Ignition Temperatures of R1234yf

Content

- Intention
- Self ignition phenomena
- Influences on IT
- Analysis of published IT
- Consequences if MIT is used
- Further thoughts
- Summary/Conclusions

JRC draft report, version 11.12.2013:

To be added for final version:

KBA experimental results in the light of SAE fault tree analysis and other work (consider different purpose; KBA tests not meant as risk analysis; confirm ca. 700 °C needed for ignition; risk of person in car to be exposed vs. risk of vehicle to catch fire?) and other work

Existing legislation, regulations, directives and standards

Many temperatures have been published so far, but

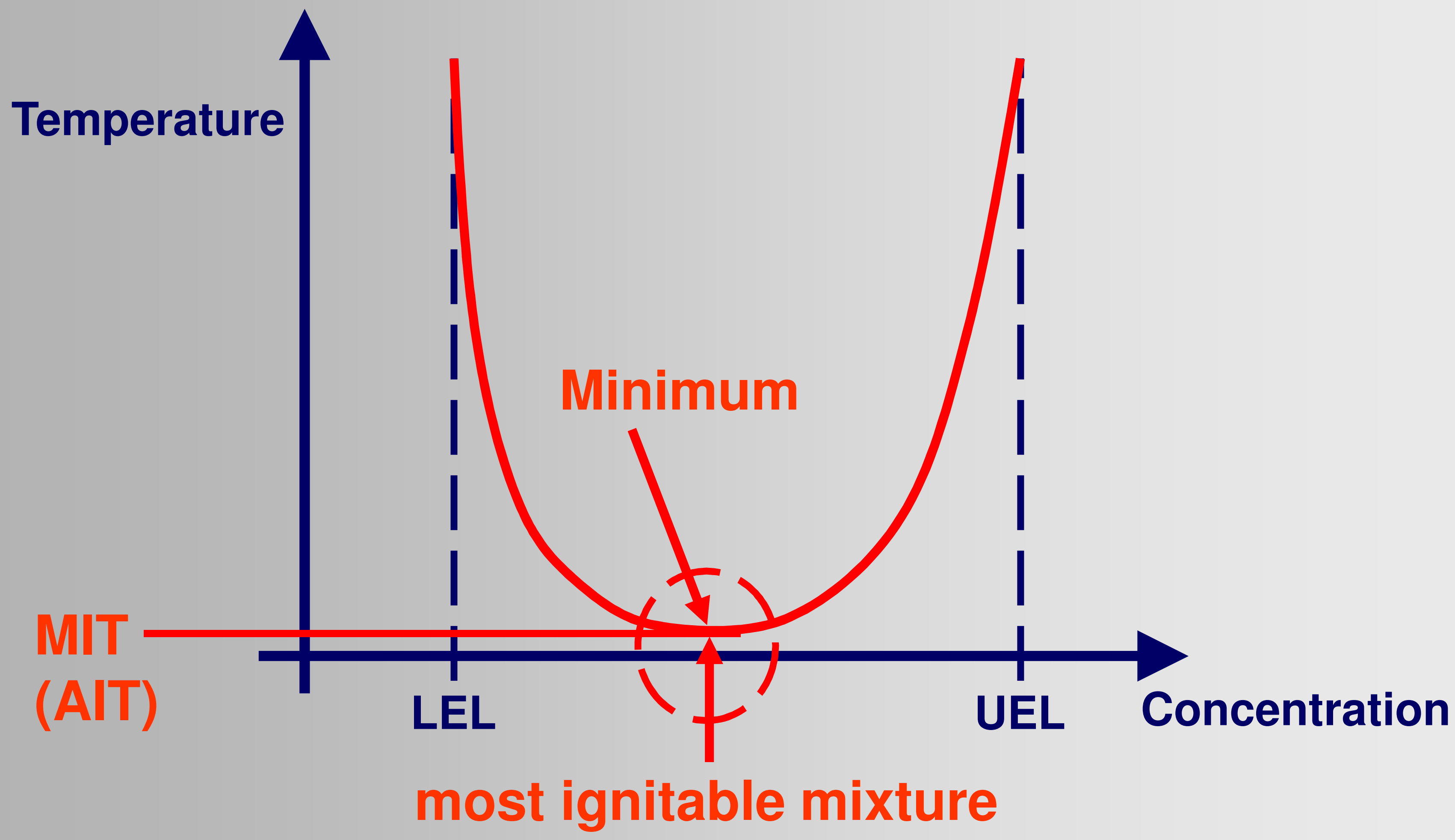
What is the most reliable ignition temperature, now and in future?

