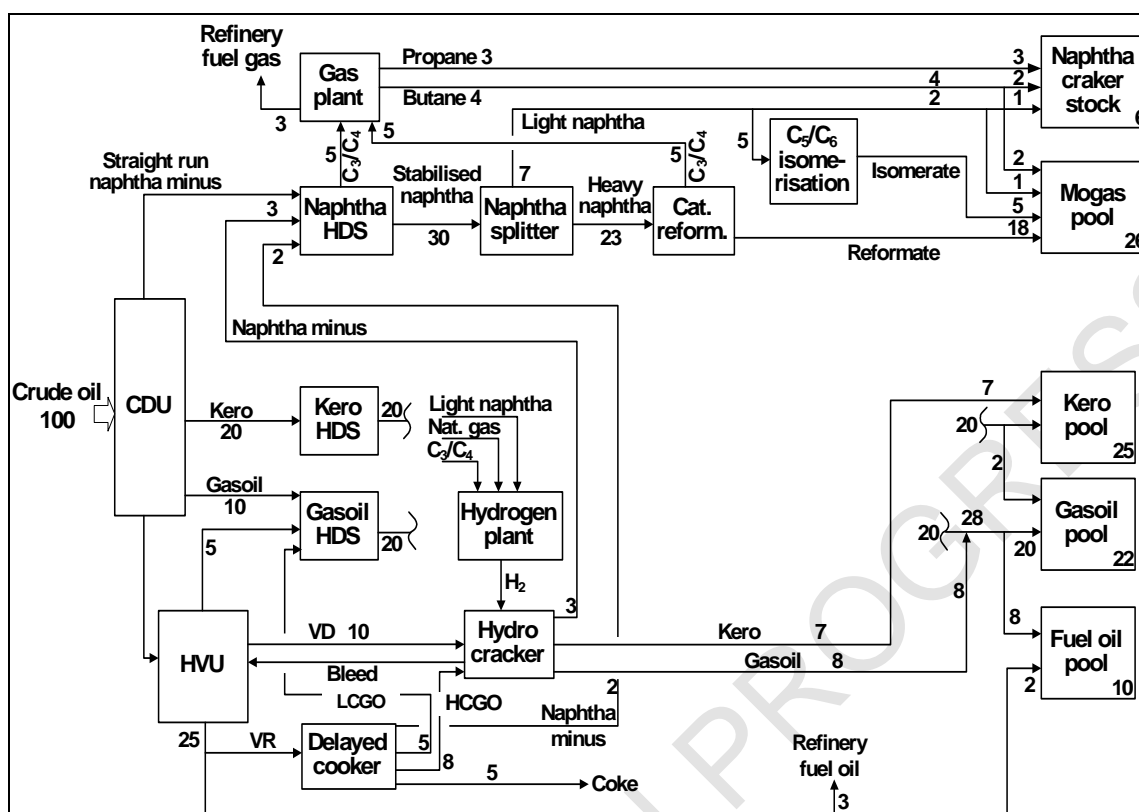


Figure 9.3: Scheme 3: Hydrocracker configuration

This type of refinery has a higher degree of flexibility with respect to either maximum gasoline or maximum middle distillate production, whereas a FCC configuration is primarily focused on increased gasoline production. About 15 % of the existing refinery complexes in Europe have already been extended with a Hydrocracker. It should be noted that such extensions require a relatively high capital investment and high energy consumption compared to the installation of a Catalytic cracker.

9.1.4 Configuration 4: complex refinery with hydroconversion and IGCC

Scheme 4 is a refinery with a Hydrocracker and additional 'deep conversion'. With a Residue Hydrocracker and/or a Gasification Unit (IGCC), so that even more conversion capacity for heavier feed stocks is introduced (see Figure 9.4). This is an example of a large complex refinery, and it includes some options to produce high value petrochemical feedstocks. This extended range of heavy residue conversion techniques can in principle eliminate the need for mixing heavy residue to the fuel oil pool or can process more heavy crude oils. The Residue Hydrocracker, i.e. Hycon, H-oil Unit or other types of Residue Hydrocrackers, converts vacuum residues to high-value transportation fuels e.g. gasolines, kerosene and diesel. The addition of a Residue Hydrocracker to a refinery provides considerable flexibility and increases production of gasoline and middle distillate fuels at the expense of fuel oil. The IGCC converts the visbreaker residue to power, steam, hydrogen, and some waste streams. The main advantage of this arrangement is the production of hydrogen by use of low-value vacuum residue instead of the more valuable light naphtha, other light hydrocarbon streams or natural gas. Moreover, the fuel oil production is reduced and the production of LPG and diesel fuels is increased.

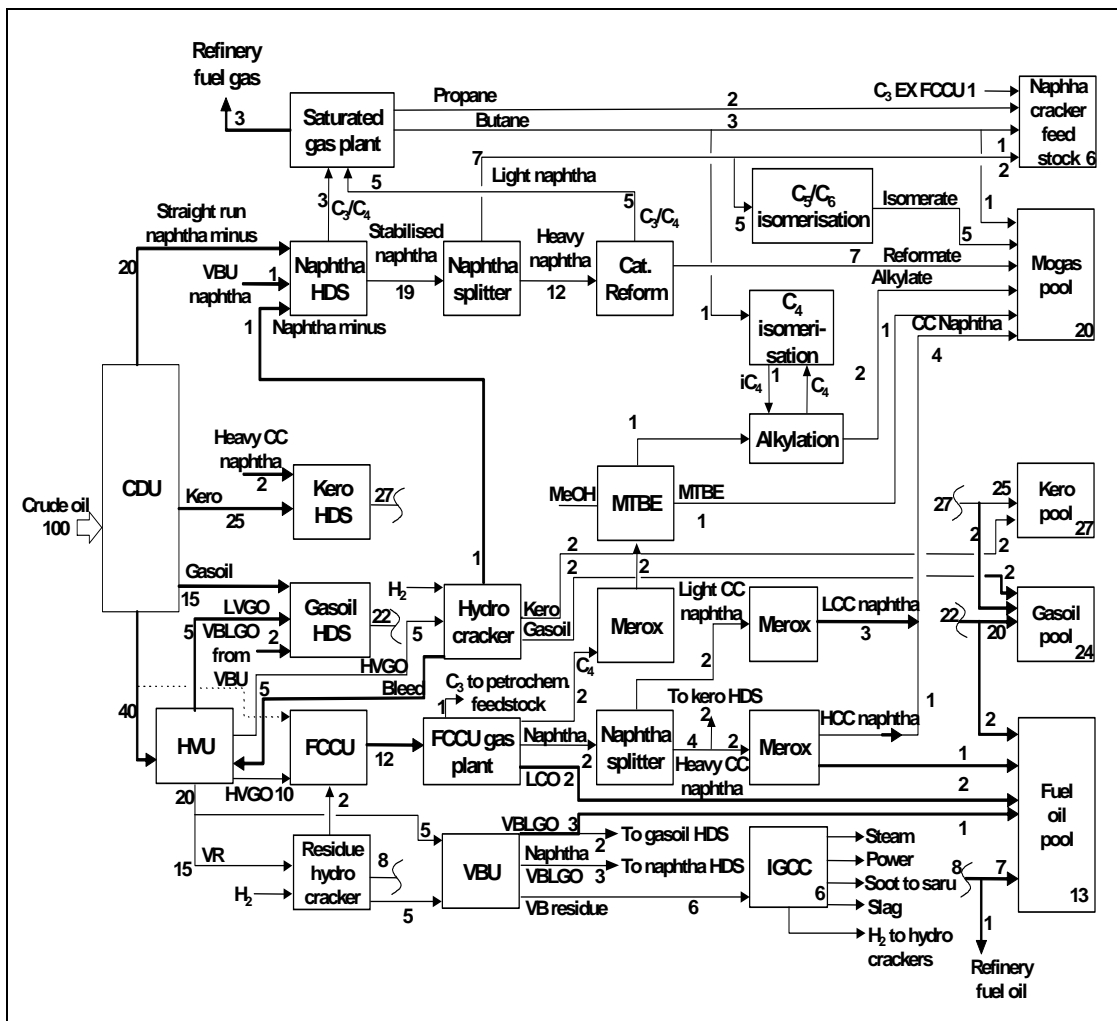


Figure 9.4: Scheme 4: Complex refinery with hydroconversion and IGCC

The visbroken residue is sent to the IGCC where it is converted into syngas (H_2/CO). The produced hydrogen can partly be used in the Hydrocracker and the Residue Hydrocracker. Remaining syngas may be combusted in a gas turbine followed by a steam turbine for electricity production and a boiler for steam production. This can be an energy efficient alternative to the classic heavy fuel-fired boilers. Waste streams from the IGCC are slag and soot recovered from the soot rework unit. The quantity and quality of the soot depends on the visbroken residue feed quality and ultimately on the crude oil processed.

9.2 Refinery feedstock, intermediates and products

This section contains a brief explanation of the chemical and physical properties of feedstock, intermediates and products available within a refinery. Because some of the terms may vary from country to country, this annex gives a short description of how these names are used within this document. Moreover this annex gives a short overview for non expert readers.

9.2.1 Crude oil

Crude oil is a mixture of hydrocarbon compounds (95 - 99 % w/w) of different chemical composition and molecular structures with some impurities. Most of these impurities, such as sulphur, nitrogen, vanadium and nickel are chemically bound to the hydrocarbon structures. Others, such as sand/clay, water and water-soluble salts of zinc, chromium and sodium are present as inorganic material.

The hydrocarbons in crude oil are a mixture of three chemical groups: paraffins (straight and branched chains are called normal- and iso-paraffins), naphthenes (saturated rings or cycloparaffins) and aromatics (one or more unsaturated rings). The most used rough distinction between crude oil types is sweet or sour. Sweet crude is normally low in sulphur and lightly paraffinic. Sour crude is usually high in sulphur and heavily naphthenic.

