Final Report – Task 2

Assessment of the need for additional IED amendments

Specific contract No. 070307/ENV/2012/627812/C3

19 July 2013

Submitted to:
European Commission
Attention:
DG ENV C.3, Industrial Emissions Team
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BELGIUM

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1. Introduction

1.1 Context

The Commission has found that for some of the provisions of the IED related to large combustion plants there is a need for clarifying the current text, particularly where some provisions can be interpreted in different ways. The driver for the clarifications is questions from Member States that have arisen during their transposition and early implementation of the IED.

In particular, DG ENV has received a number of questions regarding the criteria to use for qualifying combustion plants as “reactors used in the chemical industry”, which are excluded from Chapter III of the IED (Article 28). Such plants were already excluded from the scope of the LCP Directive 2001/80/EC (Article 2(7)(e)). Recently, a concrete case was raised by the Netherlands, after reporting their emission inventories under the LCP Directive, about the categorisation of the steam cracking units operated by Shell Nederland Chemie BV (Moerdijk). Emissions from this plant have been reported in the inventories in the past. However, Dutch authorities stated that the plant operator was arguing that the steam cracker pyrolysis furnaces should be excluded from the scope of the Directives as these are considered to fall under the “reactors used in the chemical industry”. In the data collection phase of this study it also emerged that Italy and Poland has also excluded steam cracking pyrolysis furnace units from their emission inventory submission under the LCP directive based on the same argument. According to Cefic, there is no consistency in the approach taken by Member States in reporting emissions from steam cracker pyrolysis furnaces across the EU in the LCP emission inventories.

Given that the term “reactor used in the chemical industry” is not defined in the IED, it is open to interpretation which combustion plants are exactly covered by it. Obviously, such interpretation should be seen in the context of the overall objectives and the provisions of the Directives concerned. As with all interpretations of EU Directives, the final saying on this would be for the European Court of Justice, being the instance to rule on such matters.

In this report, a technical assessment has been undertaken to explore the rationale for excluding “reactors used in the chemical industry” from the scope of the regulation and to understand the consequences of different interpretations of this term.

One possible interpretation that has been considered is that the exclusion of chemical reactors should only apply for combustion plants used in the chemical sector where the flue gases from the combustion process are in direct contact with the substances involved in or resulting from the chemical process in the reactor. The rationale for such interpretation is that such contact or mixing will affect the composition of the flue gases and applying the emission limit values set out in the LCP Directive (and in Annex V of the IED) would not be appropriate as they are aimed to control emissions resulting from the combustion of the fuels.

A second possible interpretation that could be considered argues that if the combustion process and the chemical reaction process occur within the same physical equipment and the combustion process is integral to the chemical reaction process (i.e. the combustion heat causes the chemical reaction to take place), then the equipment would be considered a “reactor used in the chemical industry.” In this case, the products of chemical reaction would not affect the composition of flue gases, as they do not come into direct contact.

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1 It should be noted that the wording used in Article 28 of the IED is slightly different from the one in Article 2(7) of the LCP Directive. It is the view of DG ENV that this should not affect the interpretation of the provision.
Evidently, the implications of interpretation of the term “reactor use in the chemical industry” are not limited to its potential application to ethylene steam crackers. Pyrolysis furnaces and similar configurations of combustion equipment are used in the commercial production of methanol, ammonia, vinyl chloride monomer, and biofuels (e.g. biodiesel), among other chemical production processes. The configurations of combustion equipment used in methanol, ammonia, vinyl chloride monomer, biofuels, and other chemical production processes, and how such configuration relates to the definition of “reactor used in the chemical industry” are described in Section 3.

1.2 Objectives

This study is intended to help the Commission to better understand this specific provision related to “reactor used in the chemical industry” of the Directives. Based on the information gathered together with the text of the LCP Directive and the IED, we will seek to develop a rationale for determining which types of combustion plants conform to the Directive definition excluding “reactors used in the chemical industry” from the scope of the LCP Directive and Chapter III of the IED. In addition, we will propose criteria to define the term “reactors used in the chemical industry” in Article 2(7)(e) of the LCP Directive and Article 28 of the IED, reflecting such rationale.

1.3 This report

This report forms the final output of Task 2 of the study ‘Collection and analysis of data for the review required under Art. 30(9) of Directive 2010/75/EU on industrial emissions (IED)’, specific contract No. 070307/ENV/2012/627812/C3 implementing Framework Contract No ENV.C.3/FRA/2011/0030.

The report is structured as follows:

- Section 2 sets out the legal definitions that are relevant;
- Section 3 sets out different process-related combustion plants used in the chemical industry examines the case of ethylene steam cracker pyrolysis furnaces and presents an overview of ethylene steam crackers operating across the EU; and
- Section 4 explores alternative definitions of the term “reactor used in the chemical industry” according to the Directive text and examines which types of combustion plants used in the chemical industry may qualify as “reactors in the chemical industry”. In this section alternative criteria are proposed to define the term “reactors used in the chemical industry” in accordance with Article 2(7)(e) of the LCP Directive and Article 28 of the IED.
2. **Legal provisions**

### 2.1 Articles in the Industrial Emissions Directive

Combustion plants which are qualified as "reactors used in the chemical industry" are excluded from the provisions of Chapter III of the IED (in accordance with Article 28) and the provisions of the LCP Directive (in accordance with Article 2(7)(e)). Neither of the Directives provides an explicit definition of what constitutes a “reactor used in the chemical industry.”

According to Article 3(25) of the IED, ‘combustion plant’ means any technical apparatus in which fuels are oxidised in order to use the heat thus generated. Therefore, any chemical reactors that do not oxidise fuel in order to use the heat that is generated would not be classed as combustion plants and would not be subject to the provisions of Chapter III. Chapter III of the IED is restricted to combustion plants of rated thermal input of 50MW or more, irrespective of the fuel used (Article 28).

Furthermore, “fuel” is defined in the IED (Article 3 paragraph 24) as “any solid, liquid or gaseous combustible material used to fire the combustion plant with the exception of waste”.

This definition is interpreted to mean that it is not relevant to consider processes such as titanium dioxide production in which an inorganic material (e.g. TiCl4)\(^2\) is oxidized in a chemical reactor to a chemical product. The interpretation of the definition is that inorganic compounds such as metals are not “combustible” (even though some inorganic compounds can react with oxygen and be oxidised). This is a narrow definition. If the definition of “combustible” is expanded to mean “oxidisable” then metallurgical and other inorganic processes could be included in the discussion.

Under Article 2(7) of the LCP Directive, ‘combustion plant’ means any technical apparatus in which fuels are oxidised in order to use the heat thus generated. However the wording is slightly different to that of the IED:

> This Directive shall apply only to combustion plants designed for production of energy with the exception of those which make direct use of the products of combustion in manufacturing processes.

### 2.2 Definition of “Reactor used in the Chemical Industry” – alternative definitions

This section explores the term “reactor used in the chemical industry” under alternative definitions and explores how the alternative definitions generally would apply to combustion equipment used in the chemical industry.

Two alternative criteria for a definition of “reactor used in the chemical industry” are explored and discussed in this report. One alternative is the “direct contact” definition, in which the qualification of a process as a “reactor used in the chemical industry” depends upon their being direct physical contact of the products of combustion and the products of chemical reaction in the chemical process. A second alternative is the “direct causation” definition in which the qualification of a process as a “reactor used in the chemical industry” depends upon the heat of combustion “directly causing” a chemical reaction to take place and the combustion being “integral” to the chemical reaction process. The alternative definitions are discussed further in this section.

\(^2\)This is based on the interpretation that TiCl4 and other inorganics are, strictly speaking, “non-combustible.”
2.2.1 Direct Contact Definition

Under Article 2(7) of the LCP, combustion plants that “make direct use of the products of combustion in manufacturing processes” are excluded from the LCP Directive:

LCP Article 2(7): “This Directive shall apply only to combustion plants designed for production of energy with the exception of those which make direct use of the products of combustion in manufacturing processes. In particular, his Directive shall not apply to the following combustion plants:
(a) plants in which the products of combustion are used for the direct heating, drying, or any other treatment of objects or materials e.g. reheating furnaces, furnaces for heat treatment;
(b) post-combustion plants i.e. any technical apparatus designed to purify the waste gases by combustion which is not operated as an independent combustion plant;
(c) facilities for the regeneration of catalytic cracking catalysts;
(d) facilities for the conversion of hydrogen sulphide into sulphur;
(e) reactors used in the chemical industry;
(f) coke battery furnaces;
(g) coopers;
(h) any technical apparatus used in the propulsion of a vehicle, ship or aircraft;
(i) gas turbines used on offshore platforms;
(j) gas turbines licensed before 27 November 2002 or which in the view of the competent authority are the subject of a full request for a licence before 27 November 2002 provided that the plant is put into operation no later than 27 November 2003 without prejudice to Article 7(1) and Annex VIII(A) and (B);”

The exclusions from both the LCP Directive and the IED include the explicit exemption of “reactors used in the chemical industry.” Chemical reactors are equipment in which a chemical reaction takes place that transforms raw materials (i.e. the chemical reaction feedstocks) to chemical products (i.e. the reaction products)\(^3\). This is to distinguish chemical reaction processes from physical processes (e.g. simple distillation) in which the raw materials are separated from one another through a physical process, but where no chemical transformation of the raw materials to products takes place through a chemical reaction.

The phrase “direct use of the products of combustion” in the LCP is interpreted to mean that the products of combustion are “directly” used in the manufacturing process and provide direct heat to the manufacturing process.

The case of “reactor used in the chemical industry” could be considered as a particular example of such a situation, when it is limited to those plants in which the products of combustion come into direct contact with the products of chemical reaction within the same physical space within the same equipment, and the products of combustion and the products of chemical reaction are com mingled within the equipment. Under such a “direct contact” definition, the rationale for exempting such reactors is that the products of combustion directly affect the composition of the exhaust gas from the chemical reaction process, as the products of combustion and the products of chemical reaction are in direct contact. Therefore, if the provisions of the LCP Directive and IED were to be applied to these plants, the air emissions limits in the Directives would apply to both the products of combustion and the products of chemical reaction from the process.

Under this “direct contact” interpretation, a “reactor used in the chemical industry” would cover a process such as the bitumen process (discussed further in Section 3.2.5), in which

\(^3\) For the remainder of this report the term “raw materials” will be used to mean the feedstocks that are chemically reacted in the chemical reactor to form chemical products; the term “fuel” will be used throughout this report to mean the material that is combusted to provide heat, and the combustion of which produces products of combustion.
the bitumen process feedstock, which for this process is both raw material (and the fuel), are fed directly into the bitumen blowing unit (BBU), and both the chemical reaction to produce the bitumen product and the fuel combustion that provides heat to the process to drive the chemical reaction occur within the BBU itself. In this case, there is no physical separation between the products of combustion and the raw materials and chemical reaction products. Other processes (e.g. ethylene oxide production, ethylene dichloride production) in which products of combustion come into direct contact with the process raw materials and products of chemical reaction would also be categorised as "reactors used in the chemical industry" under this "direct contact" definition.

Conversely, under the “direct contact” definition a process such as a pyrolysis furnace, in which the heat is created by fuel combustion within a firebox and then imparted indirectly to the raw materials undergoing a chemical reaction through a heat exchange process (furnace tubes), would not be categorized as a “reactor used in the chemical industry” because in this case the products of combustion and the products of chemical reaction do not come into direct physical contact with one another, and the combustion reaction and the chemical reaction do not occur within the same physical space. In a pyrolysis furnace, the raw materials flow through the inside of the pyrolysis furnace tubes, while the combustion process occurs on the outside of the pyrolysis furnace tubes. The heat from the combustion process is imparted indirectly to the raw materials undergoing the chemical reaction through heat exchange through the walls of the pyrolysis furnace tubes. More in general, combustion equipment that are configured such that fuel combustion takes place on the outside of furnace tubes, while the chemical reaction of the raw materials to chemical reaction products takes place inside furnace tubes, such as reformers used in the production of methanol and ammonia and direct-fired pyrolysis furnaces used in the production of vinyl chloride monomer and biofuels would not be categorised as a “reactor used in the chemical industry” under the “direct contact” definition.

2.2.2 “Direct Causation” Definition

Under the “direct causation” definition, a “reactor used in the chemical industry” would include processes such as pyrolysis furnaces, in which the heat of combustion is transferred through heat exchanger tubes to the raw material within the tubes, which undergoes a chemical reaction as a direct result of application of the heat of combustion. Under the “direct causation” definition, the combustion and chemical reaction would need to occur simultaneously within the same equipment, e.g. a pyrolysis furnace, although the combustion and chemical reaction would not necessarily need to occur within the same physical space, as is the case with the bitumen process in which the combustion and chemical reaction are physically collocated within the BBU. Under the “direct causation” definition the combustion would need to be integral to, and not physically separate from, the chemical reaction process in order for the process to qualify as a “reactor used in the chemical industry.”

Under the “direct causation” definition, the waste gases from combustion and the exhaust gas from the chemical reaction process are never in direct contact in the process. A process in which raw material is heated by a combustion process without undergoing a simultaneous chemical reaction within the same equipment would not be categorised as a “reactor used in the chemical industry.” For example, in the case of a preheater that raises the temperature of a raw material prior to the introduction of the raw material into a reactor that is a separate and distinct piece of equipment from the preheater, the preheater would not be categorised as a “reactor used in the chemical industry” because no chemical reaction is occurring within the preheater itself.
2.3 “Chemical industry”

The term ‘chemical industry’ is used in the IED under the heading section 4 of Annex I. It includes:

- production of organic chemicals (IED Annex I section 4.1),
- production of inorganic chemicals (IED Annex I section 4.2),
- production of phosphorous-, nitrogen- or potassium-based fertilisers (simple or compound fertilisers) (IED Annex I section 4.3),
- production of plant protection products or of biocides (section 4.4),
- production of pharmaceutical products including intermediates (IED Annex I section 4.5) and
- the production of explosives (IED Annex I section 4.6).

The production of organic chemicals includes “simple hydrocarbons (linear or cyclic, saturated or unsaturated, aliphatic or aromatic). Petroleum refineries can produce petrochemical feedstocks, including ethylene, propylene, and isobutene, from operation of cracker units, and other products such as bitumen that undergo chemical reaction in addition to physical separation in the production process. Therefore, where petroleum refineries produce such organic chemicals, this part of their activity may also be categorised as part of the “chemical industry”.

The production of biofuels (e.g. biodiesel) from wood or other agricultural products would also be categorised as “production of organic chemicals” and categorised as part of the “chemical industry.” Biofuels are produced from chemical reaction of (raw material) wood/other agricultural products to biofuels (the chemical reaction product) and these processes do not necessarily take place in a petroleum refinery. Biofuels may be produced from biogenic raw materials using various chemical reaction processes including fluidized bed reactors or pyrolysis furnace reactors. Regardless of the process used, in the production of biofuels chemical reactions are taking place in the chemical reactor to transform the agricultural products into biofuels, such biofuels containing "simple hydrocarbons" including linear aliphatic compounds. Therefore, production of biofuels conforms to the definition of "production of organic chemicals."

Many chemical manufacturing processes have a significant requirement for energy input. The energy source depends on the process requirements and the local availability. Many chemical plant operators sub-contract energy supply (steam and electricity generation) to third parties or use the central utility facilities that exist on many industrial plant sites. For other chemical reaction processes direct heat, steam, and/or electricity may be generated locally within the process. The main sources of process heat to chemical reaction processes are kilns (e.g. lime kilns, green coke calcining kilns, and other kilns), direct-fired furnaces (i.e. heating of process materials contained within furnace tubes), steam boilers, and heat exchangers (recovery of heat against a hotter product or raw material). Steam boilers and heat exchangers would be sources of indirect process heat to chemical processes, in that in these devices the combustion products do not directly contact the material being heated and (in the case of some types of process furnaces) chemically reacted. Kilns are sources of direct process heat to chemical processes, in that in these devices the combustion products do directly contact the material being heated and chemically reacted. Some chemical processes are exothermic processes that generate more energy (in the form of heat) than is needed for operation of the chemical reactor process. Examples of these exothermic processes include ethylene oxide and ethylene dichloride production. These chemical processes may export energy, in the form of heat exchange, steam or electricity, to other parts of the industrial plant site.
3. Process-related combustion plants used in the chemical industry

3.1 Types of process related combustion plants used in the chemical industry

3.1.1 Process heaters

Process heaters are heat transfer units in which heat from fuel combustion is transferred predominantly by radiation / conduction and secondarily by convection to fluids contained in tubes. Process heaters are generally used in heat transfer applications where steam heaters (i.e. boilers) and heat exchangers using intermediate heat transfer fluids (e.g. heat transfer oil) are inappropriate. These include applications in which heat must be transferred to the process fluid at temperatures in excess of 90° to 200°C. The process fluid stream to be heated is generally contained within single-fired tubes along the radiant section walls and ceiling, within two-sided fired tubes within the radiant section, and within convection section tubes of the process heater combustion chamber. This process fluid stream is heated for one of two reasons: (1) to raise the temperature of the process fluid stream by fuel combustion to facilitate additional downstream processing (further: “heating applications”), or (2) to raise the temperature of the process fluid stream by fuel combustion so that chemical reactions may occur within the tubes (further: “chemical reaction applications”).