EU COUNCIL REGULATION (EC) No 440/2008:

The degree of auto-ignitability is expressed in terms of the auto-ignition temperature. The auto-ignition temperature is the lowest temperature at which the test substance will ignite when mixed with air under the conditions defined in the test method.

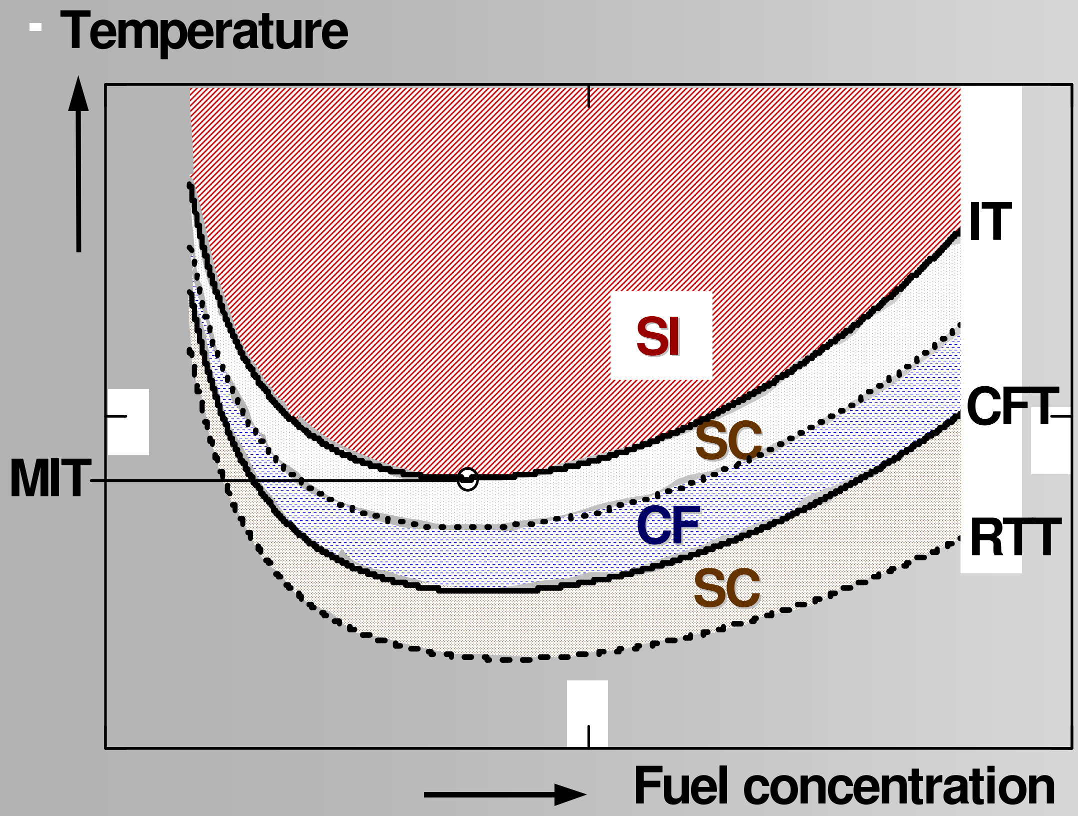
→ AIT (MIT) to be reported in Material Safety Data Sheet.