The composition of the crude is the most important parameter in establishing the range and quality of products that may be produced from a refinery. The impurities of the crude, which usually make up 1 - 5 % of the total, are also very important in establishing the value of the crude and the difficulties in converting it into marketable products. The most important impurity of crude oil is sulphur, which is present largely in the form of organic compounds such as mercaptans and sulphides. Some elemental sulphur, H₂S, and FeS may also be present but only in small quantities. The total sulphur content may be as low as 0.04 % w/w or as high as 5 % w/w. Crudes containing more than 0.5 % w/w S are commonly referred to as 'sour' and the others as being 'sweet'. In general, the sulphur content increases in the higher boiling fractions.

Examples of crude types processed in European refineries are shown in Table 9.1. A distinct shift in crude oils processed in European refineries took place between 1993 and 1997, from Middle East crude oils to 'North Sea' crudes. Market forces mainly caused this and this trend could therefore easily reverse. CONCAWE has reported that the average sulphur content processed in European refineries decreased from 1.45 % in 1979 to approx. 1.0 - 1.1 % from 1985 onwards. The availability and marketing of low sulphur crude oils has helped the European refineries to reduce SO₂ emissions and to some extent also the emissions of NO_x.

Table 9.1: Examples of crude oil types and compositions

Crude origin	Crude Oil	Density kg/m ³	Kinnetic viscosity mm ² /s	Sulphur % w/w	Vanadium mg/kg	Nickel mg/kg
Middle East	Arabian Light	864	5.18	1.91	23.7	4.6
	Iranian Heavy	870	7.85	1.67	68.2	21.4
	Arabian Heavy	889	14.54	2.92	69.8	22.3
	Iranian Light	860	5.11	1.46	55.2	17.0
	Kuwait	870	6.90	2.47	32.9	9.6
North Sea	Statfjord	830	2.70	0.26	1.5	0.7
	Oseberg	845	3.47	0.24	1.6	0.8
Russian	Ural	864	5.41	1.55	37.1	12.2

The next two tables show the metal content of crude oil. Nickel and vanadium are present as porphyrin-systems in the crude oil. In order to determine heavy metals in crude, sampling is of crucial importance. More information about that can be found in [150, Dekkers, Daane 1999]

Table 9.2: Metal content of different crude oils

Source	Metals, ppm			
	Fe	Ni	V	Cu
East Texas	3.2	1.7	12	0.4
West Texas	5.1	4.8	7.9	0.4
Mirando	7.6	1.9	1.4	0.5
Jackson	4.4	1.8	0.9	0.1
Scurry County	3.4	1.0	0.8	0.2
Wilmington	28	46.0	41.0	0.6
Santa Maria	17	97.0	223.0	0.3
Kettleman	24	35.0	34.0	0.4
Ventura	31	33.0	49.0	1.1
Tibu-Petrolea	1.6	9.0	60.0	0.9
Kuwait	0.7	6.0	77.5	0.1
Mid-Continent	3.8	4.2	7.9	0.3
Kansas	5.8	5.8	20.8	0.4
Morocco		0.8	0.6	0.1
Redwater	3.4	10.6	4.5	0.1

Source: Speight, J 0 - The Chemistry and Technology of Petroleum, Marcel Dekker Inc. 1980

Table 9.3: Range of metals and other elements contents found in crude oils

Element	Concentration (ppm)		
V	5.0	-	1500
Ni	3.0	-	120
Fe	0.04	-	120
Cu	0.2	-	12.0
Co	0.001	-	12
Si	0.1	-	5.0
Ca	1.0	-	2.5
Mg	1.0	-	2.5
Zn	0.5	-	1.0
Al	0.5	-	1.0
Ce	0.001	-	0.6
Zr	0.001	-	0.4
Ti	0.001	-	0.4
Sn	0.1	-	0.3
Pb	0.001	-	0.2
Hg	0.03	-	0.1
B	0.001	-	0.1
Ga	0.001	-	0.1
Ba	0.001	-	0.1
Sr	0.001	-	0.1

A report [150, Dekkers, Daane 1999] has shown that the quantity of Cadmium, Zinc, Chromium, Copper and Arsenic in the crudes are indeed much lower than traditionally assumed. Reasons for this include improper analytical techniques and contamination during sampling. Table 9.4 shows the results achieved in the above-mentioned report.

Table 9.4: Content of certain metals in some crude compared to other published data

Metal	Concentration ($\mu\text{g}/\text{kg}$)	
		Published data ^(*)
Arsenic	4 – 37	0.2 – 26200
Cadmium	0.40 – 4.9	0.109.1
Chromium	12 – 240	1.5 – 3170
Copper	10 – 195	30 – 7180
Zinc	59 – 1090	25 – 19500
(*) Published data from several sources reflected in the report Source: [150, Dekkers, Daane 1999]		

Physical properties and characteristics of crude oil

Crude oil is a mixture of many compounds and, apart from the lightest components, the characterisation by a complete chemical analysis is almost impossible. As a result, the general physical properties are expressed in terms of simple parameters, which can be quickly estimated. The underlying nature of the crude is then derived from this information by comparison with corresponding parameters from known feedstocks. Most of these parameters are not limited to crudes, but may be used for most petroleum products as well. One of the simplest crude properties to measure is the specific gravity, normally expressed in terms of the °API. Crudes are often classified as being 'heavy' or 'light' according to their °API, the heavy being less than about 28 - 32°API and the light over 32 – 35 °API.

9.2.2 Refinery intermediates and products

There are over a hundred of refinery products, including gaseous and liquid refinery fuels for domestic and industrial use, fuel for most forms of transport, lubricating oils for all types of machinery and the basic raw materials for the petrochemical industry. Individual refineries do not usually supply the full range of possible products, but try to select these most suited to the quality of the crude feed, the available processing equipment and the local market requirements. The composition of a product will vary between refineries, being a function of crude type and refining processes used, but the overall quality will meet the product specifications prevailing for a given market. The major refinery product groups are shown in Table 2.1 by refinery process unit. A short description of the product groups follows.

Refinery fuel gas (RFG)

Refineries use the C_1/C_2 fraction as refinery gas to cover part or most of their fuel requirements. Refinery gas can also contain H_2 . An amine wash is normally used to extract H_2S .

Liquefied petroleum gas (LPG)

Sometimes C_3 and C_4 components are also used for refinery fuel, but most of the C_3 and C_4 components will be sold as liquefied petroleum gas (LPG), which is used as a fuel for numerous applications. LPG is sold either as a mixed LPG fraction or as separated C_3 and C_4 fractions. The liquid propane normally contains a minimum of 95 %w/w C_3 compounds, the remainder being C_2 and C_4 . Butanes and butenes are also used as a petrochemical feedstock for the manufacture of MTBE, acetic acid, solvents, polybutylenes, and rubber.

Naphtha and chemical naphtha

Naphtha is the raw gasoline range fraction from crude oil distillation. As well as gasoline production, in some cases, naphtha is used as the feedstock for petrochemicals production.

Gasoline

Gasoline, the fuel for motor cars and light aircraft, represents the highest volume and one of the more valuable refinery products. Automotive gasoline, which is by far the most important gasoline type, consists of a complex mixture of hydrocarbons ranging from C_4 to C_{10} , boiling

between 38°C and 205°C. Most refiners produce gasoline in three or four octane grades, the principal difference being the anti-knock performance. Mogas is a term normally used for motor gasoline.

Jet fuel (kerosene, avtur)

Jet fuel is the name given to kerosene or kerosene blends used as fuel in aviation turbines (hence also called Avtur) by both commercial aviation and military aircraft. For most refineries the primary source of jet fuel blending stocks is the straight-run kerosene fraction (C₈ - C₁₂) from the atmospheric crude unit. For a refinery with a Hydrocracker, kerosene boiling range hydrocarbons from this unit can also meet jet fuel specifications, and is a major contributor to jet fuel production. Hydrotreated light Coker gas oil and thermally cracked gas oil can also be used as blending stock. In some developing countries, kerosene is still the primary fuel for cooking and domestic heating.

Diesel oil/heating oil/gas oil

Diesel fuels are produced by blending of kero and gas oil fractions from the crude distillation unit and gas oil fractions of the high vacuum unit and from conversion units. An upgraded and flexible processing scheme for desulphurisation of blending components is necessary in most refineries in order to arrive at the currently required and future sulphur specifications (500 ppm currently, 350 ppm from 2000 and 50 ppm from 2005 onwards). Light heating oils (kero/diesel fraction) are typically used for small domestic applications.

Middle distillates/distillate fuels

Alternative names for the fuels in the kerosene and gas oil boiling ranges.

Fuel oils

Fuel oils cover a very wide range of applications and are produced in a variety of grades. Gas oils are sometimes referred to as fuel oils, but in Europe the term is usually used to describe heavy fuel oils (atmospheric residue) which are used for electricity etc. Heavy fuel oil are used for electricity or power generation by utility companies, or sold as bunker fuel oil for seagoing vessels. Refineries use heavier fractions from crude oil distillation, from vacuum distillation or from visbreaking for generation of heat, electricity and steam in their furnaces and boilers.

Heavy fuel oils consist largely of the residue remaining from the distillation of crudes. These residues consist of large hydrocarbon structures containing components that require additional processing to convert them into more valuable, lighter products for use in gasoline and diesel engines. These residues generally have a high sulphur and ash content, are mostly very viscous and will therefore be blended with lighter gas oils in order to sell them as a commercial fuel for ships and utilities.

Lubricating oils, wax and greases

Lubricating oil feedstocks are produced from the atmospheric residue by fractionation under vacuum. The oil cuts produced from the vacuum distillation column are further processed to remove unwanted impurities (solvent extraction and dewaxing) and blended with miscellaneous additives (both organic and inorganic in nature) to give lubricating oils of various grades. Lubricating oils can be modified by mixing with thickening agents such as soap, clay or silica gel to produce lubricating greases. Dewaxing yields paraffinic or microcrystalline wax that is usually subjected to hydrofinishing to remove colours, odours and potentially carcinogenic hydrocarbons for domestic applications.