In chemical process equipment such as pyrolysis furnaces (e.g. used in ethylene and vinyl chloride monomer production) and reformer furnaces (e.g. used in methanol and ammonia production) the primary purpose of the heat transfer in the furnace/reformer is to provide the heat needed to drive the chemical reaction of the raw material to chemical reaction products. In chemical process equipment such as distillation columns, the primary purpose of the heat transfer is generally to impart heat to raise the temperature of the raw material (the process fluid), e.g. to generate vapour feed to a distillation column, and not to drive a chemical reaction involving the raw materials.

This section does not cover combustion plants such as steam boilers and gas turbines because there are no chemical reaction processes involved in steam boiler or gas turbine operation other than conventional combustion processes.

3.1.1.1 Process Heaters for Heating Applications

Process heaters whose function is to heat a process (raw material) fluid stream before additional processing or to heat an indirect heat transfer fluid include distillation column feed preheaters and reboilers, reactor feedstock preheaters, hot oil furnaces, hot sand heaters, and viscous fluid heaters. These process heaters may impart heat to the raw material itself (e.g. in a direct-fired reboiler for a distillation column) or impart heat to an intermediate heat transfer fluid (e.g. in a hot oil furnace, sand furnace, or viscous fluid heater) that is subsequently used to impart heat to the raw material. These types of process heater are found in both the petroleum refining and chemical manufacturing industries.

Direct-fired heaters are used in the petroleum refining industry principally as preheaters for various operations such as distillation, catalytic cracking, hydroprocessing, and hydroconversion. Direct-fired heaters are used in a wide variety of heating applications in the chemical manufacturing industry. They are used as feedstock (raw material) preheaters for non-fired reactors, reboilers for distillation operations, and heaters for heating heat transfer oils or other intermediate heat transfer fluids.

Heat transfer oils and other intermediate heat transfer fluids are used as working fluids to transfer heat from direct-fired oil/fluid heaters to process equipment, e.g. distillation process

4 See Section 6.1.4 of LCP BREF (2007) for a definition of process heaters.
reboilers. The direct-fired oil/fluid heaters used in these processes would not be considered chemical reactors, as the heat transfer oil/fluid being heated does not undergo any chemical reaction. Reboilers are heat exchangers that provide heat to the bottom of a distillation column to generate vapour that rises back into the distillation column. The reboiler would be considered a heat exchanger, not a chemical reactor. Distillation is a generally physical process to separate the various liquid and vapour fractions of a feedstock.

3.1.1.2 Process Heaters for Chemical Reaction Applications

Process heaters may be used to impart heat to raw materials for the purposes of driving a chemical reaction. In these processes, the primary purpose of the heat is to promote the chemical reaction, rather than only to heat the raw materials. Process heaters / furnaces may impart heat directly to the raw materials through direct contact between the products of combustion and the raw materials and chemical reaction products, or they may impart heat indirectly to the raw materials by radiation/conduction heat transfer through furnace tubes. In this case, the raw material flows through the inside of the furnace tubes, and the fuel combustion occurs in the combustion chamber outside of the furnace tubes. Heat is transferred across the furnace tube walls through radiation, conduction, and convection. In this case, there is no direct contact between the products of combustion and the raw materials undergoing chemical reaction or the chemical reaction products.

Applications of process heaters to chemical reaction processes include steam-hydrocarbon reformers used in ammonia and methanol manufacturing, pyrolysis furnaces used in ethylene and vinyl chloride monomer manufacturing, pyrolysis furnaces used in biofuel (e.g. biodiesel) production, and thermal cracking units used in petroleum refining operations.

For each of these processes heat is transferred indirectly to the raw material through furnace tubes. Other types of process heaters provide direct heat to the raw materials. These applications include direct combustion processes such as the bitumen production process in which bitumen process feedstock, which for this process is both the raw material and the fuel, is fed directly into the bitumen blowing unit along with air and steam. The volatile components of the bitumen process feedstock (i.e. the fuel) combust in the bitumen blowing unit to provide heat to drive the chemical reaction of the remainder of the bitumen process feedstock (i.e. the raw material) to produce the bitumen product, and the products of combustion directly contact the raw material and chemical reaction products in the bitumen blowing unit.

Pyrolysis Furnace/Steam Reformer Processes

There are number of processes, including ethylene, methanol, ammonia, and biofuels production, in which reformer or pyrolysis furnaces are used to provide heat to the process to drive the chemical reaction. For these processes, the combustion of fuel (e.g. natural gas, fuel gas generated by downstream processes) occurs in a firebox and heat is provided to the raw material through furnace tubes. The products of combustion do not come into contact with the raw materials or products of chemical reaction, and the products of combustion do not directly affect the composition of the vent gas from the chemical reaction or vice versa. The combustion and chemical reaction occur within the same equipment (the pyrolysis furnace, the reformer) and the combustion is integral to the process and directly causes the chemical reaction to occur.

3.1.2 Kilns

In kilns (e.g. lime kilns, green coke calcining kilns), fuel is direct-fired into the kiln along with the raw material and the combustion gases directly contact the raw material, directly
transferring heat to the raw material and thereby initiating a chemical reaction. Green coke calcining is a petroleum refinery process. These kiln processes are defined as “thermal treatment” processes involving the direct use of the products of combustion and are therefore not covered by the IED and LCP Directive (see Section 2).

3.1.3 Direct Combustion Processes

There are a number of examples of processes, including ethylene oxide, ethylene dichloride, and bitumen production, in which a portion of the feedstock to the process is completely combusted and provides heat to the process, and in which the remainder of the feedstock is chemically reacted (e.g. partially combusted) to produce the chemical product. In these processes, the products of combustion directly contact the products of chemical reaction and the direct interaction of the products of combustion and products of chemical reaction directly affect the composition of the vent gas from the process. For the bitumen process, for example, there is no “external” heat provided to the reactor by another device (e.g. a furnace) or by any supplemental fuel (e.g. natural gas); the heat needed to drive the chemical reaction is generated within the chemical reactor through the combustion process. Similarly, there is no external heat or supplemental fuel supplied to the ethylene oxide or ethylene dichloride processes.

3.1.4 Catalytic Processes and Catalyst Regeneration

Various processes including catalytic cracking and catalytic reforming use catalysts to promote chemical reactions of raw materials to products. Over time, carbon (coke) particles accumulate on the surface of the catalyst, reducing its performance. In these processes, spent catalyst needs to be periodically regenerated in order to restore its catalytic function. In this process, carbon contamination on the spent catalyst surface is directly burned off of the catalyst in a regeneration process unit. Facilities for the regeneration of catalytic cracking catalysts, which would include fluidized catalytic cracking (FCC) catalyst and other cracking catalyst regeneration, are explicitly exempt under the LCPD and Chapter III Article 28(c) of the IED. Other types of catalyst regeneration (e.g. regeneration of spent catalysts used in catalytic reforming processes) are not explicitly exempt under the LCPD and Chapter III Article 28(c) of the IED.

On-line regeneration refers to a continuous process in which the spent catalyst is directly and continuously transferred from the catalytic cracking unit to the regeneration unit, which is a separate piece of equipment. Off-line regeneration refers to the process in which the catalytic reactors are required to be taken off-line (i.e., cut-off of feedstock feed) in order for the catalyst to be regenerated. In this case, the catalyst is regenerated within the catalytic reactor itself, not in a separate piece of catalyst regeneration equipment. Multiple catalytic reactors could be used such than when one catalytic reactor is taken off line for catalyst regeneration the other catalytic reactors would continue to receive feedstock and produce chemical reaction products.

3.2 Examples of plants which are potential candidates for ‘reactor used in the chemical industry’

This section discusses the types of plants that may be considered candidates for qualification as a “reactor used in the chemical industry”.

In this section, we have assessed the relevant BREF documents including the Large Volume Organic Chemical Industry (LVOC) BREF, Refining of Mineral Oil and Gas BREF, Large Volume Inorganic Chemicals – Solids and other Industry (LVIC-S) BREF, Large Volume commercial product. Since lime kilns are categorised as “mineral industry” not chemical industry they are not analysed further in this study.

Inorganic Chemicals – Ammonia, Acids, and Fertilizers (LVIC-AAF) BREF, and other chemical process documentation to identify chemical production processes in which the combustion process occurs simultaneously with the chemical reaction process in the same equipment are deemed to be relevant.

Potential candidates include:

A. **Thermal Treatment Processes**
   - Carbon black (furnace black process) – LVIC-S BREF;
   - Green coke calcining (refinery process) – Mineral Oil and Gas Refining BREF

B. **Direct Combustion Processes**
   - Production of ethylene oxide and ethylene dichloride (precursor to vinyl chloride) – LVOC BREF.
     (Note: the ethylene oxide and ethylene dichloride processes are examples of processes in which direct combustion of a fuel (feedstock) occurs within a chemical reactor as a side reaction to a chemical process using the same raw material feedstock; in this case, ethylene is both the fuel and the raw material in the process.\(^8\)
   - Bitumen – Mineral Oil and Gas Refining BREF; this refers to the production of bitumen within a petroleum refinery.\(^9\)

C. **Catalytic Cracking Processes/Associated CO Boilers**
   - Propylene (and other hydrocarbons) production from fluidized catalytic cracking (FCC) – Mineral Oil and Gas Refining BREF, and Other catalytic cracking processes
   - CO boilers

D. **Pyrolysis Furnace Processes**
   - Ethylene cracker pyrolysis furnace process (LVOC BREF)
   - Biofuels (biodiesel) pyrolysis furnace process (no applicable BREF)
   - Vinyl Chloride Monomer pyrolysis furnace process (LVOC BREF)

E. **Steam Reformer Processes**
   - Methanol Production Steam Reformer Process (LVOC BREF)
   - Ammonia Production Steam Reformer Process (LVIC – AAF BREF)

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\(^8\) These processes are examples of major processes that would fall under this example; this is not intended to be a comprehensive list of every process that is similar to the configuration of an ethylene oxide / ethylene dichloride direct combustion process and that would have the same Directive Status as these processes. There are many of these “partial oxidation” processes described in the LVOC BREF, and the ethylene oxide and ethylene dichloride processes are used as a representative examples here.
A. THERMAL TREATMENT PROCESSES

Thermal treatment processes include kilns, furnaces, and similar equipment in which there is direct contact between the flue gases generated in the combustion process and the raw material being thermally treated. Kilns, furnaces, and other processes that are categorised as thermal treatment processes are discussed in this section.

3.2.1 CARBON BLACK

CARBON BLACK PRODUCTION (FURNACE BLACK PROCESS) PROCESS DESCRIPTION

Approximately 95% of carbon black production worldwide is through the furnace black process. The thermal black process and other processes account for the remainder of worldwide carbon black production.\(^\text{10}\) A typical furnace black process configuration is illustrated in Figure 3-1 and Figure 3-2.

The furnace black process produces carbon black from ‘carbon black feedstock’ (also referred to as ‘carbon black oil’) which is a heavy aromatic oil that may be derived either as a by-product of the petroleum refining process or metallurgical coke production process. For either petroleum-derived or coal-derived feedstock, the carbon black feedstock, referred to as the ‘primary feedstock,’ is injected into a furnace that has been preheated by a ‘secondary feedstock’ (generally natural gas or fuel oil). The carbon black feedstock is injected directly into and then rapidly mixed with the hot combustion gases generated by combustion of the secondary feedstock. Both the secondary feedstock and a portion of the carbon black feedstock are combusted to provide heat to the furnace black production process. The process heat vaporises and pyrolyzes the remaining carbon black feedstock to form the carbon black product. The carbon black is then separated from the combustion gases for further processing, pelletizing, and drying.\(^\text{11}\)

COMBUSTION PROCESSES

The furnace black process is a combustion process in which gases generated from combustion of the secondary feedstock (e.g. natural gas) are mixed directly with the primary feedstock (carbon black oil) in the carbon black furnace to form the product (carbon black), which is then physically separated from the combustion gases. The tail gas from which the carbon black product is separated contains carbon monoxide, methane, and other hydrocarbons. A portion of the tail gas is generally burned for energy recovery within the furnace black process to provide heat to the downstream carbon black product dryers, as illustrated in Figure 3-1. The remaining tail gas may also be exported from the furnace black process and burned for energy recovery in a CO Boiler to provide steam and/or electricity, or the tail gas may be flared or vented to the atmosphere without energy recovery. CO Boilers are discussed separately below.


Figure 3-1 Furnace black process (Source: LVIC-S BREF)

COMPOSITION AND DISPOSITION OF VENT GASES / EMISSIONS

The Large Volume Inorganic Chemical – Solids and Other Industry (LVIC-S) BREF reported that there is a wide range of emissions characteristics for furnace black carbon black production due to wide variability in the characteristics of the feedstocks used (e.g. sulphur content) and the application of emissions control systems (e.g. tail gas combustion). For example, tail gas sulphur content was reported to range from 5 ppmv to 250 ppmv and hydrogen sulphide from 63 ppmv to 2,500 ppmv.\textsuperscript{12}

The LVIC-S BREF reported controlled air emissions for a typical furnace black process operated in Germany for which all of the facility vent gases are vented to a single stack.\textsuperscript{13}

Table 3-1: Emissions values for carbon black

<table>
<thead>
<tr>
<th>Emission component</th>
<th>Specific emission (kg/tonne carbon black)</th>
<th>Emission concentration* (mg/Nm\textsuperscript{3} at 10 % O\textsubscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulate matter</td>
<td>0.2 – 0.4</td>
<td>10 – 30</td>
</tr>
<tr>
<td>Sulphur dioxide (as SO\textsubscript{2})</td>
<td>6.5 – 22.0**</td>
<td>400 – 1400</td>
</tr>
<tr>
<td>Nitrogen oxides (as NO\textsubscript{2})</td>
<td>6.0 – 15.0</td>
<td>400 – 900</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>2.0 – 3.0</td>
<td>120 – 200</td>
</tr>
<tr>
<td>Volatile organic compounds (as total C)</td>
<td>up to 0.7</td>
<td>up to 50</td>
</tr>
</tbody>
</table>

*Emission concentrations at 273.15 K, 101.3 kPa under dry conditions, standardised to 10 % O\textsubscript{2}. This oxygen percentage would be representative for a situation where all off-gases are emitted through a central stack.

**Range corresponds to a sulphur content in the feedstock of 0.3 – 1.0 wt-%. Actual


The figure below demonstrates that the carbon black oil (the carbon black feedstock) and the fuel gas (natural gas) enter the same piece of equipment and that there is only one tail (exhaust) gas stream that contains both the combustion products of the natural gas and the volatilized components of the carbon black oil. The exhaust gas from the carbon black furnace contains both the combustion products from the combustion of natural gas (the fuel) and the chemical reaction products from the volatilized components of the carbon black oil (the feedstock), which are directly mixed together and which are not distinguishable from one another in the exhaust gas stream. Note that the combined combustion product and chemical reaction product exhaust gas from the carbon black furnace is generally further combusted in a downstream process for the purposes of emission control and energy recovery.

