

Identifying Hazardous Conditions for Compression Heat Ignition of the Chemically Unstable Gas Tetrafluoroethylene at an Industrial Scale

Christian Liebner^{a,*}, Martyn Shenton^b

^aBundesanstalt für Materialforschung und –prüfung (BAM), Unter den Eichen 87, Berlin, Germany

^bPlasticsEurope TFE Safety Task Force, UK

christian.liebner@bam.de

Tetrafluoroethylene (TFE) is an industrial scale starting material e.g. for polymer production (PTFE, FEP). When ignited the chemically unstable TFE is capable of decomposing in an explosive way. Explosion propagation through pipe systems of production plants have led to damage and fatalities within the last seven decades.

Incident analyses identified compression heat a relevant source of ignition. Chemical plants consist of pipes, vessels, separating valves, strainers and other components. Before restarting the process after maintenance work, different parts of the plant components could be filled with TFE, nitrogen or air at different initial pressures ranging from vacuum or atmospheric to TFE at operating pressure. Valve opening procedures may cause a temperature increase in the gas phase. Compression takes place at polytropic conditions. Heat losses cannot be neglected. The temperature development in the gas depends upon the surface to volume ratio of the enclosure, geometrical influences, the state of gas flow, how fast the valve opens, and the heat capacity of the gas being compressed.

Laboratory scale tests (Meyer, 2009) revealed ignition of TFE/air due to compression heat. Tests in pipes of 28 mm inner diameter, i.e. already industrial scale, were performed by (Kluge et al., 2016). In the present contribution initial test results from a 63 mm pipe will be compared with existing 28 mm pipe data. A description of the experimental setup as well as an explanation of the hazard diagram will be given. Furthermore, a method allowing for the identification of hazardous conditions will be discussed.

1. Introduction

Handling of TFE in the process industry is a safety issue still not resolved in all its aspects. TFE is a decomposable gas. It can decompose into tetrafluoromethane and carbon black in an explosive way. Once triggered, TFE can undergo a self-propagating reaction. The strongly exothermic decomposition reaction doesn't need the presence of an oxidizer. A dimerization reaction forming octafluorocyclobutane (OFCB) out of two TFE molecules can start at temperatures as low as 200 °C and can trigger the decomposition due to its heat generation. The bimolecular gas phase reaction is described by a second order reaction rate equation (Lacher et al., 1952; Babenko et al., 1993). One of the main causes of accidents in chemical plants processing tetrafluoroethylene (TFE) is compression heat (Reza and Christiansen, 2007). Local heating from a hot surface can also lead to a TFE decomposition reaction (Kluge, 2012).

Biryulin et al. (2014) reported remarkably slow burning velocities for TFE-air mixtures. Lietze (2001) measured unexpected long run up distances for the decomposition reaction to reach the deflagration to detonation transition (DDT). Once ignition is achieved, the reaction starts slowly. Thus, relatively high deflagration pressures can be reached before the DDT. Especially in pipes at elevated conditions, i.e. pressures and temperatures relevant for production plants, explosion propagation can lead to severe damage of equipment and instrumentation, and cause serious injuries including fatalities.

The restarting procedure of a production plant after the completion of maintenance work involves filling certain volumes of the inner part of the installations with TFE at the required pressure. Pipes and vessels could still

contain some air or nitrogen at ambient pressure or technical vacuum pressure. Wherever there are two adjacent volumes of different pressures being separated by a valve, there will be the possibility for generating compression heat when the valve is opened. The apparatus used in the present work consists of two sections of a straight pipeline separated by a high-speed ball valve. In Industrial TFE plants slower operating valves are used.

2. Experimental Setup

Figure 1 depicts the flow chart diagram of the experimental apparatus. Both compression pipes provide a static pressure resistance of 325 bar. Their inner diameters are $d_1 = 28$ mm and $d_2 = 63$ mm. The complete lengths are $L_1 = 22$ m and $L_2 = 30$ m, respectively and consist of several sections connected by bolted joints and lens gaskets. To protect the test apparatus, at one end of each pipe a burst disc is installed to vent in the direction of explosion propagation. The burst disc consists of a hardened brass foil clamped between the lens gasket of the end flange. It is designed to open at a static pressure level of about 37 bar(a).