Bitumen

Bitumen (referred to as asphalt in the US) is used mainly for paving roads but also for a number of other applications, such as materials for roofing. The basic source of bitumen is the residue remaining after vacuum distillation of crude. The residue can also be treated by blowing with air at high temperature (bitumen blowing process) to increase the asphaltene content.

Petroleum coke

Petroleum coke is the residue remaining after destructive distillation of petroleum residue in a delayed coking unit. It is widely used as fuel in the cement and steel industry. It can also be used as a fuel for power plants if the sulphur content is low enough. Coke also has nonfuel applications as a raw material for many carbon and graphite products.

Table 9.5: Example of petroleum coke analysis

Petroleum coke analysis used in oxygen-blown gasification	
Ultimate analysis	% w/w
Carbon	87.1 - 90.3
Hydrogen	3.8 - 4.0
Oxygen	1.5 - 2.0
Nitrogen	1.6 - 2.5
Sulphur	2.1 - 2.3
Proximate analysis	% w/w
Volatiles	9.0 - 9.7
Fixed C	80.4 - 89.2
Moisture	0.9 - 10.2
Ash	0.2 - 0.4
<i>Source: [175, Meyers 1997]</i>	

Sulphur

Sulphur is basically a by-product of refining resulting from the removal of sulphur compounds from the main hydrocarbon product streams. The quantity of sulphur produced by a refinery depends on the amount present in the crude and the desulphurisation and sulphur recovery capacity installed. It is a valuable product which is mainly used as the raw material for sulphuric acid manufacture.

Relationship between feed (typically crude oil) and products

As a broad generalisation it is true to say that any crude can be processed into any reasonable selection of products by a suitable choice of refining unit operations. The cost of production will depend on the refining units required, which in turn depend on the crude selected. In theory the production cost can be minimised by careful selection of the crude. In practice, however, refinery designs are often compromised by factors such as: the changing availability, price and composition of crudes and changing market demands for product slate and specifications. A few relatively simple crude properties can indicate the feasibility of processing a particular crude (mix) with a given refinery complex.

In general, it is found that the heavier the crude, the higher the quantities of sulphur, Conradson carbon and heavy metals, and the lower its hydrogen content. Heavy crudes are also more difficult to process. Heavy crude normally results in high fuel-oil production while light crude is more appropriate for a high gasoline and middle distillate production. Other simple property indicators are sulphur content and pour point.

In order to evaluate the properties of the various likely products such as gasoline octane rating, the aromatics content of kerosene, etc., it is necessary to distil the crude and analyse the fractions boiling within different boiling ranges. This will give information on the process units that may be required for quality improvement, such as desulphurisation facilities, a reformer unit or an aromatics extraction plant. The residue fractions can be similarly analysed to give more detailed information on the conversion units that may be appropriate.

9.3 Cost effectiveness of implementation of some techniques

9.3.1 Basic concepts for cost effectiveness analysis

The ECM BREF [67, EC 2006] provide assistance to both Technical Working Groups (TWGs) and permit writers when considering the environmental and economic conflicts that can occur when determining which techniques to implement under the IED.

According to this document, a cost effectiveness analysis is described as follows:

The basic concept is simple: one can spend a euro only once. In the context of environmental policy this means that the aim is to achieve highest environmental yield for each euro invested for environmental purposes.

The most explicit way to compare costs and benefits of a measure is to monetarise both and compare them in a cost benefit analysis (CBA). When the comparison shows that the benefits outweigh the costs, this indicates that the measure represents a worthwhile investment. If different alternative measures give positive results, the measure with the highest result is the one offering the highest overall value for money. However, such a cost benefit analysis requires a lot of data and some benefits are difficult to monetarise.

A cost effectiveness analysis is more simplified than a CBA as environmental benefits are quantified but not monetarised. This type of analysis is typically used to determine which measures are preferable to reach a specific environmental target at the lowest cost.

Cost effectiveness (CE) of a technique typically is defined as:

CE = annual cost /annual reduction of emissions (e.g. 5 EUR/kg VOC reduced)

In the context of determination of BAT, the use of the CE concept is not straightforward.

However, ranking BAT options on the basis of ascending CE is useful, e.g. to exclude options that are unreasonably expensive in comparison with the environmental benefit obtained.'

9.3.2 Basic hypothesis and assumptions used in the REF BREF for economics

To enable an easy comparison, the following assumptions have been commonly used to estimate the abatement cost calculations.

- The annualised capital charge (ACC) is 7.4 % (equivalent to a 4 % interest rate applied over a 20 year write-off).
- The scaling rule for cost of a unit sized MW compared to the reference unit MW_{ref} is given by:

$$\text{Cost}_{\text{unit MW}} = (\text{MW}/\text{MW}_{\text{ref}})^{0.6} \text{Cost}_{\text{unit MW}_{\text{ref}}}$$

- The reference fixed operating cost is 4 %/year of the capital cost.

References: [67, EC 2006] [139, CONCAWE 6/11 2011]

9.4 Description of zeolites

Zeolites are widely used in industrial processes or laboratory (Sherman, 1999). They are microcrystalline aluminosilicates of natural or synthetic, whose structure is formed by rings consisting of tetrahedral AlO_4^- and SiO_4 are interconnected by oxygen atoms. The negative charges of Tetrahedrons- AlO_4^- cations are compensated by the compensation, present in various locations within the porous structure, which may be replaced by other cations by ion exchange full or partial (Breck, 1974).

The structure of zeolites is an open structure with large pores and channels. After complete dehydration of a zeolite, the channel can be filled with a variety of other molecules. The adsorption process is selective and depends on the particular structure of the zeolite and the size of molecules to be adsorbed. For this reason, zeolites are also called 'molecular sieves'.

Depending on the number of oxygen atoms that form the openings of pores, zeolites can be classified into pore zeolites extra large ($>9 \text{ \AA}$), large pore zeolites ($6 - 9 \text{ \AA}$), mean pore zeolites ($5 - 6 \text{ \AA}$) and small pore zeolites ($3 - 5 \text{ \AA}$), where access to the interior of the pore takes place, respectively, through rings 18, 12, 10 or 8 atoms of oxygen (Giannetto, 1990).

The acidity of zeolites is a very important property that depends not only on the material structure, but also other parameters such as total number of Brönsted acid sites and Lewis, and the strength and location of these centers (Serralha, 2001).

The Brönsted acidity is based on the existence of protons as cations compensation. This type of acid depends strongly on the structure and topology of zeolite, the chemical composition and surrounding environment, particularly the molar ratio Si/Al.

There is usually an increase in the strength of Brönsted acid sites with increasing Si/Al ratio. The NaY zeolite has a Si/Al ratio greater than 1.5 (Giannetto 1990), NaA zeolite and a ratio of 1, it is less acidic.

9.5 Soil and groundwater monitoring – An example

Description

See also Section 3.26.

As illustrated in Figure 9.5, the primary objective of a groundwater monitoring network is to:

- provide an access point for measuring groundwater levels;
- collect samples that accurately represent *in situ* conditions at the specific point of sampling.

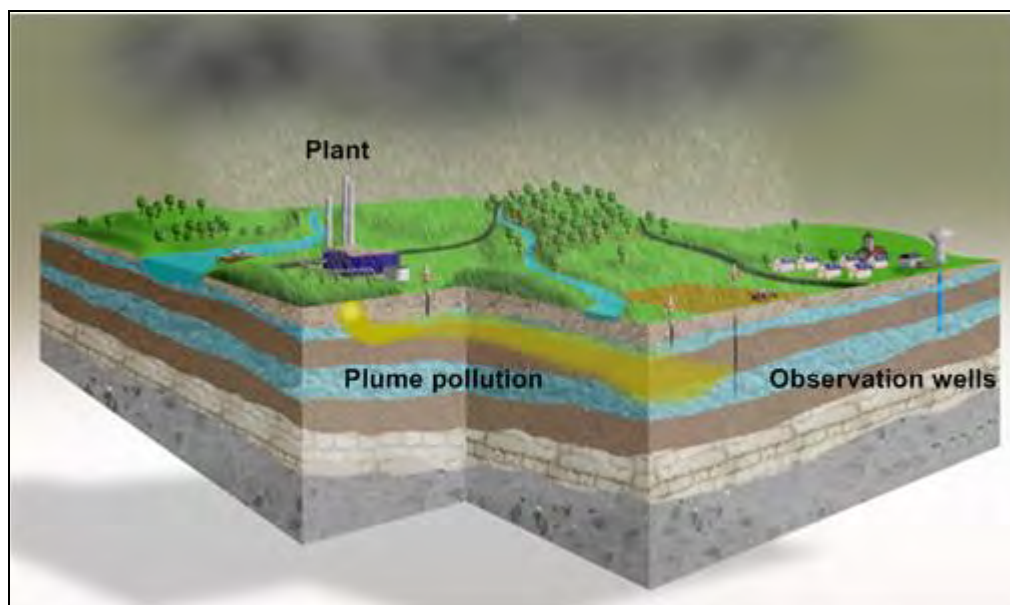


Figure 9.5: Example of a monitoring network in a case of a groundwater pollution

Achieved environmental benefits

When properly designed and implemented, a groundwater monitoring system allows to:

- determine the flow direction and groundwater table profile;
- detect the release of pollutants from a suspected or known source;
- determine the extension of the polluted area;
- help design a management strategy and monitor the effectiveness and efficiency of its implementation;
- act as an alert system (in the event of plume advancement);
- extrapolate the concentration of pollutants in the contaminated area and support a risk assessment.

Cross-media effects

Two important points are to be considered when a monitoring network is implemented:

- the risk of cross-contamination of adjacent groundwater, from one borehole to another and/or vertically within a borehole from a contaminated to an uncontaminated zone;
- the cross-contamination of an adjacent surface water with contaminated purge groundwaters should be prevented. Adequate measures should be taken, and permits should be obtained for the disposal or release of related effluents.

Operational data

The different steps and operational data required to define, implement and use a groundwater monitoring network can be summarised as explained in Figure 9.6. The installation of an adequate monitoring network (steps 1 to 3) is an iterative process, and the interpretation of results (step 6) can lead modifying it.