**Figure 3-2 Example of possible configuration of the furnace black process (LVIC-S BREF)**

**Typical Capacity**

According to Table 4.2 of the LVIC-S BREF (2007), a typical carbon black plant in the EU can have a production capacity of 100,000 metric tons per year. From Table 4.11 of the LVIC-S BREF the total energy input to the furnace black process is in the order of 74 GJ/tonne carbon black produced, including primary (carbon black oil) and secondary (natural gas) feedstock. For a 100,000 tonne per year capacity plant the total energy input including
primary and secondary feedstock is equivalent to 0.234 GJ/second heat input (234 MWth). The total energy output from the furnace black process (i.e. the energy content of the tail gas that can be burned for energy recovery) is on the order of 28 GJ/tonne carbon black produced, equivalent to 87 MW of potential heat input to downstream combustion processes (e.g. carbon black dryers, CO boilers).\textsuperscript{14}

There are two consecutive combustion processes going on in this process: the combustion going on in the reactor (the carbon black furnace) itself and the combustion going on in the tail gas energy recovery boiler that is downstream of the reactor. The tail gas combustion occurring in the carbon black dryer can be ignored because dryers are exempt from Chapter III of the IED as thermal treatment processes. Both the reactor combustion process and the energy recovery combustion process affect the final composition of the of flue gas that is ultimately released to the atmosphere.

### 3.2.2 Petroleum Refinery Green Coke Calciners

**Calciner**

Green (raw) coke is produced as a by-product of refinery processes; the green coke contains moisture and volatile organic compounds that make the material unsuitable for certain industrial applications. For certain applications therefore, the green coke should be calcined before being used or sold. The fuel to the green coke calcining kilns are direct fuel gas, natural gas and/or coke fines\textsuperscript{15} fired at the discharge end of the kiln. The coke is calcined 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 calcined 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.

**Composition and Disposition of Vent Gas / Emissions**

The draft mineral oil and gas refining BREF (Draft March 2012) reported uncontrolled emissions from green coke calcining processes, which are reproduced in the Table below.

**Table 3-2: Emission values for calcination of green coke (Source: March 2012 Draft Mineral Oil and Gas BREF Table 4.32, Page 318)**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Emission Value Range (mg/Nm\textsuperscript{3} at 3 % O\textsubscript{2})</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen Oxides</td>
<td>450 – 875</td>
<td>Without NO\textsubscript{X} emission control device</td>
</tr>
<tr>
<td>Sulphur Oxides</td>
<td>1,100 – 2,300</td>
<td>Without SO\textsubscript{X} emission control device; (300 – 700 for low sulphur coke)</td>
</tr>
<tr>
<td>Particulate Matter</td>
<td>20 – 100</td>
<td></td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons (total)</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{14} LVIC-S BREF Section 4.3.5, Energy Consumption, Table 4.11, Page 223.

\textsuperscript{15}“Coke fines” are fine particulate coke material that can be collected from the process and burned for energy recovery or recombined with the main product (the calcined coke).
**TYPICAL CAPACITY**

The draft mineral oil and gas refining BREF reported petroleum coke production capacity in Europe of 13,900 metric tons per day, corresponding to approximately 5 million metric tons per year. Petroleum coke production capacity includes facilities in Belgium, Germany, Hungary, Italy, Romania, Spain, and the United Kingdom.\(^{16}\) Petroleum coke production capacity was not reported for other countries within the EU.

**Figure 3-3 Schematic of calcining process for petroleum coke (Source: Zhang, 2007)**

**B. DIRECT COMBUSTION PROCESSES**

“Direct combustion” processes include processes in which a portion of the feedstock to the process is completely combusted within the process and provides heat to the process, while the remainder of the raw material feedstock is reacted (e.g. partially oxidised) within the process to form chemical reaction products.

### 3.2.3 ETHYLENE OXIDE

**ETHYLENE OXIDE PRODUCTION PROCESS DESCRIPTION**

Ethylene oxide is formed by reacting gaseous ethylene and oxygen over a catalyst. The exothermic reaction is carried out at elevated temperature (200 – 300\(^{\circ}\)C) and pressure (15 - 25 bar). The primary reaction to produce ethylene oxide is the partial oxidation of the ethylene feedstock to ethylene oxide:

\[
C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O
\]

The main by-products of the ethylene oxide production process are carbon dioxide and water that are formed from the highly exothermic complete oxidation (combustion) of a portion of the ethylene feedstock:

\[
C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O
\]

The ratio between the partial oxidation (to ethylene oxide) and complete oxidation (to carbon dioxide) reactions that occur in the ethylene oxide reactor catalytic defines the selectivity of

---

the ethylene oxide production process (i.e., the amount of ethylene oxide produced per amount of ethylene feedstock consumed). According to the LVOC BREF (2003) the selectivity of the process is determined by the type of catalyst used and by whether air or oxygen (supplied by an air separation unit) is used in the process. The selectivity to ethylene oxide is 65 – 75 % for the air process or 70 – 80 % for the oxygen process. The heat generated from the exothermic complete oxidation reaction is removed from the reactor through heat exchangers and is recovered for use for steam generation elsewhere in the production plant.

A typical ethylene oxide plant based on the oxygen process is shown in Figure 3-4. The configurations of ethylene oxide plants that are based on the air process are somewhat different because of the additional process steps needed to remove nitrogen from the ethylene oxide reactor vent gas.

**Figure 3-4 Schematic ethylene oxide / ethylene glycol process with pure oxygen feed**

![Diagram of ethylene oxide production process](image_url)


**COMBUSTION PROCESS**

A portion of the ethylene feedstock to the ethylene oxide reactor is completely oxidized to carbon dioxide and water as a side reaction to the primary process of converting ethylene to ethylene oxide through partial oxidation. Air or oxygen may be used in the ethylene oxide reactor. The complete oxidation of ethylene feedstock in the ethylene oxide reactor would be categorised as a combustion process, as the ethylene is converted to carbon dioxide and heat. Both the heat and the carbon dioxide generated by the ethylene oxide production process may be recovered for use.

The combustion process and chemical reaction process (conversion of the raw material ethylene to ethylene oxide) occur simultaneously within the same piece of equipment (within the ethylene oxide chemical reactor) and the components of the exhaust gas that are derived from the combustion reaction and from the chemical reaction are comingled within the same vent gas stream and cannot be distinguished from each other. For this process (and also for the ethylene dichloride process described below) the “feedstock” and the “fuel” are both the same ethylene input stream. There is no separate “supplemental fuel” such as natural gas going into the ethylene oxide or ethylene dichloride chemical reactors. The heat to these processes is coming from the combustion of a portion of the ethylene feedstock to the process.
COMPOSITION AND DISPOSITION OF VENT GAS / EMISSIONS

The vent gas\(^{17}\) stream from the ethylene oxide reactor is treated to remove the carbon dioxide, and the treated vent gas (containing crude ethylene oxide product) is sent to downstream processes for recovery of the ethylene oxide product. The carbon dioxide recovered from the vent gas may be vented to the atmosphere or sold as a commercial product (e.g. for beverage production). The carbon dioxide produced from the vent gas treatment process can be nearly pure CO\(_2\).

The exhaust gas emissions result from two processes that occur within the ethylene oxide reactor: the combustion of the fuel (the ethylene) within the reactor to combustion products (CO\(_2\) and H\(_2\)O) and the chemical reaction of the raw material (also the ethylene) to form ethylene oxide (the chemical reaction product). Therefore the composition of the exhaust gas from the ethylene oxide process is directly related to the fuel combustion (the combustion of the ethylene feedstock) in the reactor and is also directly related to the chemical reaction of the feedstock (also the ethylene) to form ethylene oxide. Both the combustion products and the chemical reaction products are components of the same exhaust gas stream.

TYPICAL CAPACITY

The LVOC BREF (2003) reports ethylene consumption for a typical ethylene oxide plant. Depending upon the process (air or oxygen) and the process selectivity, ethylene consumption can be 800 kg per 1,000 kg of ethylene oxide produced. A typical ethylene oxide plant in the EU may have a production capacity of 200,000 metric tons per year\(^{18}\), corresponding to approximately 160,000 metric tons per year ethylene feed based on the LVOC BREF (2003) ethylene consumption factor. This ethylene feed rate would correspond to a heat input greater than 50 MW (0.05 GJ/second).

But for an ethylene oxide reactor the amount of “fuel” input to the chemical reactor is somewhat subjective; The overall input of “feedstock” (i.e. the ethylene) to the reactor includes both the amount of the feedstock that is converted into the chemical product (ethylene oxide) and the amount of the feedstock that is fully combusted to CO\(_2\) and heat in the reactor. So one could define the “thermal input” to the ethylene oxide reactor as only the amount of feedstock that is fully combusted to CO\(_2\) or one could define the “thermal input” more broadly as being the total input of feedstock to the reactor.

3.2.4 ETHYLENE DICHLORIDE

ETHYLENE DICHLORIDE PRODUCTION PROCESS DESCRIPTION

Ethylene dichloride may be produced either through the direct chlorination process or the oxychlorination process, or through a combination of the two processes referred to as the “balanced process.” The direct chlorination process involves a direct gas-phase reaction of ethylene feedstock with chlorine feedstock to produce ethylene dichloride. The oxychlorination process involves a gas-phase reaction of ethylene feedstock with hydrochloric acid feedstock and oxygen to produce ethylene dichloride and water. The ethylene dichloride is then cracked to produce vinyl chloride monomer and hydrochloric acid, which is recycled to the ethylene dichloride reactor. Chemical reactions involved in the direct chlorination and oxychlorination processes are as follows:

\(^{17}\) In this case, the vent gas (as opposed to flue gas) from the chemical reactor is what contains the chemical products of the chemical reaction. The vent gas containing the chemical products is comingled with the combustion products of the direct oxidation of the feedstock (the side reaction that also occurs within the chemical reactor).

Direct chlorination process reaction:

\[ C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \]

Oxychlorination process reactions:

\[ C_2H_4 + \frac{1}{2} O_2 + 2 HCl \rightarrow C_2H_4Cl_2 + H_2O \]

\[ [C_2H_4 + 3 O_2 \rightarrow 2 CO_2 + 2 H_2O] \]

The oxychlorination process produces a process off gas containing by-product CO\(_2\) produced from the direct oxidation of the ethylene feedstock with oxygen in the ethylene dichloride reactor. The direct chlorination process produces a process off gas containing by-product chlorinated hydrocarbons. This process is similar to the ethylene oxide process described previously in that the ethylene represents both the chemical process feedstock and the fuel for the process.

**COMBUSTION PROCESS**

A portion of the ethylene feedstock to the ethylene dichloride reactor is completely oxidized to carbon dioxide and water as a side reaction to the primary process of converting ethylene to ethylene dichloride through partial oxidation in the oxychlorination process. The complete oxidation of ethylene feedstock in the ethylene dichloride reactor could be categorised as a combustion process, as the ethylene is converted to carbon dioxide and heat. Both the heat and the carbon dioxide generated by the ethylene dichloride production process may be recovered for use.

**COMPOSITION AND DISPOSITION OF VENT GAS / EMISSIONS**

The ethylene dichloride production processes are not 100 percent efficient in the utilisation of the ethylene feedstock. On the order of three percent of the ethylene feedstock is not converted to ethylene dichloride but is converted either to CO\(_2\) (by direct oxidation of the ethylene in the oxychlorination process) or to chlorinated hydrocarbons (in either the oxychlorination or direct chlorination process.) Process off gas containing chlorinated hydrocarbons is generally treated in a thermal incineration process or a catalytic incineration process to convert the chlorinated hydrocarbons to CO\(_2\) and HCl prior to venting to the atmosphere. Combined ethylene dichloride/vinyl chloride monomer plants generally recover energy from the incinerator off gases and process off gases for use in the plant.

**TYPICAL CAPACITY**

The LVOC BREF (2003) reports ethylene consumption for a typical integrated ethylene dichloride / vinyl chloride monomer plant. Ethylene consumption can be 470 kg per 1,000 kg of vinyl chloride monomer produced.\(^1\) A typical integrated ethylene dichloride/vinyl chloride monomer plant in the EU may have a production capacity of 500,000 metric tons VCM per year, corresponding to approximately 235,000 metric tons per year ethylene feed. This ethylene feed rate would correspond to a heat input greater than 50 MW (0.05 GJ/second).

**3.2.5 BITUMEN**

**BITUMEN (PETROLEUM REFINERY) PROCESS DESCRIPTION**

Bitumen is a residue derived from crude oil and is an ingredient used in the production of asphalt and roofing material. The feedstock for the bitumen production process is the

residue from the petroleum refinery vacuum distillation process. According to the draft of the revised Mineral Oil and Gas BREF (Draft 2 March 2012), 45% of petroleum refineries in the EU operate bitumen production processes.

Bitumen is produced in a bitumen blowing unit (BBU). A simplified process diagram of a BBU is illustrated in Figure 3-5). The bitumen process feedstock (vacuum distillation residue) is fed to the oxidizer unit, and air is blown into the oxidizer unit to polymerize, dehydrogenate, and partially oxidize the feedstock. Steam is also injected into the oxidized unit to prevent the oxygen in the air and the volatile hydrocarbons in the feedstock from forming an explosive mixture in the oxidizer. Bitumen product is removed from the base of the oxidizer unit. Heat generated by the exothermic oxidation process is exported from the process.

**COMBUSTION PROCESSES**

Components of the vacuum distillation residue (feedstock) are combusted in air to carbon dioxide in the oxidizer unit; other components are partially oxidized. The combustion processes take place within the oxidizer unit along with the chemical reactions that produce the bitumen product.

**COMPOSITION AND DISPOSITION OF VENT GAS/EMISSIONS**

Vent gases from the top of the oxidizer unit are treated in a vent gas scrubber to remove oil components and partial oxidation products. The treated vent gas, containing carbon dioxide, light hydrocarbons, and residual oxygen and nitrogen, is generally incinerated.  

**TYPICAL PRODUCTION CAPACITY**

According to Table 1.6 of the Mineral Oil and Gas BREF (Draft 2 March 2012), a typical petroleum refinery in the EU can have a bitumen production capacity ranging from 0.1 to 4.7 million cubic meters bitumen per year. Table 3.80 of the draft BREF reports a typical density of bitumen of 1.17 kg/litre. The feedstock energy content of bitumen is approximately 40 MJ/kg as reported by the IPCC. The energy content of the bitumen produced by a 0.5 Mm³/year capacity bitumen plant is therefore approximately 0.75 GJ/sec, corresponding to approximately 750 MW of heat content.
C. CATALYTIC CRACKING PROCESSES/ASSOCIATED CO BOILERS

3.2.6 Propylene (and other hydrocarbons) production from fluidized catalytic cracking

**FLUID CATALYTIC CRACKING (FCC) PROCESS**

Catalytic Cracking processes are operated at petroleum refineries to produce components of gasoline (petrol) and other hydrocarbons from high-boiling petroleum fractions. Propylene and other light olefins are produced as co-products of the catalytic cracking process. The main sections of a conventional fluidized catalytic cracking unit comprise the feedstock injection system, the reactor (fluidised bed), stripper, fractionator, and catalyst regenerator. A fluidized catalyst system is used to facilitate catalyst flow and heat transfer between the reactor and the catalyst regenerator. The cracking reactions in the reactor produce hydrocarbon products (including propylene) and by-products and also generate coke (carbon) particles that adhere to the catalyst particles. The cracking reactions in the reactor are endothermic reactions; the heat balance for the catalytic cracking process is obtained through the combustion, in air, of catalyst-deposited coke in the catalyst regenerator. The regenerated catalyst is recirculated back into the reactor. Make-up catalyst is added to account for losses of catalyst particles from the process. The hydrocarbon products of the FCC reactor are sent to a fractionation process where the component hydrocarbons are separated and collected for further processing. A typical (simplified) process flow diagram of an FCC Process is shown in Figure 3-6.
The exhaust gas from this process is from the catalyst regeneration process. The “fuel” for the catalyst regeneration process is the carbon (coke) particles that are contained on the spent catalyst. The heat that is needed to regenerate the spent catalyst comes from combustion of the coke particles within the catalyst regenerator. The coke particles that are contained on the spent catalyst form from the chemical reaction of feedstock that is fed to the FCC reactor (a separate piece of equipment.)

FCC processes may be operated in full combustion or partial combustion mode depending upon the characteristics of the feedstock and other process considerations. The catalyst regenerator flue gas contains carbon dioxide from oxidation of coke from the catalyst, and the regenerator flue gas may also contain carbon monoxide if operated in partial combustion mode. The regenerator flue gas is treated to remove entrained catalyst particles (catalyst fines) and then may be sent through a turbine to generate motive power to drive regenerator air compressors or other equipment or to generate electricity. For operation in partial combustion mode, regenerator flue gas containing carbon monoxide may be sent through a CO Boiler to convert the carbon monoxide to carbon dioxide. CO Boilers are discussed in Section 3.2.7.