Self ignition phenomena



Self ignition phenomena

Conceptual presentation of terms related to oxidation phenomena:



MIT	Minimum ignition temperature
IT	Ignition temperature
SI	Self Ignition
SC	Slow Combustion
CF	Cool flame
CFT	Cool flame temperature
RTT	Reaction threshold temperature

source: SAFEKINEX Deliverable No. 5 „Report on experimentally determined self-ignition temperature and the ignition delay time“ (2005)

Influences on IT

MIT (AIT) is known as one important safety characteristic for gases and vapours, but

- **explosion indices are not the type of independent physico-chemical material characteristics such as melting temperature or density, therefore**

- **explosion indices and especially the MIT (AIT) are influenced by apparatus parameters (test method) and physico-chemical properties of the fuel.**

Materials and physico-chemical properties (modified to MAC)

- **Molecular structure of substance** (unsaturated fluorinated hydrocarbon)
- **Initial temperature** (ambient temperature in engine compartment)
- **Refrigerant and/or oxygen concentration** (explosive atmosphere)
- **Effect of inert admixtures** (motor coolant, inertization, inhibition or acceleration of oxidation)

Apparatus parameters (boundary conditions)

- **Free volume and its shape** (deformation of engine compartment, flow fields, “disturbing obstacles”)
- **Size of hot surface** (surface/volume ratio of exhaust system and/or turbocharger)
- **Constitution of hot surface** (roughness, specific surface of exhaust system and/or turbocharger)
- **Material of hot surface** (catalytic effects, composition of cast metal)
- **Flow conditions, turbulences** (leak rate, leak size, flow fields (dependent on obstacles), buoyancy (chimney effect), contact time, ignition delay time, gas traps)

Analysis of published IT

Temperature	Source
405 °C	MSDS Honeywell, published 11/10/2008
525 °C	BAM presentation “Combustion of R1234yf and HF analytics in leak testing of car refrigerant R1234yf”, Annexes to KBA-MAC report
600 °C	BAM test report “Ignition behavior of HFO1234yf” (BAM Az.: II-2318/2009)
635 °C	Daimler presentation “Observations on Risk Assessments of R1234yf”, Brussels 11-12-2013
700 °C	SAE CRP IV report “Additional risk assessment of alternative refrigerent R1234yf, 24-07-2013
750 °C	SAE CRP III report “Risk assessment for alternative refrigerents HFO-1234yf and R-744 (CO2), 17-12-2009
> 800 °C	SAE CRP III report “Risk assessment for alternative refrigerents HFO-1234yf and R-744 (CO2), 17-12-2009

Analysis of published IT

405 °C, MIT

- **Only** value determined according to existing standards
- Reproducible "worst case" value

Existing Standards according to EC Council Regulation (EC) No 440/2008 (test method A.15):