Steps 1:

The concept model is based on a preliminary analysis of data that should be collected on the following aspects, including:

- geologic and hydrogeologic conditions (fractured, alluvial or karstic);
- existing observation wells (piezometers), taking into account the eventual accumulation of sediments at the bottom of the well;
- potentially contaminating substances (volatile, miscible or immiscible contaminants), classified as light non-aqueous phase liquids (LNAPLs) or dense non-aqueous phase liquids (DNAPLs);
- other anthropogenic influence (existing pollution, pumping well, irrigation,...);
- public priority protection targets.

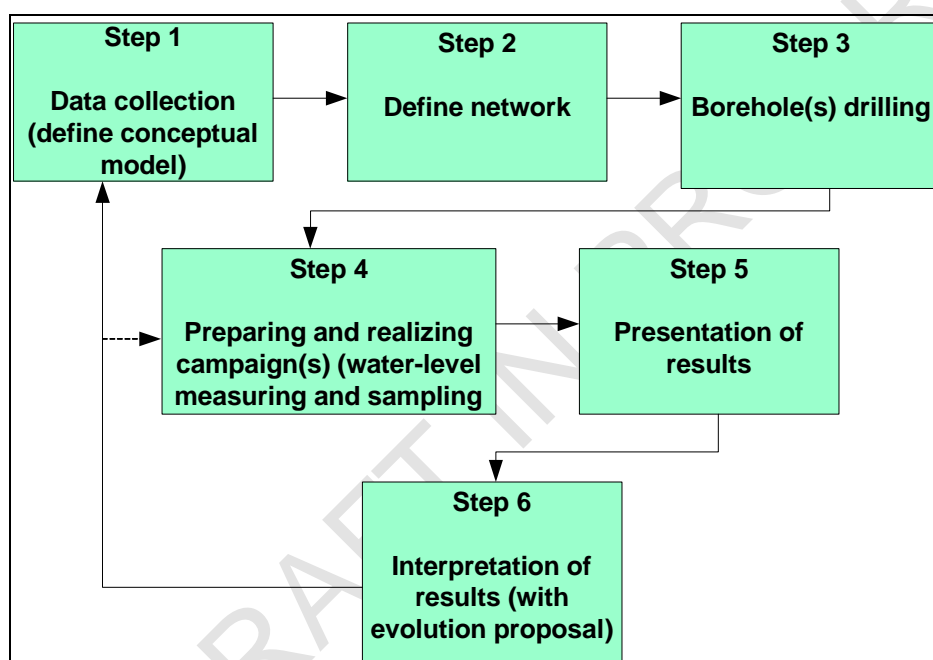


Figure 9.6: Main steps for the implementation of a groundwater monitoring system

Step 2:

This information affects the second step and the monitoring design/strategy, in particular on the well locations, screening levels, drilling and installation methods, selection of parameters, purging and sampling frequency and procedures. Usual frequencies are in the range 2–6 months, site-specific adaptation may be needed. At this stage, particular precautions and related operational choices may be taken, in particular:

- for each pathway monitored, the implementation of a minimum 3 wells is required (1 upstream for comparison of upgradient conditions to background quality, and 2 downstream for allowing groundwater flow direction by triangulation. (See Figure 9.7);
- in the presence of a pure phase, inappropriate purging can lead to redistribute or spread the contaminants: low flow purging is thus recommended (micropurging);
- for a DNAPL, sampling may also need to be performed at the bedrock of the aquifer in order to ensure collecting contaminated groundwater from the plume (as illustrates in Figure 9.8).
- a low-flow sampling method should be preferred in case of volatile compounds. Other specific procedures based on local expert requirements can be used to achieve the same results.

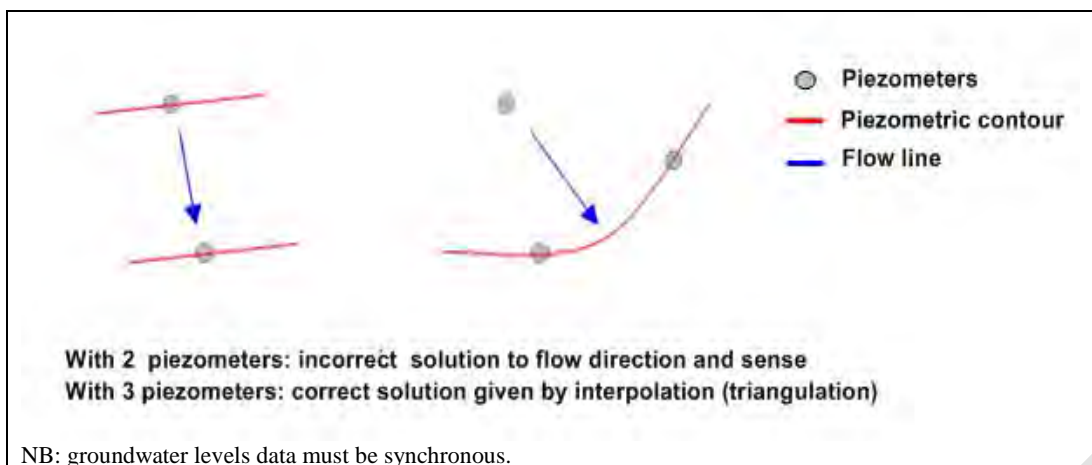


Figure 9.7: Good practice to determine the flow direction and sense

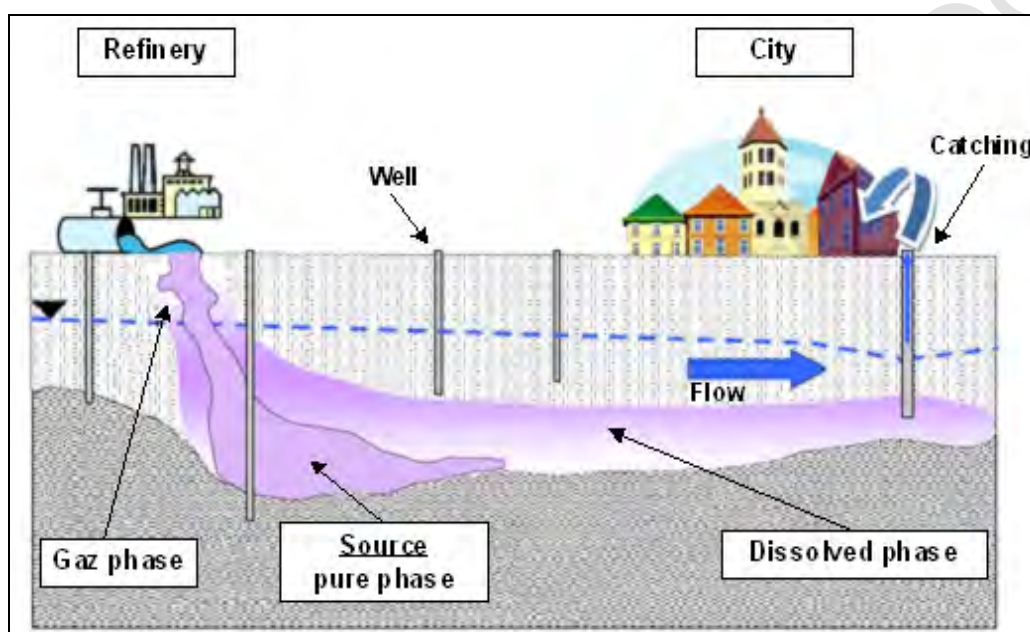


Figure 9.8: Example of DNAPL plume migration in groundwater

Steps 3 to 4: Appropriate standards or guidances might be followed, for example, the 'Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells' (US EPA, March 1991) and the ISO 5667 – 11 'Guidance on sampling of groundwater'. Laboratories performing the analyses should be accredited for each substance analysed and must achieve the analytical performances settled down (i.e. limit of quantification). Quality control procedures should also cover the prevention of drilling and sampling equipment contamination.

In the case of oil refineries, the following measures and precautions should be in particular taken:

- the monitoring of the following parameters and substances can be recommended (to be adapted to the context): BTEX, PAH, Total Petroleum Hydrocarbons, pH, temperature and conductivity;
- well construction materials (PVC or HDPE) should be selected in order not to interact with contaminants or modify the composition of the groundwater;

- on sites with aged contamination, multilevel sampling wells can be used for sampling, in order to be able to draw a detailed three-dimensional groundwater contamination profile (e.g. DNAPL).

Steps 5 to 6: the presentation of results will be facilitated using cartographic tools for piezometric and plume mapping, and chronicles of piezometric and concentration data. Figure 9.9 shows an example of groundwater level map based on a rather large number of piezometric wells, and developed using a kriging interpolation software; the rectangle corresponds to the refinery footprint. In more simple cases based on a 3 – 4 set of piezometers, an interpolation may be achieved only by triangulation. Seasonals evolution should be taken into account for the interpretation of these results.