**OTHER CATALYTIC CRACKING PROCESSES**

Catalyst regeneration for other catalytic cracking processes are also exempt under Article 28(c).

**3.2.7 CO Boilers**

**PROCESS DESCRIPTION**

Residual carbon monoxide in the cracking catalyst regenerator flue gas may be burned in a steam-generating “CO Boiler.” [CO Boilers are also applied to other processes, including carbon black furnaces, for the purposes of heat recovery and conversion of CO in the furnace vent gas to CO₂.] The steam generated by the CO Boiler may be used within the catalytic cracking process (or e.g. furnace black process) or exported from the process. The exhaust gas from the CO Boiler is subject to further treatment to remove particulate prior to
venting to the atmosphere. A (simplified) flue gas treatment system for an FCC Process illustrating the application of the CO Boiler is shown in Figure 3-7.

**Figure 3-7 Generic Process Flow Diagram for FCC Unit and Ancillary Flue-Gas Treatment**


D. **Pyrolysis Furnace Processes**

3.2.8 **Ethylene Steam Cracker Pyrolysis Furnace Process**

**ETHYLEN STEAM CRACKERS IN EUROPE**

As requested by the EC, data on ethylene steam crackers currently operating across Europe were gathered. This included up to date information on: number of crackers, thermal capacity, fuel consumption, emissions of key pollutants and abatement measures. Detailed results are presented in Appendix A. Summary data are presented in the tables below.

**Table 3 Numbers and capacity of ethylene crackers in the EU (2013)**

<table>
<thead>
<tr>
<th>Member State</th>
<th>Number</th>
<th>Rated thermal input (GWth)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>Belgium</td>
<td>10</td>
<td>1.8</td>
</tr>
<tr>
<td>Germany</td>
<td>17</td>
<td>6.7</td>
</tr>
<tr>
<td>Finland</td>
<td>2</td>
<td>0.3</td>
</tr>
<tr>
<td>France</td>
<td>3</td>
<td>0.9</td>
</tr>
<tr>
<td>Italy</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>Netherlands</td>
<td>30</td>
<td>3.9</td>
</tr>
<tr>
<td>Spain</td>
<td>10</td>
<td>2.2</td>
</tr>
<tr>
<td>Poland</td>
<td>4</td>
<td>0.2</td>
</tr>
<tr>
<td>Portugal</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>UK</td>
<td>11</td>
<td>1.1</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>92</strong></td>
<td><strong>19.5</strong></td>
</tr>
</tbody>
</table>
Table 4: Fuel used at ethylene steam cracker plants in Europe

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>Fuel used (PJ) at ethylene steam cracker plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Other solid fuels</td>
<td>0</td>
</tr>
<tr>
<td>Liquid fuels</td>
<td>62</td>
</tr>
<tr>
<td>Natural gas</td>
<td>38</td>
</tr>
<tr>
<td>Other gases</td>
<td>228</td>
</tr>
</tbody>
</table>

Table 5: Emissions from ethylene steam cracker plants in Europe

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Annual emissions (kt/yr) from ethylene cracker plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total SO₂</td>
<td>31</td>
</tr>
<tr>
<td>Amount of SO₂ from plants with liquid fuels make up &gt;30% of thermal input</td>
<td>23</td>
</tr>
<tr>
<td>Amount of SO₂ from plants with gaseous fuels &gt;50% of thermal input</td>
<td>7.3</td>
</tr>
<tr>
<td>NOₓ</td>
<td>22</td>
</tr>
<tr>
<td>Dust</td>
<td>1.5</td>
</tr>
</tbody>
</table>

STEAM CRACKING PROCESS DESCRIPTION

Ethylene is manufactured primarily by steam cracking of hydrocarbon feedstocks ranging from light gases, including ethane, propane, butane, and liquefied petroleum gases (LPG) to refinery liquid products including naphtha and gas-oil. The types and mix of feedstock used in steam cracking for ethylene production varies by region. In Europe, as well as in Korea and Japan, most ethylene is produced from steam cracking of naphtha, while in the United States most ethylene is produced from steam cracking of ethane. In the EU, liquid feedstocks (e.g. naphtha) are more commonly used than gaseous feedstocks for ethylene production.

The fundamental chemical equations for ethylene production in steam crackers are as follows:

- Ethane Dehydrogenation to Ethylene
  \[ \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \]
- Ethane → Ethylene + Hydrogen
Assessment of the need for additional IED amendments.
Specific contract No. 070307/ENV/2012/627812/C3 (Task 2)

Steam cracking of petrochemical feedstocks to produce ethylene also produces other high value (saleable) petrochemical co-products, including propylene, butadiene, and aromatic compounds. Steam cracking of heavier hydrocarbon feedstocks generally yields a higher proportion of co-products, including propylene, butadiene, and benzene. Most propylene produced worldwide is produced as a by-product of ethylene production, recovered either from steam crackers or from fluid catalytic cracking units at petroleum refineries. The steam cracking process also produces by-product hydrogen, methane and C4+ hydrocarbons that are generally burned for energy recovery within the steam cracking process or exported to other parts of the petrochemical plant for energy recovery.

Steam crackers for ethylene production can be broken down into three separate process sections: (1) pyrolysis (cracking reaction); (2) primary fractionation / compression; and (3) product fractionation, as illustrated in Figure 3-8. Combustion and chemical reaction processes occur separately in the pyrolysis section of the process, as illustrated in Figure 3-9; physical separation and purification of the ethylene and other products of the pyrolysis process occurs in the compression and fractionation sections of the process.

**PYROLYSIS FURNACE**

In a typical steam cracker (pyrolysis furnace) for ethylene production, a hydrocarbon stream (feedstock) is preheated in heat exchangers and then vaporised using superheated steam. The preheated feedstock is mixed directly with steam and, depending on the type of feedstock, further heated to incipient cracking-temperatures of 600 - 650ºC. The steam cracking reactions take place in an arrangement of metal tubes in the pyrolysis furnace at temperatures above 800ºC.23 See Figure 3-8 that illustrates a pyrolysis furnace flow diagram.

**Figure 3-8: Feed and furnace section (Source: 2003 LVOC BREF, Page 150)**

The pyrolysis furnace tubes are externally heated through the combustion of fuel-grade by-products of the pyrolysis process (e.g. methane, hydrogen) collectively referred to as "fuel gas" and, as needed, combustion of supplemental fuel (e.g. natural gas) in fuel burners that surround the pyrolysis furnace tubes. The flue gas from the combustion of fuel gas in the fuel burners does not come into direct contact with or comingle with the vent gas (ethylene

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product and by-products) from the pyrolysis furnace tubes. Steam is injected directly into the feedstock stream to reduce the partial pressure of the hydrocarbon mixture to improve the production of desired products, and also to minimise coke formation in the pyrolysis furnace tubes (LVOC BREF). Conversion of saturated hydrocarbons (e.g. ethane) to unsaturated compounds (e.g. ethylene, propylene) is highly endothermic, requiring 15 to 50 GJ heat input per tonne of ethylene produced (ibid). Neelis et al. (2003) reported an average total process energy of 34.8 GJ/tonne ethylene based on an analysis of LVOC BREF data.

**Fractionation and Compression steps**

The ethylene and other products of the steam cracker pyrolysis process are quickly quenched in transfer line exchangers (heat exchangers) to a temperature below 350 ºC to prevent further undesirable chemical reactions from taking place. The transfer line exchangers generate high-pressure steam that is used elsewhere in the steam cracking process. The quenched product stream is then sent to the primary fractionation / compression and product fractionation processes for separation. Flue gas from the pyrolysis furnace is sent to downstream heat recovery and treatment processes (e.g. nitrogen oxide control) and then vented to the atmosphere.

Compression and fractionation of the steam cracker pyrolysis reaction products separates ethylene and propylene (the primary desired products) from the other hydrocarbons produced by the pyrolysis process. These processes include primary fractionation, compression, refrigeration, and successive downstream fractionation steps to remove hydrogen, methane, ethane, acetylene, propane, C4 products (e.g. butane), and C5 products (e.g. pentane). These separation processes are illustrated in Figure 3-8.

**Fuel Gas from by-products**

As fuel grade by-products, methane and hydrogen separated from the by-product stream may be combusted as fuel gas in the pyrolysis furnace burners, but they can also be exported from the process for further processing or energy recovery. Other by-products of the separation and fractionation processes (e.g. C4) may also be mixed with supplemental fuel (e.g. natural gas) and sent back to the pyrolysis furnaces for use as fuel for the pyrolysis furnace burners. Pyrolysis fuel oil that is a by-product of the quench process and C4s separated from the by-product stream may also be exported from the steam cracker process for further processing or energy recovery, e.g. to plant utility boilers for steam generation.

Ethane and propane separated from the by-product stream may be recycled back into the pyrolysis furnaces as feedstock for the steam cracking process or may be exported from the steam cracking process to other parts of the chemical plant (e.g. to utility boilers for steam generation.) Ethane and propane separated from the steam cracker products may also be used as fuel for the pyrolysis furnace burners if not used as feedstock or exported from the process.

The type of feedstock to the steam cracker controls the primary products and saleable co-products of the steam cracker reaction\(^{25}\). As shown in Table 3.25, use of naphtha feedstock would generally produce a larger quantity of fuel-grade by-products than would use of ethane feedstock (steam crackers in Europe generally operate using naphtha feedstock). The mix of products from the steam cracker reaction indirectly affects the quantity of and composition of the fuel-grade products that are the feedstock to and that are combusted in the pyrolysis furnace. Tying the composition of the emissions from the pyrolysis furnace...
directly to the composition of the cracking unit feedstock would be a complex analysis. Note that the cracking unit feedstock and the pyrolysis furnace feedstock are not the same feedstock. The cracking furnace feedstock is naphtha; the pyrolysis furnace feedstock is fuel-grade by-products of the cracking process. See Figure 3-8 above for an illustration of the pyrolysis furnace heat input.

COMPOSITION OF FLUE GAS FROM THE PYROLYSIS FURNACE FUEL BURNERS

Depending upon the feedstock used and the process design, by-products separated from the steam cracker pyrolysis reaction products in the downstream compression and fractionation processes (e.g. methane, hydrogen, C4 products) may constitute the majority of the fuel combusted in the pyrolysis furnace burners. Flue gas from combustion in the pyrolysis process is a product of combustion of by-products from the cracking reaction (fuel gas) and also a product of combustion of supplemental fuel (as needed) supplied to the pyrolysis furnaces. Therefore, the chemical reactions that occur in the pyrolysis section of the process, and the downstream compression and fractionation processes indirectly affect the composition of the flue gas from the pyrolysis furnaces. Process design considerations concerning what by-products to export from the ethylene production process vs. what by-products to retain within the ethylene production process for use as feedstock or for energy recovery will also indirectly affect the composition of the flue gas from the pyrolysis process fuel burners.

With regards to NO\textsubscript{x}, the IED emission limits for combustion of "other gases" in existing combustion plants (except gas turbines and engines) are set out below:

- 50-500 MW\textsubscript{th}: 300 mg NO\textsubscript{x}/Nm\textsuperscript{3} (provided the plant was permitted before 27/11/2002 or started operation before 27/11/2003; if not the case the value below applies)
- >500 MW\textsubscript{th}: 200 mg NO\textsubscript{x}/Nm\textsuperscript{3}

From Table 7.6 of the LVOC BREF (2003, page 164), the reported NO\textsubscript{x} emissions from steam cracker furnaces range from ~60 mg/Nm\textsuperscript{3} to >250 mg/Nm\textsuperscript{3} (data collated during CEFIC survey 2000). The BREF reported two (unidentified) outlier ethylene steam cracker plants that reported NO\textsubscript{x} emissions > 250 mg/Nm\textsuperscript{3}. [It is important to note that this information source is now more than 10 years old; the LVOC BREF is currently being revised but a draft document was not available during this study].

Selas-Linde GmbH (which operates ethylene cracking furnaces in Europe) has reported performance metrics for (De-NO\textsubscript{x} Catalyst controlled) NO\textsubscript{x} emissions from steam cracker furnaces of <60 mg NO\textsubscript{x}/Nm\textsuperscript{3}.\textsuperscript{26} The ECN (Energy Research Center of the Netherlands) also reported that NO\textsubscript{x} emissions <100 mg NO\textsubscript{x}/Nm\textsuperscript{3} are achievable without application of external (Selective Catalytic Reduction/SCR) NO\textsubscript{x} emission controls.\textsuperscript{27}

ECN reported in their written comments on the current revision of the LCP BREF that the hydrogen content of the fuel gas used in pyrolysis furnaces and other process heaters can affect the NO\textsubscript{x} emissions from combustion, and that the correction factor relationship of fuel gas hydrogen content and NO\textsubscript{x} emissions is linear: i.e. “If, for example, a gas composition contains 15 vol% of hydrogen, the NO\textsubscript{x} requirement…is multiplied with a factor of 1.15.”

\textsuperscript{26} http://www.selas-linde.com/production_programme/process_furnaces/cracking_furnaces/ethylene.php
ECN noted that the Dutch legislation for NO\textsubscript{x} emissions from LCPs already contains this adjustment.\textsuperscript{28}

The IED does not contain any adjustments that account explicitly for the composition of gaseous fuels. There is a single standard in the IED for “gaseous fuels” as a category, which would include both natural gas and the various compositions of fuel gases used in furnaces and other process heaters at chemical plants, petroleum refineries, etc. Note that the Netherlands regulations adjust for the H\textsubscript{2} content of the fuel gas to the pyrolysis furnace and the IED doesn’t adjust for the H\textsubscript{2} content of the fuel gas. The IED also does not include any adjustment for combustion temperature.

It is pertinent to note here that the fuel to the pyrolysis furnace is largely generated by downstream equipment in the steam cracker process. This is fundamentally different from the processes described in Section 2 in which the fuel and the feedstock are the same material (e.g. ethylene to ethylene oxide) or the fuel is a conventional purpose-made fuel product (e.g. natural gas).

**Decoking**

Cracking furnace pyrolysis tubes are required to be periodically decoked using an air/steam mixture. Decoking is normally conducted by operating the pyrolysis furnace using fuel gas or supplemental fuel to supply heat and replacing the feedstock with a steam/air mixture that flows through the furnace tubes, removing the coke particles from the surface of the furnace tubes.

The decoking vent gas containing the coke particles can be routed either to the pyrolysis furnace fireboxes for combustion of the coke particles or to a separate decoke drum to remove the coke particles using a wet or dry particulate control system (LVOC BREF). Coke particles from the decoking process are combusted to CO\textsubscript{2}; some carbon monoxide is also produced by the decoking process. Typically, ethylene production plants have multiple pyrolysis furnaces, with one furnace available for decoking while the other furnaces are processing feedstock for ethylene production. A recent environmental permit application for a proposed ethylene production plant with eight pyrolysis furnaces estimated that each furnace would operate on a 50-day production cycle and that each furnace would need to be decoked up to 12 times per year (see following section for impacts on NO\textsubscript{x}, SO\textsubscript{x} etc. emissions of decoking).\textsuperscript{29} The transfer line exchangers also require periodic decoking, although not as often as the cracking furnaces.

The decoking is a different combustion process than the pyrolysis furnace process. The coke particles removed from the inside of the pyrolysis furnace tubes either by mechanical means (entrained with the air/steam mixture) or through combustion. The decoking process vent gas (the steam/air mixture, coke fines, and coke fine combustion products) are either routed to the pyrolysis furnace firebox for combustion or may be separated or combusted in a separate piece of equipment. The composition of the exhaust gas is different between normal operation and the decoking process. Decoking is a separate process that involves feeding an air/steam mixture through the inside of the pyrolysis furnace tubes rather than feeding naphtha feedstock through the inside of the pyrolysis furnace tubes. If the decoking exhaust gas is routed into the pyrolysis furnace fireboxes, then that would change the composition of the exhaust gas from the pyrolysis furnace as opposed to feeding only fuel-grade by-products into the pyrolysis furnace fireboxes. Also, the pyrolysis furnace may be


operated at a different temperature during the decoking process than during normal operation, which would also affect the emissions from the pyrolysis furnace.  

