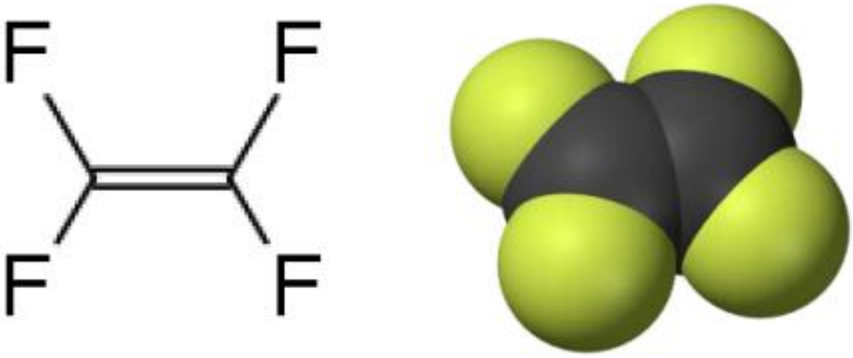
PLASTICSEUROPE TFE Safety Task Force
for world-wide safe operation to protect our industry



Guide for the Safe Handling of Tetrafluoroethylene

December 2024

Fluoropolymers
Product Group of Plastics Europe

Guide for the Safe Handling of Tetrafluoroethylene

December 2024, Revision 2

This guide was developed by the PlasticsEurope TFE Safety Task Force and first issued in November 2017. This updated version of the guide has been produced to include the latest knowledge on tetrafluoroethylene (TFE) safety from the TFE Safety Task Force sponsored testing, improved industry practices and TFE safety knowledge from elsewhere.

The PlasticsEurope TFE Safety Task Force was founded in 2003 and consists of experts working for fluoropolymer production companies all over the world (See Appendix A). The primary goal of the PlasticsEurope TFE Safety Task Force is to enhance the safe handling of TFE by sharing relevant information and identifying gaps in the know-how and investigating these. For this purpose, various research projects have been carried out over the past 20+ years initially at Bundesanstalt für Materialforschung und -prüfung (BAM)(i), Germany, and more recently with Ineris(ii), France. This guide summarizes our most important findings and provides current state-of-the-art guidance in safe TFE handling practices.

About the authors

The main contributors to December 2024 version of this guide were:

> Dr. Martyn Shenton was a member of the PlasticsEurope TFE Safety Task Force for almost 20 years and was chairperson of the group from May 2017 to December 2023. He has over 20 years experience of handling TFE at AGC Chemicals Europe, Ltd. and was the company's Global TFE Safety Expert, a position he has held for over two decades. Martyn is now a Principal Consultant at Blue Frog Scientific with expertise in process and product safety and regulations.
>
> Jeroen Robert Wanrooij has been a member of the PlasticsEurope TFE Safety Task Force since 2017 and became chairperson of the group in November 2023. He has over 15 years experience of handling TFE at The Chemours Company and is one of the company's TFE Safety Experts.
>
> Hannes Engel joined the PlasticsEurope TFE Safety Task Force in 2022 when starting in his new role as Process Safety Engineer at AGC Chemicals Europe, Ltd. Previous roles included work as Senior Process Safety Engineer at a global process safety consultancy.
>
> Matteo Gusberti, site process leader at Syensqo, has over 15 years experience of fluoropolymers and TFE handling. He has been a member of the PlasticsEurope TFE Safety Task Force since 2017 and the group's vice-chairperson since April 2024.

The biographies of the main contributors to the original guide (November 2017) are included here:

(i) https://www.bam.de/Navigation/EN/Home/home.html
(ii) https://www.ineris.fr/en

Dr. Fabio Ferrero, independent consultant, has been collaborating with the PlasticsEurope TFE Safety Task Force since 2008. During his 8-year-experience at BAM Federal Institute for Materials Research and Testing, Berlin, Germany, he worked on many TFE-related projects and provided valuable publications on TFE safety.

Dr. Martyn Shenton has been a member of the PlasticsEurope TFE Safety Task Force since 2003 and became chairperson of the group in May 2017. He has over 15 years experience of handling TFE at AGC Chemicals Europe, Ltd. and is the company's Global TFE Safety Expert, a position he has held for over a decade.

Davide Bellucci, fluoropolymers process technologist at Solvay Specialty Polymers, has over 10 years experience of TFE safe handling. He has been a member of the PlasticsEurope TFE Safety Task Force since 2012 and the group's vice-chairperson since May 2017.

Dr. Tom Spoormaker was chairperson of the PlasticsEurope TFE Safety Task Force from 2003 until April 2017. He had 37 years of experience in handling TFE at DuPont and Chemours. During his professional career experience, he covered a variety of engineering functions and gathered deep know-how of TFE safety-related issues. Furthermore, he was chairperson of the DuPont TFE Committee for over 16 years. His field knowledge was extremely useful in the preparation of this guide.

Acknowledgments

Special thanks go to the PlasticsEurope team for the organisational support given in preparation of this guide. Thanks, in particular to all members of the PlasticsEurope TFE Safety Task Force for their important suggestions.

The authors would also like to thank David Farrar, toxicology expert at CCERT Limited, United Kingdom, for providing expertise on the health hazards during TFE manufacturing.

PlasticsEurope TFE Safety Task Force
for world-wide Safe operation to protect our Industry.

This Guide for the Safe Handling of Tetrafluoroethylene is dedicated to the memory of
Dr. Tom Spoormaker, chairperson of the PlasticsEurope TFE Safety Task Force 2003 – 2017.

Fluoropolymers
Product Group of Plastics Europe

Disclaimer

Contact information

The TFE Safety Task Force can be contacted via the PlasticsEurope Fluoropolymer Product Group (FPG) at:

Email:	info@plasticseurope.org
FPG website:	https://fluoropolymers.eu/
FPG LinkedIn:	https://www.linkedin.com/company/fluoropolymers-product-group/

Joining the TFE Safety Task Force

The TFE Safety Task Force is keen to expand membership to any TFE producing or using company who wishes to improve and share their knowledge regarding TFE safety. We already have a global TFE safety community with members based in Europe, North America and Asia. Furthermore, if your interest in TFE safety is from a more academic viewpoint, we will also be pleased to engage with you. The group can be contacted via the PlasticsEurope Fluoropolymer Product Group using the contact details above.

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Introduction

Tetrafluoroethylene (TFE, CAS: 116-14-3) is a colourless, odourless gas and its main industrial application is the production of fluoropolymer resins. Fluoropolymers have a high resistance to a broad range of fuels, solvents and corrosive chemicals, and have both excellent thermal and dielectric stability. Fluoropolymer resins are used in a variety of engineering applications, ranging from seals for the automotive and aerospace industry to fire/heat resistant layers and implants for biomedical applications. According to [1], worldwide sales of fluoropolymers in 2000 exceeded \$2.0 billion compared with \$1.5 billion in 1994. More recent data for the European Economic Area (EEA) indicated that € 1.0 – 3.0 billion of EEA fluoropolymer sales plus EEA fluoropolymers downstream markets had a value of over € 700 billion in 2022 [2]. This expanding market and applications for fluoropolymers, of which polytetrafluoroethylene (PTFE), is the most common fluoropolymer resin, indicates a worldwide consumption of PTFE of around 100 000 tons each year [1], PTFE consisting of polymerised TFE monomer units.

Handling of TFE requires special attention due to its reactive decomposition (explosion) and flammability hazards [3]. Furthermore, TFE tends to polymerise spontaneously at ambient temperature. To reduce polymerization, a small amount of a terpene (typically α-pinene although similar chemicals such as d-limonene can be used) can be added as an inhibitor during TFE manufacture, storage and transport. In contact with air (oxygen), TFE tends to form explosive peroxides; the addition of the inhibitor helps minimise polymer growth initiated by these unwanted peroxides. Polymer growth is not eliminated by the addition of the inhibitor but is significantly reduced. However, the effectiveness of the inhibitor is itself reduced by high temperatures. Furthermore, terpenes are flammable substances, and appropriate procedures must be followed for their safe use, even if the amount of inhibitor added is comparatively small. Some companies render TFE inert by mixing it with an inert gas (like carbon dioxide, CO_2) or by producing it as an azeotropic mixture with hydrochloric acid (HCl).

TFE is an extremely flammable and chemically unstable gas [4] that decomposes to carbon black and tetrafluoromethane in the absence of oxygen or another oxidizing agent although an ignition source is required. The unexpected decomposition of TFE has led to many accidents in the fluoropolymer industry since the 1940s. Common ignition sources include heat (hot spots) and heat of compression. As an example, see a detailed incident report [5] where the ignition source is attributed to heat of compression. For these reasons TFE falls within the scope of the European road transport agreement and Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures [6]. As a result of its hazardous nature, it is not recommended to store or ship pure TFE. If transported within Europe in cylinders as a compressed gas, the maximum pressure of stabilized TFE is limited to 6 bar(iii) by the ADR agreement [7]. Due to this limitation, many fluoropolymer resins producers tend to manufacture TFE on the same site where it is polymerised.

TFE is classified as carcinogenic [3], [8], and repeated exposure has the potential to cause damage to organs. TFE is a registered substance according to the EU REACH regulation [9].

This guide focuses on the safe handling and processing of TFE for the manufacture of fluoropolymer resins. The hazards associated with TFE and with the toxic by-products

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(iii) If not further specified, bar will refer to absolute pressure.

generated from TFE manufacture and use, such as hydrogen fluoride (HF) and perfluoroisobutene (PFiB), are also dealt with in detail.

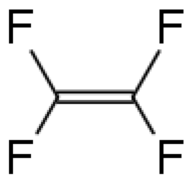
TFE contains C-F bonds but does not meet the current definitions of a Per and Poly-Fluoro Alkyl Substance (PFAS) due to the presence of the double bond. However, many of the substances that are made from TFE such as fluoropolymers are PFAS.

Chapter I – TFE properties

1. TFE chemical and physical properties

TFE (chemical formula C_2F_4) is the simplest perfluorinated alkene. At ambient temperature, TFE appears as a colourless and odourless gas. The main physical-chemical properties of TFE are summarised in Table 1 [4], [10], [11], [12].

Table 1 TFE properties

<table>
<tr><th colspan="2">Structural formula</th><th colspan="2">Names</th></tr>
<tr><td rowspan="5"> </td><td rowspan="5"></td><td>IUPAC</td><td>1,1,2,2-Tetrafluoroethene</td></tr>
<tr><td>Others</td><td>Tetrafluoroethylene
Tetrafluoroethene
Perfluoroethene
Perfluoroethylene
Fluoroplast 4
R-1114</td></tr>
<tr><th colspan="2">Numerical identifiers</th></tr>
<tr><td>CAS #</td><td>116-14-3</td></tr>
<tr><td>EC #</td><td>204-126-9</td></tr>
<tr><th colspan="2">General properties</th><th colspan="2">Thermochemical properties</th></tr>
<tr><td>Molecular formula</td><td>C_2F_4</td><td>$\Delta_f H^0$ [kJ·mol^{-1}]</td><td>-659</td></tr>
<tr><td>Molecular mass [g·mol^{-1}]</td><td>100.015</td><td>$\Delta_f G^0$ [kJ·mol^{-1}]</td><td>-624</td></tr>
<tr><td>CAS registry number</td><td>116-14-3</td><td>$C^0_{p,m}$ [J·K^{-1}mol^{-1}]</td><td>80.4</td></tr>
<tr><th colspan="4">Other chemical and physical properties</th></tr>
<tr><td colspan="2">Density at 0 °C and 1 bar(iv) [kg·m^{-3}]</td><td colspan="2">4.46</td></tr>
<tr><td colspan="2">Relative density, gas (air = 1)</td><td colspan="2">3.453</td></tr>
<tr><td colspan="2">Melting point</td><td colspan="2">-131.15 °C (142.0 K)</td></tr>
<tr><td colspan="2">Boiling point</td><td colspan="2">-75.95 °C (197.2 K)</td></tr>
<tr><td colspan="2">Critical temperature</td><td colspan="2">33.3 °C (306.4 K)</td></tr>
<tr><td colspan="2">Critical pressure [bar]</td><td colspan="2">39.4 (3.94 MPa)</td></tr>
<tr><td colspan="2">Vapour pressure at 20 °C [bar]</td><td colspan="2">29.1 (2.91 MPa)</td></tr>
<tr><td colspan="2">Solubility in water at 20 °C and 1.013 bar [% v/v]</td><td colspan="2">0.043 (110 mg/l)</td></tr>
</table>

TFE is handled in chemical plants at a range of temperatures and pressures and is processed as gas as well as liquid and sometimes even as supercritical fluid. Figure 1 shows the phase diagram of TFE. The pressure and temperature conditions for region (1) are those of liquid TFE. The region marked with (2) represents TFE in the gaseous state of matter. In region (3) TFE is found as a supercritical fluid.

(iv) If not further specified, bar will refer to absolute pressure.

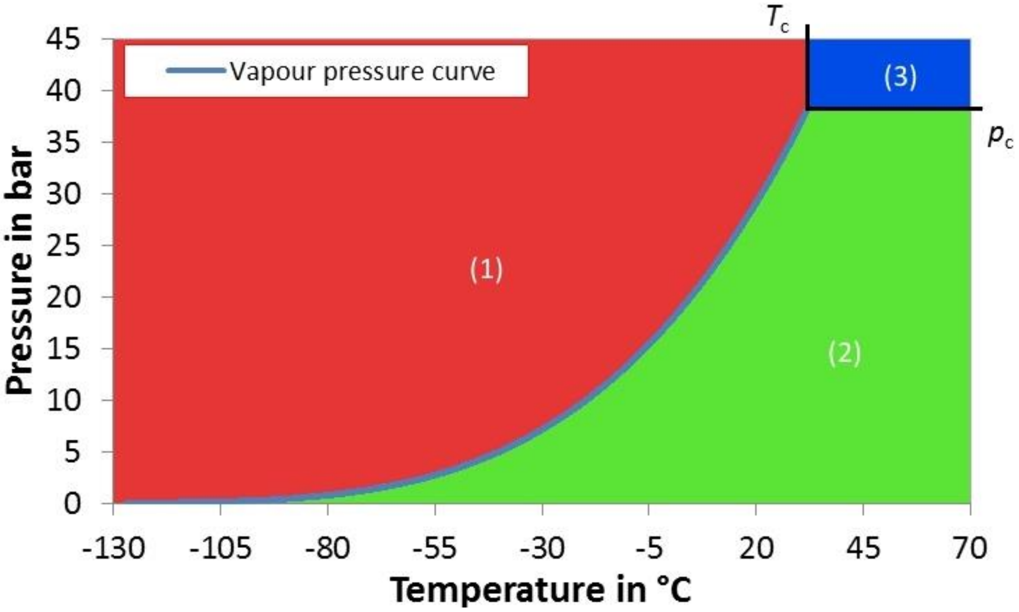


Figure 1 TFE phase diagram

There is lots of information that can be extracted from the phase diagram, i.e.:

- Gaseous TFE can be liquefied by increasing pressure only if the temperature is lower than the critical temperature (T_c). In other words, TFE cannot be found as a liquid for temperatures higher than the critical temperature, but only as a gas or as a supercritical fluid.
- For pressures above the critical pressure (p_c) TFE cannot be found as a gas, but only as a liquid or a supercritical fluid.
- TFE will appear as a supercritical fluid only if *both* temperature and pressure are above their critical values.

In Figure 1, the vapour pressure curve reports the vapour pressure (p_{vp}) of TFE as a function of temperature. The vapour pressure of a substance represents the pressure of the gas phase in equilibrium with the liquid phase of the same substance. Therefore, along the vapour pressure curve, which is valid only below the critical point, ($T < T_c$ and $p_{vp} < p_c$), liquid and gas exist in equilibrium. Typically, when liquid and gas phase are coexisting, the gas phase will be referred to as vapour, from which the name vapour pressure comes. In the industrial practice the vapour pressure curve provides, among other, information to avoid undesired condensation of gaseous TFE.

Furthermore, following considerations are valid for TFE below the critical point:

- At a specific temperature the corresponding pressure read from the vapour pressure curve represents the pressure limit above which gaseous TFE will condensate or under which liquid TFE will evaporate.
- At a specific pressure the corresponding temperature read from the vapour pressure curve represents the temperature limit above which liquid TFE will evaporate or under which gaseous TFE will condensate. This temperature is known as boiling point for that specific pressure.

There are different ways to express mathematically the vapour pressure curve of a substance. Here two equations for TFE found in literature are reported.

The vapour pressure curve of TFE expressed by Antoine's equation is:

$$\log_{10} p_{vp} = 4.029 - \frac{686.19}{(T - 26.95)} \qquad \text{Equation (1)}$$

where the equation coefficients were calculated by the National Bureau of Standards (now known as National Institute of Standards and Technology (NIST)) from empirical data between 142 and 208 K [13].

A slightly more complex formula is reported to be valid for a broader temperature range (from 146 to 306 K) [14], as shown in Equation (2). The coefficients for Equation (2) are listed in Table 2.

$$\ln(p_{vp}/p_c) = \frac{(\mathrm{VPA} \cdot \mathrm{R}) + \left(\mathrm{VPB} \cdot \mathrm{R}^{1.5}\right) + \left(\mathrm{VPC} \cdot \mathrm{R}^{3}\right) + \left(\mathrm{VPD} \cdot \mathrm{R}^{6}\right)}{T_r} \qquad \text{Equation (2)}$$

Table 2 Parameters of Equation (2)

Parameter	Value
R	$1 - T_r$
T_r	T/T_c
VPA	-6.744
VPB	0.625
VPC	-1.948
VPD	-3.789

The use of Equation (2) is recommended as it is valid over a broader temperature range.

2. TFE general toxicology

TFE has a low level of toxicity following single exposures to high concentrations [15], [16]. Repeated exposures to such very high levels or to levels in excess of the occupational exposure limit may cause damage to the kidneys and haematopoietic system and may also cause cancer. Repeated exposure by inhalation of rats or mice to TFE for their lifetime led to increases in the incidence various types of tumour in kidney, liver and the haematopoietic system [16]. Literature [17] reports that "*Studies comparing the metabolism of TFE in humans and animals, suggest that the risk for developing some of these tumours is lower for humans than for rats and mice*". The industry has concluded that TFE should be classified as a CLP Cat 1B carcinogen in its submissions to the European Chemicals Agency (ECHA) under the REACH Regulation [9]. According to the U.S. Department of Health and Human Services, TFE is listed among the "Reasonably Anticipated to Be Human Carcinogens" substances [18].

Contact of the skin, eyes or respiratory tract to splashes or sprays of liquid TFE may cause local irritation and freeze burns. Exposure to TFE gas can also cause irritation in the eyes, skin and respiratory tract [19]. Very high exposures can displace the oxygen in the air causing, dizziness, poor coordination, and unconsciousness. Table 3 shows the permissible exposure limits of TFE in air [16], [19].

A retrospective mortality study in workers occupationally exposed to TFE during its manufacture and polymerisation has shown no excess incidence of cancer at any site [20].

Table 3 Permissible exposure limits of TFE in air.

Threshold	Value	Description
ACGIH TLV-TWA	2 ppm (8.2 mg·m^{-3})	Time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.
AEGL-1 (1hour exposure)	22 ppm (90 mg·m^{-3})	Airborne concentration above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic, non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.
AEGL-2 (1 hour exposure)	55 ppm (220 mg·m^{-3})	Airborne concentration above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.
AEGL-3 (1 hour exposure)	330 ppm (1300 mg·m^{-3})	Airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.
Legend		
ACGIH TLV-TWA	American Conference of Governmental Industrial Hygienists, Threshold Limit Value - Time Weighted Average	
AEGL	Acute Emergency Guideline Levels	

3. Health hazards during TFE manufacturing and processing

TFE is manufactured on an industrial scale by the pyrolysis of chlorodifluoromethane ($CHClF_2$, R22, HCFC-22, CAS # 75-45-6). Pyrolysis is typically performed in hot tubes/reactors at temperatures around 600-900 °C in presence of hot steam in order to enhance conversion. TFE is distilled in various stages from the raw pyrolysis products in the presence of α-pinene or d-limonene, which acts as a stabiliser by reducing spontaneous TFE polymerisation at ambient temperatures. During the manufacture of TFE via pyrolysis, toxic by-products are formed. In particular, the extremely toxic compound perfluoroisobutene (i-C_4F_8, PFiB, CAS # 382-21-8) is formed; PFiB is approximately 10 times more toxic than phosgene [21]. PFiB tends to concentrate in the high-boiling stream in the TFE distillation process and must be handled with extreme care due to its extreme toxicity to humans [22]. This extreme toxicity resulted in PFiB being listed in the UN Chemicals Weapons Convention (CWC) that is monitored by the Organisation for the Prohibition of Chemical Weapons (OPCW) as a Schedule 2A chemical, since it might constitute a potential threat as a chemical weapon [23].

Understanding potential PFiB presence is vital for the safety of TFE manufacturing facilities as demonstrated by fatalities and injuries that have been reported from accidental exposure to PFiB [24]. The presence of PFiB can be inferred by online gas chromatography (GC) as although difficult to directly measure, if hexafluoropropene (C_3F_6, HFP, CAS # 116-15-4) is present, then a ratio between the HFP and PFiB concentration can be used to estimate the PFiB concentration; HFP can routinely be detected by Gas Chromatography (GC) of atmospheric air samples. The value for this ratio will depend on the production processes.

Direct measurement of PFiB concentration is possible using more sensitive analytical techniques such as Gas Chromatography-Mass Spectrometry (GC-MS). However, due to the toxicity of PFiB, there is a lack of availability of PFiB standards although PFiB tends to be included in the mass spectra libraries, for example, SpectraBase® from Wiley [25]. Alternatively, the TFE cyclic dimer, (c-C_4F_8, octafluorocyclobutane, CAS # 115-25-3) is readily available as a proxy standard (although the retention time and mass fragment pattern will slightly differ to those for PFiB).

Sampling process streams where PFiB concentrations have been concentrated should be avoided due to its extreme toxicity. Furthermore, sampling and measurements of process gas where the PFiB concentration is present in trace amounts should only be considered for analysis when fully risk assessed, and suitable control measure are in place. The risk assessment should include consideration of the risks and potential exposures during sample collection, storage, analysis and disposal.

A recent advance in PFiB exposure monitoring has come from Morphix Technologies Incorporated who have developed a SafeAir badge with one of the member companies of the TFE safety Task Force [26]. Although this badge does not stop the exposure, it can detect PFiB exposures of 3 ppm•minutes and provide warning to workers to escape from potentially harmful environments. It is noted that the AEGL-3 (lethal) value for PFiB for a 10-minute exposure is reported as 2.0 ppm [24]. Several members of the TFE Safety Task Force are either using or considering using these badges and although experience is limited with this technology, the TFE Safety Task Force members agree that this can be a useful aid in reducing the risk and harm associated with potential PFiB exposures. Some of the specification parameters for the PFiB SafeAir badge are listed in Table 4 [27]; further information is available directly from Morphix Technologies(v):

Table 4 Physical specification and sampling parameters for the PFiB SafeAir badge

Parameter	Value	Unit
Dimensions	74 x 41 x 1	mm x mm x mm
Weight	1.5	g
Refrigerated shelf life	6	months
Colour change	off-white to pink	
Exposure dose	3.0	ppm•minutes
Colour Comparator Range	3.0 – 30	ppm•minutes
Maximum recommended sampling time	12	hours
Minimum recommended sampling time	5	minutes
Relative humidity range	35 – 90	%
Face velocity range	5 – 25	cm/sec
Temperature range	0 – 37	°C
Light effect – UV (direct sunlight)	minor background discoloration	
Light effect – visible	no effect	

(v) sales@morphtec.com

Table 4 (continued)

Parameter	Value	Unit
Colour stability	12	hours
Known Interferences	• HCl at concentrations > 600 ppm for > 5 minutes • No interference from HFP or TFE	

When handling process streams containing PFiB; the approach must be to avoid exposure as any potential exposure can lead to harm and even death. Despite the positive developments in measuring and detecting PFiB, there is no cure if exposed above the fatal threshold.