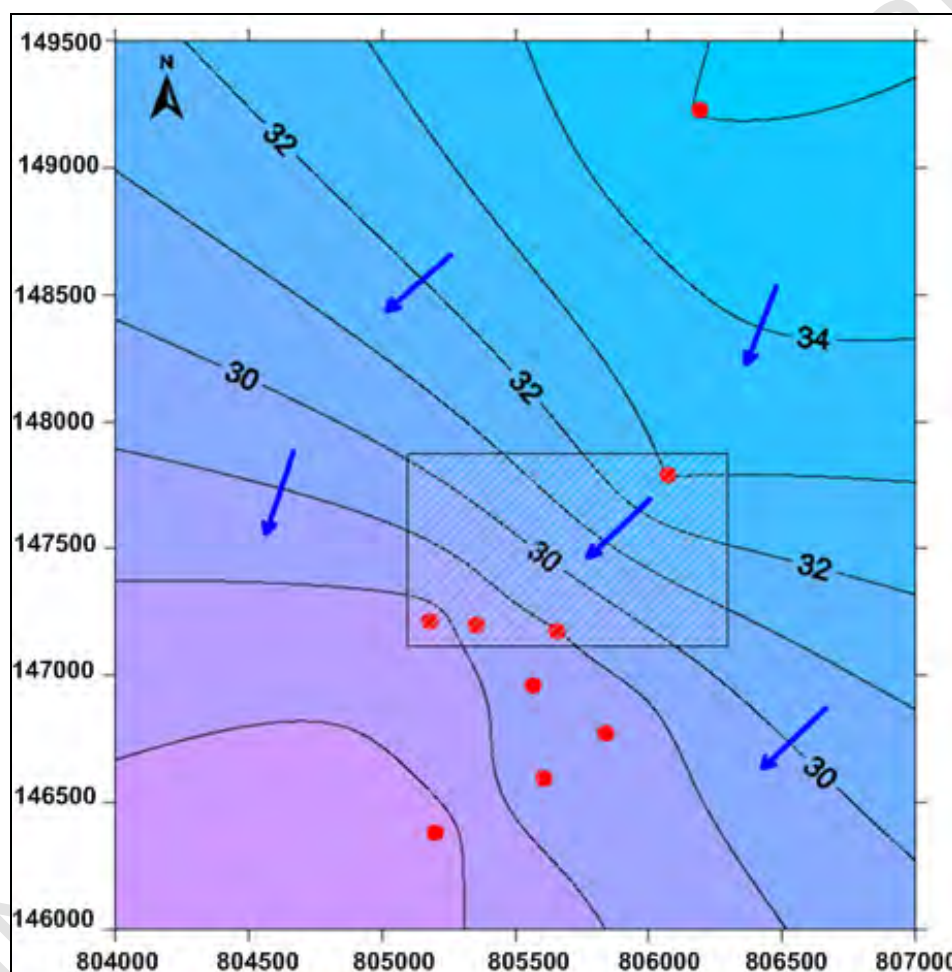


Figure 9.9: Example of groundwater levels map indicating the flow direction and sense (kriging interpolation)

Applicability

Applicable to any new and existing refinery or part of refinery.

Economics

The cost of this technique varies very much, depending in particular on the number of monitored wells, substances, and measuring campaigns.

As an example, the cost for the implementation of three piezometers at a depth of 8-10 metres (for alluvial aquifer) is estimated (2010) at around EUR 8 000 – 12 000 for steps 1 to 3. The cost of a campaign (3 piezometers, sampling, analysis and interpretation), for steps 4 to 6, is estimated at around EUR 1 500 – 2 000 for the monitoring of BTEX, PAH, Total Petroleum

Hydrocarbons, pH, temperature, conductivity. The monitoring campaign is usually realised twice a year.

Driving forces for implementation

Prevention and early detection of groundwater pollution. Monitoring of old site historic contamination in order to prevent, reduce and manage potential or actual health and environmental impacts.

Example plants

In France, groundwater monitoring is applied in all refineries.

References

[38, INERIS 2009].TWG FR 2010

WORKING DRAFT IN PROGRESS

9.6 Air emissions –The 'Bubble approach': a methodology

This annex includes 4 appendix named A to D

Introduction

To prevent the emission of pollutants in the atmosphere, the REF BREF proposed AEL for specific refining processes or combustion.

One operator could take appropriate measures in order to comply with these values 'stack by stack or unit by unit'.

A specific approach based on a 'bubble concept' can nevertheless be used by the competent authority to regulate one refining site. It will lead to define a single value as a target for the refinery as a whole.

This annex aims to provide an example methodology to make the relevant calculations.

This approach takes into account the specificity of the refining sector, in particular the following factors:

- the recognised complexity of refining sites, with a multiplicity of combustion and process units, often interlinked for their feedstock and energy supply;
- the frequent (e.g. weekly or even daily) process adjustments required in function of the quality of the crude received;
- the technical necessity for many sites to keep burning a part of their internal residues as energy fuels, and to frequently adjust the site fuel mix according to process requirements;
- the need for enabling, quantifying and monitoring a net site-level emission reduction for sites where some key specific installation controls are not possible and have to be compensated elsewhere.

This approach consists of considering all concerned emissions together, as emitted through a single 'virtual single stack'.

This approach assumes, as a prior condition, that the global result on the environment should be at least as efficient as if BAT-AEL were achieved for every individual process.

Main definition of the concepts used: What is the 'bubble approach' and how could it be applied in a refinery?

Bubble perimeter

The exact bubble perimeter to be considered for a given site will depend on the site processes. In the purpose of this document, this methodology is designed to cover **all sources of permanent emissions from a refinery** (i.e. combustion plants, catalytic crackers, sulphur recovery units, coke calciners and other processes where appropriate), as further indicated.

Bubble substances or parameters covered

Based on the work undertaken in 2009 – 2010 for the revision of this document, SO₂ and NO_x have been recognised as the two parameters which deserve, in priority, a common methodology for a site-level bubble-expressed AEL calculation, and for which enough supporting information and data have been provided. Therefore, the current methodology will address specifically these two substances.

Bubble averaging period

In the particular context of this document, the methodology proposed has been based primarily on a **yearly average**, since a long-term period has been considered as the most appropriate for reflecting the best performances achievable in normal operating conditions, and giving enough time and flexibility, in order to integrate necessary feedstock, process and fuel adjustments.

However, the efficient control of a yearly bubble requires a very frequent or continuous monitoring regime of all emissions concerned. A shorter-term bubble can, therefore, be derived from the long-term bubble using monitoring results. As real examples of bubble regulations already used by some Member States show, an associated **daily average** could be useful.

Methodology to set a bubble level based on individual BAT-AELs

The site-level bubble is expressed as a sum of two terms:

- **A first term related to the energy system**, including at least all furnaces, stand-alone boilers, central CHP or conventional power plants, and gas turbines. This term is driven by suitable AEL concentration ranges expected from each category of installations. It includes emissions from internal power plants where energy is exported and excludes emissions from external (out of permit) power plants.
- **A second term related to the process units**, including at least FCC UNIT if any, and SRU. This term should be driven by suitable AEL concentration or specific emission ranges expected from each of them when BAT is applied. It includes emissions from coking: green coke calcination, fluid coking, emissions from SRU (specially SO₂) and PERMANENT emissions from flaring (pilot flames). It excludes emissions from SWS and incondensable untreated gases.

$$\text{Site Bubble} = \frac{\text{Energy system term} + \sum \text{process units terms}}{\text{FL}_{\text{comb}} \times [\text{Comb}] + \text{FL}_{\text{FCC}} \times [\text{FCC}] + \text{FL}_{\text{SRU}} \times [\text{SRU}] + \text{FL}_{\text{other}} \times [\text{other}]}$$

Where: FL= flue-gas
[...]= concentration from process ...

In the context of this document and for the purpose of expressing meaningful AEL at the site level, the bubble determination should always be based on concentration and specific emission ranges expected from all concerned installations when BAT is applied, and should involve the following steps:

- Step1. Exhaustive identification and geographical mapping of all included sources, to be done according to Appendix A;
- Step2. Determination of the off-gas volumetric contributions expected from all included sources, to be done according to Appendix B;
- Step3. Determination of the mass contributions expected from all included sources, to be done according to Appendix C;
- Step4. Determination of the bubble-associated monitoring regime, to be done according to Appendix D.

9.6.1 APPENDIX A ON 'GOOD PRACTICES' FOR THE IDENTIFICATION AND MAPPING OF ALL INCLUDED SOURCES

Introduction

Reminder of global methodology steps:

- Step1. Exhaustive identification and geographical mapping of all included sources;
- Step2. Determination of the off-gas volumetric contributions expected from all included sources;
- Step3. Determination of the mass contributions expected from all included sources;
- Step4. Determination of the bubble-associated monitoring regime.

The first step of the methodology is crucial as the following steps (calculations) will depend on a clear identification of the sources included in the bubble.

Exhaustive listing of all emitting source (stacks) under the considered bubble area (energy production and processes) including:

- Quick estimation of emission levels for the considered emitted substance (e.g. by using emission factor);
- Prioritising the sources by ranking;
- Listing the currently used monitoring and that required for the corresponding source.

Methods

Refers to existing mapping e.g. for CO₂ emission trading scheme (ETS) taking into account:

- to include all combustion processes and **identify those using 'non standard fuels'**;
- to include all refining processes as far as they are in the bubble area;
- to exclude processes that could be on site but are not properly refining, e.g. steam cracker (petrochemical)

Report on map and table all the available operational data (flue-gas volume, load, average or spot concentration measurements,...).

References/Examples: CO₂ guidelines document decision 2007/589/EC and UE regulation 601/2012 of 21 June 2012 on the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of the European Parliament and of the Council.

9.6.2 APPENDIX B ON VOLUMETRIC GAS ESTIMATION

Summary of proposed standard flue-gas factors for the bubble calculation

Source	Fuel or process feed	Flue-gas factor (dry gas) at 3 % O ₂
Combustion	Refinery fuel oil (RFO)	12.3 Nm ³ /kg foe ⁽¹⁾
	Refinery fuel gas (RFG)	11.3 Nm ³ /kg foe
Sulphur recovery unit (SRU)	Acid gas	1 500 Nm ³ /t feed
Fluid catalytic cracking (FCC)	Coke	12.3 Nm ³ /kg foe
Coking process	Green coke calcination	Reported as from 1.8 to 3 Nm ³ per tonne of coke feed
	Fluid coking flue-gas	No data
Flaring (permanent emissions)	Use combustion emission factor <i>NB: Other than permanent emissions are not included</i>	
Sour water stripper (SWS) flue-gas and non condensables	<i>Not included</i>	
⁽¹⁾ kg foe: kg of fuel oil equivalent = 41.868 MJ (IEA defines tonne of oil equivalent to be equal to 41.868 GJ) <i>Source: [77, REF TWG 2010] [127, France 2010]</i>		

Calculation details and general explanations

A.1 FLUE-GAS FLOWRATE - GENERAL

Flue-gas flowrate is rarely measured directly. Where this is the case, the uncertainty in the result of the measurement must be established through a duly documented investigation.