Decoking affects the composition of the exhaust gas from the pyrolysis furnace when the decoking vent gas is recirculated to the pyrolysis furnace. Also, the pyrolysis furnace may be operated at a different temperature during the decoking process than during normal operation, which would also affect the pyrolysis furnace flue gas emissions.  

The decoking vent gas may be discharged to:

- a common de-coke drum to serve a number of furnaces, equipped with wet de-dusting (water spray tower, water scrubber), or
- dry de-dusting (cyclones, bag filters), or
- individual de-coke drums for each furnace, as above, or provision to route decoking air/steam mix into the furnace firebox (with adequate residence time to ensure complete combustion of the coke particles).

Depending upon the plant configuration the decoking exhaust stack may be a separate stack from the pyrolysis furnace stack. 

The steam cracker furnace is still operated during the decoking process to provide heat to the pyrolysis furnace tubes. The difference in the decoking process is that instead of feeding feedstock (naphtha) through the pyrolysis furnace tubes, air and steam are fed through the pyrolysis furnace tubes to burn off the coke deposits inside the tubes to CO$_2$ (and some CO). The furnace would still be generating flue gas (containing NO$_x$ and other combustion products) during the decoking process, but in addition decoking vent gas would be separately generated from the pyrolysis furnace tubes. 

The decoking vent gas (from the coke deposits that are removed from the inside of the pyrolysis tubes) containing PM and CO can be separately vented through a particulate control system to collect the coke fines. This is a separate stack from the furnace stack in which the fuel gas is combusted. However, the composition of the pyrolysis furnace exhaust gas may still be affected during the decoking process because the pyrolysis furnace may be operated at a different temperature during the decoking process than during normal operation, which would affect the pyrolysis furnace flue gas emissions. Decoking distinguishes pyrolysis furnaces from the general class of “large combustion plants” because natural gas-fired steam boiler tubes do not need to be regularly decoked like pyrolysis furnaces do. The BAT target for average dust (particle) emissions during the decoking is < 50 mg/Nm$^3$ (LVOC BREF, 2003). BAT for particle emissions are cyclone separation and sending the decoke effluent to furnace radiant box to burn the coke particles. The decoking vent either goes through the same stack (i.e., “stack”) or a separate (not shown in Figure 3-9) stack. Whether there is a separate decoking vent stack would not affect the composition of the decoking vent gas.

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31 idem
3.2.9 Biofuels (Biodiesel) Pyrolysis Furnace Process

PROCESS DESCRIPTION

There are a wide variety of processes that have been developed for the production of biofuels (e.g. biodiesel) from biogenic materials (e.g. agricultural waste.) Some of these processes involve pyrolysis of the biogenic material in a pyrolysis furnace. Pyrolysis is an inherently endothermic process; heat to drive the pyrolysis process may be provided directly to the biogenic material through partial oxidation of a portion of the biogenic material within the pyrolysis furnace. Alternatively, the heat can be provided to the pyrolysis furnace indirectly through combustion of supplemental fuel, or combustion of process by-products, in a separate combustion device.

Direct Combustion Processes

Processes that involve partial oxidation of a portion of the raw material in the pyrolysis furnace would be similar in general configuration to the direct combustion processes (e.g. ethylene oxide, ethylene dichloride) described above. One such partial oxidation / gasification process is the Choren process (owned by Linde). 33 34 In this process, the

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biogenic material is first preheated and dried using process heat (steam) in a heat exchanger (non-combustion) process. Then the pre-heated and dried material is pyrolysed in a pyrolysis furnace in which the heat to the process is provided through partial oxidation of a portion of the biogenic material within the furnace. The pyrolysis furnace produces pyrolysis gas and solid char, which are separated for downstream processing. The Linde/Choren process is illustrated in Figure 3-10.

**Figure 3-10: Linde/Choren Carbo-V Biofuels Process**

Indirect Combustion Processes

Processes that provide heat to the pyrolysis furnace indirectly, using an external combustion device, can be similar in general configuration to the ethylene steam cracker pyrolysis furnace. In this case, heat is supplied to the pyrolysis process through heat exchanger tubes. In this case, as for the ethylene steam cracker, there is no direct contact between the products of combustion and the products of chemical reaction. In combustion fluidized bed (CFB) pyrolysis furnaces, heat is supplied to the pyrolysis process through hot sand or other hot material that is externally heated in a sand furnace and then recirculated through the fluidized bed. Heat is transferred from the hot sand to the biogenic materials, and the biogenic materials undergo pyrolysis in the CFB furnace. An example of this process is illustrated in Figure 3-11. As shown in the Figure, sand is heated in the sand furnace and supplied to the fluidized bed furnace. The fuel for the sand furnace, in this case, is the char generated by the pyrolysis process and separated from the pyrolysis gases in the downstream cyclone separator. The combustion gases from the combustion of the char in sand furnace are used in a heat exchanger to preheat and dry the biogenic raw materials prior to their introduction into the CFB pyrolysis furnace. However, the combustion gases from the sand furnace do not directly contact the biogenic raw materials or products of the chemical pyrolysis process.

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Assessment of the need for additional IED amendments.
Specific contract No. 070307/ENV/2012/627812/C3 (Task 2)

Direct Combustion Processes

The Linde/Choren process and similar direct combustion processes in which the heat to the process is provided by partial oxidation (combustion) of the biogenic raw material would meet the “direct contact” definition of a reactor used in the chemical industry. The process is similar in configuration to direct combustion processes such as the bitumen process in which heat is provided to the process through partial combustion of the bitumen process raw material. For the Linde/Choren process and similar processes, there is direct contact between the products of combustion (the partial combustion of the biogenic raw material) and the products of chemical reaction (the pyrolysis gas and the char products.)

Indirect Combustion Processes

Combustion fluidized bed processes and other processes in which heat is provided to the pyrolysis furnace through external combustion sources would not meet the directive definition of a reactor used in the chemical industry under the “direct contact” definition, and may or may not meet the “direct causation” definition depending upon the process configuration. These indirect combustion processes are either similar in configuration to the ethylene steam cracker pyrolysis furnace process, in which heat is provided to the pyrolysis process through heat exchanger tubes, or are otherwise configured such that the combustion process occurs in different equipment than the chemical reaction process. For the CFB pyrolysis process the combustion process occurs separately from the pyrolysis process in the sand furnace and there is no direct contact between the products of combustion (e.g. the combustion of the char product of the pyrolysis process) and the products of chemical reaction (the pyrolysis gas and the char products) or direct causation of the chemical reaction by the combustion process. For this process, the sand furnace would be categorised as a conventional combustion plant subject to the LCP Directive and the IED and would not be exempt under either the “direct contact” or “direct causation” definitions. Biofuels production processes that are similar in configuration to pyrolysis furnace processes would similarly meet the “direct causation” definition of “reactor used in the chemical industry.”
3.2.10 Vinyl Chloride Monomer Pyrolysis Furnace Process

**PROCESS DESCRIPTION**

Vinyl Chloride Monomer (VCM) is produced from the cracking of ethylene dichloride (EDC), generally in the gas phase in a thermal (non-catalytic) process, in a pyrolysis furnace. The EDC cracking process is illustrated in Figure 3-12. In this process the EDC (the raw material) is fed through pyrolysis furnace tubes which are externally heated by combustion of fuel (e.g. natural gas) in the pyrolysis furnace combustion chamber. The heat applied to the outside of the furnace tubes cracks the EDC raw material into VCM and HCl chemical reaction products. The chemical reaction gas, containing VCM, HCl, and residual unreacted EDC, is cooled in a quench tower/condenser to separate the liquid-phase EDC and the gas-phase HCl from the VCM. The products of combustion are separately vented from the pyrolysis furnace and do not directly contact the raw materials or products of the chemical reaction process. The separated EDC is purified and then recycled into the cracking furnace. The VCM is purified and used in downstream chemical processing, e.g. to manufacture polyvinyl chloride.

The EDC cracking process used to produce VCM is similar in configuration to the steam cracking pyrolysis furnace process used to produce ethylene. For each process, a raw material input (ethane, ethylene dichloride) is fed to furnace tubes in a pyrolysis furnace, and the furnace tubes are externally heated by a fuel. The EDC/VCM process differs from the ethylene process in that the EDC/VCM process does not generate fuel gas for use in the pyrolysis furnace, as does the ethylene production process. The EDC/VCM process is similar to the ethylene process in that the products of combustion do not directly contact the raw materials or chemical products of the process.

A portion of the reaction products of the EDC cracking process and the impurities in the EDC raw material further thermally decompose to carbon black or coke in the pyrolysis furnace tubes, and therefore the EDC pyrolysis furnace needs to brought off line periodically and subjected to a decoking process. The decoking process for the EDC pyrolysis furnace is similar to that for ethylene steam cracker pyrolysis furnaces; instead of EDC raw material, a mixture of steam and air is fed through the inside of the furnace tubes, which removes and partially combusts the carbon black and coke particles from the inside of the furnace tubes. The vent gas from the pyrolysis furnace decoking process is generally subject to some form of particulate air emissions control such as a wet scrubber and then discharged through a common stack. Thyssen-Krupp reported that the period between scheduled decoking events could be more than one year depending upon how the process is designed and operated.

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Figure 3-12: Ethylene Dichloride Cracking Furnace Process (Source: ThyssenKrupp Uhde GmbH)

E. Steam Reformer Processes

3.2.11 Methanol Steam Reformer Process

**PROCESS DESCRIPTION**

Methanol is mainly produced from steam reforming of natural gas feedstock (raw material input.) In the methanol steam reforming process, natural gas and steam are fed to a reformer, in which the natural gas and steam are reacted over a catalyst to form “reformer gas.” The reformer gas consists of hydrogen, carbon dioxide, carbon monoxide, methane, water. The reformer gas is further reacted in downstream sections of the production process over a different catalyst to form methanol.

Process heat to the steam reformer is provided by combustion of fuel, usually natural gas and fuel gas that is produced by the downstream sections of the methanol production process. The natural gas and fuel gas (heat input) are combusted in the reformer furnace to heat the outside of furnace tubes. The chemical reaction to form the reformer gas from the steam and natural gas (raw material input) occurs inside of the reformer furnace tubes. The reformer furnace is similar in its physical configuration to a pyrolysis furnace in an ethylene steam cracker plant. Similarly, in each case, the natural gas/fuel gas (heat input) is combusted outside of the furnace tubes and the chemical reaction to form the chemical products from the raw material input takes place inside of the furnace tubes.

Schematic diagrams of the reformer furnace for the production of reformer gas is shown in Figure 3-13. As shown, natural gas and fuel gas are combusted in the furnace chamber to provide heat to the furnace tubes. The natural gas and steam flowing through the inside of the furnace tubes undergo a chemical reaction to form the reformer gas that is further reacted in downstream process equipment.

The downstream methanol synthesis process that produces the methanol from the reformer gas is shown in Figure 3-13. As shown, the downstream synthesis process produces both the methanol product and fuel gas (purge gas) that is recirculated back into the reformer furnace for use as fuel (heat input.) In this regard, the methanol production process is similar to the ethylene production process in that the ethylene production process also produces fuel gas that is recirculated back into the furnace for use as fuel (heat input).
Figure 3-13: A Simplified Overview of the ‘Front End’ Production Of Reformed Gas For Methanol Production (Source: AMPCO, 2006)

Figure 3-14: A Methanol Synthesis Process (Source: AMPCO, 2006)
3.2.12 Ammonia Production Reformer Process

**PROCESS DESCRIPTION**

Ammonia (NH₃) is generally produced from steam reforming of a hydrocarbon feedstock (raw material input), usually natural gas. In the ammonia production process, the hydrocarbon (generally natural gas) raw material and steam are fed to a primary reformer, in which the natural gas and steam are reacted over a catalyst to form “primary reformer gas.” The primary reformer gas consists of hydrogen, carbon dioxide, carbon monoxide, methane, water. The primary reformer gas is further reacted with input of air, or nitrogen (N₂) in a second “secondary reformer” to further reduce the methane content for the reformer gas and further increase the hydrogen (H₂) content. The air, or nitrogen, provides the N₂ reactant to the ammonia production process. The H₂ and N₂ in the secondary reformer gas are reacted in the ammonia synthesis section of the production process over a different catalyst to form NH₃.

**Primary Reformer Process**

Process heat to the primary reformer is provided by combustion of fuel, usually natural gas. Purge gas produced by the downstream section of the ammonia production process may also be used as a fuel gas to the primary reformer. The natural gas (or other conventional fuel) and fuel gas are combusted in the primary reformer furnace to heat the outside of furnace tubes. The chemical reaction to form the primary reformer gas from the steam and natural gas (raw material) occurs inside of the primary reformer furnace tubes. The primary reformer is similar in its physical configuration to a pyrolysis furnace in an ethylene steam cracker plant; similarly in each case, the natural gas/fuel gas is combusted outside of the furnace tubes and the chemical reaction to form the chemical products from the raw material input takes place inside of the furnace tubes.

A schematic diagram of the primary reformer for the production of primary reformer gas is shown in Figure 3-15. As shown, natural gas and potentially also fuel gas generated by downstream processes are combusted as fuel in the furnace chamber to provide heat to the furnace tubes. The natural gas (raw material) and steam flowing through the inside of the primary reformer furnace tubes undergo a chemical reaction to form the primary reformer gas that is further reacted in the secondary reformer and downstream process equipment to form ammonia.

**Secondary Reformer Process**

The secondary reformer process that produces the secondary reformer gas is shown in Figure 3-15. The main objective of the secondary reforming process is to add the nitrogen required for the ammonia synthesis and to complete the conversion of the hydrocarbon feed to hydrogen. For this purpose, the reaction heat and the required temperature for the secondary reformer chemical reaction are achieved by an internal combustion of part of the primary reformer gas before it is passed over the catalysts containing nickel. No supplemental fuel is needed to drive the chemical reaction for the secondary reformer process.

The process air is compressed and pre-heated in the primary reformer convection section to around 500–600°C, with the result that the methane contained in the natural gas raw material is converted down to a residual content of around 0.2–0.3%. The secondary reformer chemical reaction proceeds adiabatically, resulting in a process gas outlet temperature of approximately 1000 °C. Heat may be removed from the secondary reformer process gas using a waste heat steam boiler, a superheater/boiler, or a boiler/preheater. Removal of heat from the secondary reformer gas cools the gas to approximately 330–380°C in preparation for the downstream ammonia synthesis reaction (LVIC-S BREF).
Figure 3-15: Ammonia production process flow diagram

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Natural gas

ZnO → Desulphurisation → ZnS

H₂O, fuel → Primary reformer → Flue-gas

Air, power → Secondary reformer → Heat

Shift conversion → Heat

Heat, power → CO₂ removal → Condensate, CO₂

Methanation

Power → Compression

Power → NH₃ synthesis → Purge/flash gas

NH₃
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4. **Assessment and interpretation of ‘reactors used in the chemical industry’**

4.1 **Coverage of different types of plants under the alternative definitions**

As discussed above, two alternative definitions of “reactor used in the chemical industry” are considered in this report. This section discusses how the above-listed processes would be categorised under each of the definitions.

Before considering whether a plant might fall under this particular category (“reactor”), the following checks are done:

1. Determine whether the process is explicitly exempt by the Directive under another entry (LCPD Article 2(7) and IED Article 28), e.g. catalytic cracking catalyst regeneration processes.

2. Determine whether the process is categorised as a “thermal treatment” process in which the products of combustion are directly used.

In further determining which processes may qualify as a ‘reactor used in the chemical industry’ there are two sequential issues:

3. Determine whether there is a chemical reaction going on within the device that is being heated. In a simple raw material preheater (e.g. a conventional direct-fired distillation column reboiler) there is no chemical reaction taking place within the equipment; this equipment is therefore clearly not a “reactor used in the chemical industry,” but rather a “conventional” combustion plant. In a pyrolysis furnace, there is a chemical reaction taking place within the equipment and the primary purpose of the heat provided to the equipment is to drive the chemical reaction; similarly, for a carbon black furnace, the primary purpose of the heat is to drive the chemical reaction occurring within the equipment. So these equipment are not conventional “combustion plants” but rather are process heaters/furnaces.