TFE is also listed in the CWC as a discrete organic chemical containing phosphorous, sulphur or fluorine (DOC/PSF). Plants that manufacture DOC/PSFs may have the capability for making chemicals that could be used as chemical weapons. Manufacturers of TFE are likely to have declaration responsibilities relating to the CWC and may be subject to inspections by the OPCW to ensure compliance with the CWC. Further information on these obligations will be available from your CWC National Authority.

A short description of the main toxic by-products formed during manufacturing and processing of TFE is given in Table 5. Under common working conditions, all compounds listed are in their gaseous form. Upon contact with water, hydrogen fluoride (HF) and hydrogen chloride (HCl) will easily dissolve and generate solutions, which are extremely poisonous and corrosive. For this reason, contact with water in body tissues for these substances can be extremely dangerous.

Quantities of TFE may be supplied by the manufacturers for laboratory testing or the preparation of calibration gases although this tends to be limited volumes of stabilised TFE and only to organisations that have been approved by the TFE supplier as having sufficient experience, knowledge, processes and the equipment to handle the TFE safely. There are other synthetic methods for manufacturing TFE on a millimole scale [28], but the authors of this report do not have experience of these. Regardless of the quantity of TFE or how it is made or supplied, the flammability, decomposition and toxicity hazards must be well understood and appropriate processes followed to ensure its safe handling.

In plants processing TFE into polymer resins, the so-called “Polymer Fume Fever” might constitute a toxicity issue [17]:

“TFE is used as a monomeric building block in the manufacture of solid polymeric materials such as PTFE and other fluoropolymers that are normally sold as powders, granules or aqueous dispersions. […] During the hot processing of fluoropolymer resins into finished articles, some fume will be generated at the temperatures reached during normal processing(vi) *and the resulting fume does present a potential health hazard. It is essential that adequate ventilation is provided to prevent worker exposure to fume in the workplace. […] The potential consequence of over exposure to fumes from fluoropolymers decomposing under these conditions is “Polymer Fume Fever”. This is a temporary, influenza- like illness with symptoms such as fever, chills and a cough that can last approximately 24 to 48 hours. Onset of symptoms may not be apparent for up to 24 hours. As a precaution, any person thought to be suffering from polymer fume fever should seek medical attention. The illness is also associated with exposure to the decomposition*

(vi) 200-380 °C, depending on the resin type *products produced by smoking tobacco goods, such as cigarettes, which have become contaminated by fluoropolymer resins, even by trace quantities. It is essential that smoking and carrying tobacco products is banned in work areas where fluoropolymer resins are handled.*”

Further information on hazards and handling of fluoropolymer resins can be found in [17].

Table 5 Toxic by-product during the manufacturing and processing of TFE

By-product	Threshold [29]	Description
Carbonyl fluoride, formula: COF_2	2 ppm* ($5.4\ mg\cdot m^{-3}$)	Effects following inhalation, or skin or eye contact with carbonyl fluoride may initially include: skin irritation with discomfort or rash; eye corrosion with corneal or conjunctival ulceration; irritation of the upper respiratory passages; or temporary lung irritation effects with cough, discomfort, difficulty in breathing, or shortness of breath. Respiratory symptoms may be delayed for several hours.
Carbon monoxide, formula: CO	25 ppm* ($29\ mg\cdot m^{-3}$)	An odourless gas which reduces the oxygen carrying capacity of the blood, resulting in a decreased capacity for exertion, increased load on the heart and with severe exposure, unconsciousness and death.
Chlorodifluoromethane, formula: $CHClF_2$	1000 ppm* ($3534\ mg\cdot m^{-3}$)	A colourless gas with a slight ethereal odour which may cause anaesthetic-like effects and may also cause effects on heart function (cardiac arrhythmia) when inhaled at extremely high concentrations.
Hexafluoropropylene, formula: C_3F_6	0.1 ppm* ($0.6\ mg\cdot m^{-3}$)	An odourless gas which can cause signs of respiratory irritation and Central Nervous System (CNS) depression when inhaled at high concentrations. May cause significant kidney damage upon repeated or prolonged exposure.
Hydrogen chloride, formula: HCl	2 ppm** ($3.0\ mg\cdot m^{-3}$)	Hydrogen chloride forms corrosive hydrochloric acid on contact with water found in body tissue. Inhalation of the fumes can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary oedema, circulatory system failure, and death. Skin contact can cause redness, pain, and severe skin burns. Hydrogen chloride may cause severe burns to the eye and permanent eye damage.
Hydrogen fluoride, formula: HF	0.5 ppm* ($0.4\ mg\cdot m^{-3}$) 2 ppm** ($1.6\ mg\cdot m^{-3}$)	The odour threshold of hydrogen fluoride is significantly less than the occupational exposure limits. Inhalation of hydrogen fluoride at higher concentrations will give rise to symptoms of choking, coughing and severe eye, nose and throat irritation. In severe cases, and possibly following a symptomless period, fever, chills, difficulty in breathing, cyanosis, and pulmonary oedema may develop, which may lead to death. Acute overexposure to hydrogen fluoride can also result in injury to the liver and kidneys.
PFiB (perfluoroisobutylene), formula: $i\text{-}C_4F_8$	0.01 ppm** ($0.08\ mg\cdot m^{-3}$)	PFiB is highly toxic by acute inhalation, and exposure to concentrations above 1 ppm for any significant period of time can be fatal.
Legend		
* ACGIH TLV-TWA	American Conference of Governmental Industrial Hygienists, Threshold Limit Value - Time Weighted Average	
** ACGIH TLV-C	American Conference of Governmental Industrial Hygienists, Threshold Limit Value – Ceiling limit	

4. TFE REACH Registration

Further details about the properties of TFE are included in the EU REACH registration that is available at the ECHA Chem website [30]. The Lead Registrant (LR) for TFE in the EU is AGC Chemicals Europe, Ltd. based in the Netherlands. The Lead Dossier for the TFE EU REACH registration was last updated in 2014, but the LR is currently working on an EU dossier update. TFE is one of several fluorinated monomers that form part of the EU REACH Fluoromonomer Consortium (FMC). The data used for the EU REACH registration of TFE is owned by FMC members and is available for purchase through a Letter of Access (LoA) for other companies that wish to join the TFE EU REACH registration to access the EU market. The registration of TFE covers the following uses at the tonnage band "> 1000 tpa"; further details about the use descriptors is available in the ECHA Guidance document [31]:

- ERC 1 (manufacture).
- ERC 6c (use of monomer in polymerisation processes at industrial site (inclusion or not into/onto article)).
- PROC 1 Chemical production or refinery in closed process without likelihood of exposure or processes with equivalent containment conditions.
- PROC 3 Manufacture or formulation in the chemical industry in closed batch processes with occasional controlled exposure or processes with equivalent containment condition
- PROC 15 Use as laboratory reagent.
- PC 32 (polymer preparation).

Further information about the EU REACH registration is available from the LR, FMC consortium or ECHA. LoA data for non-EU territories is available from the FMC however, the FMC does not have any REACH responsibilities outside the EU.

5. TFE Harmonised Classification

ECHA published a harmonised classification for TFE in Annex VI to CLP_ATP17 that applied from the 17th December 2022 [32]. The EU harmonised classification for TFE is:

- Carcinogen 1B
- GHS 08
- Danger
- H350 May cause cancer

This classification was supported by the industry expert at RAC 51 [33] as the PlasticsEurope member companies already used the above classifications. Carcinogenicity was the only hazard open for comments during the public consultation, so a harmonised flammability classification was not considered. An assessment of the flammability classification for TFE is presented in the next section. Further details for the non-harmonised classifications that are agreed by the REACH registrants are presented in Appendix D, Table 20.

The UK adopted the same carcinogenicity classification for TFE; this is listed in the GB Mandatory Classification List (GB MCL) and came into legal effect from the 20th October 2023 [34].

6. TFE unstable gas classification

The EU CLP Regulation [6] includes a criteria for classifying flammable gases. Since TFE is flammable and is chemically unstable, i.e., has a decomposition hazard [5] an assessment of TFE against these criteria is presented in Table 6:

Table 6 Flammable gas assessment for TFE

			Summary of criteria*	TFE properties [35], [36]	Assessment
1A	Flammable gas		Ignitable < 13 % or range > 12 %	Flammability range 13.0 – 43.4 %	Not ignitable < 13 % but flammable range is > 12 % so meets this criteria
	Pyrophoric gas		Spontaneous ignition < 54 °C	AIT = 235 °C	Does not meet this criteria
	Chemically unstable gas	A	Chemically unstable at 20 °C and 1 atmosphere	Not chemically unstable at atmospheric pressure	Does not meet this criteria
		B	Chemically unstable at > 20 °C and > 1 atmosphere	MITD at 2 atmospheres is 600 °C	Meets this criteria
1B	Flammable gas		Meet 1A and upper flammability limit (UFL) > 6 %	UFL = 43.4 %	Meets this criteria
			Or burning velocity below 10 cm s^{-1}	Burning velocity 55 – 60 cm s^{-1}	Does not meet the criteria
2	Flammable gas		Other gases that have a flammable range in air	Already met other criteria	Not applicable

* Full criteria are given in Table 2.2.1 of regulation (EC) 1272/2008 [6].

It is noted that the AIT value reported in Table 6 is from tests where the TFE was stabilised with α-pinene [35]. However, as part of the same study, an AIT for unstabilised TFE was also recorded and found to be within the experimental error of +/- 5 °C of the AIT value for stabilised TFE.

With reference to the assessment in Table 6 and the guidance in the CLP regulation [6], particularly the sentence in section 2.2.2.1, "*Flammable gases that are pyrophoric and/or chemically unstable are always classified in Category 1A*", it is concluded that TFE shall be classified as Flammable 1A; this is the most severe flammability classification for a chemically unstable gas. Furthermore, the CLP regulation also states that the following information must be used when labelling TFE containers [6]; this is much less than the classification information found under the EU C&L inventory (see Table 20 in Appendix D):

7. Per- and Poly-Fluoroalkyl Substances

Many compounds with CF_2 groups meet the Organisation for Economic Co-operation and Development (OECD) [37] and/or EU [38] definitions of a Per- and Poly-Fluoroalkyl Substance (PFAS). However, due to the presence of the double bond, TFE is not classified as a PFAS and hence not directly impacted by the regulatory attention that PFAS are receiving. However, the main use of TFE is as a monomer for fluoropolymers and these fluoropolymers do meet the PFAS definitions of both the OECD and the EU, so awareness and compliance with relevant PFAS regulations is necessary for manufacturers and users of TFE. Further information on PFAS current and emerging regulations is available from many sources including the ECHA hot-topics PFAS website [39], the universal PFAS Registry of Intension (RoI) ECHA website [40], and the PlasticsEurope Fluoropolymer Product Group (FPG) website [41].

Chapter II – Fire and explosion hazards

TFE instability as well as its reactivity has been the cause of a number of accidents in chemical plants in the last years ([5], [42]-[47]). These accidents involved a number of fatalities as well as enormous economic losses, due to significant equipment damage and to partial or total plant shutdown. Images showing the typical damage caused to a valve and some pipework following a TFE decomposition are shown in Figure 2.

Figure 2 Damage from a TFE decomposition

The reactivity of TFE resides in its double C=C bond. At ambient conditions, gaseous TFE tends to spontaneously polymerize. For pressures around 2-3.5 bar, the uncontrolled polymerisation may lead to an explosion [19]; the exact pressure depends on the local conditions such as temperature and pipe/equipment. Hence specific preventive actions, such as polymerisation inhibition or inerting, and mitigation action, such as installation of rupture discs, venting and so on are required. Typical polymerisation inhibitors are terpenes, in particular α-pinene. However, terpenes are flammable substances and appropriate safety measures for their use must also be adopted, even if the amount of inhibitor added to TFE is comparatively small.

Despite the presence of an inhibitor, TFE can still decompose explosively in fire, under pressure, or upon contact with materials with which it can react exothermically. Remarkably, TFE decomposition does not require the presence of air or of an oxidizing agent, just TFE and an ignition source. Other reactive gases including acetylene [48] and ethylene [49] also share this explosive decomposition property. The knowledge from separate studies on TFE, acetylene and ethylene share common themes as highlighted in the recent investigation on flame arrestors for decomposable gases where testing with TFE is discussed with reference to acetylene and ethylene [50].

Furthermore, inhibited and uninhibited TFE can react violently with air, oxygen and other oxidizers as well as with halogen compounds [19]. TFE also tends to spontaneously form peroxides upon contact with air.

In this section, the main concerns on the stability and reactivity of TFE will be described.

1. Decomposition reaction

The decomposition reaction of TFE, which forms tetrafluoromethane and carbon black (soot), is shown in Equation (3). Once triggered by an ignition source (such as a spark, external heat or contact with incompatible materials) the decomposition runs explosively [51]. Gases like TFE, which can decompose without the presence of air, oxygen or another oxidizer, are commonly called chemically unstable gases.

$$C_2F_{4\,(g)} \rightarrow CF_{4\,(g)} + C_{\,(s)} \qquad \Delta H_r = -257\ \mathrm{kJ.mol^{-1}} \qquad \text{Equation (3)}$$

Soot formed during a TFE decomposition is often seen as black smoke (following pipe/vessel rupture) and deposits in equipment. Figure 3 shows the top of a reactor filled with soot following some TFE decomposition testing [52].

Figure 3 Soot formation from TFE decomposition tests

The higher the pressure, the lower is the required temperature for TFE to decompose [52]. In order to quantify the hazard connected to the contact of TFE with hot surfaces, the so-called Minimum Ignition Temperature for Decomposition (MITD) can be used. The MITD is the lowest temperature of a hot surface, e.g. the walls of a reactor or of a pipe, at which the decomposition of a chemically unstable gas like TFE occurs without the presence of an oxidiser like air. The MITD is therefore analogue to the standard Auto Ignition Temperature (AIT aka. MIT) for flammable gases, which represents the lowest temperature of a hot surface, where the most ignitable mixture of a flammable gas with air may register an ignition [53], [54]. MITD dependence on pressure and on vessel geometry is presented graphically in Figure 4. The results refer to tests in a fully heated cylindrical stainless-steel vessels with volumes ranging from 0.2 to 100 L. Figure 4 shows the decrease of the MITD of TFE with increasing pressure and vessel volume, which indicates a larger affinity to ignition. For larger vessels at high pressure, MITD can drop to values around 200 °C. The vessel orientation may also play a role in enhancing the possibility of an ignition, as it can be seen in Figure 4(vii) [52].

The influence of α-pinene, the most common inhibitor for spontaneous polymer growth of TFE at ambient temperature, on the ignition of TFE by contact with hot surfaces was tested in a series of experiments [55]. MITD of stabilized and non-stabilized TFE were compared, showing no relevant effect of the inhibitor on the ignition properties (Figure 5). In the same study, TFE contaminated with 2 % air was also tested for ignition by contact with hot surfaces, as to analyse the influence of impurities which in the practice could arise upon improper evacuation of equipment or pipelines. Results are presented in Figure 5[(vii)] [55].

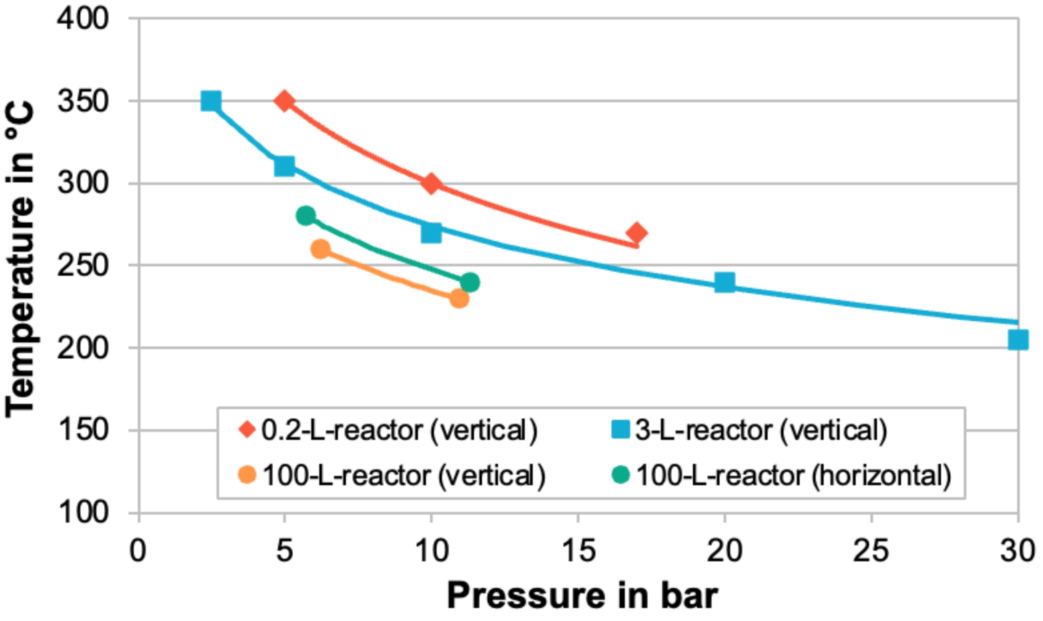


Figure 4 Dependence of the MITD of TFE on pressure

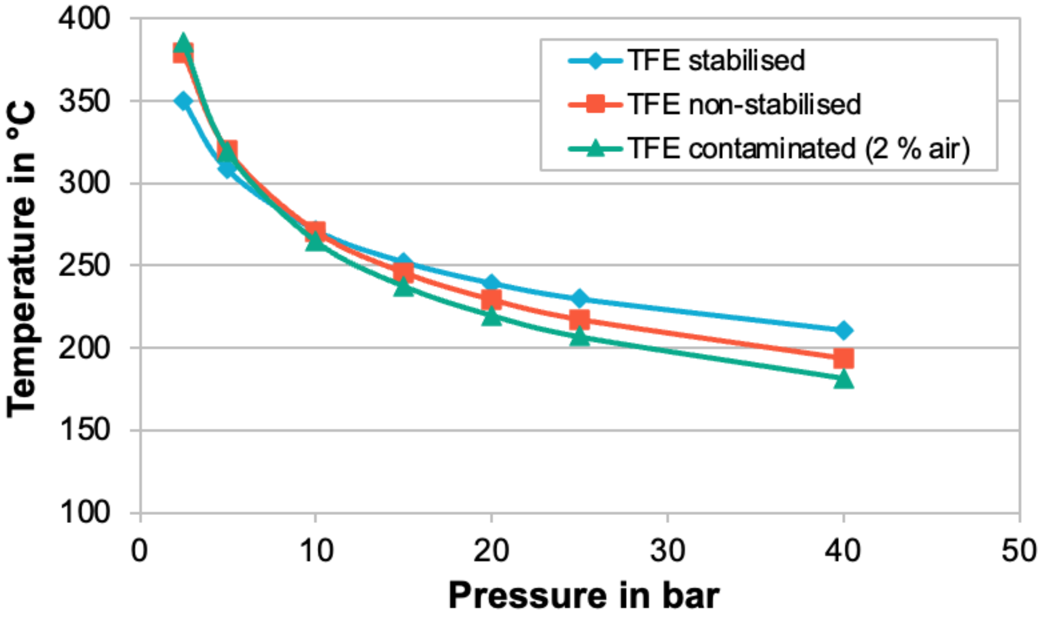


Figure 5 Effect of inhibitor and air impurities on the ignition properties of TFE

(vii) Plotted points calculated from equations presented in the literature source.

Not only is the spontaneous ignition of TFE upon contact with hot surfaces relevant, but also the triggering of TFE decomposition by an external ignition source, such as a spark from an electrostatic discharge. Tests with induced ignition of TFE showed a Pressure Limit of Stability for Decomposition (PLSD aka. MIPD) around 2-3.5 bar at ambient temperature [56]: this means under that pressure a common energy source will not be able to trigger TFE ignition. It is known that the PLSD drops for increasing temperatures, but this has not been comprehensively studied. The energy required to ignite pure TFE at different initial pressures is reported in Table 7 (data from confidential reports shared by the PlasticsEurope TFE Safety Task Force member companies). A large scatter in the values presented can be noticed. This can be attributed to a variation in test conditions.

Table 7 Minimum Ignition Energy for Decomposition (MIED) for pure TFE at different initial pressures

Pressure (bar)	MIED (mJ)
5	5000
7	2000 - 40000
14	190 - 200
21	20 - 255

TNT equivalence is commonly used to give an estimate of the force of an explosion. Based on the heats of reaction of TFE and TNT, it can be concluded that the explosive power is as high as about 2/3 that of TNT. However, as TNT is much more effective at converting the chemical energy into mechanical energy, a more realistic value of 1/3 tends to be used [46].

2. Reaction in air (combustion)

The combustion reaction of TFE is shown in Equation (4). Like the decomposition reaction, TFE combustion can proceed explosively. Since TFE will be present as gas at ambient conditions (see Figure 1), if released, it will readily mix with air, which may result in the formation of flammable atmospheres. Depending on TFE/air concentration and additional factors such as confinement and congestion, ignition of such flammable atmosphere may result in an explosion.

$$C_2F_{4\,(g)} + O_{2\,(g)} \rightarrow 2COF_{2\,(g)} \qquad \Delta H_r = -628\ \text{kJmol}^{-1} \qquad \text{Equation (4)}$$

The ignition temperature (AIT or MIT) of TFE-air mixtures upon contact with hot surfaces according to [53], [54] is reported in [4] to be around 240 °C at atmospheric pressure. As for pure TFE, the temperature required to trigger ignition of TFE-air mixtures upon contact with a hot surface decreases with increasing pressure. This is shown in Table 8 for tests performed in a stainless-steel cylindrical reactor with the volume of 3 L [57]. No tests in larger vessels were found in literature, but the ignition temperature of TFE-air mixtures is expected to decrease for increasing volume.

Table 8 Ignition temperatures of stoichiometric TFE-air mixtures and of pure TFE in a 3-L-vessel

Initial pressure (bar)	Ignition temperatures of 18 % TFE in mixture with air (°C)	Ignition temperatures of pure TFE (°C)
1.0	245*	>450
2.5	210*	350
5.0	195	310
10.0	175*	270
15.0	165	250*
20.0	160*	240
25.0	155	215*

* marked values are inter- or extrapolated

The flammability range of TFE in air at ambient conditions is 12– 59 % v/v [4] and this range widens with increasing pressure and temperature.

The Minimum Ignition Energy (MIE) of TFE-air mixtures is reported to be around 4 mJ [4]. Further values of ignition energies of TFE-air mixtures are provided in Table 9 (data from confidential reports shared by the PlasticsEurope TFE Safety Task Force member companies). The energy required to trigger the combustion reaction (Table 9) is therefore much lower than one required to initiate the decomposition reaction (Table 7). Due to lower ignition temperature and ignition energy, TFE-air mixtures are easier to ignite than pure TFE.

Table 9 Ignition energies of TFE-air mixtures at different initial pressures

Pressure (bar)	TFE composition in air (% v/v)	Ignition energy (mJ)
1	24 - 27	14 - 34
5	24	ca. 12

3. Further notes on stability, reactivity and incompatibilities

The C=C double bond is responsible for reactivity of TFE with a large range of materials. Violent reactions between TFE and other materials have led to fatalities [44]. The most common reactive agents are detailed here, based on information gathered in the literature [4], [30], [58] - [62]. To prevent any further incompatibility, reactive or stability issues it is advisable to check all process chemicals vs. reaction with TFE.