- IEC 60079-4
- DIN 51794
- ASTM 659-78
- B.S. 4056 : 1966
- EN 14522

} Open Glass Flasks

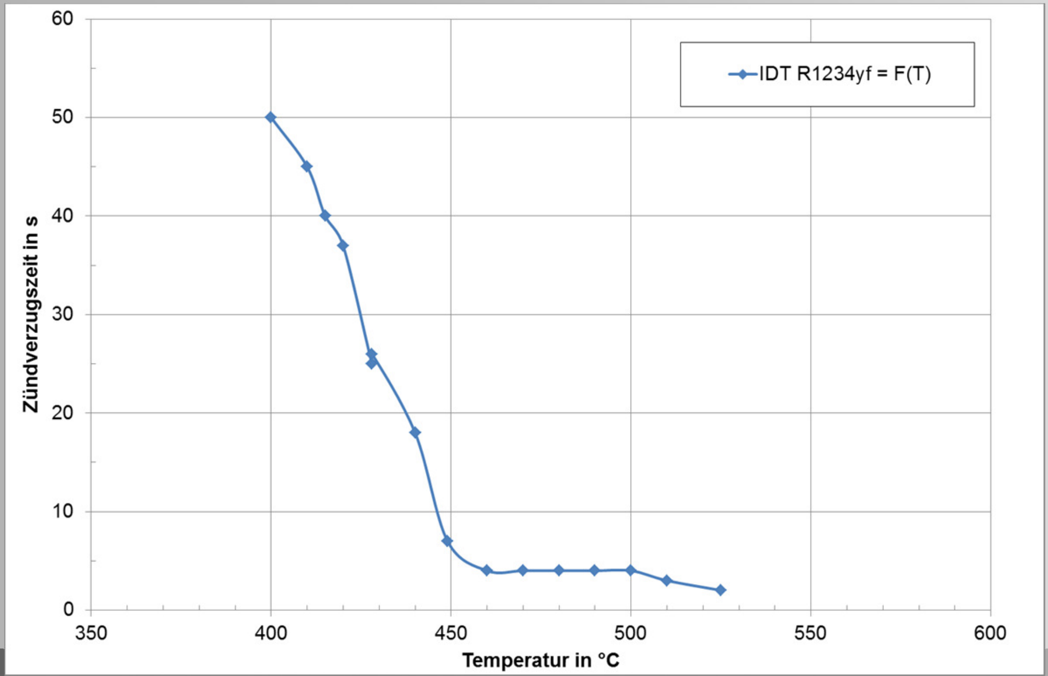
EN 14522:2005   ASTM 659-78

Usually MIT (AIT) determined according to the ASTM standard are lower compared to EN standard!

BAM

525 °C, IDT = "0s" (immediate ignition)

- Value determined according to existing standards
- Reproducible value, also often used in chemical industry to consider flow conditions and contact times
- Not standardized value!

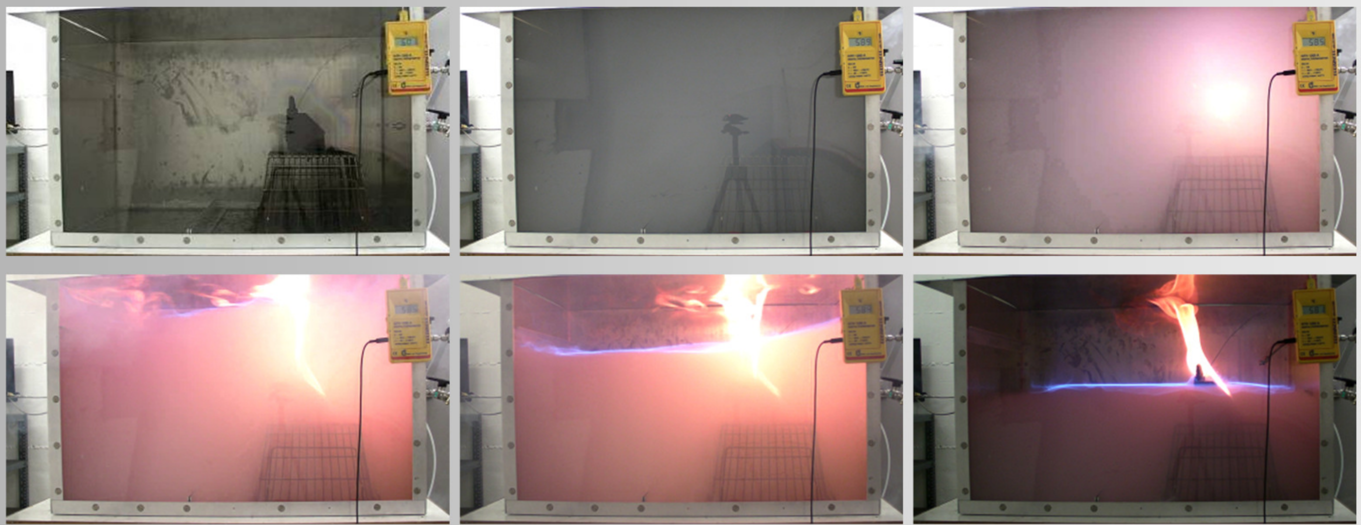


As surface temperature rises, the ignition delay time reduces. Taking account of the triggering time of 2s for 20ml of R-1234yf, at temperatures > 525 °C immediate ignition is to be expected.