For application of the “direct contact” definition, the following final decision level applies to determine whether the process should be categorised as a “reactor used in the chemical industry”:

4. Determine whether there is direct contact between the products of combustion and the raw material within the equipment (because of which the combustion process directly affects the composition of the vent gas stream from the chemical reaction process). If there is direct contact, then the reactor is a “reactor used in the chemical industry”; if there isn’t direct contact then the reactor is not a “reactor used in the chemical industry.”

Under the “direct causation” definition, in determining which processes may qualify as a “reactor used in the chemical industry”, instead of the step mentioned under point 4 above, the following final decision level applies to determine whether the process should be categorised as a “reactor used in the chemical industry”:

5. Determine whether the heat resulting from the fuel combustion directly causes the chemical reaction of the raw material to take place within the equipment and whether the combustion process is integral to the chemical reaction process. If there is direct causation and the combustion process is integral to the chemical reaction process then the process is a “reactor used in the chemical industry; if there
isn’t direct causation and/or the processes are not integral to one another then the process is not a “reactor used in the chemical industry.”

4.1.1 Applicability of Directive Definitions to Specific Processes

Of the plants described in Section 3.2:

- Category A has been exempted;
- Category B (direct combustion) is covered under the “direct contact” definition.
- Category C has been exempted.
- Categories D and E are assessed below under the “direct causation” definition.

**ETHYLENE STEAM CRACKER PYROLYSIS FURNACE PROCESS**

Note that the Linde/Choren process and the CFB Pyrolysis Furnace process represent only two examples of the many available biofuels production processes. There are a large number of biofuels production processes that are either installed or in development that may have some characteristics similar to either or both of these example processes. Therefore, each biofuels production process will need to be evaluated individually to determine whether the process meets the definition of “reactor used in the chemical industry”

**Direct Combustion Processes**

The Linde/Choren process and similar direct combustion processes in which the heat to the process is provided by partial oxidation (combustion) of the biogenic raw material would meet the “direct contact” definition of a reactor used in the chemical industry. The process is similar in configuration to direct combustion processes such as the bitumen process in which heat is provided to the process through partial combustion of the bitumen process raw material. For the Linde/Choren process and similar processes, there is direct contact between the products of combustion (the partial combustion of the biogenic raw material) and the products of chemical reaction (the pyrolysis gas and the char products.)

**Indirect Combustion Processes**

Combustion fluidized bed processes and other processes in which heat is provided to the pyrolysis furnace through external combustion sources would not meet the directive definition of a reactor used in the chemical industry under the “direct contact” definition, and may or may not meet the “direct causation” definition depending upon the process configuration. These indirect combustion processes are either similar in configuration to the ethylene steam cracker pyrolysis furnace process, in which heat is provided to the pyrolysis process through heat exchanger tubes, or are otherwise configured such that the combustion process occurs in different equipment than the chemical reaction process. For the CFB pyrolysis process the combustion process occurs separately from the pyrolysis process in the sand furnace and there is no direct contact between the products of combustion (e.g. the combustion of the char product of the pyrolysis process) and the products of chemical reaction (the pyrolysis gas and the char products) or direct causation of the chemical reaction by the combustion process. For this process, the sand furnace would be categorised as a conventional combustion plant subject to the LCP Directive and the IED and would not be exempt under either the “direct contact” or “direct causation” definitions. Biofuels production processes that are similar in configuration to pyrolysis furnace processes would similarly meet the “direct causation” definition of “reactor used in the chemical industry.”
VINYL CHLORIDE MONOMER PYROLYSIS FURNACE PROCESS

Applying the same reasoning to both the ethylene production process and the VCM production process, under the “direct causation” definition the pyrolysis furnace used in the VCM production process would also be categorised as a “reactor used in the chemical industry.” Both types of pyrolysis furnaces combust fuel (fuel gas/natural gas heat input) to provide heat to the outside of furnace tubes, and in each case the chemical reaction of the raw materials to reaction products occurs inside of the furnace tubes. Conversely, if the ethylene steam cracker pyrolysis furnace is categorised as a non-exempt “combustion plant” then the pyrolysis furnace used in the VCM production process would also be categorised as a non-exempt “combustion plant.”

METHANOL STEAM REFORMER PROCESS

Applying the same reasoning to both the ethylene production process and the methanol production process, if the ethylene steam cracker pyrolysis furnace is categorised as a “reactor used in the chemical industry” under the “direct causation” definition then the steam reformer furnace used in the methanol production process would also be categorised as a “reactor used in the chemical industry.” Both processes produce fuel gas that is used in the furnaces as fuel (fuel gas / natural gas heat input), both types of furnaces combust fuel gas to provide heat to the outside of furnace tubes, and in each case the chemical reaction of the raw materials to chemical reaction products occurs inside of the furnace tubes. Conversely, if the ethylene steam cracker pyrolysis furnace is categorised as a non-exempt “combustion plant” then the methanol steam reformer furnace would also be categorised as a non-exempt “combustion plant.”

AMMONIA PRODUCTION REFORMER PROCESS

Applying the same reasoning to both the ethylene production process and the ammonia production process, if the ethylene steam cracker pyrolysis furnace is categorised as a “reactor used in the chemical industry” under the “direct causation” definition then the primary reformer used in the ammonia production process would also be categorised as a “reactor used in the chemical industry.” Both processes produce fuel gas from downstream separation processes that may be used in the fuel, both processes combust natural gas (or other conventional fuel) and fuel gas to provide heat to the outside of tubes, and in each case the chemical reaction of the raw materials to reaction products occurs inside of the tubes. Conversely, if the ethylene steam cracker pyrolysis furnace is categorised as a non-exempt “combustion plant” then the ammonia process primary reformer would also be categorised as a non-exempt “combustion plant.”

Applying the “direct contact” definition of “reactor used in the chemical industry” the secondary reformer would be categorised as a “reactor used in the chemical industry” and not as a “combustion plant.” In the secondary reformer, the heat needed to drive the chemical reaction that occurs in the secondary reformer is provided by combustion of part of the primary reformer gas within the same equipment in which the chemical reaction takes place, i.e., the secondary reformer process is a “direct combustion” process. The chemical reaction products and combustion products are combined within the same equipment to produce the secondary reformer gas. The combustion products within the secondary reformer come into direct contact with the chemical reaction products, corresponding to the “direct contact” definition of “reactor used in the chemical industry.”

4.1.2 Summary of combustion processes

Table 4-6 summarises all the different combustion processes that were discussed in section 3.2 including those that have been discarded as exempt under the IED or LCP Directive.
### Table 4-6 Summary of Combustion Equipment Types and Directive Status

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
<th>Fuel</th>
<th>Raw Material</th>
<th>Exempt under IED/LCP Directive on other grounds than qualifying as “reactor”</th>
<th>Covered by “direct contact” definition</th>
<th>Covered by “direct causation” definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green coke calciner kiln</td>
<td>Calcination of green coke raw material to calcined petroleum coke; direct contact of the fuel and raw material in the calciner kiln</td>
<td>Conventional fuels (e.g. natural gas); volatile components of green coke raw material</td>
<td>Green coke raw material</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon black furnace</td>
<td>Production of carbon black from carbon black oil feedstock by direct heating of feedstock in furnace</td>
<td>Conventional fuels (e.g. natural gas); volatile components of carbon black oil raw material</td>
<td>Carbon black oil raw material</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrolysis furnace</td>
<td>Conventional and/or alternate fuels are burned in combustion chamber outside of pyrolysis furnace tubes; the chemical reaction of raw material to chemical product occurs inside of furnace tubes. No direct contact of the raw material and the fuel in the pyrolysis furnace</td>
<td>Conventional fuels (e.g. natural gas) / process-generated fuels (e.g. fuel gas)</td>
<td>Ethylene steam cracker: ethane, naphtha, other hydrocarbons. VCM: Ethylene dichloride Biodiesel: Biogenic material (e.g. agricultural waste)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Direct Combustion Process (e.g. ethylene oxide; ethylene dichloride; bitumen)</td>
<td>The same feedstock (e.g. ethylene) constitutes both the fuel and the raw material; some of the feedstock is combusted and provides heat to the process and the remainder is reacted to chemical products.</td>
<td>Ethylene (fuel)</td>
<td>Ethylene (raw material)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>Description</td>
<td>Fuel</td>
<td>Raw Material</td>
<td>Exempt under IED/LCP Directive on other grounds than qualifying as “reactor”</td>
<td>Covered by “direct contact” definition</td>
<td>Covered by “direct causation” definition</td>
</tr>
<tr>
<td>----------------------------------------------------------------------</td>
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<td>---------------------------------------------------------------------------------</td>
<td>----------------------------------------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>Steam reformer (methanol production, ammonium production)</td>
<td>Conventional and/or alternate fuels are burned in the combustion chamber outside of steam reformer tubes; the chemical reaction of raw material to chemical product occurs inside of the steam reformer tubes. There is no direct contact of the combustion products with the raw material in the steam reformer process.</td>
<td>Conventional fuels (e.g. natural gas) / process-generated fuels (e.g. fuel gas)</td>
<td>Generally natural gas feedstock</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Catalyst regeneration (Catalytic Cracking Unit)</td>
<td>Catalyst containing coke particles is regenerated using steam/air; the coke particles on the catalyst are combusted and removed from the catalyst.</td>
<td>Coke particles</td>
<td>None: No supplemental fuel is needed for the catalyst regeneration process</td>
<td>Exempt from IED and LCP Directive (the directive explicitly exempts catalytic cracking catalyst regeneration from categorization as a combustion plant.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst regeneration (other than the exempt catalytic cracking type of unit)</td>
<td>Catalyst containing coke particles is regenerated using steam/air; the coke particles on the catalyst are combusted and removed from the catalyst.</td>
<td>Coke particles</td>
<td>None</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>CO Boiler (e.g. for FCC unit or carbon black furnace)</td>
<td>Partially combusted gases from catalyst regenerator process containing CO are combusted to CO₂, with recovery of heat and also potentially with use of supplemental fuel.</td>
<td>Carbon monoxide (in catalyst regenerator exhaust gas stream); supplemental fuel (e.g. natural gas)</td>
<td>None</td>
<td>Processes that fully combust a partially combusted exhaust gas stream from another process are not categorised as post-combustion plants (therefore these are not exempt).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst regeneration (other than the exempt catalytic cracking type of unit)</td>
<td>Catalyst containing coke particles is regenerated using steam/air; the coke particles on the catalyst are combusted and removed from the catalyst.</td>
<td>Coke particles</td>
<td>None</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>
4.1.3 Conclusions

As illustrated in Table 4-6, the following process combustion plants do not require further consideration with respect to the definition of “reactor used in the chemical industry”:

- Kilns (excluded under point of IED Article 28(a) as “thermal treatment” units);
- Catalytic cracking catalyst regeneration processes (excluded under point of IED Article 28(c)).

4.2 Industry Feedback

The European Chemical Industry Council (Cefic) reached out to its members to investigate how the term “reactor” is widely understood by industry. As such, the expert working group working on the revision of the LVOC BREF was consulted with (this includes 16 companies which covers the majority of steam crackers operating across the EU). The group arrived at the following definition for a “reactor” under the IED:

**A reactor is a piece of equipment purposely designed to ensure that (a) defined reaction(s) take(s) place with or without non reaction fluids being present in the reaction medium and independent of the type of heating and/or cooling required to ensure the reaction(s) take(s) place and/or are controlled.**

According to Cefic, the key issue at stake is the intention of combustion. Cefic’s members maintain that in a reactor the main purpose is on making specific reaction products (and the generation of heat is a side effect), whereas in a true combustion plant, the main intention is to generate heat. The full rationale is provided in Box 1.
Assessment of the need for additional IED amendments.
Specific contract No. 070307/ENV/2012/627812/C3 (Task 2)

August 2013

Box 1 Cefic Rationale as to why Steam Cracker Furnaces are Chemical Reactors (provided on March 20th 2013)

Steam cracker furnaces are solely designed and operated for the purpose of creating the correct thermo-chemical reaction conditions to produce the required mixture of products. Within these steam cracker furnaces both the combustion of fuel and the chemical conversion of hydrocarbons into products with new chemical properties occurs.

Furnaces used to generate steam or electricity on the other hand are designed for maximum thermodynamic efficiency and only the combustion of fuel takes place.

A steam cracker furnace consists of a series of reactor tubes installed inside a combustion chamber. The burners in the combustion chamber are placed in a carefully designed pattern in order to create a unique flame pattern which will achieve a desired temperature profile inside the reactor tubes, across their entire length. The tube temperature is chosen in order to generate the correct thermo-chemical reaction conditions to produce the desired mix of products from the specific feedstock being used whilst minimizing undesired by-products. Indeed the main operational control parameter is reactor tube outlet temperature. Too low a temperature will result in insufficient conversion to the desired products whilst too high a temperature creates excessive amounts of coke as an undesired by-product. Maintaining this critical temperature for the right amount of cracking to occur is most economically achieved by direct combustion onto the reactor tubes rather than via an intermediate heat transfer medium such as steam or electrical heating. Thus the combustion conditions, the burner design, as well as the uniquely designed reactor are completely different to furnaces designed for steam or electricity generation where the aim is for thermodynamic efficiency rather than the optimum reaction kinetics inside a reactor tube.

The steam cracking operation inevitably produces a small layer of coke inside the reactor tubes and as a result there is a periodic need to decoke the tubes to maintain the desired reaction conditions. This again is not an operation that would occur in a simple combustion furnace.

The steam cracking process is highly integrated with the downstream units that use the products it makes to develop a wide range of plastics and other chemicals. Thus in order to ensure the maximum efficiency of operation it is customary to have a bank of furnaces with reaction tubes of which some can be off-line. The furnaces that are on-line also do not necessarily all operate at the same conditions as some may be processing recycled by-products in order to increase the yields of the desired products.

The emissions from a steam cracker furnace will thus not only vary with the fuel type and combustion conditions but will also vary based on the operating conditions being used. These are dependent on the feedstock, the desired mix of products and the amount of coke inside the reactor tube.

Cefic also noted in their comments that the ethylene process is a unique process in that the steam cracker furnace is required to operate at a high temperature in order to drive the cracking reaction, and in that fuel gas for the process is generally produced by downstream in the ethylene production process. Thereby the ethylene steam cracker furnace is fully integrated with the overall ethylene production process and is not a separately operated piece of equipment.
4.3 Rationale for excluding reactors used in the chemical industry from scope of Chapter III of the IED

The generation of heat in an ethylene steam cracker furnace cannot be considered a “side effect.” The steam cracking process is a highly endothermic process. The heat generated by the combustion of fuel gas and supplemental fuel is integral to the cracking process; the chemical reaction of the raw materials would not occur if the heat from the fuel combustion were not provided. This is fundamentally different from an exothermic chemical reaction process, in which the heat generated by the chemical reaction may not be desired (i.e., actually is a side effect), and in fact may need to be removed from the process in order for the chemical reaction to continue. This analysis is similar for other pyrolysis and reformer processes that require heat to drive the chemical reaction, including methanol production, ammonia production, and certain types of biodiesel production, in which heat is not generated by the chemical reaction itself and therefore must be provided by a combustion process in order to drive the chemical reaction.

The fact that the pyrolysis furnace is required to operate a high temperature in order to drive the cracking reaction is not relevant to whether the steam cracker should be categorised as exempt under a “direct causation” definition. The fact that the steam cracker is required to operate at high temperature is relevant to whether the or not the pyrolysis furnace exhaust gas concentrations can or cannot meet the numerical limits in the LCP Directive and the IED that are applicable to combustion plants, and whether or not add-on emission control equipment is required to do so. Technical reports (e.g. ECN) have indicated that emissions from pyrolysis furnaces can meet current Directive limits with or without add-on controls. Therefore, it is not clear that the suggested inability of pyrolysis processes to meet the current Directive limits is sufficient justification to apply the “direct causation” definition and exempt such processes from the Directive. However, there are no data available concerning the performance of each pyrolysis furnace in the EU with respect to the current Directive limits applicable to combustion plants.