TFE is incompatible with polymerization catalysts (e.g. triboron/triborane pentafluoride), peroxides (e.g. chloroperoxytrifluoromethane, dioxygen difluoride) and other oxidisers (i.e. sulphur trioxide, oxygen difluoride, iodine pentafluoride, difluoromethylene dihypofluorite, permanganates, perchlorates, chlorates, and nitrates). Oxygen gas added to an uninhibited compound will produce a polymeric peroxide which is a powerful explosive that is sensitive to heat, impact or friction. TFE can also form peroxides upon contact with air. It has been reported that liquid TFE, collected in a liquid nitrogen-cooled trap open to air, formed a peroxidic polymer which exploded.

TFE experiences exothermic reactions with substances capable of breaking a double bond (e.g. chlorine, bromine and other halogen compounds). Additionally, it can react violently if in contact with aluminium, copper and their alloys. Contact with other metals (such as sodium, potassium) and organometallic compounds should be avoided. TFE is also incompatible with metal alkoxides.

Ammonia also reacts with TFE to form difluoroacetonitrile (CHF_2CN) and hydrogen fluoride (HF). The HF tends to further react with ammonia to form ammonium fluoride, whereas the difluoroacetonitrile will react with any water present to form difluoroacetamide (CHF_2CONH_2) or trimerises to form 2,4,6-tris(difluoromethyl)-1,3,5-triazine; the triazine is toxic.

4. Note on TFE in mixtures

In the production of fluoropolymer resins, TFE is often mixed with co-monomers, in order to achieve specific properties of the end product [17]. Typical co-monomers are hexafluoropropylene, perfluorinated vinyl ether, ethylene and vinylidene fluoride. Depending on the mixture, the explosive properties of TFE can be enhanced or reduced. This has enormous effect on the design of reactors and process equipment as well as their corresponding safety devices. When TFE is mixed with co-monomers, it is extremely important to acquire sufficient know-how on the hazardous behaviour of the mixture under process conditions via specific testing and/or literature search.

There is limited data available for TFE mixture flammability although a member company of the PlasticsEurope TFE Safety Task Force was able to share TFE flammability information at atmospheric temperature and pressure for TFE mixtures with the inert gas, HCFC-22; this is included in Figure 6. It should be noted that the data indicates that for any mixture of TFE and HCFC-22 with a TFE concentration less than 67 %v/v was not flammable in these tests.

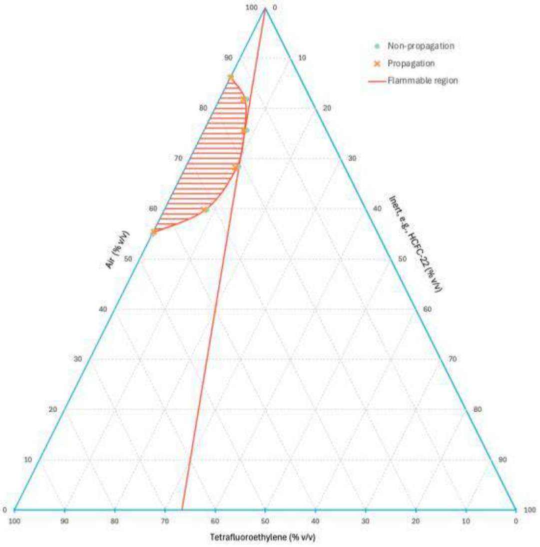


Figure 6 TFE-air-HCFC-22 flammability diagram

5. Ignition sources

Different energy sources can trigger the ignition of TFE and its explosive mixtures with air or co-monomers. Table 10 contains a list of the most common ignition sources; there may be other ignition sources which are not covered here.

Table 10 Ignition sources

Ignition source	Description
Heat from spontaneous polymerisation of TFE	TFE spontaneously polymerises at ambient conditions unless an inhibitor is added. The effect of the inhibitor is removed if sufficient energy is provided (for instance via external heat input or spark).
Heat from peroxide formation by contact of TFE with air or oxygen	Peroxides tend to initiate polymerisation hence the comments for the spontaneous polymerisation are valid for the spontaneous formation of peroxides. TFE Safety Task Force members have a maximum oxygen concentration of 10 ppm prior to the introduction of TFE into a pipe or vessel. However, for TFE of high purity, it is recommended that the oxygen content is significantly lower to avoid peroxide formation and unwanted polymerisation.
Heat from further exothermic reactions	This could be heat from chemical reaction of TFE with other substances such as chlorine [63] or sulphur dioxide [64] or from the contact of TFE with a reactive substrate or from reaction of TFE with finely divided metals.
External heat source	This might be heating input upon contact with a hot surface (e.g. as a result of welding or 'hot work') or the formation of hot spots due to improper heating. The laser beam of an optical measuring device could also provide enough energy for ignition.
Spark or electrostatic discharge	Ignition energies required to trigger decomposition and combustion reaction of TFE are presented in Table 7 and Table 9, respectively. Spark or electrostatic discharge can provide that energy.
Mechanical energy / Heat of friction	Fluid flowing through pipelines of rough materials or metal-to-metal contact can provide energy for the ignition [65].
Fluid energy (adiabatic compression)	Upon fast opening of valves separating plant sections with high-pressure difference, low pressure gas is compressed and therefore heated. If the gases involved are flammable or chemically unstable, the energy delivered can generate an ignition. For chemically unstable gases like TFE ignition can propagate back to connected equipment, since air or other oxidizers are not required to sustain the reaction. Furthermore, ignition induced by adiabatic compression can be an issue in compressors which must be carefully designed.
Fluid energy (sudden flow stop)	Another form of fluid energy that could provide an ignition could be the heat produced by suddenly stopping the fluid flow, due to the conversion of kinetic energy in thermal energy [65].
Ionising radiation	Some forms or radiation (*e.g.* gamma rays, X-rays) carry enough energy to liberate electrons from atoms or molecules, thereby ionizing them. This can then initiate polymerisation which generates heat that can trigger an ignition.
Propagation from elsewhere (domino effect)	Accidents in neighbouring equipment can provide the energy required for ignition (for instance heat from explosions or fires within a plant).

Among the listed ignition sources, the contact of TFE with hot surfaces/hot spots and the adiabatic compression are considered to be responsible for the majority of the severe accidents occurred in chemical plants within the last 25 years (see Figure 7, data from publications [5], [42] - [47] and confidential reports shared by the PlasticsEurope TFE Safety Task Force member companies).

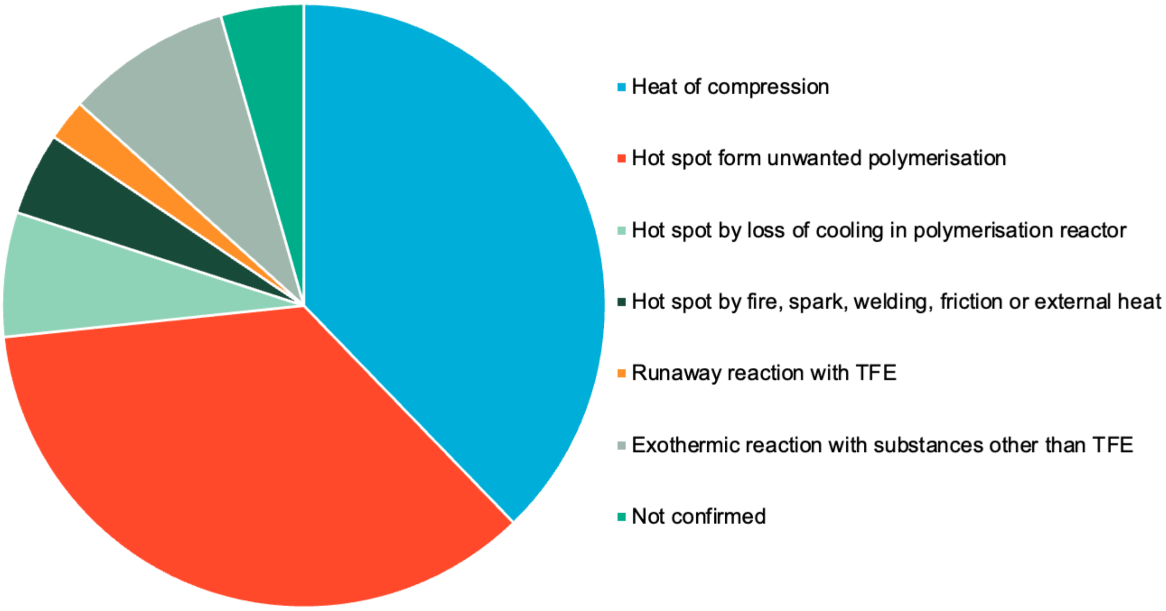


Figure 7 Distribution of ignition sources for accidents involving TFE (January 1999 – December 2023)

6. Explosion types (deflagration vs. detonation)

An explosion is a rapid event during which gases created from the reacting materials cause an increase in the local pressure or volume, usually with the generation of high temperatures. The overpressure which is produced can cause serious damage to structures, property and surrounding environments. Fragments generated during an explosion may travel long distances, with enough energy to cause secondary damage due to impact or penetration or to initiate secondary incidents in the surrounding.

Explosions are categorized as deflagrations or detonations, depending on their force and dynamics.

In a deflagration, the combustion or reaction wave propagates at a velocity less than the speed of sound. Only the expanding gases generate the overpressure, and the propagation of the explosion occurs due to the heat released by the reaction, or, in other words, unburnt gas ignites due to heating within the flame front. The overpressure in a deflagration is relatively low compared to the overpressure in a detonation. Still, deflagration can and does cause severe damage.

In a detonation, the combustion or reaction wave propagates at a velocity faster than the speed of sound. Here the flame front is coupled with a shock wave that triggers the propagation of the reaction by igniting unburnt gas. The resulting overpressure is much higher than in a deflagration and has a higher damage potential.

Under the common working conditions used in TFE manufacturing and processing plants, if pure TFE or TFE rich mixtures are ignited, the explosion will run in the form of a deflagration. In confined spaces, especially in longer pipelines, a deflagration can be accelerated and turn into a detonation. At the Deflagration-to-Detonation Transition (DDT) point the highest overpressures are generated. Should DDT overlap with the reflection of the reaction front (e.g. at a closed fitting/armature), the overpressure would be further enhanced. It is important to design plants so that a DDT is not possible, since most protective equipment and measures will work only in the deflagrative and not in the detonative range.

A comprehensive study on TFE decomposition in pipelines is reported in [66]. Pipes with internal diameters up to 25 mm were tested, in order to check if they could withstand stresses, which occur during the decomposition of TFE at initial pressures up to 23 bar. Under the analysed boundary conditions, TFE showed relatively long run-up distances to detonation (around 200 times the pipe internal diameter), which was the reason for high explosion pressures at the reflection of the reaction front and tail at the pipe end or at a closed fitting/armature there installed. This was valid also for pipe lengths of many times the run-up distance to detonation. In some tests for the simulation of many interference points a spiral wire was incorporated in the pipes: the distance to detonation of TFE could be halved by this arrangement.

The deformation at the pipe end during the decomposition of TFE with 22 bar initial pressure in pipes Ø 30 mm x 5 mm, material: steel (type St 35 GBK [67], [68]) for different pipe lengths is shown in Figure 8.

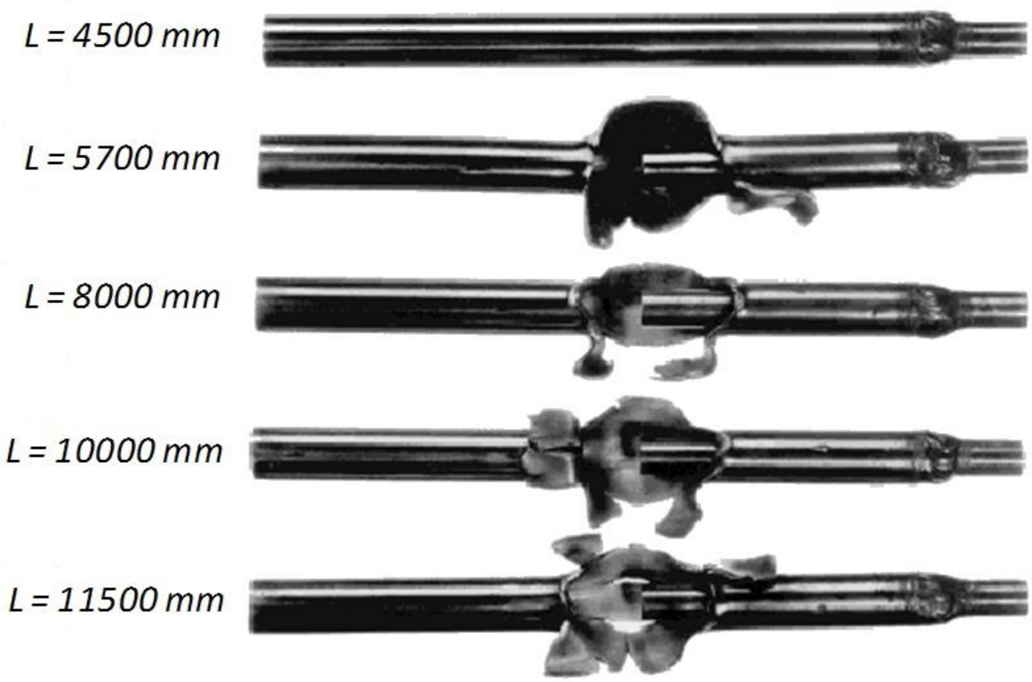


Figure 8 **Deformation of the pipe end during the decomposition of TFE with 22 bar initial pressure**

Source [66]

It is known that a minimum pipe diameter is required for a detonation to be sustained and therefore for a DDT to occur [69]. Some companies take advantage of this effect and use bundles of small diameter tubes within their pipeline system as flame arrestors. These can avoid the propagation of a TFE decomposition and therefore minimize damage. The higher the pressure and temperature the smaller the diameter required for quenching. Furthermore, in order for the quenching to be effective, a minimum length of the pipe with small diameter is required.

7. Adiabatic compression (heat of compression)

Many processes are not truly adiabatic due to the non-ideal nature of real-life examples. This is also the case for adiabatic compression where the theoretical compression temperatures are not reached due to gas mixing and heat losses. However, the actual heat of compression may still be enough to act as an unwanted ignition source in TFE industrial accidents [5]. The theoretical temperature rise for adiabatic compression depends primarily on the gas being compressed (composition and pressure) and the compressing pressure; the heat rise can be calculated using the following equation:

$$T_1 = T_0 \times (P_1/P_0)^{(\gamma-1)/\gamma} \qquad \text{Equation (5)}$$

Where:
T_0 is the initial temperature in K.
P_0 is the initial pressure.
γ is the ratio of specific heats of the gas being compressed.
P_1 is the final pressure.
T_1 is the final temperature in K.

Note: The pressure units are not important if they are absolute values and consistent.

The ratio of specific heats (γ) depends on the complexity of the gas being compressed, the fewer the atoms, the higher the value of γ [70]. Hence compressing helium gas (1 atom) or nitrogen (2 atoms per molecule) will both lead to a significantly higher temperature rises compared to compressing TFE (6 atoms per molecule). Table 11 contains some examples of the gases that may be present in a TFE plant, and the adiabatic temperature rises for two scenarios:

Condition A: Compressing a gas under vacuum (gas pressure 0.3 bar(a)) with 10 bar(a) TFE. Initial gas and TFE temperature 26.85 °C (300.00 K).

Condition B: Compressing a gas at elevated pressure (gas pressure 2.0 bar(a)) with 10 bar(a) TFE. Initial gas and TFE temperature 26.85 °C (300.00 K).

Table 11 Adiabatic temperature rises when gases are compressed under two scenarios

Gas	Ratio of specific heats (γ)	Theoretical adiabatic temperature reached; condition A (°C)	Theoretical adiabatic temperature reached; condition B (°C)
Helium	1.667	947	298
Argon	1.667	947	298
Air	1.401	545	203
Nitrogen	1.400	544	202
TFE	1.126	171	86

It is critical to understand the risks associated with adiabatic compression and the impact that the gas being compressed, and pressure conditions have on the potential temperature rise. The data in Table 11 is illustrates the dangers of compressing common gases and highlights the additional risks that compressing gases under vacuum also present. Although the temperature rise from compressing higher pressure gases is lower, the temperature rise may still present a hazard. The adiabatic temperatures should be compared to the MITD data for TFE of about 270 °C at 10 bar(a) (from Figure 5); with a downstream (compressed) pressure of 2 bar nitrogen, when compressed to 10 bar, the temperature rise should not be sufficient to initiate a TFE decomposition. However, a potential temperature rise to 200 °C would not be considered to leave enough of a safety margin in industrial facilities.

Heat of compression has been attributed to be the cause of many accidents that have occurred in chemical plants manufacturing or processing TFE. An example of a serious accident where the ignition source for the TFE was adiabatic compression is described below [5]:

"A 1999 explosion in the purification area of a fluorinated polymer manufacturing plant in the United States caused fatal injuries to three employees. Another employee was severely injured. The affected plant personnel were attempting to locate a suspected polymer plug in lines containing tetrafluoroethylene (TFE) monomer upstream of the polymerization plant. In an attempt to dislodge a possible plug in an elbow leading off a pressure vessel, one of the employees rapidly actuated a manually operated ball valve. High-pressure TFE upstream of the valve rushed into the downstream piping, which likely contained air at sub atmospheric pressure. Adiabatic compression against a blind flange created temperatures sufficient to ignite a TFE/air mixture. The initial deflagration provided ample energy for a self-sustaining decomposition reaction to propagate within the TFE line into the upstream pressure vessel. Liquid TFE had been collecting in the pressure vessel as the result of a deliberate increase in the flow of cooling brine associated with a separate process. This allowed the decomposition to continue, causing a rapid increase in pressure inside the vessel, sufficient for the bolts on the upper flange to fail. The four employees were exposed to burning TFE sprayed from the pressure vessel and were also injured by shrapnel created by the explosion."

Adiabatic compression of low pressure gas by high pressure TFE could occur, among others, during the fill-up or discharge processes of pipeline, reactors or other equipment, if no proper valve management, plant design and operational plan is considered. Adiabatic compression could also be an issue in vent lines/devices, if the design is incorrect. Due to the importance of the topic, this review includes a dedicated paragraph on experimental results from adiabatic compression tests involving TFE. It is hoped that this helps to identify conditions where adiabatic compression resulting in a significant temperature rise is expected to occur.

A laboratory scale investigation of the ignition of TFE induced by the adiabatic compression that can arise by activating a high speed valve (opening times under 50 ms) separating two portions of a pipeline with a high pressure difference was carried out [71]. In the tests performed, the high pressure zone contained TFE at pressures between 15 and 30 bar, reflecting practical conditions of interest in chemical plants. For the low pressure zone, experiments with air, nitrogen, and TFE were carried out. The pressure range in the low pressure zone was between 0.05 and 1 bar; this was representative of leakage of air into evacuated pipes or of remaining of purge or process gas upon incomplete evacuation. The pipe diameters analysed were 15 and 20 mm and the pipe lengths of the low pressure pipe, referred to as compression pipe, spaced between 180 and 1145 mm. Numerical simulations supported the experimental finding. The study reported following conclusions [71], [70]:

"With the compression pipes tested […] *ignitions were achieved if and only if the compression pipe was at least 540 mm long, TFE at 25 bar in the high pressure zone was present and the low pressure section contained air at 1 bar. Reproducible ignitions were achieved only in the longer compression pipe (diameter of 15 mm and length of 1020 mm), provided the air had an initial temperature of at least 105 °C. In one of the ignitions the decomposition propagated*

completely in the high pressure zone. Under the same or even harsher conditions, no ignitions were achieved if nitrogen instead air was present in the compression pipe, which suggests that combustion of TFE may act as a precursor for decomposition. A comparison between the compression temperatures recorded during the tests without ignition with the theoretically achievable values showed that potentially much higher temperature could be generated by the adiabatic compression. With help of numerical simulations, it could be observed that the theoretical temperatures are more likely to be achieved and maintained for a longer time (in a larger portion of the pipeline) in compression pipes with larger diameter and length. It was also shown that for the diameters tested, the heat losses to the tube walls and surroundings are not negligible. For a complete safety assessment of the TFE decomposition initiated by adiabatic compression, larger and longer pipes should be tested in further experiments."

In order to extrapolate the data collected in the laboratories [71] to a larger scale, a facility was designed and constructed on the BAM Test Ground Technical Safety (TTS). Results of this investigation on industry scale are reported in [72]. By actuation of a high-speed ball valve (opening times between 100 and 120 ms), low pressure air in a compression pipe (diameter = 28 mm) was rapidly compressed by incoming TFE at high pressure from a donor reservoir. The donor reservoir was initially a 65-L-vessel and was later substituted for a donor pipe for practical reasons. The compression pipe lengths tested ranged between 1 m and 7 m. During the tests it was possible to achieve ignition for milder initial conditions (lower initial pressure in the donor reservoir as well as lower temperatures in the compression pipe) than in the laboratory experiments [71], which highlighted the suspected effect of the pipe diameter on the tendency to decomposition induced by adiabatic compression. Figure 9 shows a photo shot during the induced ignition in a test with TFE at 25 bar in the donor section and air at 1 bar in a 5-m-compression pipe (initial temperature ~35 °C) with the setup with the 65-L-vessel as TFE donor. The decomposition initiated at the compression pipe end propagated back toward the donor zone and partially damaged the facility [Figure 9, #1]. Fortunately, the burst disc equipped on the vessel activated [Figure 9, #2] releasing the pressure build-up and guaranteed the integrity of the donor reactor. Temperatures around 520 °C and pressures above 125 bar were recorded in the TFE donor vessel. Near the compression pipe end temperatures above 1000 °C were achieved.

Figure 9 **Picture taken during an ignition of TFE induced by adiabatic compression of air in a large-scale facility**

The main output of the study reported was the “hazard diagram” shown in Figure 10 [72]. The diagram was derived from tests with TFE compressing air in a 5-m-compression pipe, considering an initial temperature of 35 °C. The hazard diagram summarizes the experimental outputs in a donor pressure vs. receiving pressure graph.

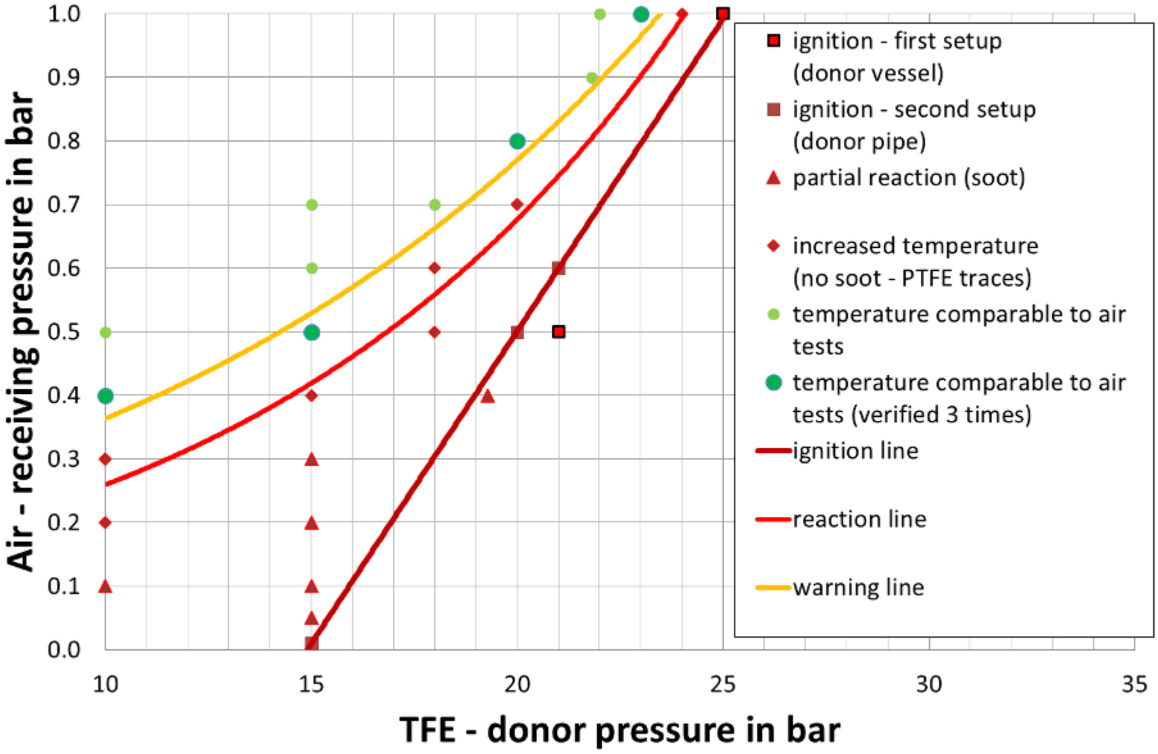


Figure 10 Hazard diagram for TFE compressing air in a 5-m-compression pipe, diameter = 28 mm, initial temperature 35 °C

The hazard diagram is described as [72]:

“With increasing donor pressure the critical receiving pressure for “ignition” rises. In the “hazard diagram” this tendency is visualized by the “ignition line”. In the range of high donor pressure the transition between “safe” and “ignition” is sharp. For decreasing donor pressure a transition range occurs, which is enclosed by “ignition line” and “reaction line”. The “reaction line” results from tests, in which the measured compression temperature was higher than in the equivalent air/air-system. […] *Locally limited reactions were also attended by peaks in the pressure time history. In tests within the transition range some undefined polymerization products and/or soot were found in the region of the end flange.”*

The hazard diagram in Figure 10 can be taken for a first approximation if hazardous conditions are possible for a specific pressure ratio within a plant or installation. However, as the plant geometry and conditions are going to vary from the test conditions, a precautionary approach should be taken as the results may differ. Any point above the ‘*warning line’* is expected, but not guaranteed to be safe. Nonetheless, the validity of the diagram is confirmed only for the investigated conditions, which means a 5-m-pipe as compression pipe, TFE as donor gas at pressure up to 25 bar, air as a receiving gas at pressure up to 1 bar and an initial system temperature up to 35 °C, with valve opening times around 120 ms, or more conservative conditions.