B.1.1 EXPRESSION OF MEASUREMENTS

In all circumstances, the quantity of flue-gases has to be expressed under the same conditions as the other parameters to which they relate.

As far as temperature and pressure conditions are concerned, normal conditions will be systematically used, namely:

- Temperature = 273.15 K or 0°C
- Pressure = 101 325 Pa or 1 atm

The normal written form will be used to express these conditions, preceding the unit of volume by the letter N: for example Nm³.

Conversely, the conditions of flue-gas composition in which measurements are expressed will be systematically specified:

- water content: actual content or corrected to 0 % (dry flue-gases);
- oxygen content: actual content or content corrected to a standard value (0 %, 3 % or other value).

Conversion formulae relating to flue-gas composition:

Dry flue-gas flow = wet flue-gas flow x (1 - % water in the flue-gas)

*Flow at y % O₂ = flow at x % O₂ * (21-x)/(21-y).*

B.1.2 USING THE RESULTS

Flue-gas flows are used to calculate the quantities of pollutants emitted based on an analysis of flue-gases.

Special care must be taken to ensure that the 2 terms of the product are expressed using the same units and conditions.

B.2 FLUE-GASES FROM FURNACES AND BOILERS (COMBUSTION)

B.2.1 GENERAL

Flue-gases emitted by these plant items originate from the combustion of fuels and possibly other fluids.

The rule below is to be used for fuels: Flue-gas flow = fuel flow x flue-gas factor

The flow of fuel is to be measured in accordance with the rules described before.

Flue-gas factor represents the quantity of flue-gases produced per unit fuel.

It is often expressed as Nm³ of dry flue-gas corrected to 3 % O₂ per standard tonne (or tonne of oil equivalent - it is convenient when summing flue-gas volumes generated by different types of fuels (e.g. solid, liquid, gaseous) to express the mass of fuel consumed as tonnes of oil equivalent (toe). The International Energy Agency defines one tonne of oil equivalent (toe) to be equal to be 41.868 GJ), *as a result of which an approximate fixed factor can be used regardless of what the fuel is.*

The standard flue-gas factor approach is not however sufficiently accurate for complying with the level of uncertainty required by the EU ETS provisions. Statutory obligations for drawing up CO₂ balances have led refineries to obtain a better understanding of the atomic composition of the fuels which they use. The calculations proposed below are based on these characteristics.

B.2.2 FLUE-GAS FACTOR FOR LIQUID FUEL OILS

Liquid fuel oils are analysed on the basis of their compositions by mass:

a % C + b % H + c % S + d % N + e % O

$$QFO_{\text{flue-gases}} = [0.0889 C \% + 0.211 H \% + 0.0333 S \% + (6.8 \times k + 0.8) N \% - 0.0263 O \%] \times (21/18) / \text{NCVFO}$$

in Nm³/kg of fuel oil equivalent at 3 % O₂ dry gases

With k the proportion of nitrogen which is wholly oxidised.

NCVFO: Net calorific value of fuel oil expressed as MJ/kg

Examples:

For k = 0.2 (typical value)

The fuels in the table have been taken from an Heavy Fuel oils survey and the refinery FO analysed in the context of the CO₂ balance.

Corrected stoichiometric formula for nitrogen with a nitrogen % oxidised to 20 % NO ₂ (in Nm ³ /kg)								
Vf = 0.0889 C % + 0.211 H % + 0.0333S % + 0.0216 N % - 0.0263 O %								
	C %	H %	S %	N %	Vf as Nm ³ /kg neutral	NCV as th/t	Vf as Nm ³ /kg at 3 % O ₂ dry gases	Vf as Nm ³ /kg foe at 3 % O ₂ dry gases
HF FO survey of LSC	87.8	10.2	1.6	0.4	10.02	9650	11.69	12.11
HF FO survey of HVF	86.8	10.1	2.4	0.7	9.94	9400	11.60	12.34
HSC type HVF	85.5	10	3.5	1	9.85	9200	11.49	12.49
LSC type HVF	87.5	10.5	1	1	10.05	9500	11.72	12.34
'LSC' FO	87.3	12	0.5	0.2	10.31	9900	12.03	12.15

HF = Heavy Fuel oil

LSC = Low sulphur content

HSC = high sulphur content

HVF = high viscosity fuel

It will be noted that there is very little variability in the flue-gas factor for liquid fuels.

Analysis of liquid fuels composition is performed 6 to 12 times a year.

Flue-gas factor for the calculation of the bubble (combustion component):

Based on the above, it is proposed to take the typical value of 12.3 Nm³/kg of fuel oil equivalent at 3 % O₂ (dry gases) as a standard flue-gas factor for liquid fuels.

B.2.3 FLUE-GAS FACTOR OF GASEOUS FUELS

FG are analysed on the basis of their mass composition: a HC + b H₂ + c inerts

Hydrocarbons are written as the generic form C_nH_p

Q flue-gases = (a x (4.76n + 0.94p) + b x 1.88 + c) x 22.4 / (a x (12 n + p) + b x 2 + c x 28)
as Nm³/kg

This flue-gas volume is expressed per kg of fuel gas at 0 % O₂ (neutral combustion) on dry gases.

In order to have the factor expressed in Nm³/kg foe, the result has to be divided by the fuel Net Calorific Value.

See the formula above to convert the result at a different O₂ content.

Examples:

The table below also indicates the Net Calorific Values for the various molecules and expresses flue-gas factor (dry gases) in relation to quantity of energy.

	HC							H2	inerts
	CH4	C2H6	C3H8	C4H10	C2H4	C3H6	C4H8		
n/p	0.25	0.33	0.375	0.4	0.5	0.5	0.5	/	/
neutral flue gas factor as Nm ³ /kg	11.9	11.3	11.1	11.0	10.6	10.6	10.6	21.06	0.80
flue gas factor at 3 % O ₂ as Nm ³ / kg	13.9	13.2	12.9	12.8	12.4	12.4	12.4	24.6	0.9
NCV (MJ/kg) source : norm NF EN ISO 6976	50.01	47.79	46.36	45.75	47.20	46.00	45.3	120	0
NCV as th/t	11945	11414	11073	10927	11274	10987	10820	28662	0
flue gas factor at 3 % O ₂ as Nm ³ / kg std	11.7	11.6	11.7	11.7	11.0	11.3	11.5	8.6	/

The table below provide values for a typical FG corresponding to the averaging of 700 measurements of different FG with varying composition. The measurements were performed on 12 different units coming from 3 refineries (average of 58 measurements for each unit).

	%vol	MM	%m	Dry flue-gas at 3 % O ₂ Nm ³ /kg dry gases	NCV	Dry flue-gas at 3 % O ₂ Nm ³ /kg std dry gases
CH ₄	25.0 %	16	23 %	13.92	50.01	11.65
C ₂ H ₆	19.0 %	30	33 %	13.23	47.79	11.59
C ₃ H ₈	7.0 %	44	18 %	12.95	46.36	11.69
C ₄ H ₁₀	3.5 %	58	12 %	12.81	45.75	11.73
C ₅ H ₁₂	1.0 %	72	4 %	12.70	45.35	11.72
H ₂	40.5 %	2	5 %	24.57	120	8.57
N ₂	3.5 %	28	6 %	0.93	0	
CO	0.5 %	28	1 %	2.47	10.11	10.23
Total	100 %	17.5	100 %	13.02	48.07	11.34

Flue-gas factor for the calculation of the bubble (combustion component):

Based on the above, it is proposed to take the typical value of 11.3 Nm³/kg of fuel oil equivalent at 3 % O₂ (dry gases) as a standard flue-gas factor for gaseous fuels.

B.3 FLUE-GASES FROM SOUR WATER STRIPPER (SWS) GASES

Flue-gases and/or incondensables from SWS gases are not taken into account in the calculation of the flue-gas volume used for determining the bubble.

As it has been considered that such practises cannot be BAT, including such emissions in a permanent bubble calculation could have a counter productive effect by tolerating them over time and preventing the operator taking drastic actions.

B.4 FLUE-GASES FROM SULPHUR RECOVERY UNITS

The calculations are a simplified formulation based on the flow of acid gas (AG) feeding the unit. The molar composition of acid gas is modelled as three main families, to which ammonia must be added if SWS gases are treated: $a \text{ H}_2\text{S} + b \text{ HC} + c \text{ inerts}$.

Where:

$a = \% \text{ v H}_2\text{S}$

$b = \% \text{ v hydrocarbons}$

$c = \% \text{ v inerts}$

and $a + b + c = 1$

For simplicity the HC are considered to be C_2H_6 (MM= 30) and the inert components are essentially CO_2 . (MM = 44). These approximations generally have little effect on the result (with a low HC content).

B.4.1 MAKE-UP FUEL GAS

Fuel Gas (FG) is injected in the incinerator in order to entirely burn residual H_2S . The flow of FG is represented by the ratio: $j = \% \text{ m of FG to AG}$

B.4.2 ANALYSERS

Gas analysers are mainly:

- H_2S and SO_2 , in the tail gas (TG) downstream of the main reaction zone;
- SO_2 and O_2 in the flue-gas at the exit of the incinerator.

In the following, unless specified otherwise, concentrations are given on dry gases.

B.4.3 CALCULATIONS

Taking into account the actual conversion in the sulphur unit, the molar flow (corresponding to 1 Mol of AG) of the dry residual gas for 0 % O_2 is:

$$f = Q \text{ TG mol} = (1.88a + 15.2b + c)/(1 - 4.76 * \% \text{ SO}_2 \text{ TG} + 0.88 * \% \text{ H}_2\text{S TG})$$

Flue-gas volume exiting the incinerator:

$$Q_{\text{incin vol}} = (1 + 5.64 * \% \text{ H}_2\text{S TG}) * (1.88a + 15.2b + c)/(1 - 4.76 * \% \text{ SO}_2 \text{tg} + 0.88 * \% \text{ H}_2\text{Stg}) + j * \% \text{ x QGA} * 1000 * \text{PF} \text{ (Nm}^3\text{/h of dry flue-gas at 0 \% O}_2\text{)}$$

Examples:

a) Complete conversion:

Molar composition	H_2S	HC	Inerts	MM AG	Mol flue gas/mol AG	Flue-gases $\text{Nm}^3\text{/t AG}$
Case 1	100 %	0 %	0 %	34	1.88	1 239
Case 2	90 %	0.5 %	9.5 %	35	1.86	1 208
Case3	80 %	1 %	19 %	36	1.85	1 178

In the table above, cases 1 and 3 correspond to extreme values: case 1 would be an AG flux originating from amine treatment of FG, while case 3 would be an AG flux from an FCC, with a high CO₂ content. In practice these fluxes are mixed and case 2 reflects a typical AG composition.