The fact that the pyrolysis furnace is not a “separately operated piece of equipment” is relevant to the “direct causation” definition in that in this definition the combustion process and the chemical reaction process must be “integrated.” However, from a purely physical perspective, whether the combustion process occurring in a pyrolysis furnace is providing heat to raw materials that undergo chemical reaction or to a process fluid (e.g. sand) that does not, the combustion process itself would not be affected. Whether the heat is being provided to a chemically reactive raw material or a chemically inactive process fluid, fuel would be combusted and combustion products would be generated, and the chemical reaction, or lack thereof, in the equipment would not affect the composition of the exhaust gas from the combustion process. This provides the fundamental difference between applying a “direct contact” definition and a “direct causation” definition. If “direct contact” processes were not exempt, the air emissions limits in the Directive would apply to both the products of combustion and to the products of chemical reaction, as in “direct contact” processes the products of combustion and the products of chemical reaction are in direct contact and the composition of both the products of combustion and the chemical reaction affect the composition of the exhaust gas from the process. One could argue that it was clearly not the intent of the LCP Directive and the IED to regulate emissions that directly emanate from and are determined by a chemical reaction, and that therefore it would be reasonable to apply the “direct contact” definition to avoid the situation where the air emissions limit values in the Directive would be applied to exhaust gases for which the composition is directly determined by a chemical reaction.

It is somewhat less straightforward to argue that a “direct causation” definition should apply to processes such as pyrolysis furnaces and steam reformers, in which the chemical reaction does not directly affect the composition of the exhaust gas from the combustion process. Regardless of whether the combustion process associated with the pyrolysis
process or steam reforming process is “integral” to the chemical production process, the combustion process remains a conventional combustion process in which fuel is combusted and products of combustion are generated.

Ethylene steam cracker process, methanol production process, and other furnace/reformer processes may generate by-products from downstream processing equipment that may be burned in the furnace / reformer as “fuel gas.” It has also been argued that this relationship between the furnace/reformer fuel combustion and downstream processes establishes an “integral” relationship between the combustion and chemical reaction processes. However, the use of fuel gas in these processes is not strictly necessary. Whether the heat was provided to the chemical reaction by combustion of fuel gas in the furnace or by combustion of conventional fuels (e.g. natural gas) in the furnace, the chemical reaction for which the heat is needed would still occur. Therefore, it is not clear that the generation and use of fuel gas in these processes should itself be a criterion for application of the “direct causation” definition.

Part of the determination of whether to apply the “direct contact” definition or the “direct causation” definition depends upon consideration of the purpose of the exempting “reactors used in the chemical industry.” If the purpose of the exemption is to avoid applying the LCP Directive and IED air emissions limitations to exhaust gas that emanates from and is directly affected by a chemical reaction, then application of the “direct contact” definition is sufficient for that purpose. By applying the “direct contact” definition, application of the LCP Directive and IED air emissions limitations to exhaust gas that is directly affected by a chemical reaction would be avoided. Application of the “direct causation” definition is not needed for this narrow objective.

However, if the objective of the exemption of reactors used in the chemical industry is more broad, e.g. to avoid applying the LCP Directive and IED air emissions limitations to combustion processes that operate outside of the operating conditions that are typical of conventional combustion plants (e.g, steam boilers, gas turbines) or that are “indirectly affected” by a chemical process, then application of the “direct causation” definition should be considered. These operating condition aspects of pyrolysis furnaces, steam reformers, etc., may include operation of the combustion process at a higher temperature than typical of conventional combustion plants, operation using fuel gases that are generated by the production process itself, periodic emissions from furnace decoking operations, etc. Application of the “direct contact” definition would not be sufficient to account for the variability of operating conditions of pyrolysis furnaces, steam reformers, etc.

Note that available air emissions data are not sufficient to demonstrate whether ethylene steam cracker pyrolysis furnaces are capable of operating within the air emissions limits of the LCP Directive and IED, either with or without add-on control systems. Technical reports suggest that pyrolysis furnaces can operate within these limits. No data have been collected related to air emissions of other processes that would be exempt from the air emissions limits of the LCP Directive and the IED under the “direct causation” definition, including methanol, ammonia, vinyl chloride, and biofuels production. Therefore no conclusions can be drawn concerning whether an exemption would be warranted with respect to application of the LCP Directive and IED air emissions limits to these processes.

Note also that the characteristics of these other processes are sufficiently similar to those of ethylene steam cracker pyrolysis furnaces that if steam cracker pyrolysis furnaces were to be exempt under a “direct causation” definition, it would be reasonable to expect that these other processes would also qualify for exemption. Each of these other processes involves the application of heat of combustion to drive a chemical reaction, and in each process the combustion process is integral to the chemical production process, i.e., the combustion process does not occur in a separate and distinct piece of equipment from the chemical reaction. Therefore application of the “direct causation” definition would result in the
exemption not only ethylene steam cracker pyrolysis furnaces but also exemption of a wide range of other processes in which heat is applied within a piece of equipment to drive a chemical reaction.

As set out Section 2.2 two alternative definitions of “reactor used in the chemical industry” are considered in this report. A summary of the results of the analysis for each of the processes discussed above follows:

**THERMAL TREATMENT PROCESSES**

*Carbon black (furnace black process)*

Carbon black production in the furnace black process would be exempt as a “thermal treatment process” under Article 28(a). In this process, the raw material (carbon black oil) and supplemental fuel (e.g. natural gas) are both fed directly into the carbon black furnace and the combustion of the supplemental fuel (and a portion of the carbon black oil) occurs within the furnace. The combustion products directly contact the raw material and directly heat the raw material. Therefore this activity would fall under “the direct heating, drying, or any other treatment of objects or materials” under the definition of “thermal treatment.”

*Green coke calcining (refinery process)*

Green coke calcining would be exempt as a “thermal treatment process” under Article 28(a). In this process, the raw material (green coke, the reaction feed) is directly contacted with the products of combustion from combustion of the fuel that is fired directly into the kiln. Combustion of the supplemental fuel (and a portion of the green coke) occurs within the kiln. The combustion products directly contact the raw material and directly heat the raw material. Therefore this activity would fall under “the direct heating, drying, or any other treatment of objects or materials” under the definition of “thermal treatment.”

*Other catalyst regeneration processes*

Catalyst regeneration processes other than those for catalytic cracking processes are not explicitly exempt under Article 28(c). These processes would, however, be exempt under Article 28(a) as thermal treatment processes. In these processes carbon (coke) particles on the surface of the catalyst are combusted to regenerate the catalyst. The products of combustion of the coke particles directly heat the catalyst material. Therefore this activity would fall under “the direct heating, drying, or any other treatment of objects or materials” under the definition of “thermal treatment.”

**DIRECT COMBUSTION PROCESSES**

*Production of ethylene oxide and ethylene dichloride*

Ethylene oxide, ethylene dichloride, and similar direct combustion processes would be categorised under the “direct contact” definition as reactors used in the chemical industry and would therefore be exempt from categorization as combustion plants. The combustion process and chemical reaction process occur simultaneously in the ethylene dichloride and ethylene oxide production processes, and the components of the vent gas from the process are derived from both the combustion reaction and chemical reaction. For the ethylene oxide and ethylene dichloride production processes, the raw material and the fuel are the same substance (i.e., ethylene).

*Production of Bitumen*

Bitumen and similar direct combustion processes would be categorised as reactors used in the chemical industry and would therefore be exempt under the “direct contact” definition
from categorization as combustion plants. In the bitumen production process, components of the vacuum distillation residue (the feedstock) are combusted in air to carbon dioxide in the oxidizer unit; other components of the vacuum distillation residue are partially oxidized to bitumen product. The combustion processes take place within the oxidizer unit along with the chemical reactions that produce the bitumen product and provide direct heat to the process. In production of bitumen the combustion process and chemical reaction process occur simultaneously and the components of the exhaust gas from the process are derived from both the combustion reaction and the chemical reaction, thereby qualifying the processes as “reactors used in the chemical industry” under the “direct contact” definition.

**Catalytic Cracking Processes**

*Propylene (and other hydrocarbons) production from fluidized catalytic cracking and other exempt catalytic cracking processes*

Catalyst regeneration for catalytic cracking processes are explicitly exempt under Article 28(c) and therefore do not need to be further considered with respect to other potential exemptions.

**CO Boilers**

CO boilers that are used to combust carbon monoxide generated from upstream combustion processes such as catalyst regeneration and carbon black furnaces are not categorised as exempt post-combustion processes and therefore are not exempt from categorization as combustion plants. CO boilers constitute an “additional downstream oxidation process” downstream of the catalyst regenerator or carbon black furnace and therefore to not meet the definition of exempt post-combustion process.

**Pyrolysis Furnace Processes**

*Ethylene steam cracker pyrolysis furnace process*

Ethylene steam cracker pyrolysis furnace processes would not be categorised as “reactors used in the chemical industry” under the “direct contact” definition and would therefore not be exempt from categorization as combustion plants. In the steam cracker process, the heat is supplied to the process by combustion of supplemental fuel (e.g. natural gas) and the raw material is heated by transfer of heat through pyrolysis furnace tubes. There is no direct contact between the raw material to the process (e.g. naphtha, ethane) and the products of combustion in this process. For the steam cracker process the raw material and the fuel are provided separately to the equipment with no direct contact.

This process would be exempt under the “direct causation” definition, as the heat provided by the combustion directly causes the chemical reaction to take place and the combustion process is integral to the ethylene production process.

*Biofuels (biodiesel) pyrolysis furnace process*

Pyrolysis furnace processes to produce biofuels may or may not be categorised as “reactors used in the chemical industry” under the “direct contact” definition or the “direct causation” definition depending upon the source of the heat provided to the pyrolysis process. In some biofuels processes, the heat to the process is provided by direct partial oxidation of a portion of the biogenic raw material. These processes are similar in configuration to direct combustion processes such as the ethylene oxide and ethylene dichloride processes, in which also partial oxidation of the raw material provides heat to the process. For these types of processes, the raw material and the fuel are the same substance (i.e., the biogenic material). These types of processes would be categorised as “reactors used in the chemical industry” under the “direct contact” definition.
In other biofuels processes, the heat to the pyrolysis process is provided by an external combustion source and the products of combustion do not directly contact the raw materials or products of chemical reaction. For example, the fluidized bed combustion pyrolysis process the heat to the process may be provided by hot sand that is heated in a separate sand furnace. For these types of processes the raw material and the fuel are provided separately to the equipment with no direct contact, and would not be categorised as “reactors used in the chemical industry” under either the “direct contact” or “direct causation” definitions.

**Vinyl Chloride Monomer pyrolysis furnace process**

Vinyl chloride monomer is produced by the pyrolysis of ethylene dichloride. The pyrolysis process for production of vinyl chloride monomer is similar in configuration to the ethylene steam cracker pyrolysis process and thereby would be categorised as a “reactor used in the chemical industry” under the “direct causation” definition but not the “direct contact” definition. In both processes, there is no direct contact between the raw material to the process (e.g. ethylene dichloride) and the products of combustion in this process. For the vinyl chloride monomer process, the raw material and the fuel are provided separately to the equipment with no direct contact. In both processes, the heat of combustion directly causes the chemical reaction to occur and the combustion process is integral to the chemical process. Thereby the process would be categorised as a “reactor used in the chemical industry” under the direct causation” definition but not the “direct contact” definition.

**STEAM REFORMER PROCESSES**

**Methanol Production Steam Reformer Process**

Methanol is produced by the steam reforming of raw material, typically natural gas. In the steam reforming process, conventional and/or alternate fuels are burned in a combustion chamber outside of steam reformer tubes; the chemical reaction of the raw material to chemical product occurs inside of the steam reformer tubes. There is no direct contact of the combustion products with the raw materials or products of the steam reformer process. The raw material and the fuel are provided separately to the equipment with no direct contact. The heat of combustion directly causes the chemical reaction to occur and the combustion process is integral to the chemical process. Thereby the process would be categorised as a “reactor used in the chemical industry” under the direct causation” definition but not the “direct contact” definition.

**Ammonia Production Steam Reformer Process**

Ammonia is produced by the steam reforming of raw material, typically natural gas. The steam reformer process for production of ammonia is similar in configuration to the steam reformer process for the production of methanol. In both processes, there is no direct contact between the raw material to the process and the products of combustion in this process. For the ammonia production process, as for the methanol production process, the raw material and the fuel are provided separately to the equipment with no direct contact. The heat of combustion directly causes the chemical reaction to occur and the combustion process is integral to the chemical process. Thereby the process would be categorised as a “reactor used in the chemical industry” under the direct causation” definition but not the “direct contact” definition.

Rationale for categorisation of ethylene steam crackers as reactors used in the chemical industry
4.3.2 Analysis of Industry-proposed categorization of ethylene steam crackers as “reactors used in the chemical industry”

Regarding the industry-proposed definition of ethylene steam crackers as a “reactor used in the chemical industry”, the following conclusions are made:

- The chemical reactions related to steam cracking of naphtha (or ethane) feedstock to form the ethylene product (and chemical reaction by-products) take place inside pyrolysis furnace tubes, while the combustion process takes place outside of the pyrolysis furnace tubes.
- The ethylene product produced by the steam cracker process is separated from the chemical reaction by-products of the steam cracker process in downstream fractionation equipment.
- The by-products separated from the ethylene (the primary product) include fuel-grade by-products that are used as fuel for the pyrolysis furnace.
- The pyrolysis furnace tubes are externally heated by combustion that occurs in a furnace firebox;
- The pyrolysis furnace is [generally] fired by fuel gas (fuel-grade by-products) that is generated by the downstream ethylene product fractionation process.
- No chemical product or by-product is produced by the pyrolysis furnace itself; the furnace produces exhaust gas composed of the combustion products of the fuel gas (fuel-grade by-product) combustion.
- The exhaust gas from the combustion of the fuel gas in the pyrolysis furnace firebox (outside of the pyrolysis furnace tubes) does not directly contact or comingle with the ethylene-containing vent gas from the inside of the pyrolysis furnace tubes.
- The pyrolysis furnace firebox is not intended to produce a chemical and no chemical reaction occurs within the pyrolysis furnace firebox other than a conventional combustion process. No chemical product is recovered from the pyrolysis furnace firebox exhaust gas. The feedstock (naphtha) flows through the pyrolysis furnace, but inside the heat exchanger pyrolysis furnace tubes, not in direct contact with the combustion gas from the pyrolysis furnace firebox.
- The chemical reactions that occur inside the pyrolysis furnace tubes affect the composition of the exhaust gas from the pyrolysis furnaces indirectly by affecting the composition of the fuel gas that is burned in the pyrolysis furnaces. i.e., the mode of operation of the chemical process that produces the ethylene, and the mode of operation of the downstream fractionation process that produces the fuel-grade by-products, determines the composition of the fuel gas to the pyrolysis furnace, which in turn determines the composition of the exhaust gas from the pyrolysis furnace firebox.
- Thereby under the “direct contact” definition it is possible to conclude, because the pyrolysis furnace tubes vent gas (containing the ethylene product and co-products) and furnace exhaust gas (containing the fuel gas combustion products) are not in direct contact, because no chemical reaction (other than combustion-reactions) occurs in the pyrolysis furnace itself, and because the composition of the flue gas is not directly affected by the chemical reaction that produces the ethylene, that the pyrolysis furnace is not a reactor used in the chemical industry as referred to in Article 28.
The counterargument, under the “direct causation” definition, is that, as practically operated, the entire ethylene steam cracker process is an integrated recycle process in which the composition of the fuel gas to the furnace is directly affected by the mode of operation of the chemical (pyrolysis) reaction process that produces the ethylene and co-products and also directly affected by the composition of the (fractionated) products and by-products of the chemical reaction process.\(^{37}\) This translates to an ‘indirect’ effect of the chemical reaction on the pyrolysis furnace exhaust gas composition.

This [indirect] connection between the chemical reaction (occurring inside the pyrolysis tubes) vent gas composition and the furnace combustion fuel gas composition (occurring outside of the pyrolysis tubes) and resulting flue gas composition is integral to how the steam cracker process is practically operated.

### 4.3.3 Emissions profiles of ethylene steam cracker furnaces

Data collection in this study found evidence that there was concern that the naphtha-feedstock ethylene steam cracker pyrolysis plants could have trouble meeting the NO\(_x\) emissions limits that were set in the then LCP Directive due to the higher operating temperature of the pyrolysis processes than conventional combustion processes (i.e. there is the potential for greater production of thermal NO\(_x\) from a steam cracker than from a natural gas-fired boiler). It was perhaps because of this issue that the exemption of ‘reactors used in the chemical industry’ in the Directive came about.