In the same industry scale study further substances of practical interest were tested as receiving gas, namely TFE and nitrogen [72]. Tests were performed at conditions which led to ignitions in the TFE/air system, but no noticeable reaction could be initiated. Furthermore, tests with TFE compressing air in a 0.1-m-compression pipe were performed, but no critical compression temperatures were achieved, confirming that a minimum length of the compression pipe is needed to observe and ignition.

Finally, the industrial scale study also reports following conclusions of practical interest [72]:

"It could be seen that a self-propagating decomposition reaction can cause massive damages to pipes and instrumentations especially when it transits into a detonation. A venting of a pipe system in a case of decomposition is only effective if the burst disc is in line with the propagating reaction. A venting perpendicular to the flow direction of the pipe can even lead to an acceleration of the decomposition reaction and is therefore ineffective. Besides the self-propagating reaction, it could be observed that even reactions within the transition range might be hazardous, too. [...] *High temperature and pressure strains might lead to damages of gaskets or make shut-off devices ineffective. Additionally, the inside system can be contaminated by soot which might lead to impurities of further products or can even act as a promoter of unwanted reactions as well."*

Figure 11 includes data on four recent industrial accidents (marked with squares (■)) involving TFE where the ignition source has been attributed to adiabatic compression are compared with reaction and ignition lines from the hazard diagram (Figure 10). Information on the accidents has been provided by the PlasticsEurope TFE Safety Task Force member companies. It is important to note that the geometries of the test conditions used to prepare the hazard diagram (Figure 10) are not the same as those for all the reported accidents although in some cases, there are similarities. For instance, the industrial accident #1 involved pipes of larger diameters than the ones tested [72]. Accident #4 is operating in the same pressure conditions but with larger diameter pipes. Larger pipes are likely to result in less heat loss resulting in a higher compression temperature rise and are therefore should be viewed as 'less safe' although with sufficient diameter, the reduction in the pressure rate rise may reduce the temperature rise. Table 12 explicitly highlights which parameters and conditions are comparable and which not.

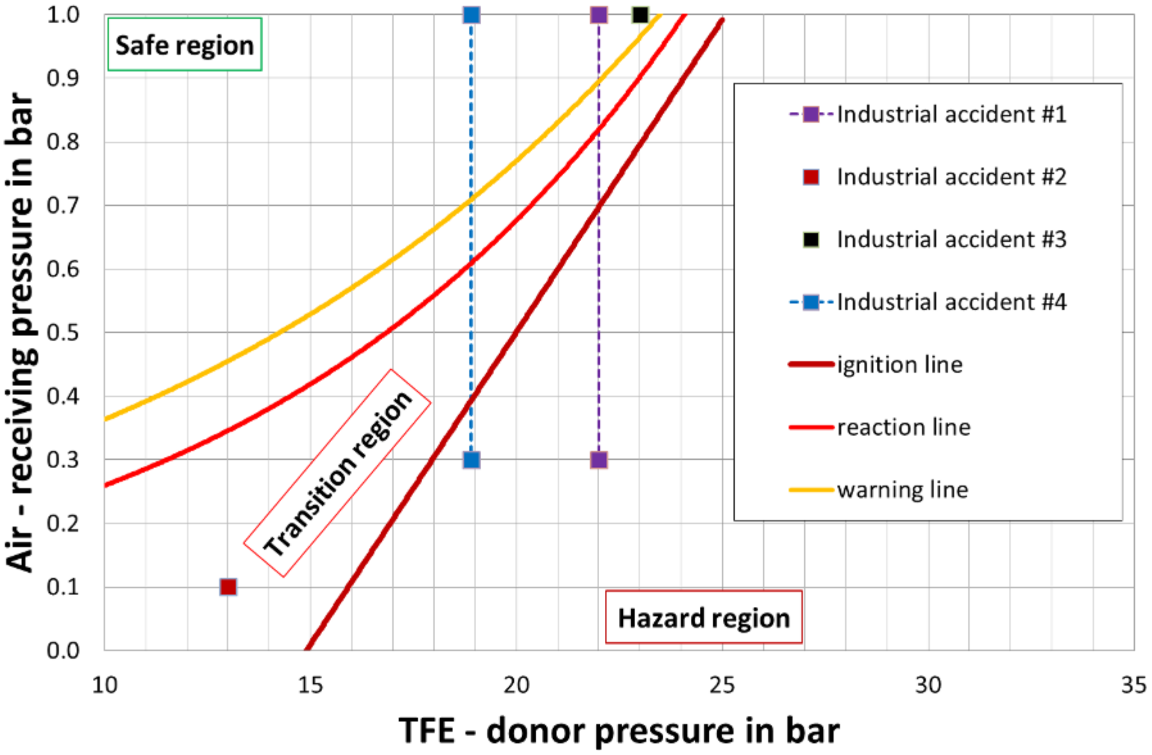


Figure 11 Comparison of industrial adiabatic compression accidents with the hazard diagram

Table 12 Information on adiabatic compression accidents in the chemical industry

Equipment parameters and initial conditions								
		Receiving pipe					***TFE Donor***	
Accident ID	**Compression Ratio**	**Gas**	**Diameter (cm)**	**Length (m)**	**Pressure (bar)**	**Temperature (K)**	**Pressure (bar)**	**Temperature (K)**
#1	🟩 20	🟩 Air	🟥 3.81	🟥 1	🟩 ≤ 1	🟩 300	🟩 20	🟩 < 300
#2	🟩 130	🟩 Air or nitrogen	🟩 1.9	🟩 4	🟩 0.1	🟩 274	🟩 13	-
#3	🟩 23	🟩 1 bar nitrogen and 0.2 bar air likely	🟩 2.5	🟩 5	🟩 1.0	🟩 293	🟩 23	🟩 293
#4	🟩 63	🟩 Air or nitrogen	🟥 5	🟥 ~1	🟩 0.3-1	🟥 343	🟩 19	🟥 343
Legend	🟩	Comparable with hazard diagram		🟥		Not comparable with hazard diagram		

Notes		
Accident ID	**Notes on TFE Donor**	**Further notes**
#1	Donor pipe with a length larger than 10 m.	Accident in a feed line. Valve type: plug and explosion-resistant valves. Valve opening times under 4 s. No elements of turbulence in the region where adiabatic compression occurred. Accident occurred during maintenance work.
#2	TFE header with a length larger than 30 m and a diameter of 2".	Accident in a feed line. Valve type: ball valve. Valve opening times unknown. Unknown if elements of turbulence were present.
#3	Donor pipe with 2.5 cm diameter with a length of 300 m for a total volume of 100 L.	Accident in a feed line. Valve type: ball valve (1"). Valve opening times > 1 s. No elements of turbulence in the region where adiabatic compression occurred.
#4	Reactor with a volume of 300 L (partially full of latex).	Accident in a vent line. Valve type: ball valve (2"). Valve opening times > 1 s. No elements of turbulence in the region where adiabatic compression occurred.

The data points for industrial accidents #2 and #3 are directly comparable to the experimental testing done and would be expected to lay in the hazard or transition region, i.e. under the ignition, or reaction or at worst warning line. This is the case for the industrial accident #2, but not for the industrial accident #3. This can be explained by some uncertainties in scaling-down industrial conditions, especially in terms of the impact some piping internals might have on the fluid dynamics (strainers, elbows, instrumentation, valves, etc.), which are commonly installed in TFE feed lines. It is expected that these add some turbulence to the system, but their impact has not been fully investigated although some observations from these more complex arrangements are included in this section.

For industrial accidents #1 and #4 there is uncertainty on the pressure conditions at ignition hence these are displayed as lines between the possible maximum and minimum receiving pressures. Furthermore, the pipe diameters are bigger than those used for the testing, so the data are not directly comparable to the testing. These factors mean that we cannot be certain whether the condition for accidents #2 and #3 were in the hazard, transition or safe region.

Although the hazard diagrams such as those shown in Figure 10 and Figure 11 that plot donor and receiving pressures are useful for guidance, it is important to understand that these diagrams only relate to the conditions tested. For the data presented in both Figures, the compressed pipe had a length of 5 m, inner diameter of 28 mm and was at 35 °C. The gas pressures, the gas being compressed, valve opening speed, the presence of restrictions such as orifices, strainers, instruments, changes in pipe diameter, bends and connecting pipework and equipment etc. must also be considered. Restrictions have the possibility of becoming a location where gas compression occurs, i.e., could mimic an end-flange, or could reduce gas flow (although there is still likely to be a temperature rise at the restriction) and enhance mixing that may reduce temperature rise further downstream [73]. The presence of pipe spurs also present additional locations where adiabatic compression could be a concern. It can be difficult to remove air or nitrogen from spurs, particularly for instrumentation on longer pipes.

Although non-adiabatic, it has already been demonstrated that the heat of compression can be sufficient to initiate TFE decompositions in both experimental work [71] and industrial accidents [5]. The identity of the compressing substance is not significant regarding the temperature rise (but may have an impact for other reasons such as mixing and the consequence of the temperature rise); it is the gas that is being compressed and the pressures of compressing (donor) and compressed (receiving) gas that are important. A series of air-air compression tests were conducted using the 2.5-inch internal diameter test pipe over a range of receiving and donor pipe pressures that are representative of typical operating conditions in TFE manufacturing facilities; the results are presented in Figure 12 [74]; the typical valve opening time for the 2.5-inch valve was 400 – 500 ms. As with the hazard diagrams, these results are only valid for the geometry/equipment tested but may be useful as guidance.

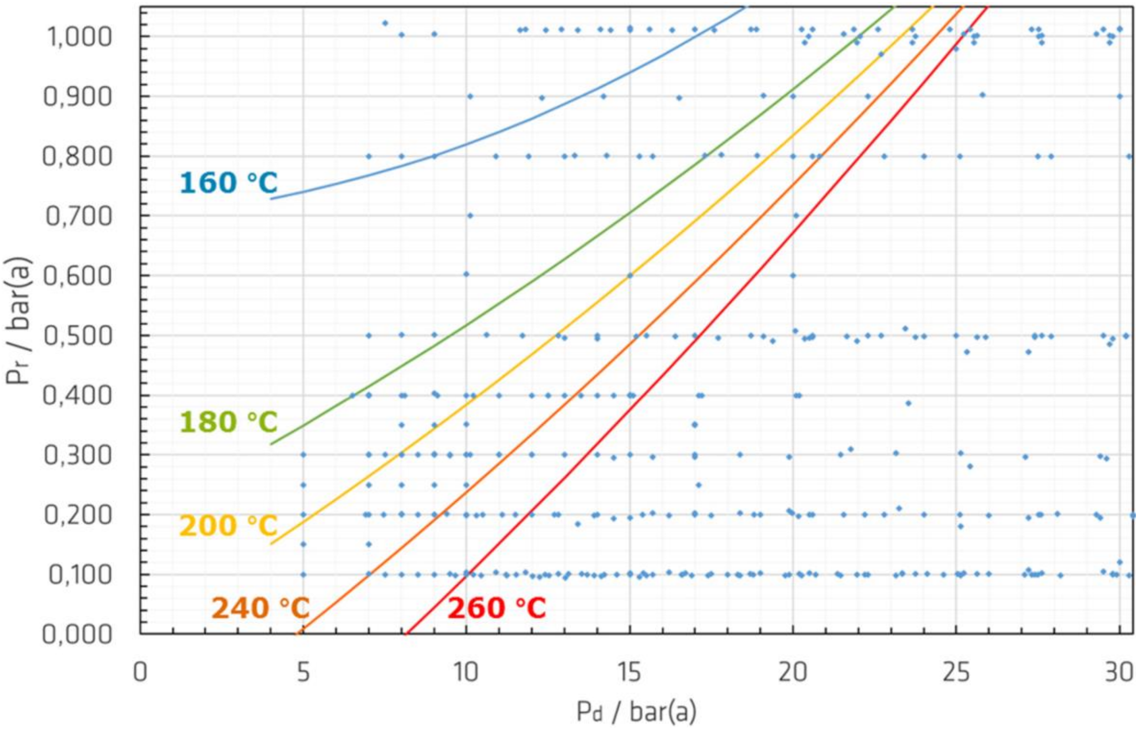


Figure 12 Air-air compression isotherms diagram for an internal pipe diameter of 2.5-inches
Each single compression test is represented by a small blue dot.

The speed of opening for the quarter turn ball valve between the high-pressure donor and low-pressure receiving pipe was also investigated using the 2.5-inch internal diameter pipe [74]. These experiments demonstrated that the gas flow rate through the ball valve opening is not proportional with the turn angle. The gas flow did not start until the valve was partly turned (around 10° turn from closed). Furthermore, due to the limited volumes of the pipes in these experiments, the gas in both the donor and receiving pipes reached a pressure equilibrium long before the valve was fully open.

Although the valve opening speeds used for the data shown in Figure 13 and Figure 14 are much slower than those used for the air-air compression isotherm diagram where the valve opening time were typically 0.4 – 0.5 s (Figure 12), the measured compression temperatures of 384 °C and 299 °C were still reached.

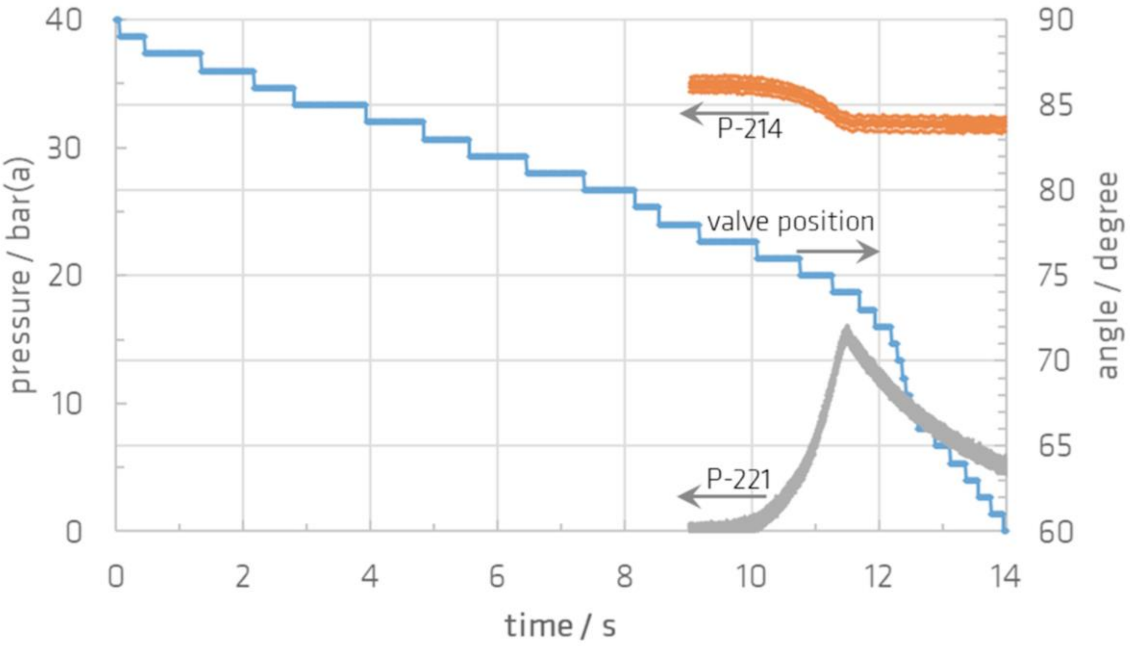


Figure 13 Pressure and ball vale angle versus time plot
Initial donor pipe pressure (P-214) = 35.1 bar; initial receiving pipe pressure (P-221) = 1.02 bar, closed valve angle = 90 °, opened valve angle = 0 °, valve turn speed = 25.8 °s^{-1}.

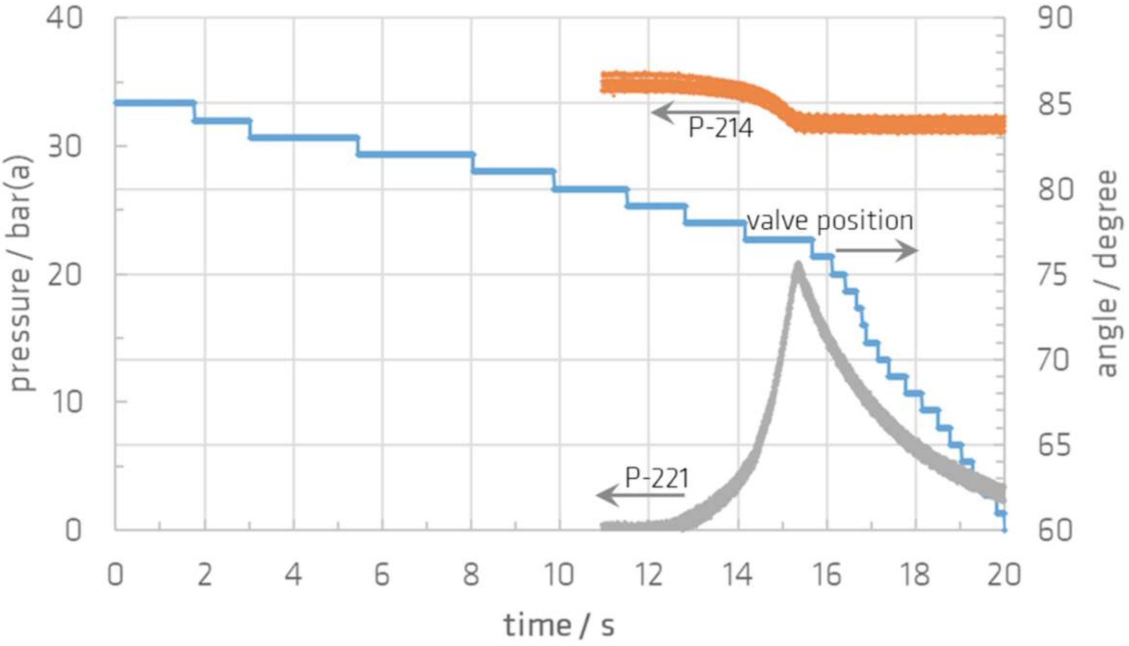


Figure 14 Pressure and ball vale angle versus time plot
Initial donor pipe pressure (P-214) = 35.1 bar, initial receiving pipe pressure (P-221) = 0.101 bar, closed valve angle = 90 °, opened valve angle = 0 °, valve turn speed = 0.8 °s^{-1}.

This is an important result that should be considered for ball valves and similar valves that have a potential for rapid opening in situations where heat of compression may be a risk. However, these situations should be avoided, if possible, by reducing donor gas pressure, increasing receiving pipe pressure and avoiding pressures below 1 bar, consideration of receiving pipe gas, valve type and pipe diameter etc.

8. Gas vs. liquid phase decomposition

TFE is typically manufactured and processed as gas. For some applications, like intermediate storage or transport within a plant, TFE might be liquefied by compression and/or cooling. Handling of liquid TFE requires special attention, due to the related hazards and significantly increased TFE inventory compared to gas. For this reason, some companies categorically avoid the use of liquid TFE or the pumping of liquid TFE. Other companies choose to handle liquid TFE in mixtures with inerting substances. Typically, liquid TFE is mixed with carbon dioxide (CO_2) or hydrochloric acid (HCl). In the second case, an azeotropic mixture is formed. Liquid mixtures of TFE with CO_2 or HCl might still be flammable, but the risk of explosions related to the handling of pure TFE is highly reduced/avoided. It has to be noted that HCl is a toxic compound (see Table 5) and necessary precautions must be taken.

The greater hazards of having liquid TFE is shown by the effects of an explosion in case an undesired event triggers the decomposition reaction. In fact, the overpressure generated if liquid TFE decomposes will be much higher than for gaseous TFE, due to the higher mass and potential energy involved. Therefore, equipment is much more likely to rupture. Failure of equipment would let liquid TFE to expand with possible release of toxic substances and formation of a fireball and ejection of fragments. This phenomenon is known as Boiling Liquid Expanding Vapour Explosion (BLEVE). The authors of this report do not know of any BLEVE accidents involving TFE, but there have been many fatalities caused by BLEVEs of other liquefied gases [75], [76]. Figure 15 shows pictures of fireballs generated by BLEVEs involving flammable gases.

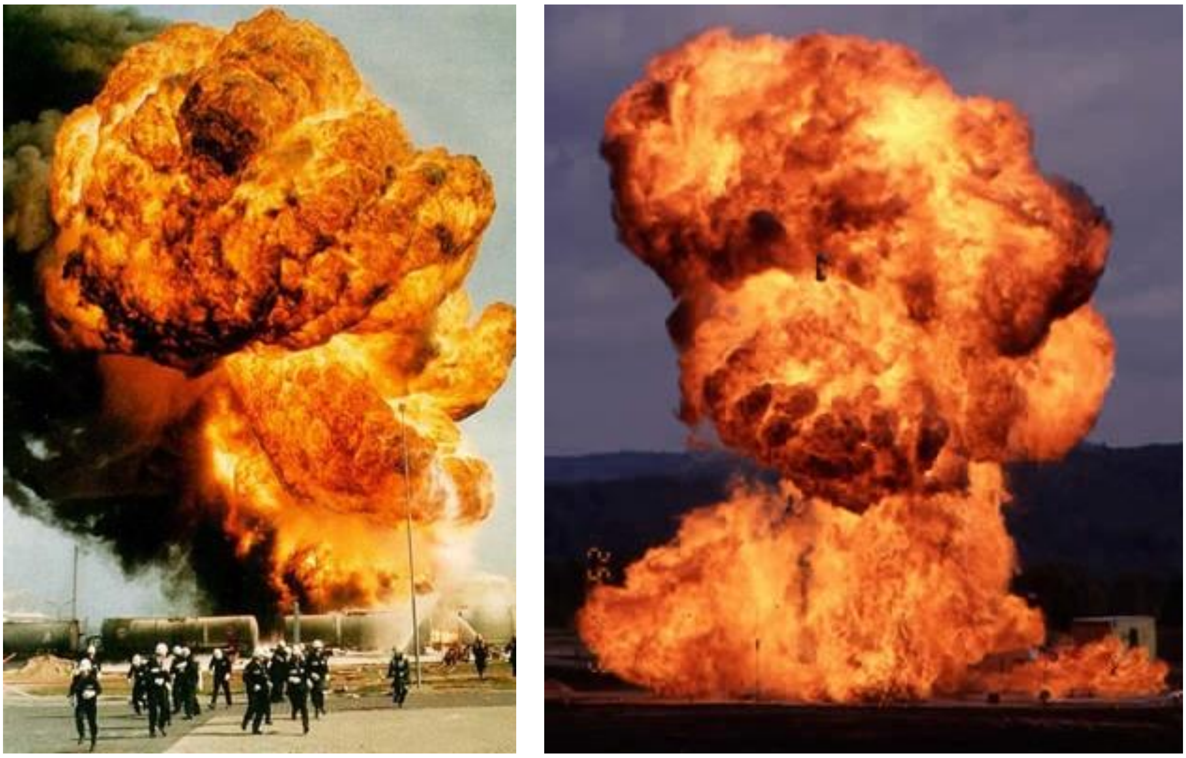


Image courtesy of Rudy Pospisil

Image courtesy of Dr. A.M. Birk,
Queen's University Canada

Figure 15 Fireballs formed as a consequence of BLEVEs
(Sources, left: [77], right [78])

9. Risks and hazards

Table 13 presents an overview of risks and hazards which could lead to fire and explosion in chemical plant while handling TFE. Note that the list presented might not include plant specific issues, which must be accounted for.