source: BAM presentation "Combustion of R1234yf and HF analytics in leak testing of car refrigerant R1234yf", Annexes to KBA-MAC report

600 °C, BAM test "Box 09"

- Model volume, high leak rate, refrigerant/oil mixtures
- "Only" temperature was varied, other parameters were fixed!
- Oil ignited when leakage was stopped
- Criticized as "not real life test" → to be excluded almost certainly considering all crash scenarios and resulting conditions ?



source: BAM test report "Ignition behaviour of HFO1234yf" (BAM Az.: II-2318/2009)

635 °C, Daimler observation

- Leak tests with cars
- No details available regarding test conditions
- Presumption: Temperature was not the only parameter varied and therefore the ignition temperature is a limiting (lowest) value of plenty ignition temperatures determined at various conditions
- If conditions have been comparable to tests Daimler published in September 2012 this ignition temperature confirms the complexity of hot surface ignition phenomena
- Ignition temperature is valid for the specific test conditions (leak rate, deformations, damages, ambient temperature etc.)

700 °C, SAE CRP IV

- More than 800? leak tests with cars
- Some details available regarding test conditions
- Different type of cars were tested → test conditions changed (all) the time (size and shape of engine/hot surface, leak rate etc.)
- Presumption: Temperature was not the only parameter varied and therefore the ignition temperature is a limiting (lowest) value of plenty ignition temperatures determined at various conditions
- Does this limiting value cover **all** conditions considering **all** crash scenarios and resulting conditions ?
- Or is that value only one additional temperature valid for the specific test conditions ?

BAM point of view: Yes, since it is not possible to study all parameters influencing hot surface ignition considering actual and future test set-ups (type of cars, constructional changes, optimization of fuel consumption, crash scenarios and resulting conditions)!

750 °C, INERIS test

- Model volume
- Main differences to standards: ambient temperature, vertical tube as hot surface → comparability to engine? (material, shape etc.)
- Critical: flow field? (empty volume, no obstacles etc.)
- Presumption: test series varying “only” surface temperature?
- Reproducible value?
- Ignition temperature is valid for the specific test conditions (leak rate, deformations, damages, ambient temperature etc.)

- Temperature > 800 °C: Not evaluated!

Assuming MIT as most reliable ignition temperature:

- SAE FTA already roughly considered that case by carrying a sensitivity analysis (SAE CRP IV report) regarding the time a hot surface of more than 700 °C is available from 1% to 10% → Risk of exposure to vehicle fire increases by one order of magnitude to 3E-11
- Assuming the presence of a 700 °C hot surface is available 100% time → risk increases by another order of magnitude to3E-10
- BUT: Daimler pointed out global problems carrying out any FTA (architecture, definition of top events, links between events, quality of input values etc.)
- Assuming that different FTA with different top event, input values etc. can lead to lower, but also higher risk → How to deal with numbers in the range of 1E-8 to 1E-12 keeping in mind a two order of magnitude change by using MIT or a hot surface present all time?