The flue-gas factor increases inversely with the inerts content and in the same direction as HC concentration. In the 3 situations above, the 2 parameters partly cancel out and the resulting variability is small.

b) Actual conversion:

Qvol dry flue-gas with combustion of FG in incinerator in Nm³ dry/t AG at 3 % O₂

Qvol dry flue-gas with combustion of FG in incinerator in Nm ³ dry/t AG at 3 % O ₂				Composition AG Case 2		
FG=50 %m C1, 50 %m C2	PF (moles dry flue-gas at 3 % O ₂ /g FG) =	0.52	MMFG =	20.87	Ratio H ₂ S/SO ₂ =	2
%S [= %vol SO ₂ % + % vol H ₂ S]-->		0.25 %	0.50 %	1.00 %	2.00 %	3.00 %
Mass ratio FG/GA						
0 %		1 517	1 529	1 553	1 602	1 652
1 %		1 652	1 665	1 689	1 738	1 788
2 %		1 788	1 800	1 825	1 874	1 923
3 %		1 924	1 936	1 960	2 010	2 059
4 %		2 060	2 072	2 096	2 145	2 195

This method should be used for reporting purposes.

Simplified calculation of flue-gas volume from SRU:

This simplified method allows expressing the flue-gas volume with a reduced number of parameters.

Qincin VOL = (2 + 5.76 x %S TG + j % x 18.32) x QGA/MMGA x 22.4 x 10³ x 21/18 (at 3 % O₂ dry gases)

Qvol dry flue-gas with combustion of FG in incinerator in Nm ³ dry/t AG at 3 % O ₂		Q incin				
%S TG [= %vol SO ₂ % + % vol H ₂ S]-->		0.25 %	0.50 %	1.00 %	2.00 %	3.00 %
Mass ratio FG/AG (j %)						
0 %		1 532	1 544	1 568	1 617	1 666
1 %		1 671	1 683	1 707	1 756	1 805
2 %		1 810	1 822	1 847	1 895	1 944
3 %		1 949	1 961	1 986	2 035	2 083
4 %		2 088	2 101	2 125	2 174	2 223
5 %		2 227	2 240	2 264	2 313	2 362
6 %		2 367	2 379	2 403	2 452	2 501
7 %		2 506	2 518	2 542	2 591	2 640
8 %		2 645	2 657	2 682	2 730	2 779
9 %		2 784	2 796	2 821	2 870	2 919

The table above allows determining the flue-gas volume emitted by the SRU as a function of the mass ratio of make-up fuel gas in the incinerator to the acid gas feeding the unit.

The variability of the result is twofold for a given sulphur content in tail gas. However a typical mass ratio FG/AG of 4 % can be considered as an average value, as it reflects operational constraints (need to ensure an excess of FG to convert residual H₂S), as well as energy efficiency constraints (need to minimise FG consumption as much as possible).

This ratio is very specific to SRU configurations and operating parameters.

B.4.4 FLUE-GAS FACTOR FOR THE CALCULATION OF THE BUBBLE (SRU COMPONENT)

A simplified flue-gas factor which can easily apply to all SRU, regardless of their specificities, has to be established in order to determine the proportion of flue-gas generated by SRU.

Such a flue-gas factor should be:

- Independent from variable parameters such as the quantity of FG burnt in the incinerator, which anyway is already taken into account in the refinery fuel balance (even if it is a negligible amount, compared to combustion).
- Based on available, verifiable, commonly used parameters (such as the quantity of AG feeding the unit and sulphur recovery efficiency).

B.4.5 DETERMINATION OF THE FLUE-GAS VOLUME AS A FUNCTION OF THE SULPHUR RECOVERY EFFICIENCY

By definition the S recovery efficiency is: $\eta = 1 - \%H_2S \text{ unconverted}$

For 1 mole of AG it gives %S incin mol expressed as a function of η :

$$\%S \text{ incin mol} = (100 \% - \eta) \times a/Q \text{ incin mol} \quad (i)$$

$$\%S \text{ incin} = (100 \% - \eta) \times a/(f_0 + 4.76 \times (100 \% - \eta) \times a)$$

$Q \text{ incin vol} = (f_0 + 4.76 \times (100 \% - \eta) \times a) \times 22\,400/\text{MMGA}$
in Nm³ of dry flue-gas at 0 % O₂/t of AG

With $f_0 = 1.88a + 15.2b + c$

Let's consider the standard case where:

- $b=1$ (HC in AG = 1 % and HC is C_2H_6)
- make up FG is CH_4 (PF = $11.93 \text{ Nm}^3/\text{kg}$)
- $f_0 = 1.88a + 0.152 + (100 \% - a - 1 \%) = 0.88 * a + 1.142$

The calculations lead to the following results for the sulphur recovery efficiency:

Flue-gas volume (Nm^3 at 3 % O_2)/t of AG		MM_{GA} (g)	f_0	Sulphur recovery efficiency			
				99.90 %	99.50 %	99.00 %	98.00 %
H ₂ S content of AG (%vol)	99 %	34.0	2.01	1 553	1 567	1 585	1 619
	90 %	34.9	1.93	1 453	1 466	1 481	1 511
	80 %	35.9	1.85	1 348	1 359	1 372	1 399

B.4.6 STANDARD FLUE-GAS FACTOR FOR THE DETERMINATION OF THE BUBBLE (SRU COMPONENT)

The variability of the previous result is relatively small (less than 15 % for a given recovery efficiency).

It can be shown that even with a 30 % variability on the flue-gas volume from SRUs, the influence on the bubble value is very limited (average standard deviation is 1.3 %).

Based on this, it is proposed to take the typical value of $1\,500 \text{ Nm}^3/\text{t}$ of acid gas at 3 % O_2 (dry gases) as a standard flue-gas factor for SRU.

It corresponds to a H₂S content of 95 % and a sulphur recovery efficiency of 99.5 %, but as mentioned the variability of the factor is small even when AG composition and efficiency vary.

B.4.7 DETERMINATION OF THE SRU SO₂ EMISSION LEVEL AS A FUNCTION OF SULPHUR RECOVERY EFFICIENCY

Using the same calculations and knowing %Sincin, it is possible to determine the SO₂ emission level for SRU expressed as a concentration of SO₂ at the exit of the incinerator (without dilution from the make up fuel gas).

The SO₂ emission level is then directly related to the recovery efficiency of the unit:

$$[SO_2] = \%Sincin \times 64/22.4 \times 106 \times 18/21$$

Expressed in mg/Nm^3 at 3 % O_2 dry gases

Leading to the following results:

SO ₂ (mg/Nm^3 at 3 % O_2) incin		MM_{GA} (g)	f_0	Sulphur recovery efficiency			
				99.90 %	99.50 %	99.00 %	98.00 %
H ₂ S content of acid gas (% vol)	99 %	34.0	2.01	1 201	5 952	11 768	23 009
	90 %	34.9	1.93	1 137	5 636	11 150	21 826
	80 %	35.9	1.85	1 059	5 252	10 399	20 385

B.5 FLUE-GAS FLOW FROM THE FCC

The methodology presented under is the most precise and is used within the framework of the ETS reporting. However it requires a significant amount of data, including measurements which are site and unit-specific.

This is why a simplified method is presented further, based on a standard flue-gas factor. This latter method will be the one used for determining the flue-gas volume contribution of FCC UNIT to the total flue-gas of the refinery for the bubble calculation.

B.5.1 GENERAL CASE

In the catalytic cracking process there is a build-up of coke on the catalyst during the reaction. The coke is burnt in the regenerator, which provides the heat necessary for the reaction and re-establishment of the normal activity of the catalyst.

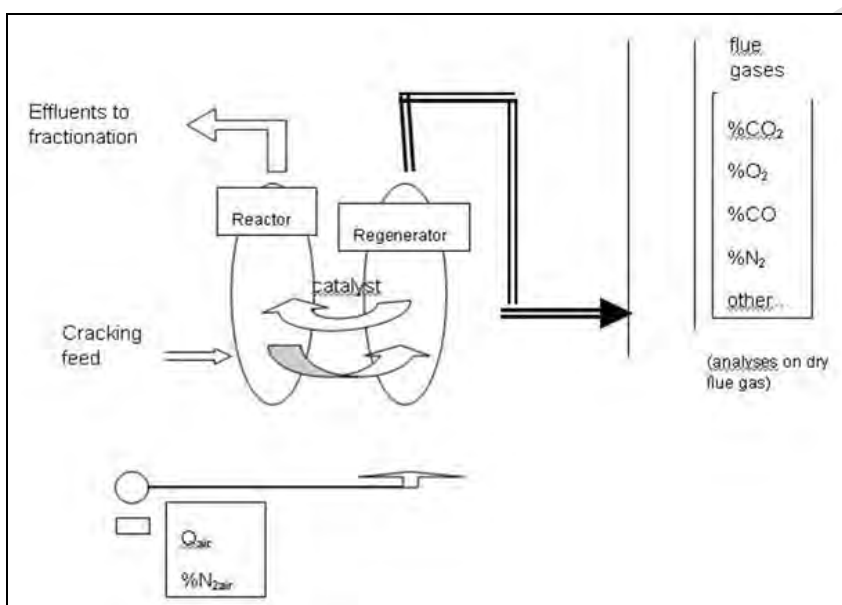


Figure 9.10: Fluid catalytic cracking (FCC) simplified diagram

$Q_{vol \text{ flue-gases}} =$

$$\frac{Q_{mass \text{ of entering air}} \times 0.79 \times \frac{1}{MM_{dry \text{ air}} + MM_{H_2O} \times \frac{\%water}{1 - \%water}} - Q_{N_2 \text{ mass to fraction}} \times \frac{1}{MM_{N_2}}}{\%N_2 \text{ flue gases}} \times 22.4 \times 1000 \text{ as Nm}^3/\text{h}$$