Table 13 Risks and hazards while handling TFE in chemical plants

Equipment / Process	Hazard(s)	Note
Storage (gaseous)	• Hot surface • Hot spot	Impinging fire, internal or external heat source, hot spots, lack of cooling could lead to decomposition and to explosion of containers.
Storage (liquid)	• Hot surface • Hot spot • BLEVE	Impinging fire, internal or external heat source, hot spots, lack of cooling could lead to decomposition and to explosion of containers. Upon rupture expanding overheated TFE could lead to BLEVE with potential formation of a fireball.
Feed lines, vent lines, pipe systems and headers	• Adiabatic compression • Detonation	Fast opening of valves in pipelines containing TFE toward low pressure area could cause ignition by adiabatic compression of low-pressure gas. Poor conditioning or procedures (e.g. air residuals, pipe working under vacuum) might enhance occurrence of ignition via adiabatic compression. Back flow of the decomposition front could turn the initial deflagration into detonation. Internals might enhance the possibility of detonation.
Distillation columns	• Hot surface • Hot spot	Temperature control failure as well as flame impingement could lead to decomposition and to explosion. Uncooled polymerisation leading to a local hot spot which acts as an ignition source for a TFE decomposition. Poor oxygen management is a common cause for polymer build-up. TFE Safety Task Force members have a maximum oxygen concentration of 10 ppm prior to the introduction of TFE into a pipe or vessel.
Polymerisation vessels	• Hot surface • Hot spot • Agitator rubbing • Excess initiator	Temperature control failure as well as flame impingement could lead to decomposition and to explosion of the vessel. Formation of hot spots (e.g. polymer build-up initiated by poor oxygen management) within the vessel is possible. Agitator might generate sparks (metal to metal rubbing or friction). Incorrect recipes can lead to run away reactions.
Compressors	• Adiabatic compression • Hot surface • Hot spot	Poor design and operation, lack or failure of cooling could lead to ignition by adiabatic compression, hot spot formation or local heating.
Pumps	• Hot surface • Hot spot	Poor design, lack or failure of cooling could lead to ignition on a hot surface or hot spot formation.
Process involving fluid flow	• Ignition by static electricity	Static electricity can ignite flowing TFE/TFE mixtures as gas, liquid or mist of particles, if proper grounding is missing.

Table 13 (continued)

Equipment / Process	Hazard(s)	Note
Electrical equipment	• Hot surface	If equipment of the wrong class is chosen, excessive heating can cause ignition.
Maintenance	• Adiabatic compression • Hot surface • Hot spot • Gas leak	Unusual operations and conditions can present significant risk as illustrated by major incidents occurring during maintenance activities [5] including start-up [47]. Operator awareness of abnormal conditions is important so inadvertent action leading to hazardous conditions can be avoided.

Chapter III – Handling hazards and precautions

1. Training and general organizational protective measures

Only trained personnel should be allowed to handle TFE.

Training programs should be annually repeated and should cover all aspects of TFE handling, with particular focus on its dangerous properties. Safety Data Sheet (SDS) and other specific documentation must be provided to workers. The number of employees who work directly with TFE should be kept as low as possible. An operational area should only be accessed by qualified and authorised employees. Concentration of TFE in air must be minimized. Procedures for the handling, use, and storage of cylinders should be in compliance with all relevant regulations.

2. Protective measures

2.1. Storage and transport by road

As mentioned, TFE can potentially explode at pressures above 2.7 bar(viii) due to spontaneous polymerisation; the likelihood of an explosion is reduced when an inhibitor is added. TFE is normally stored in tanks or gas cylinders in a stabilised form and must be transported stabilised. The ADR agreement [7], classifies the TFE for transport as Liquified, Flammable Gas under UN 1081 TETRAFLUOROETHYLENE, STABILIZED. ADR specifies how that stabilisations is achieved, special provision 386 refers to stabilisation by temperature control or/and chemical stabilisation. The level of stabilisation shall be sufficient to prevent dangerous polymerisation at a bulk mean temperature of 50 °C. Most commonly, an inhibitor such as α-pinene is added although at around atmospheric pressure, the low pressure itself could be considered as stabilising the TFE as a decomposition should not occur below a pressure of 2.7 bar. When transporting TFE under the ADR entry UN 1081, there are also other transport compliance requirements that must be followed. Further information is included in Appendix E. Advice from a qualified Dangerous Goods Safety Advisor shall be sought. No exemption applies whatever the quantity of TFE is transported.

The effectiveness of the inhibitor is removed by heat hence it is recommended to keep the storage area of gas cylinders below 25 °C and out of direct sunlight. In general, TFE cylinders should not be exposed to temperatures above 50 °C [4].

ADR agreement [7] instructs that TFE in pressurised gas cylinders should not exceed a pressure of 6 bar (5 barg) for transportation, but specific countries regulation might have different pressure limits. Generally, the pressure limit for transportation is applied also for storage purposes as well. Further details on the transportation classification of TFE are presented in Appendix E. Cylinders must be correctly labelled, secured against falling and protected from sunlight. Gas cylinders for TFE storage should not be kept in workspaces. Cylinder valves must be opened carefully and checked for leakages. Ingress of water and gas backflow into cylinders must be avoided. If moved, cylinder valves must be sealed via a valve plug and the protective cap must be used. For the filling or transfer of TFE within cylinders sealed equipment with venting should be provided.

(viii) If not further specified, bar will refer to absolute pressure.

TFE should not be stored with oxidizers, and/or other incompatible materials (see section 3 of Chapter II). Storage should be in cool, well-ventilated area (with exhaust at low spots to prevent accumulation of heavier than air TFE), protected against physical damage, from heat and other sources of ignition. Storage should be accessible by authorised persons only and kept away from food, drink and animal feed. Fire protection and spill control systems should be provided. Gas sensors should be employed to provide early warning of a potential formation of explosive mixtures in air and oxygen [19]. It is strongly advised to store TFE separately from all other flammable materials, and from combustible materials.

Cylinders for TFE should be marked in red for flammable materials on their shoulder (Figure 16): while within Europe gas cylinders colours are being standardised according to DIN EN 1089-3 [79] in the United States, colour-coding is not regulated by law.

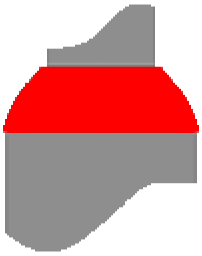


Figure 16 European colour-coding for flammable gases. Shoulder colour: red. Picture from [4]

For some applications, like intermediate storage within plants, TFE is stored as liquid. This requires special attention, for instance, a proper temperature control to avoid uncontrolled evaporation/boiling of liquid. Some companies create an azeotropic mixture of TFE with HCl to render TFE inert and safer to handle.

More information on storage regulations and procedures can be found in the GESTIS database [4].

TFE may also be stored as a mixture; if transported, these mixtures must be allocated a generic and/or N.O.S. (not otherwise specified) UN number under the ADR agreement [7] based on their composition and corresponding classification. These mixtures include:

a) TFE/HCl (hydrochloric acid) azeotropic mixture; this mixture achieves a non-explosive nature by dilution with a non-flammable gas. However, this mixture in addition has a toxicity hazard due to the HCl and still presents the normal risks of a compressed gas. Transportation of this mixture has been done with the following ‘not otherwise specified (N.O.S.)’ UN number and proper shipping name:
   - UN 3309 LIQUEFIED GAS, TOXIC, FLAMMABLE, CORROSIVE, N.O.S. (Hydrogen Chloride Anhydrous, Tetrafluoroethylene Azeotropic Mixture) [80].

b) TFE/CO_2 (carbon dioxide) vapour mixture has also been shown to achieve a non-explosive TFE mixture by dilution with an inert gas that may be transported [81]. The compressed, liquified gas mixture has the normal compressed gas hazards. The UN number and proper shipping name for this mixture is:
   - UN 3163 LIQUEFIED GAS, N.O.S. (Tetrafluoroethylene, Carbon Dioxide) [82].

c) TFE/HFP liquid/gas mixture [83], aiming to be non-explosive by dilution. The authors of this report are not aware of any company has yet attempted the transport this mixture.

A comparison of the CLP and ADR labelling for TFE and the three TFE mixtures is given in Table 14:

Table 14 TFE and TFE mixtures labelling summary

	TFE	TFE/HCl	TFE/CO_2	TFE/HFP
UN number	1081	3309	3163	Not assessed
Transport label				Not assessed
TFE concentration * /% w/w	100	55 - 60	30 - 50	-
TFE concentration * / mol %	100	-	-	35 - 65
CLP Signal word	Danger	Danger	Danger	Not assessed
CLP pictogram(s)				Not assessed

* TFE mixture concentrations are taken from references [80], [82] and [83] and are only indicative concentrations as actual concentrations are withheld as trade secrets.

When transported by road, TFE and/or TFE mixtures shall be compliant with the provisions of the ADR agreement [7]; guidance from Dangerous Goods Safety Advisors and TFE experts must be taken.

2.2. Handling

Workspaces should be properly labelled and well-ventilated. As TFE is heavier than air, bottom ventilation should be provided. Vented air cannot be redirected to working areas. If released to atmosphere, emission limits must be compliant with local regulations, meaning that some waste air will need to be treated. Gas sensors for the detection of flammable gases should be mounted at representative spots.

TFE should be always handled in closed equipment. Containers, equipment and pipelines should be properly labelled and protected from heat sources. Periodic checks for leakages should be performed. Prior to feeding of TFE, air residuals must be removed from equipment. Multiple purges with nitrogen are necessary prior to maintenance operations. This is also important for plant start up after maintenance.

Before the introduction of TFE into pipes (or systems with small volume with respect to the feed line), it is recommended that the pipe (or system) is filled with an inert gas, typically nitrogen just above atmospheric pressure and the TFE is added at a low rate, in order to reduce the possibility of ignition by adiabatic compression.

TFE supplies should be remotely isolated from a safe position.

See the GESTIS database [4] for more information on TFE handling.

2.3. Fire and explosion

TFE, also in its inhibited form, is chemically unstable at higher pressure and/or temperature. Mixtures of TFE in air are flammable at atmospheric conditions (see section 2 in Chapter II) and therefore working areas may be exposed to fire and explosion hazards. Firefighting equipment should be provided, and explosion protection techniques should be used as described in Table 15.

Table 15 Explosion protection techniques

Technique	Description
Primary explosion protection	Techniques devoted to avoiding the formation of explosive mixtures (reduction and control of the concentration of the flammable material, inerting, tightness, ventilation, etc.).
Secondary explosion protection	Techniques to control the occurrence of ignition sources, which are applied if no primary explosion protection is possible. These include the use of explosion proof electrical equipment and electrical grounding to avoid electrostatic discharge.
Tertiary (aka. constructional) explosion protection	Techniques devoted to the protection of equipment if ignition cannot be avoided. These include explosion resistant construction, explosion pressure venting and explosion suppression, among others.

Smoking should be prohibited in work areas. Equipment must be protected from undesired heating. Sparks should be avoided, and accordingly non-sparking tools must be used. Welding is not allowed in work areas. Maintenance of equipment and pipelines is possible only after careful purge and inerting. TFE is heavier than air so will collect in low areas and may travel long distances to ignition sources and flashback. It is therefore important to avoid TFE emissions in areas where ignition sources are present/nearby.

Appropriate electrical equipment should be used in areas where TFE is processed and might leak to the atmosphere. TFE has the electrical classification of IIA T3 with respect to ATEX (or its UK implementation DSEAR) [4]. IIA refers to the gas group classification and T3 to the temperature classification. Some companies use stricter temperature classification when it is considered not only the presence of pure TFE but also the possibility of its gas mixtures with more temperature sensitive co-monomers.

Specific arrangements, procedures and devices to improve safety in chemical plants manufacturing and processing TFE will be dealt in the following two paragraphs. A checklist with some guidelines for inspecting the safety status of TFE in a plant is reported in Appendix G.

2.4. Substantiated selection of process conditions

Careful selection of the process conditions helps to improve the safety in chemical and industrial plants. Table 16 includes hazards and potential control measures used in TFE process and manufacturing plants for different equipment that help in the avoidance of explosions; these control measures are in addition to risk assessed standard operating procedures, frequent staff training and risk assessments such as Hazard and Operability (HAZOP) studies.

Table 16 Equipment, hazard and proposed control measures to avoid TFE explosions

Equipment / Process	Hazard(s)	Preventive measure / Correct selection of process condition
Storage (gaseous)	• Hot surface • Hot spot	• Pressure and temperature control, so that ignition temperature (MITD/MIT) is not achievable • Measures to avoid hot spot formation (oxygen reduction, inspection, etc.)
Storage (liquid)	• Hot surface • Hot spot • BLEVE	• Pressure and temperature control, so that ignition temperature (MITD/MIT) is not achievable • Measures to avoid hot spot formation (oxygen reduction, inspection, etc.)
Feeding lines, vent lines, pipe systems and headers	• Adiabatic compression • Detonation	• Open valves slowly (> 10 s) • Keep pipeline lengths shorter, to avoid DDT • Limit pipe diameter • Provide fire protection, where required • Avoid internals, elbows, elements of turbulence • Proper design (e.g. interspace gas in vent equipment) • Proper operations (e.g. conditioning)
Distillation columns	• Hot surface • Hot spot	• Pressure and temperature control, so that ignition temperature (MITD/MIT) is not achievable • Proper oxygen management (including measurement) to avoid polymer build-up • Further measures to avoid hot spot formation (Oxygen reduction, inspection, addition of polymerisation inhibitor, etc.)
Polymerisation vessels	• Hot surface • Hot spot • Agitator rubbing • Excess initiator	• Pressure and temperature control, so that ignition temperature (MITD/MIT) is not achievable • Proper oxygen management (including measurement) to avoid polymer build-up • Further measures to avoid hot spot formation (Cleaning, inspection, etc.) • Specific agitator design • Recipe properly chosen / concentration control
Compressors	• Adiabatic compression • Hot surface • Hot spot	• Specific compressor design • TFE not exposed to oil • Proper cooling
Pumps	• Hot surface • Hot spot	• Specific pump design • Proper cooling
Processes involving fluid flow	• Ignition by static electricity	• Proper grounding

Table 16 (continued)

Equipment / Process	Hazard(s)	Preventive measure / Correct selection of process condition
Electrical equipment	• Hot surface	• Employ equipment with proper electrical class
Maintenance	• Adiabatic compression • Hot surface • Hot spot • Gas leak	In addition to the details included in this table for the equipment/process, the following should also be considered: • Maintenance procedures including control of work • Oxygen analysis • Gas detection

2.5. Examples of explosion protection procedures and devices

Examples of explosion protection procedures and devices used in TFE manufacturing and processing plants are reported in Table 17 and Table 18, respectively.

Table 17 Examples of explosion protection procedures

Safety procedure	Details	Application/Equipment
TFE combustion inerting at low pressure	Mixtures of TFE and an inert gas, where TFE concentration is less than 67 %, will not generate explosive mixtures, if released to atmosphere(ix). This is valid for ambient temperature, but not for elevated temperatures (> 60 °C).	• Storage • Transport
TFE decomposition inerting at high pressure	TFE is mixed with materials with inerting properties (like R22, HFP or HCl). At 20 bar, 50 % of inert gas is required to inert decomposition.	• Storage • Transport • Polymerisation vessels
Pressure and temperature limitation	Operating conditions are controlled and kept under conditions to lead to MIT or MITD.	• Polymerisation vessels • Distillation columns • Compressors / Pumps
Pipe design	Avoid internals and take other procedures to avoid DDT (limit pipe length and/or diameter), avoid elbows, internals and other elements of turbulence.	• Pipelines
Valve management	Use of multiple valves in a line should be avoided. If not possible, valve opening sequence is extremely important. Automatic devices are recommended but for some applications, manual valves will be required.	• Pipelines

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(ix) Data provided by a member company of the TFE Safety Task Force from historical experimental testing (see Figure 6).

Table 17 (continued)

Safety procedure	Details	Application/Equipment
Valve opening	Avoid quick opening valve. It is suggested to open valves with opening times typically longer than 10 s.	• All valves in (feed and discharge) lines where adiabatic compression is an issue
Select appropriate electrical equipment	If explosive atmosphere could be present, select ignition free equipment. Follow area classification procedures; see [84].	• Areas with explosive atmosphere • Vent or discharge areas
Explosion venting	Protect by releasing part of the overpressure from equipment where runaway reaction might occur. Vent lines should be designed to avoid risk of adiabatic compression and DDT (short, straight vent lines are suggested).	• Polymerisation vessels • Distillation columns • Compressors /Pumps
Barricades	Excluding people/equipment from areas where there is a sufficiently high likelihood of runaway reaction to avoid injury/death and/or equipment damage.	• Polymerisation vessels • Distillation columns
Leak detection	Periodic leak test to protect air inlet into process and to avoid loss of TFE or process mixture.	• Equipment • Pipelines
Multiple evacuation and pressurization	Provided a comprehensive leak testing has been completed, multiple evacuation and pressurization cycles with nitrogen or another inert gas are required before process gas (TFE or TFE based mixtures) is injected in a plant section. This is especially important for plant start up after maintenance (avoid air or oxygen residuals).	• Equipment • Pipelines
Fill-up/Feed procedures	While injecting, a positive pressure of an inert gas with low heating potential upon compression is suggested, as to reduce the pressure shock and the risk of ignition by adiabatic compression. Pressure shock is reduced by discharging toward large volumes.	• Pipelines • Small volume equipment compared to feed line
Ventilation	Proper ventilation must be provided (see section 1 of Chapter IV)	• General rule where TFE might leak

Table 17 (continued)

Safety procedure	Details	Application/Equipment
Operational design / Risk assessment	Operating, shutdown and maintenance procedures must be properly conceived, and risk assessed. Users must be trained to follow such procedures.	• General rule for whole plant

Table 18 Examples of explosion protection devices

Flame (aka. propagation) arrestors
A flame arrestor (also spelled arrester) is a device designed to extinguish a flame that travels through it. Depending on the flow regime, these may also be called deflagration or detonation arrestors. A deflagration arrestor is designed to absorb the heat from a flame front traveling at subsonic velocities, thus reducing the temperature of the burning gas or mixture below its ignition temperature. A detonation arrestor needs to not only extinguish a supersonic flame but attenuate any accompanying shockwave. Detonation arrestor elements tend to be physically more robust due to the much higher pressures involved and are larger than deflagration elements. In both cases the heat is absorbed through channels designed into an element. Flame arrestors can be either uni- or bidirectional; for uni-directional flame arrestors, using two back-to-back to protect from both directions may be appropriate. Furthermore, there are different types of channels, regular or irregular, and the size of the channels needed to stop the flame front can vary significantly depending on the gas or gas mixture and on the local operating conditions. In the case of high pressure TFE, commercial flame arrestors generally fail to avoid the propagation of the decomposition reaction. Therefore, companies have special designs for their propagation arrestors, whose functionality must be tested prior their use on the field. To allow for additional pressure release, propagation arrestors might be equipped with rupture discs. A recent TFE Safety Task Force project compared industry designed TFE flame arrestors with a commercially available flame arrestor [50]; further details are provided in section 2.6 of this Chapter. There are several key design elements that all three flame arrestors that were tested have in common: • The provision of an expansion volume. • The 90 ° inlet angle as this reduces load of flame arrestor element and also allows for the addition of a rupture disc. • A rupture disc. • The active part of the flame arrestor. • Position of the flame arrestor element. Furthermore, it is critical that no damage occurs to the flame arrestor during installation and maintenance and hence these activities should only be performed by trained personnel according to a risk assessed procedure. Flame arrestors should be inspected and replaced at appropriate intervals based on the risks of blockage and failure.

Table 18 (continued)

Rupture discs
Rupture discs are devices designed to protect vessels or other equipment from dangerous under- or overpressure conditions by the bursting of a one-time-use membrane that fails at a designed differential pressure. The membrane is usually made out of metal, but different types of materials (e.g. graphite or plastic) can be used for specific applications. The bursting pressure of a rupture disc is influenced by temperature. Rupture discs offer the advantage of an instant response time (within milliseconds), a high reliability and low cost. Rupture discs also require minimum maintenance and guarantee leak-tightness if properly mounted. Once the membrane has burst, it will not reseal and must be replaced after each use. Upon opening a rupture disc will allow venting until pressure equilibrium, which means the entire contents of the upstream process equipment will be released and this might be undesirable. In chemical plants manufacturing or processing TFE rupture discs are typically used to protect polymerisation vessels, distillation columns and other equipment from unexpected pressure rise due to uncontrolled exothermal reaction, for instance TFE decomposition. Rupture discs might provide successful venting of equipment upon TFE explosion only if the course of the explosion is deflagrative. Detonation will not be effectively vented, since in that case the pressure increase rate is larger than the pressure release rate. As with flame arrestors, it is critical that no damage occurs during installation and maintenance and hence these activities should only be performed by trained personnel according to a risk assessed procedure. Rupture discs should be inspected and replaced at appropriate intervals based on the risks of blockage and failure.
Pressure relief valves
Pressure relief valves are spring-loaded devices used to protect vessels or equipment by releasing excess pressure, which can build up during a process upset, instrument or equipment failure, or exposure to external fire. When the system pressure rises due to one or a combination of more undesired events, the fluid force on the valve disc overcomes the opposing internal spring force and the valve opens. Once the pressure excess is released and the normal conditions have been restored, the valve recloses to prevent the further release of fluid. The set pressure of a relief valve is influenced by the operating temperature, as it is for the burst pressure of a rupture disc but is adjustable within a specific range. Special relief valves can also be used to protect equipment from vacuum pressures. Nonetheless, pressure relief valves have a higher cost and require a larger maintenance effort than rupture discs. In chemical plants manufacturing or processing TFE pressure relief valves can be used to protect polymerisation vessels, distillation columns and other equipment from unexpected pressure rise due to uncontrolled exothermic reaction. For the venting of explosions, pressure relief valves are less suitable than rupture discs. Pressure relief valves that already experienced a venting where TFE was involved should be replaced.

Table 18 (continued)

Rupture discs and pressure relief valves combination

Sometimes, the use of systems which combine rupture discs and pressure relief valves might be suitable. Typically, a pressure relief valve is isolated from the process and from the discharge area via a rupture disc at both valve's inlet and outlet. The rupture disc at the inlet protects the relief valve from the process fluid, which might be an important issue when using corrosive substances. This way the lifetime of the relief valve is extended, and less expensive trim material can be used. The avoidance of the contact between process fluid and relief valve can also save resources, since the periods between major overhauls might be extended.