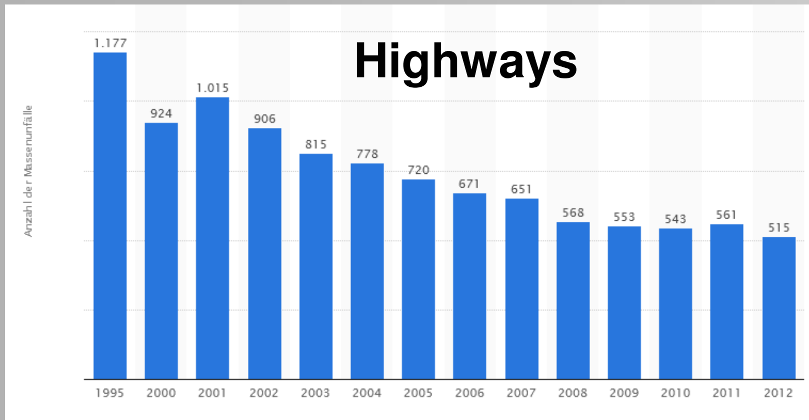
Consequences if MIT is used

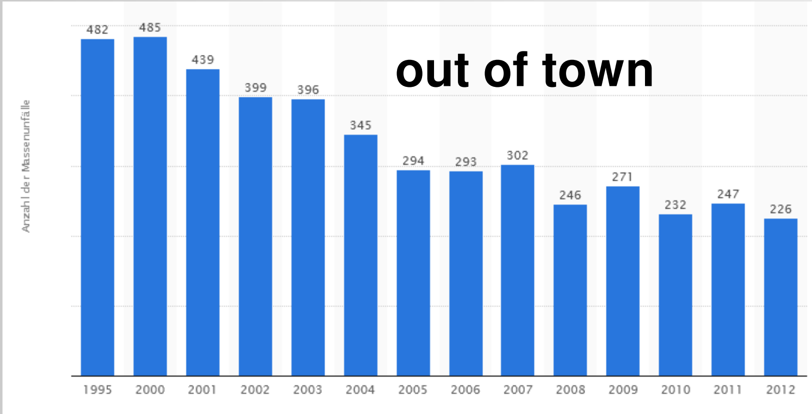
Usual risk analysis if a flammable substance is used in a process/application:

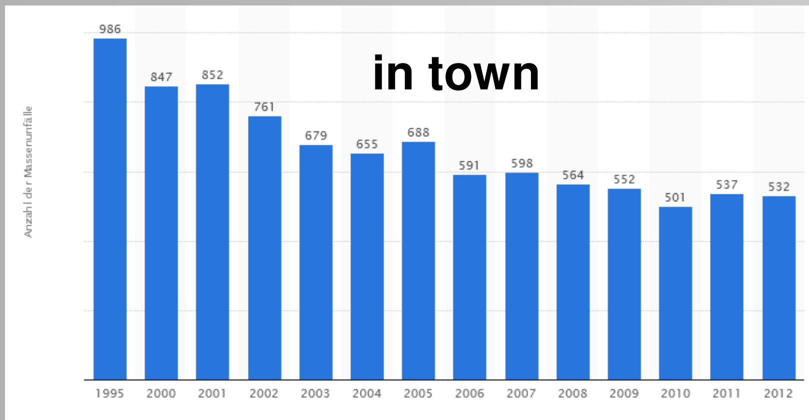
- If the formation of an explosive atmosphere can occur at any time or many times one or a combination of the following three explosion protection concepts are applied (modified to MAC):
  - *Primary explosion protection*: Avoidance or restriction of release of the refrigerant and therefore formation of an explosive atmosphere (limiting the refrigerant, additional ventilation, fast acting valves to subdivide the MAC circuit etc.)
  - *Secondary explosion protection*: Avoidance of ignition sources capable to ignite the explosive atmosphere (sparks, hot surfaces, flames etc.)
  - *Constructive (tertiary) explosion protection*: Avoidance of explosion (flame) propagation or limitation of explosion severity (flame extinguisher, additional ventilation etc.)