As indicated above, it is correct that steam crackers operate at a higher temperature (~850°C) than conventional combustion processes in order to provide the heat needed to drive the pyrolysis process, and that NO\(_x\) emissions may therefore be higher from a steam cracker furnace than from conventional natural gas-fired boilers. One of the specific drivers of NO\(_x\) emissions from combustion sources is the peak flame temperature (see Page 14 of the LCP BREF) and another driver for NO\(_x\) emissions is the nitrogen content of the fuel (see Table 1.7 of the LCP BREF, also Page 14). It may also be the case that the specific composition of the “fuel gas” used in steam cracker furnaces has specific characteristics (e.g. higher nitrogen content than natural gas) that would increase fuel-related NO\(_x\) emissions over that from conventional natural gas-fired boilers.

The LCP Directive; Annex VI Section A Emission Limit Values for NO\(_x\) contains only one limit for “gaseous fuels” for existing plants (200 mg/Nm\(^3\) for > 500 MWth existing plants; 300 mg/Nm\(^3\) for < 500 MWth existing plants); there are separate standards for “natural gas” and for “other gases for new plants under Annex VI Section B (100 mg/NM\(^3\) for new > 300 MWth plants for natural gas and 200 mg/NM\(^3\) for new > 300 MWth for other gases.) Note that ECN, citing Selas-Linde technical data, reported that commercially available De-NO\(_x\) technologies can control NO\(_x\) emissions from ethylene steam cracker furnaces to < 60 mg NO\(_x\)/Nm\(^3\) and that achieving < 100 NO\(_x\)/Nm\(^3\) without application of De-NO\(_x\) technology is feasible.\(^{38}\)

Therefore, if the objective is to distinguish the combustion process in a steam cracker furnace from the combustion process in a conventional natural gas-fired boiler, the operating temperature in a steam cracker furnace may be higher, and the fuel gas nitrogen content may be higher than the nitrogen content of natural gas. However, industry reports indicate that NO\(_x\) emissions from ethylene steam cracker pyrolysis furnaces are controllable to within the limits of the LCP Directive either with or without application of De-NO\(_x\) control.

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\(^{37}\) It is possible that this could apply to other furnaces within the petrochemical industry but this has not been researched specifically.

technology. Depending upon the specific process conditions the methods applicable to control NO\textsubscript{x} emissions may be different from those that would be applied to conventional combustion processes. The fuel gas composition and the pyrolysis furnace operating temperature may both be affecting the composition of the flue gas from the steam cracker furnace and may be distinctions between steam cracker furnaces and conventional natural gas-fired boilers. However, this does not necessarily mean that NO\textsubscript{x} emissions from steam cracker pyrolysis furnaces are not controllable to within the LCP directive standard for combustion plants.

However, potential differences between the process characteristics of steam cracker pyrolysis furnaces and conventional natural gas-fired combustion processes related to the processes potential NO\textsubscript{x} emissions profiles are not sufficient to support classification of ethylene steam cracker furnaces as “reactors used in the chemical industry.” It is difficult to characterize the steam cracker furnace itself as a “chemical reactor” without making an explicit change to the definition in the Directive because no “chemical reaction” occurs in the steam cracker furnace equipment, except for combustion reactions. Nor is there any direct contact between the products of the chemical reaction (the vent gas containing the ethylene) and the flue gas from the steam cracker, or any direct relationship between the composition of the flue gas from the steam cracker furnace and the vent gas from the pyrolysis reaction. From the Task 2 Scope of Work description, the categorisation of a “reactor used in the chemical industry” depends on there being a direct relationship between and direct contact between the flue gas and the chemical reaction taking place, which is not the case for ethylene steam cracker pyrolysis furnaces.
References


Edelweiss (2011) Ethylene Global Demand-Supply Scenario


Sedan (2010) Ethylene crackers in Europe (EU27) for year 2010


Appendix A: Overview of Ethylene crackers operating across the EU

DATA COLLECTION EXERCISE FOR THIS TASK

There are a number of existing inventories of ethylene crackers in Europe (e.g. Sedan, 2010; APPE, 2011). These existing data sources have been used alongside the existing LCP inventory for 2009 to identify relevant Member States for consultation. The latest data source (APPE, 2011) indicates that ethylene crackers are located in nine Member States: Austria, Belgium, Germany, Finland, Italy, France, the Netherlands, Spain, Sweden, Portugal and the UK. At the time of writing responses had been received from Austria, Belgium (Walloon region), Germany, Finland, Italy, the Netherlands, Poland and Portugal. No response has been received from Belgium Flanders region, France, Spain, Sweden or the UK.

Follow-up communications by email were made with Member State representatives by ICF. Information was sought on up to date information on ethylene crackers operating in Member States including: number of crackers, thermal capacity, fuel consumption, emissions of key pollutants and abatement measures. The data collected is presented below.

IMPLICATIONS OF AGGREGATION RULES TO CRACKER FURNACES

Installations for the production of ethylene generally have multiple steam cracker furnaces. As an example, an installation with eight separate steam cracker furnaces may have seven on-line with the naphtha feedstock and one in decoking mode at any one time. Each furnace could have a separate flue gas stack and would therefore have its own NOx emission control system (Lo-NOx burners, selective catalytic reduction). One ethylene production installation therefore typically comprises multiple combustion plants, where each combustion plant would typically consist of one combustion unit (one steam cracker furnace).

For decoking, the decoking vent gas would either be routed back into the pyrolysis furnace or would be emitted to the atmosphere (after treatment) through a separate stack. So there may be separate decoking stacks for each unit in addition to the pyrolysis furnace stacks. Multiple combustion (pyrolysis) furnace stacks are the norm either with each connected to a common decoking stack or with each connected to a separate decoking stack. In either case the decoking process is a scheduled (routine) part of the ethylene production process and would be considered to be normal operation. The emissions profile for operation of the steam cracker furnace during decoking would differ from the emissions profile for operation of the steam cracker furnace during the production of ethylene.

For the purposes of data collection for this study, data has been requested on combustion plants (at the stack level), in accordance with the scope of combustion plants in Chapter III of the IED.

NUMBER OF ETHYLENE CRACKERS

The data reported by Member States on the numbers of ethylene crackers (at the plant level) are summarised below in Table A-1. In total 92 plants have been identified. The final column in the table notes where data is missing/has not been verified by Member States.
### Table A-1 Number of ethylene crackers reported by Member States, split by capacity class

<table>
<thead>
<tr>
<th>Member State</th>
<th>Total number of ethylene crackers</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50-100MW</td>
<td>101-300MW</td>
</tr>
<tr>
<td>Austria</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Belgium</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Germany</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Finland</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>France</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Italy</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Austria**: Included in the LCP 2009 inventory (ID: AT051).
- **Belgium**: Included in the LCP 2009 inventory (ID: BE020, BE021, BE022, BE023, BE024, BE033, BE041, BE052, BE053, BE058).
- **No information received from Belgium Walloon region specifically (although the Flanders representative thought it was not aware of any ethylene crackers in the region).**
- **The MSCA reported that there are a further 3 crackers for which no further information is available.**
- **Finland**: Information on these two cracker furnaces was provided by the MSCA – they are not reported in the LCP inventory.
- **France**: Included in the LCP 2009 inventory (ID: FR077, FR095, FR194). [These have not been verified by MSCA]
- **Italy**: These data have been received at the installation level from the MSCA (they are not included in the LCP inventory). At one installation, 12 cracking furnaces are discharged through 7 stacks; at the second, 15 furnaces are discharged through two stacks and at the third, 13 furnaces are discharged through 1 stack. Therefore we estimate that there are between 1-6 LCPs.
### Assessment of the need for additional IED amendments

**Specific contract No. 070307/ENV/2012/627812/C3 (Task 2)**

August 2013

<table>
<thead>
<tr>
<th>Member State</th>
<th>Total number of ethylene crackers</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50-100MW</td>
<td>101-300MW</td>
</tr>
<tr>
<td>Netherlands</td>
<td>26</td>
<td>2</td>
</tr>
<tr>
<td>Spain</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Poland</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Portugal</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>UK</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

26 of the crackers are report in the LCP 2009 inventory (ID: NL062, NL069, NL068, NL064, NL071, NL070, NL063, NL078, NL079, NL081, NL083, NL085, NL077, NL080, NL076, NL075, NL074, NL086, NL072, NL084, NL066, NL065, NL073, NL082, NL087, NL067). The 4 crackers operated by Shell are not reported in the inventory.

Included in the LCP 2009 inventory (ID: ES129, ES128, ES126, ES127, ES131, ES132, ES135, ES136, ES133, ES134, ES162). [These have not been verified by MSCA]

Information on these four cracker furnaces was provided by the MSCA – they are not reported in the LCP inventory.

Included in the LCP 2009 inventory (ID: PT027).

Included in the LCP 2009 inventory (ID: UK014, UK015, UK016, UK065, UK235, UK236, UK237, UK242, UK243, UK244, UK245). [These plants have not been verified by the MSCA.]
CAPACITY

The data reported by Member States on the capacity of ethylene cracker are summarised below.

Table A-2 Rated thermal capacity (MW\textsubscript{th}) of ethylene crackers, split by capacity class

<table>
<thead>
<tr>
<th>Member State</th>
<th>Total capacity of ethylene crackers</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50-100MW</td>
<td>101-300MW</td>
</tr>
<tr>
<td>Austria</td>
<td></td>
<td>421</td>
</tr>
<tr>
<td>Belgium</td>
<td>105</td>
<td>1225</td>
</tr>
<tr>
<td>Germany</td>
<td>104</td>
<td>1496</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Finland</td>
<td>296</td>
<td></td>
</tr>
<tr>
<td>France</td>
<td>470</td>
<td>466</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Italy</td>
<td></td>
<td>757</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Netherlands</td>
<td>1600</td>
<td>398</td>
</tr>
<tr>
<td>Spain</td>
<td>370</td>
<td>466</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poland</td>
<td>224</td>
<td></td>
</tr>
<tr>
<td>Portugal</td>
<td>387</td>
<td></td>
</tr>
<tr>
<td>UK</td>
<td>565.8</td>
<td>551</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FUEL CONSUMPTION OF PLANTS

It should be noted that for an ethylene furnace the “fuel consumption” is the amount of “fuel gas” plus the amount of any supplemental fuel (e.g. natural gas) that is fed to the pyrolysis furnace burners. Note also that there may be other areas of the ethylene plant that consume fuel (e.g. for the purposes of producing plant-wide utility steam/electricity.) The table below shows total amounts of fuel used including, but not limited to, the amount of fuel combusted in the steam cracker pyrolysis furnaces.
Assessment of the need for additional IED amendments
Specific contract No. 070307/ENV/2012/627812/C3 (Task 2)

Table A-3: Fuel used as ethylene steam cracker plants in Europe

<table>
<thead>
<tr>
<th>Fuel used at ethylene steam cracker plants</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Other solid fuels (TJ)</td>
<td>0</td>
</tr>
<tr>
<td>Liquid fuels (TJ)</td>
<td>61,744</td>
</tr>
<tr>
<td>Natural gas (TJ)</td>
<td>37,582</td>
</tr>
<tr>
<td>Other gases (TJ)</td>
<td>227,712</td>
</tr>
</tbody>
</table>

Further information has been reported for four Member States:

- Borealis Porvoo plant (FI): refinery fuel gas (RFG);
- Schwechat Refinery (AT): refinery fuel gas (RFG);
- Versalis plants (IT): methane and hydrogen (self-produced);
- Olefins II installation (PL): high-pressure fuel gas (consisting mainly of methane), and own fuel gas produced on-site.39

Edelweiss (2011) shows the types of feedstocks (raw materials) being used at ethylene plants worldwide including the EU. This report indicates that none of the plants use natural gas as a feedstock, which would indicate that the natural gas reported consumed in the ethylene plants is being used as a supplemental fuel in the steam cracker furnace, or is being used as a fuel elsewhere in the production plant (e.g., for steam generation), rather than as a feedstock to the steam cracker pyrolysis furnace (i.e., raw material for ethylene production.)

**EMISSIONS OF KEY POLLUTANTS**

Emissions of dust, SO$_2$ and NO$_x$ from ethylene steam cracker plants in the EU are presented below. These have been estimated based on the identification of relevant plants in the LCP 2009 inventory and where steam crackers are not included in the inventory from information provided by MSCAs. It is important to reiterate here that some of the plants identified in the inventory have not been verified as ethylene crackers and therefore the data presented has significant uncertainties. Consequently, analysis of total emission load is best assessed at EU level rather than subdivided further.

The table shows estimated SO$_2$, NO$_x$ and dust emissions for ethylene cracker plants in the EU for 2009, and compares the estimates to total emission estimates reported for LCPs from the 2009 LCP inventory, and against “total industrial combustion emissions from inventories reported for 2009 under NECD.”

Total industrial combustion is taken as being the sum total of the following NFR codes, in line with AMEC (2012):

- 1A1a (Public Electricity and Heat Production);

39 It was noted that fuel gas streams are combined whereby there is a mixture of those gases used as a single common fuel gas in steam cracker furnaces. Gas mixture consists of methane (%), ethane, ethylene, propylene, propane (in total 1%) and hydrogen the remaining 9%.
• 1A1b (Petroleum refining);
• 1A1c (Manufacture of solid fuels and other energy industries);
• 1A2a (Stationary combustion in manufacturing industries and construction: Iron and Steel);
• 1A2b (Stationary combustion in manufacturing industries and construction: Non-ferrous metals);
• 1A2c (Stationary combustion in manufacturing industries and construction: Chemicals);
• 1A2d (Stationary combustion in manufacturing industries and construction: Pulp, Paper and Print);
• 1A2e (Stationary combustion in manufacturing industries and construction: Food processing, beverages and tobacco); and
• 1A2f (Stationary combustion in manufacturing industries and construction: Other).

Emissions of SO$_2$ are broken down by fuel type to illustrate the association between high SO$_2$ emissions and use of liquid fuels (rather than gaseous fuels).

**Table A-4: Emissions from ethylene cracker plants across Europe**

<table>
<thead>
<tr>
<th>Annual pollutant emission (kt)</th>
<th>Ethylene cracker plants</th>
<th>Comparison with LCP inventory</th>
<th>Comparison with total industrial combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2009 LCP</td>
<td>% of LCP</td>
</tr>
<tr>
<td>Total SO$_2$</td>
<td>31.00</td>
<td>2,564</td>
<td>1.2%</td>
</tr>
<tr>
<td>Amount of SO$_2$ from plants with liquid fuels make up &gt;30% of thermal input</td>
<td>22.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amount of SO$_2$ from plants with gaseous fuels &gt;50% of thermal input</td>
<td>7.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_x$</td>
<td>21.86</td>
<td>1,525</td>
<td>1.4%</td>
</tr>
<tr>
<td>Dust</td>
<td>1.50</td>
<td>123</td>
<td>1.2%</td>
</tr>
</tbody>
</table>

The estimates presented in the table above suggest that ethylene steam cracker plants do not contribute significantly to the total SO$_2$, NO$_x$ or dust emission inventories of the LCPs.
ABATEMENT MEASURES

Information has been received on abatement measures in a limited number of plants. This is presented below.

Techniques to reduce NO\textsubscript{x} emissions to air from steam cracker furnaces

- **Dow Benelux plant (NL):** De-NO\textsubscript{x} systems are installed in the cracker complex that serves to convert nitric oxides from the flue gases into nitrogen using a catalytic converter. According to the literature, the De-NO\textsubscript{x} operation can be improved even further and the incinerators of the furnaces of the oldest cracker will gradually be phased out and replaced in the period up to 2015, therefore a further reduction in NO\textsubscript{x} emissions is expected for the coming years.

- **Borealis Porvoo plant (FI):** All furnaces are equipped with low-NO\textsubscript{x} burners and gases from carbonized coal combustion are burned.

- **Schwechat Refinery (AT):** In the years 2005 through 2007, two measures were installed:
  - Construction of an SNO\textsubscript{x} facility for flue gas cleaning, and
  - Installation of low-NO\textsubscript{x} burners.

- **Olefins II plant (PL):**
  - Installation of low-NO\textsubscript{x} burners.

Techniques to reduce SO\textsubscript{2} emissions to air from steam cracker furnaces

No information reported.

Techniques to reduce PM emissions to air from steam cracker furnaces

No information reported.