The combined systems allow the relief valve to be tested on the spot by one man with a portable pressure source. While working with flammable gases or chemically unstable gases like TFE, it is extremely important that the choice of the gas to fill the interspace between the relief valve and the rupture discs is suitable. Air must not be used because presence of oxygen. Furthermore, when air (or nitrogen) is compressed by TFE, it generates a large temperature rise (adiabatic compression) which is often sufficient to rapidly decompose the TFE. The choice should be for gases which experience a small temperature rise upon compression. In chemical plants manufacturing or processing TFE the combination of rupture discs with pressure relief valves can be used to protect polymerisation vessels, distillation columns and other equipment from unexpected pressure rise due to uncontrolled heat input and some exothermic reactions.

The combination of a rupture disc and a relief valve is not suitable for venting a TFE explosion. However, depending on its design this combination may be suitable to protect against equipment damage arising from thermal expansion of pure TFE or TFE mixtures. The risk associated with TFE explosions, if credible, must be mitigated using alternative measures. In chemical plants manufacturing or processing TFE the combination of rupture discs with pressure relief valves is typically used to protect polymerisation vessels, distillation columns and other equipment from unexpected pressure rise due to uncontrolled exothermal reaction (a relatively slow temperature rise).

Rupture discs in series with high pressure switch

Another possible combination is to employ two rupture discs in series with a high pressure switch installed in between: the first disc opens at a slightly lower pressure than the second one which is designed to open at the maximum relief pressure. If the first disc fails during normal working conditions (no overpressure), the second one will prevent unwanted gas leakage. The pressure switch will detect the presence of gas and a disc substitution can be planned. Choice of the type and pressure of interspace gas between the disc is extremely important. This equipment combination could be suitable for explosion venting of TFE decomposition in the deflagrative region. Detonations are unlikely to be effectively vented as they may occur in localized areas of the piping/equipment and the pressure rise is quicker than the rupture disc opening rate, so equipment damage or rupture remains likely.

Table 18 (continued)

Gas detectors
Gas detectors are sensors which reveal the presence of a specific gas within an atmosphere and are therefore very important for the identification of gas leaks within plants. For safety purposes, gas sensors can be used to detect combustible, flammable and toxic gases, and oxygen depletion. Gas detectors use different technologies, depending on the type of substance to be perceived. Typically, electrochemical and metal oxide semiconductor technologies detect toxic gases while catalytic and infrared sensors identify combustible gases. Gas sensors can be portable or stationary, depending on their application. Portable detectors are used by personnel to enter area suspected of contamination, while fixed systems are employed to monitor gas concentration over larger time and can be part of a more sophisticated control system for process shut down. Generally, gas detectors are equipped with an audible and/or visible alarm to alert personnel. Gas detectors are reliable devices, but require proper maintenance and particularly frequent calibration. Contaminated sensors may not register dangerous gas levels and excessive exposure can drop their lifetime. Some types of sensors might deteriorate with contact with fluorocarbons, which might be an important issue in TFE processing and manufacturing plants.

2.6. Flame arrestors

Two flame arrestors developed by industry, identified as 'block' and 'tube bundle' elements, and a third commercially available design with flame arrestor being based on a coil were tested for their effectiveness to extinguish TFE decompositions that were initiated with 100 J ignitors in industrial scale pipework. Basic schematics for the three flame arrestor designs are shown in Figure 17. Full details of the tests are available [50].

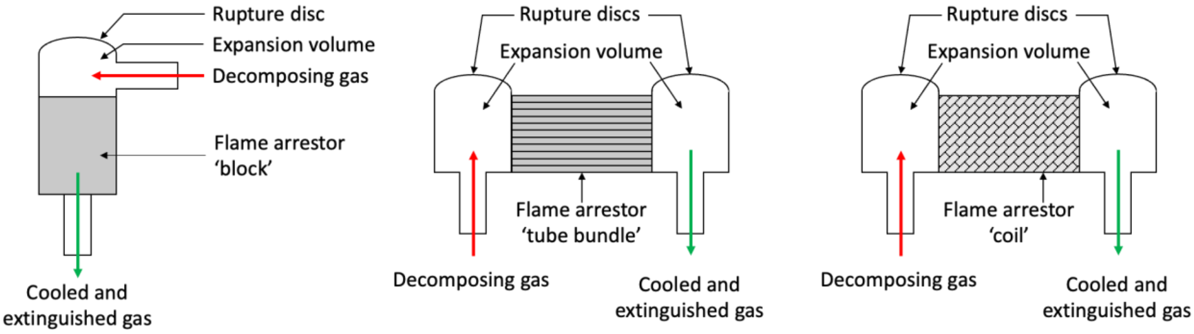


Figure 17 Basic flame arrestor design schematics with the differing flame arrestor element identified as block, tube bundle, and coil

All three designs of flame arrestor proved effective at extinguishing TFE decompositions under the conditions tested with a TFE pressure up to 21 bar. The 'block' flame arrestor provided the best flame extinguishing characteristics and was most efficient at absorbing the energy. It also has a relatively high flow resistance that reduces the likelihood of compression effects in adjacent pipes. However, TFE, particularly in the absence of a stabilizer, can undergo unintended polymerization in the flame arrestor element resulting reduced TFE flow under normal operating conditions and ultimately leads to blockages and subsequent maintenance requirements. The element may be damaged resulting in debris formation following a decomposition and the design is uni-directional which means that often two flame arrestors configured back-to-back are required to get bi-directional protection.

The ‘tube bundle’ flame arrestor also absorbs the decomposition energy efficiently and its medium flow resistance sufficiently protects adjacent pipes from excessive compression. Polymer can still block the single channels after extended periods of polymer growth with cleaning and tube replacement processes both possible during maintenance. In the event of a decomposition, no significant damage or debris is expected to the tube bundle up to the flame arrestor design pressure.

The commercially available ‘coil’ flame arrestor was also effective in the test conditions although the short length at low flow resistance might not sufficiently cool the TFE to avoid re-ignition, i.e., the gas temperature could remain above the MITD. Moreover, the low flow resistance may cause compression in the adjacent piping. Although polymer can block the single channels after some extended unwanted polymerization; cleaning or replacement of the coil should be straightforward. Extending the element coil length of the commercial flame arrestor should enable this flame arrestor to be used in TFE processing chemical plants although further testing of this improved design would be required.

Figure 18 contains screen shots from one of the videos taken during the flame arrestor testing (21.1 bar TFE, 27.5 bar rupture discs (RD); TFE amount 4.36 kg).

Figure 18 Flame arrestor testing (21.1 bar TFE)

a) prior to ignition, b) post ignition, RD before the flame arrestor has opened with a decomposition flame visible, c) large decomposition flame from the RD before the flame arrestor, unburnt TFE (grey gas cloud) released from the RD after the flame arrestor, d) the characteristic black soot from a decomposition reaction is being emitted from the RD prior to the flame arrestor and e) soot and unburnt TFE continue to be released from the RDs before and after the flame arrestor respectively.

3. Accident procedures

Information in the following paragraphs was taken from [4], [19] and [58].

3.1. Accidental release

Upon accidental release, gaseous TFE tends to accumulate on the floor because its density is higher than that of air. The TFE may be detected many 10s of meters away from the leak point. In case of a gas leak, stop the flow of gas if this can be done safely and ventilate the area. If the source of leak is a cylinder and the leak cannot be stopped, allow the TFE to be released to atmosphere. If the cylinder can be moved to a well-ventilated area (or outside) without ignition sources or any risks to the operator, this should be done. Otherwise allow the cylinder to vent ensuring that all personnel are kept well away from the cylinder.

If TFE is released as a liquid, it will persist for a short time, due to its low boiling point, high vapour pressure, and tendency to evaporate at a high rate. The same procedures as for gaseous TFE are suggested, i.e., the isolation of the source if possible and removal of personnel from the vicinity. Absorption of liquid TFE in vermiculite, dry sand, earth, or a similar material is not recommended; allow spillages to evaporate.

Upon accidental release, evacuate and restrict personnel. The affected area must be properly signposted. Once no further explosion hazards are given, if employees are required to clean up spills, they must be properly trained and equipped. Following completion of clean up, remove contaminated clothing and wash the skin thoroughly with soap and water.

Due to TFE explosive properties it is extremely important to remove all ignition sources and to avoid the use of sparkling tools during any clean-up procedures; clean-up should be delayed until TFE has been dispersed and the formation of a flammable atmosphere is no longer credible Furthermore, entering an area with high concentrations of TFE should be avoided and only be considered for the purpose of escalation prevention and only after risks have been assessed and suitable risk reduction measures have been implemented. These measures may include use of BA and avoidance of sources of ignition. It is important to ventilate the area of a leak to disperse the gas. Refer to ventilation and disposal information presented in Chapter V. High concentrations of TFE in air can cause a deficiency of oxygen with the risk of unconsciousness or death. Check that oxygen content is at least 19 % before entering a storage or spill area and that no flammable atmosphere is present. Respiratory equipment must be worn.

3.2. Firefighting

If there is a fire at a TFE manufacturing or processing plant, the risk of the explosive decomposition of TFE in supplying pipes or near-by equipment must be considered; most known TFE fires have led to decomposition. It is therefore advised to consider deluge systems for cooling of involved equipment/plant sections; this can reduce the likelihood of a TFE decomposition. Furthermore, the feed to any fire should be remotely isolated if possible and not approached. Due to the peculiar hazards of TFE, firefighting must be undertaken by trained personnel. The following recommendations for firefighting are given.

Suitable extinguishing media: dry chemical, foam, carbon dioxide (CO_2), fine water spray.

Firefighting measures: do not extinguish the fire unless the flow of gas can be stopped and any remaining gas is out of the line. Specially trained personnel may use fog lines to cool exposures and let the fire burn itself out. From a secure, explosion-proof location, use water spray to cool exposed containers. If cooling streams are ineffective (venting sound increases in volume and pitch, tank discolours, or shows any signs of deforming), withdraw immediately to a secure position. If cylinders are exposed to excessive heat from fire or flame contact, withdraw immediately to a secure location. If a fire becomes uncontrollable or a container is exposed to direct flame, consider an evacuation of at least 800 meters. Use only explosion-proof equipment.

Specific hazards: Hazardous decomposition products are formed under fire conditions. Toxic gases produced in a fire include hydrogen fluoride and carbonyl fluoride and potentially PFiB. Exposure to decomposition products may be hazardous to health. In the event of fire and/or explosion do not breathe fumes. Under prolonged exposure to fire or intense heat the containers may rupture violently and rocket great distances. Gaseous TFE is heavier than air and will collect in low areas and may travel long distances to ignition sources and flashback. Stay upwind and keep out of low areas. Gaseous TFE in confined areas may explode when exposed to fire.

Special protective equipment for firefighters: in the event of fire, wear self-contained breathing apparatus. Use personal protective equipment.

Further information: extinguishing measures must be appropriate to local circumstances and the surrounding environment. Keep unnecessary people away, isolate the hazard area and deny entry. Contaminated fire extinguishing water from water spray cooling must be collected separately and must not be discharged into drains. Fire residues and contaminated fire extinguishing water must be disposed of in accordance with local regulations. If material or contaminated runoff enters waterways, notify downstream users of potentially contaminated waters and notify local health, fire officials and pollution control agencies.

Chapter IV – Occupational hygiene

1. Ventilation

Personnel should be instructed to avoid exposure to TFE and to avoid the accumulation of accidentally released TFE. Personnel in TFE manufacturing and processing plants should regularly check equipment (supply pipelines, polymerisation vessels etc.) for leakages. Local area exhaust ventilation should be applied wherever there is an incidence of point source emissions or dispersion of TFE in the workplace, for instance in storage areas. Appropriate exhaust ventilation should be selected dependent on the nature of the process involved and local conditions to ensure that released TFE is directed away from workers. Ventilation systems should always be designed or supplied by competent ventilation specialists. The fact that TFE gas is heavier than air and will tend to accumulate in lower areas must be considered.

2. Personal protective equipment

As mentioned in Chapter II, TFE is reported to cause eye irritation or damage and requires eye protection [19]. The use of spectacles with side protection and of tight-fitting safety goggles combined with a face protection is advised when working with compressed TFE and liquefied TFE [4]. Emergency showers and eyewash should be provided and easily accessible [19].

Wear suitable respiratory equipment with positive air supply where there is insufficient ventilation or where operational procedures demand it. Also wear suitable, impervious gloves and protective eyewear. While handling gas cylinders, protective boots should be worn [4].

More information on the respirator selection for TFE can be found in [19].

Anti-static Protective Clothing is Not Normally Required

It is accepted that ignition of TFE mists or vapor clouds can occur by static ignition charge from ungrounded personnel. A person can accumulate dangerous charges of up to about 20 kV maximum when relative humidity is low. The corresponding static electricity discharge from personnel is typically less than 15 mJ. This is sufficient energy to ignite most flammable vapours and gases including TFE/air mixtures.

However, where TFE is contained and an accidental release is not credible or extremely unlikely, the use of anti-static clothing, including conductive footwear is not usually required. In areas where accidental releases are credible, ignition sources should be controlled, this would include the avoidance of electrostatic discharges from personnel by use of suitable PPE.

3. Personal hygiene

Smoking must be prohibited at the workplace. It is important to instruct personnel not to carry or use tobacco products in work areas. Personnel are recommended to store their work clothing separately from their normal clothing. Contaminated clothing should be ventilated well away from ignition sources. Contaminated clothing should not be taken home at the end of shift but should remain at employee's place of work for professional cleaning. Personnel should be provided with adequate washing facilities and required to use these regularly.

While handling TFE personnel should follow general industrial hygiene practices [85] and avoid breathing vapours, mists or gas. Workers should also avoid contact with skin, eyes and clothing. They are advised not eat, drink or smoke in the work area. Personnel should wash hands before breaks and at the end of workday. Contaminated clothing should be washed before re-use.

4. First aid measures and medical surveillance recommendations

First aid measures for personnel who come into contact with TFE, and appropriate medical treatment recommendations are available in [19] and in SDS. These are reported in Table 19.

Table 19 First aid measures upon exposure to TFE and medical surveillance recommendations

First aid measures
On inhalation, remove patient from exposure, keep warm and at rest. Obtain medical attention as a precaution. On contact with skin, thaw affected areas with water and remove contaminated clothing. Caution: clothing may adhere to skin in the case of freeze burns. After contact with skin, wash immediately with plenty of warm water. If irritation or blistering occurs obtain medical attention. On contact with the eyes, immediately irrigate with eyewash solution or clean water, holding the eyelids apart, for at least 15 minutes. Obtain immediate medical attention. Ingestion is an unlikely route of exposure. Do not induce vomiting. Provided the patient is conscious, wash out mouth with water and give 200-300 mL (half a pint) of water to drink.
Medical surveillance recommendations
Provide symptomatic treatment and supportive therapy as indicated. Medical surveillance should focus on potential reduced kidney function and adverse changes to the haematopoietic system.

Chapter V – Environmental information

General note on this chapter: this information was extracted from on-line databases of the U.S. National Library of Medicine [58] and of the European Chemicals Agency (ECHA) [30].

1. Environmental fate

During the production of TFE or its further processing to fluoropolymers, occasional releases to the environment through different types of waste streams may occur. Due to its high vapour pressure and low solubility practically all TFE released into the environment will be found in the air. The amounts found in water, soil and sediment are negligible.

TFE released to the atmosphere will quickly react with photochemically-produced hydroxyl radicals (•OH), with an atmospheric lifetime of less than 2 days. Subsequent decomposition leads to carbonyl fluoride (COF_2) that is further hydrolysed in the presence of atmospheric water to form hydrogen fluoride (HF) and carbon dioxide (CO_2); the HF is washed out by rain. Due to its fast decay, TFE does not contribute directly to the greenhouse effect so that its Global Warming Potential (GWP) is minimal and TFE is not covered by the “Montreal Protocol” [86].

TFE is expected to be mobile in soil because of its low sorption affinity (estimated soil organic carbon-water partition coefficient, log K_{oc} = 1.05). Volatilization from moist soil surfaces is expected to be an important fate process based upon an estimated Henry's Law constant of 0.63 $atm \cdot m^3/mol$. TFE may volatilize from dry soil surfaces based upon its vapour pressure.

As a highly fluorinated molecule, TFE is not expected to be readily biodegradable in aquatic media; however, since it is a gas of low solubility, TFE will readily partition to atmosphere and thus will not be persistent in the aquatic environment. If released into water, TFE is not expected to adsorb to suspended solids and sediment based upon the estimated K_{oc}. Volatilization from water surfaces is expected to be an important fate process based upon this compound's estimated Henry's Law constant. Volatilisation half-lives of about 1 hour for rivers and 95 hours for lakes were estimated. Furthermore, the half-life of TFE in marine water is not expected to exceed a few days with respect to volatilisation. Therefore, impact on aquatic life will be minimal.

Finally, TFE is not bioaccumulative, i.e., has a low tendency to accumulate in organisms, based on its estimated octanol-water partition coefficient (log K_{ow} = 1.21).

Consequently, TFE is not considered as a PBT (Persistent, Bioaccumulative and Toxic) nor as a vPvB (very Persistent, very Bioaccumulative) substance according to the REACH regulation [9] , [30].

2. Disposal methods

Depending on the concentrations involved, it may be necessary to contain and dispose of TFE as a hazardous waste. As for all chemicals, disposal of TFE should comply with local and national regulations. Provided those regulations are fulfilled, the following recommendations can be suggested.

Due to its flammable properties, TFE should not be discharged into areas where there is a risk of forming an explosive mixture with air. Furthermore, release to any place where TFE accumulation could be dangerous, for instance sewers (unless designed to prevent the build-up of explosive conditions) should be avoided. As mentioned, TFE can react explosively even without presence of air, or an oxidant and its discharge should be directed to areas free of possible ignition sources. Procedures for the handling of TFE waste streams from normal operations (2.1), for the discharge of TFE from accidental release from safety relief systems (2.2) and for the disposal of TFE-contaminated wastewater (2.3) are dealt in separate sections.

2.1. TFE waste handling

Waste gas discharged to atmosphere should be converted in a suitable burner (e.g. a thermal oxidizer) with flash back arrestor. Toxic and corrosive gases formed during production, processing or combustion of TFE should be scrubbed before discharge to atmosphere.

Gas cylinders containing TFE can be generally sent back to the supplier. In order to avoid air back flow, it is strongly suggested not to empty the cylinders up to pressure compensation. Empty containers should be clearly labelled.

2.2. Accidental TFE releases from relief systems

In the industrial production of fluoropolymers from TFE, it is common to discharge TFE from a waste stream or from safety relief into specifically designed “no entry areas”, where dilution is ensured, possibly at the highest point of the plant: this procedure avoids formation of explosive mixtures with air, prevents undesired decomposition reaction by control of ignition sources and allows for recycling of gas.

2.3. Wastewater contaminated with TFE

Wastewater contaminated with TFE, for instance from cleaning of protective clothing or equipment, or from contaminated sites, should be contained and analysed prior discharge to environment. Pre-treatment or discharge to a permitted wastewater treatment facility is acceptable only after review by the governing authority.

Appendix A – Addresses of PlasticsEurope TFE Safety Task Force Members'.

AGC CHEMICALS EUROPE, LIMITED
Hillhouse International
Fleetwood Road North
Thornton Cleveleys
Lancashire
FY5 4QD
United Kingdom
Tel: +44 (0) 1253 209600
Web: www.agcce.com
Email: Info@agcce.com

ARKEMA*
Rue d' Estienne d'Orves
92705 Colombes CEDEX
France
Tel: +33 (1) 49 00 80 80
Fax: +33 (1) 49 00 83 96
Web: www.arkema.com

Chemours INTERNATIONAL
2, Chemin du Pavillon
P.O. Box 50 CH-1218
Le Grand-Saconnex (Genève)
Switzerland
Tel: +41 (22) 717 51 11
Fax: +41 (22) 717 51 09
Web: www.chemours.com

DAIKIN CHEMICAL EUROPE
Immermannstrasse 65D
40210 Düsseldorf
Germany
Tel: +49 211 179 22 50
Fax: +49 211 164 0732
Web: www.daikinchem.de / www.daikin.com

DYNEON GmbH**
Industrieparkstrasse 1
84508 Burgkirchen
Germany
Tel: +49 (0) 8679-74709
Fax: +49 (0) 8679-3992
Web : www.dyneon.com / www.dyneon.eu

Zhejiang Jusheng Fluorochemical Co.,Ltd
Juhua factory zone
Kecheng district
Quzhou City
Zhejiang Province
324004
China
Tel: +86 -570-3615116
Web: http://www.juhua.com.cn
Email: salla1989@juhua.com
W.L. Gore & Associates GmbH
Industrieparkstrasse 1
Gebäude 250
D-84508 Burgkirchen
Germany
Tel: +49 (0) 8679-9138-0
Web: www.gore.com

GUJARAT FLUOROCHEMICALS Ltd
Inox Towers, Polot no 17 - Sector -16-A, Noida
Uttar Pradesh 201301
India
Tel: +91 120 614 9600
Web: www.gfl.co.in
Email: contact@gfl.co.in

SYENSQO - SOLVAY SPECIALTY POLYMERS ITALY S.p.A
Via Lombardia 20
20021 Bollate (Milano)
Italy
Tel: +39 (02) 2909 21
Web: www.syensqo.com

* ARKEMA stopped using TFE in 2023 but will continue to support the testing work of the TFE Safety Task Force until the end of 2024.

** DYNEON will stop manufacturing and using TFE by the end of 2025 and will leave the TFE Safety Task Force at the end of 2025.

Joining the TFE Safety Task Force

The TFE Safety Task Force is keen to expand membership to any TFE producing or using company or other stakeholder who wishes to improve and share their knowledge regarding TFE safety. The group can be contacted via the PlasticsEurope Fluoropolymer Product Group using the contact details given on page IV.

Appendix B – TFE Safety Task Force Projects

This section provides brief summaries of the projects that the TFE Safety Task Force have sponsored with Bundesanstalt für Materialforschung und -prüfung (BAM)(x), Germany and Ineris(xi), France. Publications resulting from these studies are listed in Appendix C.

1. BAM R&D Project VH 2152 "*Explosion characteristics of Tetrafluoroethylene (TFE) and TFE mixtures*" started in April 2004.

For classification purposes the minimum ignition temperatures in mixture with air (MIT) of stabilized and non-stabilized TFE were determined according to the European Directive 67/548/EC, Annex A.5, Method A.15 "Ignition temperatures of liquids and gases". The experimental set-up is shown in Figure 19, and the values measured are:

- MIT(stab. TFE) = 235 °C ± 5 °C
- MIT(non-stab. TFE) = 240 °C ± 5 °C

Therefore, the TFE must be classified into the temperature class T3.

Figure 19 Experimental set up for the MIT determination of TFE and TFE mixtures

The dimerization reaction of TFE to c-octafluorobutane plays an important role as an initiation reaction for the explosive decomposition.

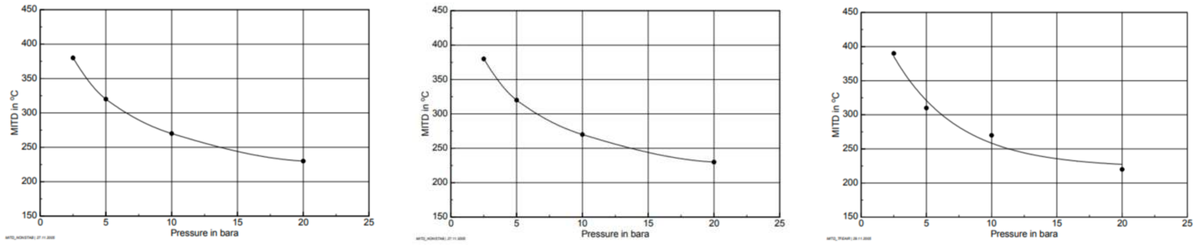
$$C_2F_4 \rightarrow 0.5\ c\text{-}C_4F_8 \qquad \Delta H_r = -\ 103\ \text{kJ mol}^{-1}\ \text{(Dimerization)}$$
$$C_2F_4 \rightarrow CF_4 + C \qquad \Delta H_r = -\ 257\ \text{kJ mol}^{-1}\ \text{(Decomposition)}$$

Dimerization can lead to a delayed ignition times for TFE decompositions. Polymerization can also occur during testing, examples of polymer formation are included in Figure 20.