Where:

$Q_{mass \text{ entering air}}$ as t/h moist air

$MM_{dry \text{ air}} = 28.97 \text{ kg/kMol}$

$MM_{H_2O} \times \%water / (1 - \%water) = 0.25 \text{ kg/kMol}$ for air at 20 °C and 60 % relative humidity

$Q_{N_2 \text{ mass to fraction}}$ as t/h

$MM_{N_2} = 28 \text{ kg/kMol}$

Let:

$$Q_{\text{vol flue-gases}} \approx \frac{Q_{\text{mass of entering air}} \times 605 - Q_{\text{N}_2 \text{ mass to fraction}} \times 800}{\%N_{2\text{flue gases}}} \text{ as Nm}^3/\text{h dry flue-gas with the measured O}_2 \text{ content}$$

Note 1: if the atmospheric pollutant analyser is located in a different place from the other analysers involved in the calculation of flue-gas flow, the quantity of gas entering the flue-gas circuit between the 2 measuring points must be added to the calculated flue-gas flow above.

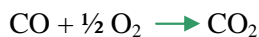
Note 2: the above formula is based on an assumed mean water content corresponding to 60 % relative humidity at 20°C. The accurate formula is to be preferred, as the corresponding parameters are generally available. Note also that the temperature conditions at the point where the air flow is measured may differ from these for the air sampled.

B.5.2 PARTICULAR CASE OF CO BOILERS

If the atmospheric pollutant analyser is located *on the flow on the boiler output*, the quantity of flue-gases to take into account is the sum of that from the regenerator and that from the combustion of the fuels in the boiler.

The first function (flue-gases from FCC) is calculated as from the above formula by adding the additional flue-gas generation by combustion of the CO in the same way as for the other fuels.

Both functions must be expressed under the same excess air conditions, which shall be taken as nil (that is to say, stoichiometry) to simplify the formulae.



As the volume flowrate of the CO₂ is equal to that of the CO. The additional quantity of flue-gases generated by CO combustion is:

Q_{flue-gas CO} = quantity of nitrogen in air used for combustion of the CO.

Q_{flue-gas CO} = quantity of nitrogen in air used for combustion of the CO.

Hence:

$$Q_{\text{flue-gas CO}} = \% \text{CO} \times Q_{\text{vol flue-gas}} \times \frac{1}{2} \times \frac{0.79}{0.21} = \% \text{CO} \times Q_{\text{vol flue-gas}} \times 1.88$$

$$Q_{\text{vol flue-gas at 0 \% O}_2} = Q_{\text{vol flue-gas}} \times \frac{21\% - \% \text{O}_2}{21\%}$$

Q_{flue-gas CO} = %CO x Q_{vol flue-gas} x = %CO x Q_{vol flue-gas} x 1.88

Q_{vol flue-gas at 0 % O₂} = Q_{vol flue-gas}

%O₂ being the content in O₂ on the regenerator output (measurement point) used in the expression for Q_{vol flue-gas}.

The total volume of flue-gases generated by the FCC, expressed for 0 % O₂ becomes:

$$Q_{\text{total flue-gas}} = Q_{\text{vol flue-gas}} \times \left[\frac{21\% - \% \text{O}_2}{21\%} + \% \text{CO} \times 1.88 \right] \text{ in Nm}^3/\text{h dry flue-gas for 0 \% O}_2$$

B.5.3 FLUE-GAS FACTOR FOR THE CALCULATION OF THE BUBBLE (FCC UNIT COMPONENT)

Coke consumption is an easy-to-obtain variable as its annual consumption in FCC UNIT regenerator is reported to the authorities. *It is established on the basis of the methods used for ETS reporting (the coke burnt is deducted from quantities of CO₂ emitted) which offer the best accuracy.*

A benchmark based on 6 FCCs, shows very little variability of the flue-gas volume generated by 1 kg of coke as fuel oil equivalent (foe).

Note: The standard flue-gas factor may also be expressed per tonne of feed processed, but the factor will have a larger variability, as the quality of the feedstock can vary significantly.

It is therefore proposed to take the value of 1.2 Nm³/kg of coke (foe) at 3 % O₂ (dry gases) as a standard flue-gas factor for FCC Units.

9.6.3 APPENDIX C ON MASS/LOAD EMISSION ESTIMATION

NOTE: These two tables are based on the BAT-AEL and EPLs agreed at the final TWG meeting (See details in Chapter 5)

The following tables show the reference values based on individual BAT-AEL to consider when setting a bubble level for the refinery site for SO₂ emissions and NO_x emissions.

Unless stated otherwise, BAT-AEL refer to 3 % oxygen by volume.

Table 9.6: BAT-AEL and EPL values for SO₂ emissions

Source	Type	BAT-AEL/EPL Values	Additional information
Combustion	Gas firing	5 – 35 mg/Nm ³	
	Multi-fuel firing	Existing ⁽¹⁾ : 35 – 600 mg/Nm ³	⁽¹⁾ Refers to the weighted average emissions from multi-fuel firing in combustion units with the exception of gas turbines and stationary gas engines
Sulphur recovery unit (SRU)	Existing units	Sulphur recovery efficiency: ≥ 98.5 %	
	New units	Sulphur recovery efficiency: 99.5 % – >99.9 %	
Fluid catalytic cracking (FCC)	New units	≤ 300 mg/Nm ³	
	Existing units/full combustion	<100 – 800 ⁽²⁾ mg/Nm ³	⁽²⁾ Where selection of low sulphur (e.g. < 0.5 % w/w) feed (or hydrotreatment) and/or scrubbing is applicable ≤ 600 can be achieved
	Existing units/partial combustion	100 – 1 200 ⁽²⁾ mg/Nm ³	
Calcining of green coke		{No BAT-AEL}	
Flares (permanent emissions only)		Use combustion BAT-AELs	

Table 9.7: BAT-AEL and EPL values for NO_x emissions

Source	Type	BAT-AEL/EPL Values	Additional information
Combustion	Gas turbine Existing units	40 – 120 (at 15 % O ₂)	⁽¹⁾ For high H ₂ content fuel (i.e. above 10 %), the upper end of the range is 75mg/Nm ³
	Gas turbine New units	20 – 50 ⁽¹⁾ (at 15 % O ₂)	
	Gas firing Existing units	30 – 150 ⁽²⁾ mg/Nm ³	⁽²⁾ For existing units using high air pre-heat (i.e. > 200 °C) or with H ₂ content in the fuel gas higher than 50 %, the upper end of the BAT-AEL range is 200 mg/Nm ³
	Gas firing New units	30 – 100 mg/Nm ³	
	Multi-fuel firing Existing units	50 – 300 ⁽³⁾ mg/Nm ³	⁽³⁾ For existing units < 100 MW with fuel oil nitrogen content higher than 0.5 % (w/w) or with percentage liquid firing > 50 % or using air preheating values up to 450 mg/Nm ³ may occur
Sulphur recovery unit (SRU)		NO _x emissions considered negligible	
Fluid catalytic cracking (FCC)	New units/all mode	<30 – 100 mg/Nm ³	⁽⁴⁾ When Sb injection is used for metal passivation, NO _x levels up to 700 mg/Nm ³ may occur.
	Existing units/full combustion mode	<100 – 300 ⁽⁴⁾	
	Existing units/partial combustion mode	100 – 400 ⁽⁴⁾	
Calcining of green coke		{No BAT-AEL}	
Flares (permanent emissions only)		Use combustion BAT-AELs	

9.6.4 APPENDIX D BUBBLE MONITORING

Setting appropriate monitoring requirements to each stack identified in the mapping

To fully benefit from the existing ETS CO₂ *monitoring plan* to identify the relevant sources and to assess the emissions level (both volumetric and mass contributions) for each substance covered by the bubble.

To define the type of monitoring in accordance with the relevant tier, as for example, following a growing level of emissions:

- use of emission factor and activity parameter monitoring;
- idem previous item and add periodic stack measurements;
- idem first item and add continuous stack measurements.

The following requirements can be associated to the correspondent emissions sources (to be considered alongside the requirements from the monitoring of emissions in Chapter 5):

Source	Type of monitoring	Observations
Combustion	Continuous direct measurements of SO ₂ or calculation based on S % in fuel Continuous direct measurements of NO _x	Technical provisions on monitoring of IED Annex V may be applicable See also detailed monitoring depending on the capacity (MW) in Section 5.1.4
	Periodic measurements of SO ₂ and NO _x for the smallest sources	
Sulphur recovery unit (SRU)	Continuous direct measurements of SO ₂	Possible calculation from fixed S % recovery and S inlet measurement
Fluid catalytic cracking (FCC)	Continuous direct measurements of SO ₂ or calculation based on S % in feed/coke Continuous direct measurements of NO _x	Measurements generally required when using deSO _x and/or DeNO _x catalysts
Coking process	Continuous direct measurements of SO ₂ and NO _x	
Flares	Permanent emissions of flares monitored from additional fuel consumptions	

Elaborating a formal monitoring plan

The monitoring plan contains the following contents:

- a description of the process to be under monitoring;
- a list of emissions sources and source streams to be monitored for each process;
- a description of the calculation-based methodology or measurement-based methodology to be used and the associated level of confidence.
- a description of the measurement systems, and the specification and exact location of the measurement instruments to be used at emission source, i.e. the points of measurement, frequency of measurements, equipment used, calibration procedures, data collection and storage procedures and the approach for corroborating calculation and the reporting of activity data and, emission factors.