Mass accidents in Germany, time period: 1995 to 2012

(source: http://de.statista.com; public area)







- Number fortunately decreased, but in newer times stable
- **Total 2012: 1273 crashs**
- No information how many cars involved
- Assuming min. 3 cars → **> 3800 cars**

Further thoughts

Pictures/damages of mass accidents

A31 close to Münster, 19/11/2011: more than 50 cars at night and fog

source: http://www.t-online.de/nachrichten/panorama/id_51596832/massenkarambolage-tote-und-viele-verletzte-auf-a31-.html

A6 close to Schwäbisch Hall, 19/02/2013: more than 40 cars

source: http://www.schwarzwaelder-bote.de/inhalt.kreis-schwaebisch-hall-zwei-tote-bei-massenkarambolage-auf-a6.1d174514-76ae-48e4-bff5-90d448df0fe5.html

In a single mass accident many cars are damaged differently → many different leak scenarios!

How to evaluate ignition risk with respect to “free volume, leak rates, size/shape of hot surfaces …” or **Does any test series regarding ignition temperatures cover all scenarios occurring in only one mass accident?**

Not to mention HF exposition for people involved!

Ignition temperatures

- Different ignition temperatures have been reported in a range from 405 °C (MIT) up to 750 °C and higher!
- Ignition temperatures are strongly dependent on test conditions!
- Most ignition temperatures published so far are valid for specific and limited conditions!
- No ignition temperature exists which cover **all** conditions occurring in "real life" considering **all** crash scenarios and resulting conditions!
- Future developments might lead to different concepts operating a combustion engine (optimization of the fuel consumption) considering "new" materials as well → New extensive studies to determine new ignition temperature?
- If another ignition temperature than the MIT will be accepted what about future risk assessment for e.g. hybrid vehicles and electrical vehicles?

Most reliable ignition temperature is the MIT of 405 °C

Statement supported by **ISO 13043:2011-04 (E) Road vehicles - Refrigerant systems used in mobile air conditioning systems (MAC) -Safety requirements**

- 4.3.2 R-1234yf MAC Systems

  The refrigerant safety strategy will be for each vehicle manufacturer to carry out a risk assessment for R-1234yf refrigerant systems that will be used in new vehicles. The risk assessments shall include, but not be limited to consideration of, the inputs below (values are given in Annex A):

  … Autoignition Temperature ….

Most reliable ignition temperature is the MIT of 405 °C

Statement also supported by **SAE J2773 Standard for Refrigerant Risk Analysis for Mobile Air Conditioning Systems**

- APPENDIX A- EXAMPLE RISK ASSESSMENT INPUTS

  A.5 Other factors

  Flammability properties including those shown in the table below

TABLE A1 - FLAMMABILITY PROPERTIES

Upper Flammability Limit, Vol. % in air (21°C, ASTM E681)
Lower Flammability Limit, Vol. % in air (21°C, ASTM E681)
Minimum Ignition Energy, mJ at 20°C and 1 atm (per IEC 79-3, 3rd ed., 1990)
Autoignition Temperature, °C (EC Physico/Chemical Test A15)
Heat of Combustion, MJ/kg per ASHRAE Standard 34
Fundamental burning velocity, cm/s (per ISO 817)
Minimum Ignition Current (per IEC 79-3, 3rd ed., 1990)
Minimum Ignition Current Ratio (per IEC 79-3, 3rd ed., 1990)

BAM

A compromise might be the temperature for immediate ignition (following test method A.15)

525 °C

- Close to the 550 °C published in SAE CRP III "4.2 Refrigerant Ignition, Engine Compartment Scenarios" (p. 73 ff.)

release and ignition. In terms of the temperature required for the hot surface to ignite the HFO-1234yf/oil mixture, the CRP decided to conservatively assume that temperatures of 550°C would be sufficient to cause ignition, although testing conducted at INERIS indicated that the temperature at which the HFO-1234yf/PAG oil mixture ignites in air is approximately 750°C and one test conducted at Hughes Associates indicated refrigerant/oil ignition at 700°C. It should be noted that the boundary conditions employed in this fault tree represent extreme use conditions (*e.g.*, vehicle engine surface temperatures would only exceed 550°C during times of extreme use and are not indicative of normal city driving). Refer to Fault Tree I4 in