(x) https://www.bam.de/Navigation/EN/Home/home.html
(xi) https://www.ineris.fr/en

Figure 20 Formation of PTFE during the tests (left; with the spiral wire, right; 3-L autoclave after the tests with the naked heating cartridge)

Understanding the MITD properties of TFE are critical to being able to handle TFE Safety at Laboratory and Industrial Scale. There was not a significant difference between the MITD of stabilised and unstabilised TFE and even the presence of trace oxygen did not have an impact greater than experimental variation on the MITD as indicated by the similar MITD variation with pressure plots in Figure 21.



a) Stabilised TFE

b) Non-stabilised TFE

c) TFE/air mixture (98 : 2 mol %)

Figure 21 MITD versus pressure plots for various TFE samples

Unwanted polymer formation can lead to hot spots that can become ignition sources for TFE in industrial settings.

2. BAM R&D Project VH 2509 “*Prevention of TFE explosions by numerical predictions of hazardous conditions*” started in May 2007.

COMSOL (Computational Fluid Dynamics) and Excel models were prepared to simulate and predict MITD in closed vessels and by heat of (adiabatic) compression. The models were complex and specific to geometries in the models.

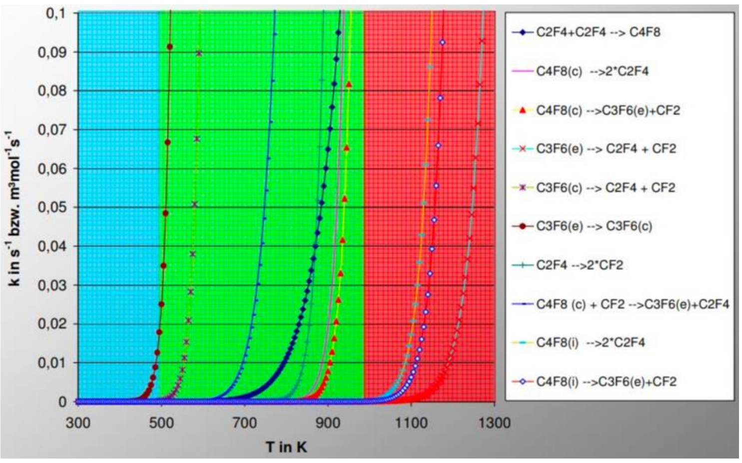


Figure 22 Modelled reaction rates versus temperature for reactions that occur when TFE is at elevated temperatures

The modelling of multiple reactions highlights the importance of these reactions in the temperature region where a TFE decomposition is most likely (green area in Figure 22). These additional reactions can provide energy that may lead to a delayed ignition of the decomposition reaction.

3. BAM R&D Project VH 2427/2527 “*Preventing of Tetrafluoroethylene explosions induced by adiabatic compression by experimental determination of hazardous conditions*” started in July 2012.

In parallel to the computational studies that continued, experimental studies on the heat of compression started. Testing on small scale test apparatus (Figure 23) were initially investigated before heat of compression testing on industrially scale pipework, with a pipe internal diameter of 1.5 inches were commenced (Figure 24).

Figure 23 **Initial (left) and second (right) experimental set-up for heat of compression experiments**

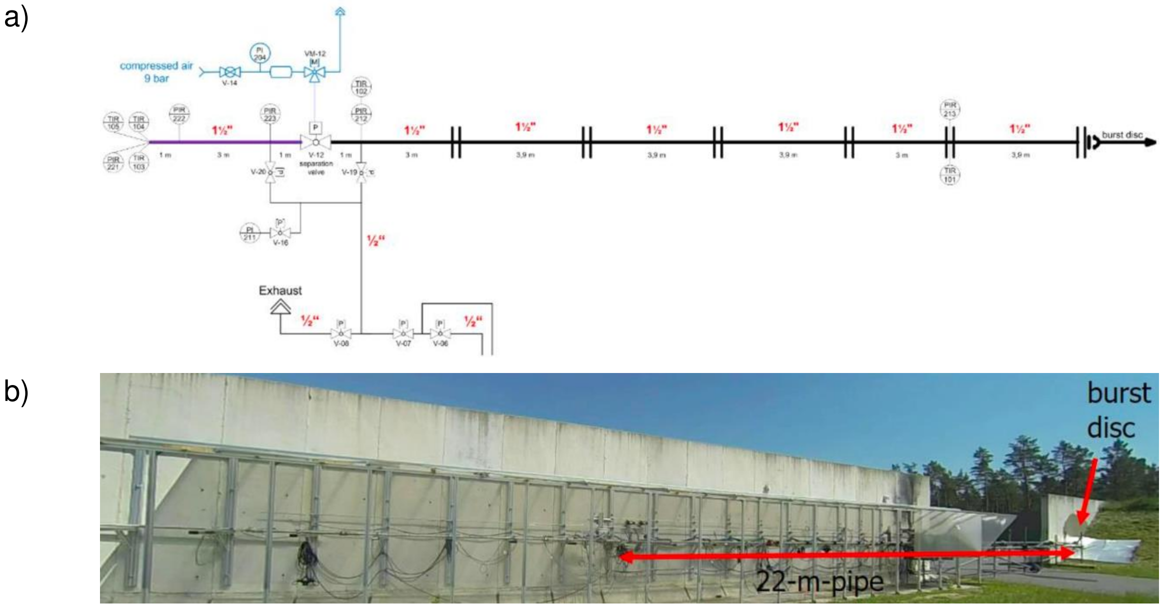


Figure 24 **Industrial scale heat of compression experimental set-up a) line diagram and b) photo**

Many tests were carried out with the following gas combinations between 1 – 40 bar pressures:

- Air compressing air
- TFE compressing nitrogen
- TFE compressing air
- TFE compressing TFE

Although it was shown that the temperatures were not adiabatic due to heat loss to the equipment and from gas mixing, temperature rises that would be sufficient to ignite a TFE decomposition were routinely measured.

4. BAM Project VH 2400 "*Rapid compression of Tetrafluoroethylene in 2-inch tubes*" started in January 2016.

This project continued the industrial scale studies looking at heat of compression as a significant ignition source for TFE decompositions. A new experimental pipe with a larger 2.5-inch internal diameter (63 mm) was installed (Figure 25 and Figure 26). As with previous tests, videos were captured which were made available to member companies for information and training purposes. The videos/screen shots from the videos were also useful in following the release of the burning gas and soot following a TFE decomposition (as shown in Figure 27).

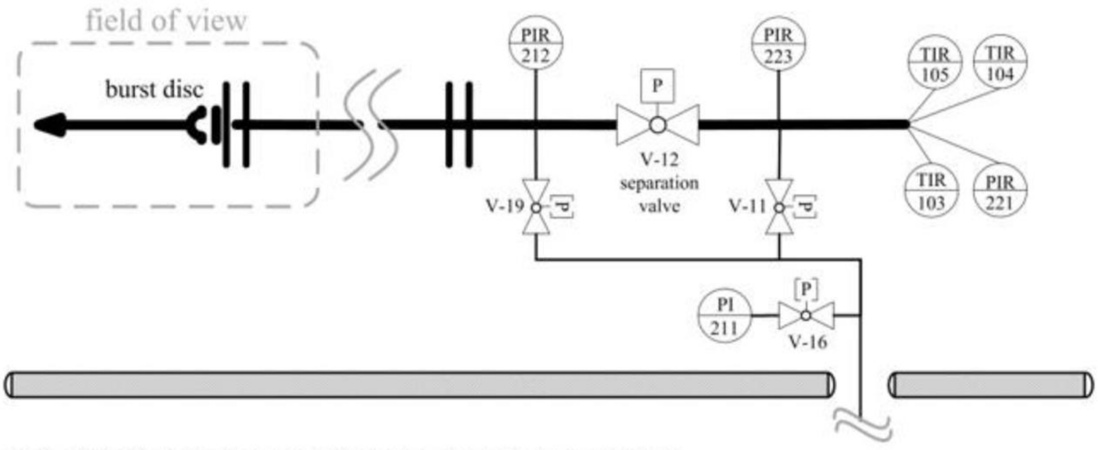


Figure 25 Simplified diagram of the industrial scale compression test apparatus

Figure 26 Industrial scale compression test apparatus during the installation of the 2.5-inch pipe without the thermal insulation present

Figure 27 Series of images showing the venting of a TFE explosive decomposition with 10 bar TFE compressing 0.4 bar air.

(a) shortly before the burst disc opens; (b) release of unburn TFE; (c) release of soot and dirt; (d) and (e) TFE flame and (f) release of decomposition products including carbon soot.

Many experiments were done to investigate heat of compression temperature for many industrial scenarios including straight, bends, ‘T-junction and strainers (Figure 28). Combined with data from real plant incidents and TFE testing, a ‘Hazard Diagram’ as shown in Figure 29 was developed. The ‘Hazard Diagram’ is one of the most important results from these studies. However, it is noted that the hazard diagram in Figure 28 is specific for the conditions tested, including the pipe geometries (such as pipe diameter, length, bends etc.). The hazard diagram along with the theoretical temperature rise from adiabatic compression (see Chapter 2, section 7) are useful tools for safe plant design.

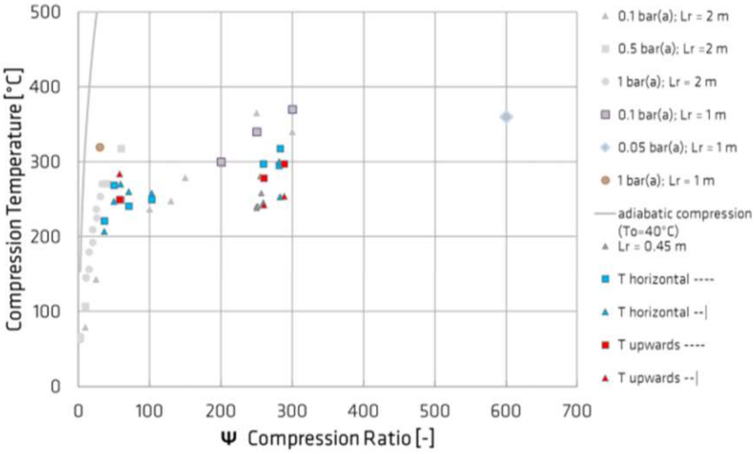


Figure 28 Compression temperature versus compression ratio for a pipe with an internal diameter of 1.1-inch

The grey line in Figure 28 indicates the theoretical temperature rise for adiabatic compression. For low compression ratios, the measured heat is close to the theoretical temperature rise but for higher compression ratios, the measured temperature deviates significantly. This lower temperature may be due to heat losses but also could be an artifact of the difficulty in measuring the temperatures.

It does not matter what causes the compression, whether it is high pressure TFE or a piston in a compressor (or for example a diesel engine). The temperature rise is not affected by the compressing medium, however in the case of TFE, the compressing medium can explosively decompose.

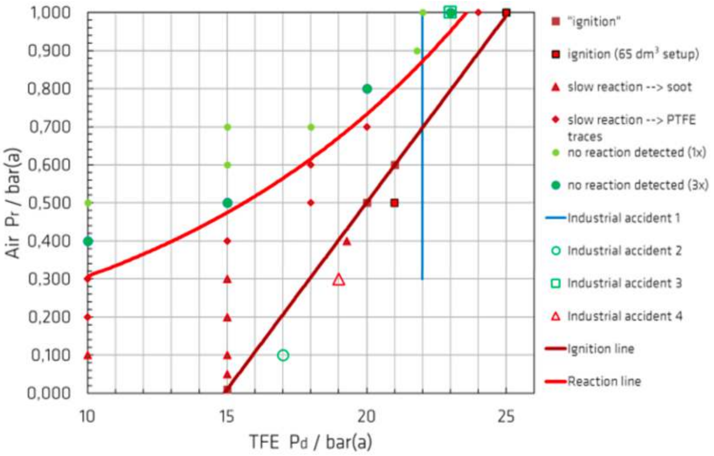


Figure 29 **Hazard Diagram for TFE compressing air in a 5 m long, 1.1-inch internal diameter receiving pipe with an initial temperature of ~ 35 °C**

Also included in Figure 29 are the conditions that are believed to have occurred for four industrial accidents.

5. BAM Project VH 2473 “*Polythermal compression of Tetrafluoroethylene in 1” and 2” tubes and adjacent standard deflagration arrestor*” started in February 2019.

Several TFE manufacturers had developed their own technologies for flame arrestors. This project compared the effectiveness of these flame arrestors with a commercially available flame arrestor. The typical experimental set-up for these tests is shown in Figure 30.

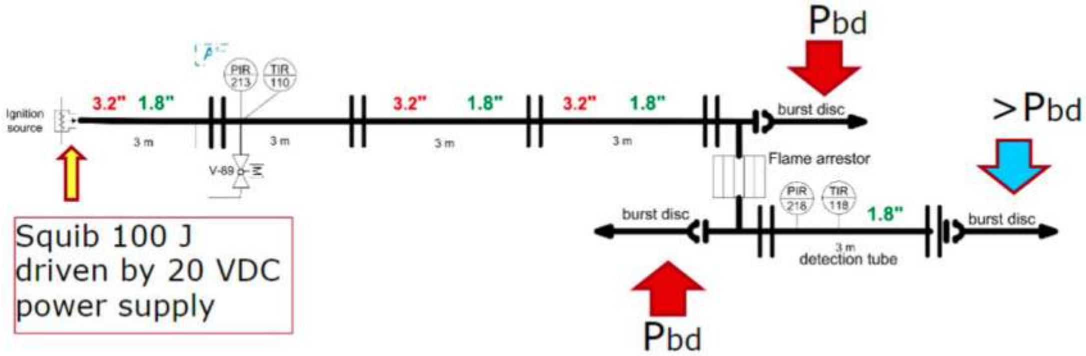


Figure 30 **Experimental set-up for flame arrestor testing**

Three types of flame arrestor were tested with TFE pressures from 11.5 – 21.1 bar with a distance between the ignition source and flame arrestor of 12.6 – 12.7 m. These test conditions correspond to about 2 – 5 kg of TFE per test. Rupture disc pressures also influence the test results but were set at 5.0 ± 1.5 bar higher than the TFE pressure. All three flame arrestors were shown to be effective at extinguishing TFE decompositions under the tested conditions; some screen shots from three tests are shown in Figure 31

a)

15.5 bar TFE, element style flame arrestor. Flame and soot being emitted from the inlet rupture disc.

b)

15.5 bar TFE, tube bundle style flame arrestor. Flame and soot being emitted from the inlet rupture disc. Unburnt TFE (i.e., the decomposition has been stopped) can also be seen being released from the rupture disc after the flame arrestor.

c)

21.1 bar TFE, tube bundle style flame arrestor. The greater TFE amount leads to a larger flame and later, more soot generation.

Figure 31 **Screen shots from flame arrestor testing**

6. Ineris Project 209669 “*Measurement of MIT of Pure and Stabilised TFE started*” in February 2023.

The TFE Safety Task Force selected Ineris, France as the new partner for TFE testing. As Ineris were new to TFE, it was decided to repeat the MIT tests that were previously performed at BAM (project VH 2152) so Ineris could gain understanding and experience handling TFE. The experimental set up used for MIT tests is shown in Figure 32:

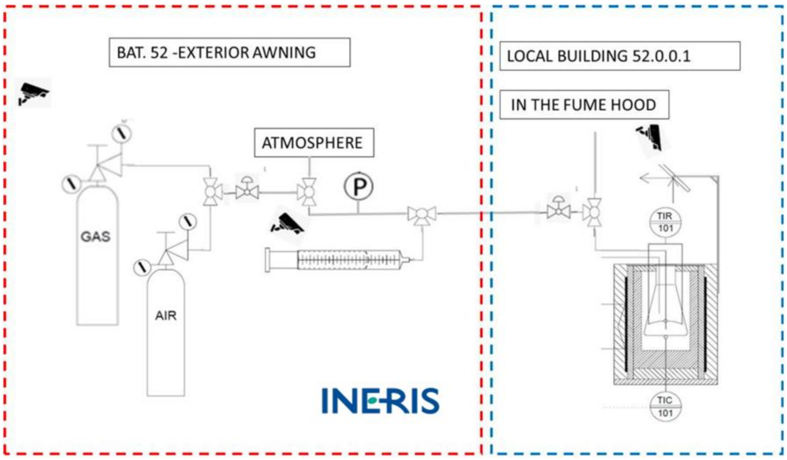


Figure 32 Experimental set-up for MIT testing

The AIT measured by Ineris was 245 °C; as expected, this was in excellent agreement with the previous measurements performed by BAM (235 ± 5 °C). Some examples of the flames seen during the Ineris testing are shown in Figure 33.

Figure 33 Examples of flames from MIT testing of TFE

Appendix C – TFE Safety Task Force Publications

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2) Andrews, G.; Self ignition of tetrafluoroethylene at elevated initial pressures. *Bachelor thesis*, Bundesanstalt für Materialforschung und –prüfung (BAM) and Technical University (TU) of Delft, Germany and The Netherlands, 2005.

3) Gula, M.; Heiße Oberflächen als Zündquelle für den Zerfall von Tetrafluorethylen. Hot surfaces as an ignition source for the decomposition of tetrafluoroethylene. *Thesis,* Bundesanstalt für Materialforschung und –prüfung (BAM) and Technical University (TU) of Berlin, Berlin, Germany, 2005 [in German].

4) Beckmann-Kluge, M., Krause, H., Schröder, V., Acikalin A. & Steinbach, J.; Study of a Self Heating Process of Tetrafluoroethylene by the Exothermic Dimerization Reaction to Octafluorocyclobutane. *Proceedings of the COMSOL Conference 2008*, Hannover, November 2008.

5) Meyer, R.; Untersuchung des Zündverhaltens des Tetrafluorethens (TFE) durch adiabatische Kompression. Study of the ignition characteristics of TFE through adiabatic compression. *Diploma thesis*, Bundesanstalt für Materialforschung und –prüfung (BAM) and Technical University (TU) of Berlin, Berlin, Germany, 23 October 2009 [in German].

6) Kluge, M.; Experimentelle Bestimmung und Modellierung von sicherheitstechnischen Eigenschaften der Zerfallsreaktion von Tetrafluorethen. Experimental determination and modelling of safety properties of the decomposition reaction of tetrafluoroethylene. *Doctoral thesis*, Bundesanstalt für Materialforschung und –prüfung (BAM), Germany, 08 June 2012 [in German].

7) Ferrero, F., Beckmann-Kluge, M., Spoormaker, T. & Schröder, V.; On the Minimum Ignition Temperature for the explosive Decomposition of Tetrafluoroethylene on hot walls: Experiments and calculations. *Journal of Loss Prevention in the Process Industries*, **25 (2)**, 293–301, March 2012.
DOI: http://dx.doi.org/10.1016/j.jlp.2011.11.005.

8) Ferrero, F., Zeps, R., Beckmann-Kluge, M., Schröder V. & Spoormaker, T.; Analysis of the self-heating process of tetrafluoroethylene in a 100-dm^3-reactor. *Journal of Loss Prevention in the Process Industries*, **25 (6)**, 1010–1017, November 2012.
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DOI: http://dx.doi.org/10.1016/j.jlp.2012.10.006.

10) Meyer, R., Kluge, M., Ferrero, F. & Grasse, D.; Zündung zerfallsfähiger Gase wie Acetylenn und Tetrafluorethen durch adiabate Kompression. Ignition of decomposable gases such as acetylene and tetrafluoroethene through adiabatic compression. BAM-PTB Colloquium, Braunschweig, Germany, 18-19 June 2013 [in German].

11) Ferrero, F., Meyer, R., Kluge, M., Schröder, V. & Spoormaker, T.; Study of the Spontaneous Ignition of Stoichiometric Tetrafluoroethylene–Air Mixtures at Elevated Pressures. *Journal of Loss Prevention in the Process Industries*, **26 (4)**, 759-765, July 2013. DOI: http://dx.doi.org/10.1016/j.jlp.2013.02.008.

12) Ferrero, F., Zeps, R., Kluge, M., Schröder V. & Spoormaker, T.; The Explosive Decomposition of Tetrafluoroethylene: Large Scale Tests and Simulations. *Chemical Engineering Transactions*, **31**, 817 – 822, 2013.
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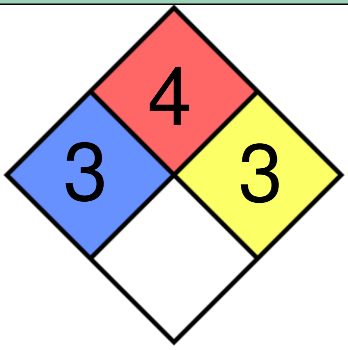
Appendix D – TFE hazards classification

Table 20 Hazard classification of TFE according to EU C&L inventory (source: [8])

Hazard symbols		
 Flammable	 Compressed Gas	 Health hazard

Statements	
Hazard statements	H220: Extremely flammable gas H231: May react explosively even in the absence of air at elevated pressure and/or temperature H280: Contains gas under pressure; may explode if heated **H350i: May cause cancer** by inhalation H371: May cause damage to organs (Kidney) if inhaled
Precautionary statements	P201: Obtain special instructions before use. P202: Do not handle until all safety precautions have been read and understood. P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking. P260: Do not breathe dust/fume/gas/mist/vapours/spray P280: Wear protective gloves/protective clothing/eye protection/face protection. P281: Use personal protective equipment as required. P308 + P313: IF exposed or concerned: Get medical advice/attention. P377: Leaking gas fire: Do not extinguish, unless leak can be stopped safely P381: In case of leakage, eliminate all ignition sources. P405: Store locked up. P410 + P403: Protect from sunlight. Store in a well-ventilated place P501: Dispose of contents/container to...

Table 21 Hazard classification of TFE (United States): NFPA 704 “fire diamond” (source: [19], [88])

<table>
<tr><th colspan="3">NFPA 704 “fire diamond”</th></tr>
<tr><td colspan="3">
</td></tr>
<tr><th colspan="3">Codes</th></tr>
<tr><td>**Flammability**</td><td>**4**</td><td>Will rapidly or completely vaporize at normal atmospheric pressure and temperature, or is readily dispersed in air and will burn readily. Flash point below 23 °C (73 °F).</td></tr>
<tr><td>**Health**</td><td>**3**</td><td>Short exposure could cause serious temporary or moderate residual injury.</td></tr>
<tr><td>**Instability/reactivity**</td><td>**3**</td><td>Capable of detonation or explosive decomposition but requires a strong initiating source, must be heated under confinement before initiation, reacts explosively with water, or will detonate if severely shocked.</td></tr>
</table>

Appendix E – TFE transport information

Table 22 TFE transport information

Consult a qualified DGSA for prior to transporting TFE (source [4], [63])

<table>
<tr><th>UN number</th><th>Labelling (ADR/RID, IMDG, IATA)</th></tr>
<tr><td>1081 (stabilized)</td><td>
2.1: Flammable gas</td></tr>
<tr><th colspan="2">Land transport (road/rail)</th></tr>
<tr><td>ADR/RID Hazard Identification nr:</td><td>239</td></tr>
<tr><td>UN proper shipping name:</td><td>TETRAFLUOROETHYLENE, STABILIZED</td></tr>
<tr><td>Transport hazard class(es):</td><td>2</td></tr>
<tr><td>ADR/RID Classification code:</td><td>2 F</td></tr>
<tr><td>Packing Instruction(s):</td><td>P200</td></tr>
<tr><td>Transport Category:</td><td>2</td></tr>
<tr><td>Tunnel Restriction:</td><td>Tank carriage: Passage forbidden through tunnels of category B, C, D and E;
Other carriage: Passage forbidden through tunnels of category D and E</td></tr>
<tr><th colspan="2">Sea transport</th></tr>
<tr><td>IMO-IMDG code</td><td></td></tr>
<tr><td>Proper shipping name:</td><td>TETRAFLUOROETHYLENE, STABILIZED</td></tr>
<tr><td>Class:</td><td>2.1</td></tr>
<tr><td>IMO Packing group:</td><td>P200</td></tr>
<tr><td>Emergency Schedule (EmS) - Fire:</td><td>F-D</td></tr>
<tr><td>Emergency Schedule (EmS) - Spillage:</td><td>S-U</td></tr>
<tr><td>Instructions - Packing:</td><td>P200</td></tr>
<tr><td>Marine pollutant:</td><td>no</td></tr>
<tr><th colspan="2">Air transport</th></tr>
<tr><td>ICAO/IATA</td><td></td></tr>
<tr><td>Proper shipping name:</td><td>TETRAFLUOROETHYLENE, STABILIZED</td></tr>
<tr><td>Class:</td><td>2.1</td></tr>
<tr><td>Passenger and Cargo Aircraft:</td><td>Cargo Aircraft only</td></tr>
<tr><td>Packing instruction:</td><td>200</td></tr>
<tr><th colspan="2">General information / precautions for transport</th></tr>
<tr><td colspan="2">Avoid transport on vehicles where the load space is not separated from the driver's compartment.
Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency. Before transporting product containers:
- Ensure that containers are firmly secured.
- Ensure valve is closed and not leaking.
- Ensure valve outlet cap nut or plug (where provided) is correctly fitted.
- Ensure valve protection device (where provided) is correctly fitted.
- Ensure there is adequate ventilation.
- Ensure compliance with applicable regulations.</td></tr>
</table>

Table 23 TFE transport by road, ADR provisions (source: [7])

UN No.	Name and description	Class	Classification code	Packing group	Labels	Special provisions	Limited and excepted quantities		Packaging			Portable tanks and bulk containers	
									Packing instruct-tions	Special packing provisions	Mixed packing provisions	Instructions	Special provisions
	3.1.2	2.2	2.2	2.1.1.3	5.2.2	3.3	3.4	3.5.1.2	4.1.4	4.1.4	4.1.10	4.2.5.2 7.3.2	4.2.5.3
1081	TETRAFLUOROETHYLENE, STABILIZED	2	2F		2.1	386 662 676	0	E0	P200		MP9	(M)	

ADR tank		Vehicle for tank carriage	Transport category (Tunnel restriction code)	Special provisions for carriage				Hazard identifycation No.	UN No.	Name and description
Tank code	Special provisions			Packages	Bulk	Loading, unloading and handling	Operation			
4.3	4.3.5, 6.8.4	9.1.1.2	1.1.3.6 (8.6)	7.2.4	7.3.3	7.5.11	8.5	5.3.2.3		3.1.2
PxBN(M)	TU40 TA4 TT9	FL	2 (B/D0	V8		CV9 CV10 CV36	S2 S4 S20	239	1081	TETRAFLUOROETHYLENE, STABILIZED

Appendix F – Workplace labelling

Table 24 Workplace labelling according to German ASR A1.3 (source: [4], [89])

<table>
<tr><th colspan="6">Prohibition labels</th></tr>
<tr>
<td colspan="2">
No open flame; fire, open ignition sources and smoking prohibited</td>
<td colspan="2">
No admittance for unauthorized persons</td>
<td colspan="2">
No eating and drinking</td>
</tr>
<tr><th colspan="6">Warning labels</th></tr>
<tr>
<td colspan="3">
Caution - gas cylinder</td>
<td colspan="3">
Caution - explosive atmosphere</td>
</tr>
<tr><th colspan="6">Mandatory labels</th></tr>
<tr>
<td colspan="2">
Use safety goggles</td>
<td colspan="2">
Wear safety shoes</td>
<td colspan="2">
Wear safety gloves</td>
</tr>
</table>

Appendix G – Safety checklist

The list presented here is intended to offer a practical tool to check if the most important safety aspects related to TFE handling have been taken into account. The aim is to provide a comprehensive to-do-list for the safe handling of TFE. Still, the list might not be complete, e.g. issues for specific applications in plants or laboratories might not be covered.

Table 25 Safety checklist

Hazards		
Toxicology issues		
	Contact of workers with TFE minimized?	☐
	Design to avoid or control PFiB formation?	☐
	Design to avoid or control other toxic products formation?	☐
	Airborne concentration limits respected?	☐
Fire and explosion hazards		
	Decomposition reaction of TFE risks known?	☐
	Reaction of TFE in air risks known?	☐
	Other reactions or stability issues considered?	☐
	Possible ignition sources known?	☐
	Further hazards and risks known (i.e. equipment specific issues)?	☐
TFE in mixture with co-monomers		
	Formation of toxic substances not listed in this guide considered?	☐
	Fire and explosions hazards of mixture known?	☐
	Effect on equipment design considered?	☐
Safety procedures and precautions		
General safety procedures		
	Risk assessment performed?	☐
	Personal trained?	☐
	MSDS and specific documentation provided to workers?	☐
	Workspace labelled?	☐
	Ventilation guaranteed (bottom ventilation)?	☐
	Concentration of TFE in air minimized?	☐
	Use of non-sparkling tool taken into account?	☐
	Appropriate electrical equipment used?	☐
	Proper grounding?	☐
	Local and global regulations (transport, storage, disposal, etc.) fulfilled?	☐

Table 25 (continued)

Safety procedures and precautions		
Storage and transportation		
	Gas cylinders stored separately from other cylinders?	☐
	Gas cylinders protected from falling?	☐
	Storage in a ventilated area?	☐
	Storage area temperature under 25 °C?	☐
	Transport/storage in gas cylinders, pressure limitation known?	☐
	If intermediate storage/transport of liquid TFE necessary precautions taken?	☐
Process specific safety procedures		
	Conditions chosen to avoid adiabatic compression?	☐
	Conditions chosen to avoid ignition on hot surfaces/hot spots?	☐
	Conditions chosen to avoid detonation?	☐
	Explosion protection plan available?	☐
	Periodic leak tests performed?	☐
	Gas detection guaranteed?	☐
	Nitrogen purges prior to TFE inlet or maintenance operation made?	☐
	Feed procedures safe?	☐
Accidental release		
	Gas leak: flow stopped, if it can be done safely?	☐
	Gas leak: if flow cannot be stop, let container empty to a safe location?	☐
	Spill: let TFE evaporate to a safe location (“no entry area”)?	☐
	Evacuate personnel not wearing protective equipment?	☐
	Ignition sources avoided?	☐
Fire fighting		
	Deluge systems provided?	☐
	Firefighters trained?	☐
	Fire feed isolated? If not, evacuate.	☐
	If fire feed can be isolated, water spray cooling of containers done?	☐
	Evacuation if containers in contact with fire or heat?	☐
	Evacuation if cooling ineffective?	☐
	Suitable extinguishment media chosen?	☐
	Respiratory equipment worn (self-contained breathing apparatus)?	☐
	Fire extinguishing water from collected separately?	☐

Table 25 (continued)

Safety procedures and precautions		
Personal protective equipment		
	Contact lenses avoided?	☐
	Protective clothing worn?	☐
	Eyewash/emergency shower available?	☐
Personal hygiene		
	Smoking prohibited?	☐
	Carrying tobacco prohibited?	☐
	Work clothing separately stored?	☐
	Work clothing regularly washed?	☐
Disposal		
	Small amount: release to air.	☐
	Large amount: releases should be minimised (e.g. by consumption or thermal destruction), but if made to atmosphere they must be to “no entry area”.	☐
	Contaminated wastewaters analysed?	☐

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Symbols

Symbol	Definition	SI Units
$C^0_{p,m}$	Standard molar heat capacity	$J.K^{-1}.mol^{-1}$
K_{oc}	Soil organic carbon-water partition coefficient	-
K_{ow}	Octanol-water partition coefficient	-
L	Pipe length	m
p	Pressure	bar(xii)
P_0	Initial pressure	bar
P_1	Final pressure	bar
P_{bd}	Pressure of bursting disc	
p_c	Critical pressure	bar
p_{vp}	Vapour pressure	bar
R	$1 - T_r$	-
T	Temperature	K
T_0	Initial temperature	K
T_1	Final temperature	K
T_c	Critical temperature	K
T_r	Reduced temperature	-
VPA	Constant used to calculate the vapour pressure	-
VPB	Constant used to calculate the vapour pressure	-
VPC	Constant used to calculate the vapour pressure	-
VPD	Constant used to calculate the vapour pressure	-
$\Delta_f G^0$	Standard molar Gibbs energy of formation	$J.mol^{-1}$
$\Delta_f H^0$	Standard molar enthalpy of formation	$J.mol^{-1}$
ΔH_r	Heat of reaction	$kJ.mol^{-1}$
γ	Ratio of specific heats	-
Ψ	Compression ratio	-
Ø	Diameter	m
% v/v	Volume fraction	-

(xii) If not further specified, bar will refer to absolute pressure.

List of abbreviations

Abbreviation	Definition
ACGIH TLV-TWA	American Conference of Governmental Industrial Hygienists, Threshold Limit Value - Time Weighted Average Time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.
ACGIH TLV-C	American Conference of Governmental Industrial Hygienists, Threshold Limit Value – Ceiling limit: Absolute exposure limit that should not be exceeded at any time.
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road (derived from French: Accord européen relatif au transport international des marchandises Dangereuses par Route)
AEGL	Acute Emergency Guideline Levels
AIT *	Auto Ignition Temperature
BAM	Bundesanstalt für Materialforschung und -prüfung
BLEVE *	Boiling Liquid Expanding Vapour Explosion
C	Carbon (elemental)
C&L	Classification and labelling
CAS	Chemical Abstracts Service
CNS	Central Nervous System
C_2F_4	Tetrafluoroethylene
C_3F_6	Hexafluoropropene
$c\text{-}C_4F_8$	Octafluorocyclobutane
Carc.	Carcinogen
CF_4	Tetrafluoromethane
CHF_2CN	Difluoroacetonitrile
CHF_2CONH_2	Difluoroacetamide
CO	Carbon monoxide
CO_2	Carbon dioxide,
COF_2	Carbonyl fluoride
$CHClF_2$	Chlorodifluoromethane
CPR	Cardiopulmonary resuscitation
CWC	Chemicals Weapons Convention
DDT	Deflagration to Detonation Transition
DOC/PSF	Discrete Organic Chemical Containing Phosphorous, Sulphur or Fluorine
DIN	Deutsches Institut für Normung
EC	European Commission
EEA	European Economic Area
ECHA	European Chemicals Agency

Abbreviation	Definition
ERC	Environmental Release Categories
EU	European Union
FPG	Fluoropolymer Product Group
FMC	Fluoromonomer Consortium
g	Gas
GB	Great Britain
GC	Gas Chromatography
GC-MS	Gas Chromatography Mass Spectrometry
GESTIS	Information system on hazardous substances of the German Social Accident Insurance (derived from German Gefahrstoffinformationssystem der Deutschen Gesetzlichen Unfallversicherung)
GHS	Globally Harmonized System
GWP *	Global Warming Potential
HAZOP	Hazard and Operability
HCFC	Hydrochlorofluorocarbon
HCl	Hydrochloric acid
HF	Hydrogen fluoride
HFP	Hexafluoropropene
IUPAC	International Union of Pure and Applied Chemistry
i-C_4F_8	Perfluoroisobutene
IATA	International Air Transport Association
ICAO	International Civil Aviation Organization
IMDG	International Maritime Code for Dangerous Goods
IMO	International Maritime Organization
LoA	Letter of Access
LR	Lead Registrant
MCL	Mandatory Classification List
MIE *	Minimum Ignition Energy
MIED *	Minimum Ignition Energy for Decomposition
MIP *	Minimum Ignition Pressure
MIPD *	Minimum Ignition Pressure for Decomposition
MIT *	Minimum Ignition Temperature
MITD *	Minimum Ignition Temperature for Decomposition
MSDS	Material Safety Data Sheet
NFPA	National Fire Protection Association
NIST	National Institute of Standards and Technology
N.O.S.	Not otherwise specified
OECD	Organisation for Economic Co-operation and Development

Abbreviation	Definition
OPCW	Organisation for the Prohibition of Chemical Weapons
PBT	Persistent, Bioaccumulative and Toxic
PC	Chemical Products Categories
PFAS	Per- and Poly-Fluoroalkyl Substance
PFiB	Perfluoroisobutene
PI	Pressure indicator
PIR	Pressure indicator Recorder
PLS *	Pressure Limit of Stability
PLSD *	Pressure Limit of Stability for Decomposition
PROC	Process Categories
PTFE	Polytetrafluoroethylene
ppm	Parts per million
Rxx	Refrigerant xx where xx is a numerical value relating to the substance composition
RAC	Risk Assessment Committee (of ECHA)
RD	Rupture disc
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RID	International Rule for Transport of Dangerous Substances by Railway (derived from French: Règlement concernant le transport International ferroviaire des marchandises Dangereuses)
s	Solid
SCC	Strictly Controlled Conditions
Stab.	Stabilised
SU	Sectors of use
TFE	Tetrafluoroethylene
TIR	Temperature Indicator Recorder
TLV	Threshold Limit Value
TNT	Trinitrotoluene
TTS	BAM Test Ground Technical Safety
TWA	Time Weighted Average
UN	United Nations
U.S.	United States (of America)
V	Valve
vPvB	very Persistent, very Bioaccumulative

* marked abbreviations are defined in the glossary.

Glossary

Term	**Definition**
adiabatic compression	A compression, i.e. an induced reduction in volume and increase in pressure of a *gas*, which happens so rapidly that the process is adiabatic, i.e. without heat transfer between a system and its surroundings. The whole energy produced by the compression increases the system temperature.
airborne concentration	The amount of chemical per unit volume of air.
alkoxide	An alkoxide is the conjugate base, i.e. a species formed by the removal of a proton (H^+) from an acid, of an alcohol and therefore consists of an *organic* group bonded to a negatively charged oxygen atom.
alkene	An alkene is an unsaturated *hydrocarbon* that contains at least one carbon–carbon (C=C) double bond
azeotropic mixture	An azeotropic mixture (or simply “azeotrope”) is a mixture of two or more *liquid*s whose proportions cannot be altered by simple *distillation*. The reason for this peculiarity is that the *vapour* phase has the same proportions of constituents as the liquid phase and therefore the boiling of the mixture occurs without change of composition.
Auto Ignition Temperature (AIT)	(see *Minimum Ignition Temperature*)
Boiling Liquid Expanding Vapour Explosion (BLEVE)	An *explosion* caused by the rupture of a vessel containing a pressurized *liquid* above its boiling point. In case the liquid is *flammable* the *explosion* can lead to a fireball.
CAS registry number	A unique numerical identifier assigned by Chemical Abstracts Service (CAS) to every chemical substance described in the open scientific literature.
catalyst	A substance which acts as a promoter of a chemical reaction, by increasing its reaction rate. Opposite of *inhibitor*.
chemically unstable gas	A *gas* which can experience *decomposition* without the presence of air, oxygen or another *oxidizer*.
combustion	An exothermic chemical reaction between a fuel and an *oxidant*, usually atmospheric oxygen. In a rapid combustion, otherwise known as a *fire*, large amounts of heat and light energy are released, which often results in a visible flame. If the combustion is accompanied by increase in the local pressure or volume, it is spoken of *explosion*.
critical pressure	The pressure required to liquefy a *gas* at its *critical temperature*.
critical temperature	The temperature at and above which a *gas* cannot be liquefied, no matter how much pressure is applied.
decomposition	The breakup of a substance into smaller molecules or atoms.
deflagration	An *explosion*, where the reaction wave propagates at a velocity less than the speed of sound.

Term	Definition
deluge system	A *fire* sprinkler system used where the application of water over a large hazard or area is required. In this type of systems all sprinkler nozzles are open and when water from the water supply is released via a deluge valve into the system it flows simultaneously from all discharge devices. The fate and collection of run-off deluge water and potential new hazards such as spreading of flammable/burning organic components should be considered.
detonation	An *explosion*, where the reaction wave propagates at a velocity faster than the speed of sound.
distillation	In industrial chemistry a distillation is a physical process which exploits differences in the volatility, i.e. the tendency of a substance to vaporize, of the components of a *liquid* mixture, in order to separate them one from another.
explosion	An explosion is a rapid event during which *gas*es created from the reacting materials cause an increase in the local pressure or volume, usually with the generation of high temperatures. It can be the consequence of a rapid *combustion* or *decomposition*. Explosions are categorized in *deflagration*s and *detonation*s, depending on their force and dynamics.
fire	The rapid oxidation of a material in the exothermic chemical process of *combustion*, releasing heat, light, and various reaction products.
flammable	(see *flammability*)
flammable gas	A *gas* which is *flammable*.
flammability	The ability of a substance to burn or ignite.
flammability range	The concentration range over which a *gas* will form a *flammable* mixture with air.
flash point	The temperature at and above which a *liquid* will generate *vapour*s in a concentration sufficient to create a *flammable* mixture in air.
fluid	A substance that continually deforms (flows) under an applied *shear stress*.
fluorocarbon	*Organic* compound in which fluorine replaces some or all hydrogen atoms.
fluoropolymer	A *fluorocarbon*-based *polymer* with multiple strong carbon–fluorine bonds.
gas	A state of the matter that will expand indefinitely if not contained. Unlike *liquid*s, gases can be compressed.
greenhouse gas	(see *greenhouse effect*)
greenhouse effect	The process by which radiation from the Earth's atmosphere warms its surface to a temperature above what it would be in the absence of atmosphere. Responsible for this effect are *gas*es which absorb part of the incoming sun radiation and reradiate it in all directions, thus increasing Earth's surface temperature. These gases are called greenhouse gases and the increase of their concentration in the atmosphere within the last two centuries is considered as the reason for the Earth's global warming.
Global Warming Potential (GWP)	A measure of how much heat a *greenhouse gas* traps in the atmosphere. Is expressed as a relative value to carbon dioxide.
haematopoietic	(see *haematopoiesis*)
haematopoiesis	The formation of blood cellular components.

Term	Definition
halogen	Halogens are a group in the periodic table consisting of five chemically related elements: fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). Halogens are highly reactive materials.
Henry's law	A correlation governing the solubility of *gas*es in *liquid*s.
Henry's law constant	A substance specific experimental constant of *Henry's law*.
hydrocarbon	An *organic* compound consisting entirely of hydrogen and carbon.
ignition source	A mechanism offering the amount of energy required to trigger a reaction like a *combustion* or *decomposition*.
inert	A substance that is not chemically reactive.
inerting	To render a *gas* or gas mixture not reactive by addition of an *inert*.
inhibitor	A substance that decreases the rate of a chemical reaction or prevents it from happening. Opposite of *catalyst*.
liquid	A state of the matter that conforms to the shape of its container but retains a constant volume. Liquids are nearly incompressible *fluid*s.
Minimum Ignition Energy (MIE)	The minimum amount of electrical energy stored in a capacitor that is sufficient to trigger the *combustion* of the most ignitable mixture of a *flammable* gas with air by discharge.
Minimum Ignition Energy for Decomposition (MIED)	The minimum amount of electrical energy stored in a capacitor that is sufficient to trigger the *decomposition* of a *chemically unstable gas*.
Minimum Ignition Pressure (MIP)	(see *Pressure Limit of Stability*)
Minimum Ignition Pressure for Decomposition (MIPD)	(see *Pressure Limit of Stability for Decomposition*)
Minimum Ignition Temperature (MIT)	The lowest temperature of a hot surface, at which the *combustion* of the most ignitable mixture of a *flammable* gas with air might be triggered.
Minimum Ignition Temperature for Decomposition (MITD)	The lowest temperature of a hot surface, at which the *decomposition* of a *chemically unstable gas* might be triggered.
molecular formula	An expression of the number and type of atoms that are present in a single molecule of a substance.
molecular mass	The mass of a molecule. It is calculated as the sum of the mass of each constituent atom multiplied by the number of atoms of that element in the *molecular formula*.
monomer	A molecule that may bind chemically to other molecules to form a *polymer*.
octanol-water partition coefficient	A coefficient representing the ratio of the solubility of a compound in octanol to its solubility in water. The higher this value, the higher is the tendency to accumulate in the food chain (bioaccumulation).
organic	In chemistry an organic compound is a member of a large class of chemical compounds whose molecules contain carbon.
organometallic compound	*Organic* compounds incorporating carbon-metal bonds.
overpressure	A transient air pressure greater than the surrounding atmospheric pressure, like that caused by an *explosion*.
oxidant	A chemical species that transfers electronegative atoms, usually oxygen, to a substrate or removes electrons from other reactants.

Term	Definition
oxidizer	(see *oxidant*)
oxidizing agent	(see *oxidant*)
perchlorate	Salt derived from perchloric acid.
perfluorinated	(see *perfluorinated compound*)
perfluorinated compound	*Fluorocarbon* in which fluorine replaces all hydrogen atoms.
permanganate	Salt derived from permanganic acid.
peroxide	A compound containing a peroxide group (i.e. an oxygen-oxygen single bond).
polymer	A large molecule composed of many recurring subunits. Natural and synthetic polymers are obtained via polymerization of many small molecules, known as *monomer*s.
Pressure Limit of Stability (PLS)	The minimum initial pressure at which the *combustion* of a *flammable* mixture of a *gas* in air can be initiated (i.e. by ignition via electrical spark).
Pressure Limit of Stability for Decomposition (PLSD)	The minimum initial pressure at which the *decomposition* of a *chemically unstable gas* can be initiated (i.e. by ignition via electrical spark).
pyrolysis	An irreversible thermochemical *decomposition* of *organic* material at elevated temperatures in the absence of oxygen (or any *halogen*).
reduced temperature	The temperature of a substance normalized to its *critical temperature*.
run-up distance to detonation	For an *explosion* accelerating within a confined space, the distance between the ignition spot and the point of transition from *deflagration* to *detonation.*
shear stress	A stress state where the stress is parallel to the surface of the material
soil organic carbon-water partition coefficient	A parameter used to express the mobility of *organic* chemicals in soils. Higher values correlate to less mobile substances, which therefore are unlikely to leach into groundwater.
solid	A state of the matter that retains constant shape and volume.
sorption	A physical and chemical process by which one substance becomes attached to another.
standard molar heat capacity	The amount of heat energy required to raise the temperature of 1 mole of a substance, at *standard conditions*.
standard molar Gibbs free energy of formation	The change of Gibbs free energy that accompanies the formation of 1 mole of a substance from its component elements, at their *standard states*. Gibbs free energy is a property of a substance, which is used to predict whether a process will occur spontaneously at constant temperature and pressure.
standard molar enthalpy of formation	The change of enthalpy that accompanies the formation of 1 mole of a substance from its component elements, at their *standard states*. Enthalpy is a property of a substance, which represents its capacity to release heat.
standard state	A reference point used to calculate the properties of a substance under different conditions, typically 1 atm of pressure and 298.15 K of temperature.
standard conditions	(see *standard state*)

Term	Definition
supercritical fluid	Any substance at a temperature above its *critical temperature* and at a pressure above its *critical pressure*. In this state of matter no distinct *liquid* and *gas* phases exist, but a *fluid* with intermediate properties.
vapour	A *gas* at a temperature below its *critical temperature*, so that it can be liquefied by *compression*, without lowering the temperature. Vapours of a substance can coexist with their other phases, for instance water vapour can coexist with *liquid* water and with ice.
vapour pressure	The pressure exerted by a *vapour* in equilibrium with its condensed phases (*solid* or *liquid*) at a given temperature in a closed system.

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