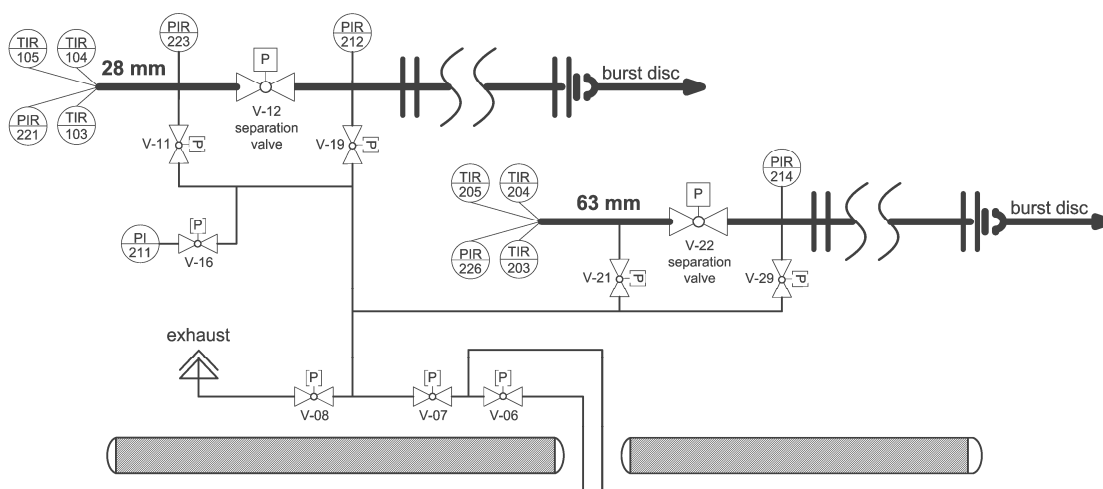


Figure 1: Experimental setup showing two compression pipes with different inner diameters. left: receiving pipe, right: donor pipe separated by a high-speed ball valve

The pipes including valves and instrumentation are equipped with a heating device. Temperature controllers keep the initial temperature between 30 to 40 °C. The right section of each pipe contains air or TFE at relatively high pressure and is therefore called the donor. A compressor from Maximator type DLE 30 and a vacuum pump from Edwards type E2M18 are used to adjust for the initial conditions. The left section is called the receiving pipe and always contains air at a low pressure, i.e. atmospheric to vacuum pressure representing the situation one could find in a production plant after some maintenance work. During opening of the high-speed ball valve, the receiving pipe receives either air or TFE from the donor pipe. Receiving sections of different lengths and shapes could be mounted. This included an elbow, a strainer and other flow restrictions (orifice plates).

Valve opening is fast but still takes some time. Limit switches are used to determine the integral opening times of the valves. The separation valve of the smaller pipe V-12 is capable to open within approximately 0.1 s while the separation valve of the bigger pipe V-22 has an opening time of at least 0.4 s. The valves are capable to apply extended opening times as well. Even fast valve opening procedures hardly result in ideal adiabatic compressions but mimic worst-case scenarios that have already led to incidents in production plants. Depending on the initial conditions the resulting compression temperature can come close to the adiabatic case. Aiming at the simplification of the description, the situation commonly is called adiabatic compression. Compression can be fast enough to produce a high temperature increase in the gas phase. This may lead directly to a TFE decomposition or may cause other reactions to occur such as dimerization which may after some time cause a decomposition. In these experiments, a delay of a few seconds was common.

The measurement of the dynamic temperature of the gas phase during the compression process is done using open junction thermocouples of $d = 160$ μm diameter, Type K, IEC 584 class 1. Due to their low response time the temperature record is slightly below the true gas phase temperature. Due to the missing electromagnetic insulation at the measurement tip a variety of noise signals are observed. The tips of the thermocouples are positioned in approximately 10 to 20 mm from the end flange. Signal amplification is

performed using a J.E.T. amplifier Type Bedo SAM 146. Thus, peak temperatures measured are erroneous, of course, but they are used only for comparison of different initial conditions. The shortcomings of this type of measurement therefore are acceptable.

Dynamic pressure measurement is performed using piezoelectric pressure transducers from PCB Type 102 providing a measurement range from 0 to 140 MPa with a resonant frequency better than 250 kHz. An amplifier from PCB Type 481A02 is used for the signal conditioning. Static pressure measurement is performed using piezo resistive pressure transducers from Keller type PA 10 with a resonant frequency of 30 kHz and amplifiers from J.E.T. Type PMV100.

All signals are sent to A/D converters and recorded at a sampling rate of 200 kS/s using a data recorder from Yokogawa, Type ScopeCorder DL 750.

Tests were performed with different combinations of geometries and pressures in the receiving and donor sections. The compression temperature values were measured in many air-air tests. Thereafter TFE-air tests were performed to verify the critical temperatures.

Figure 2 depicts a modification made to the experimental setup. A pipe of 2 m length, warmed up and bent to become an approximately 90° elbow, was installed on the left side of the separation valve instead of the straight receiving pipe.

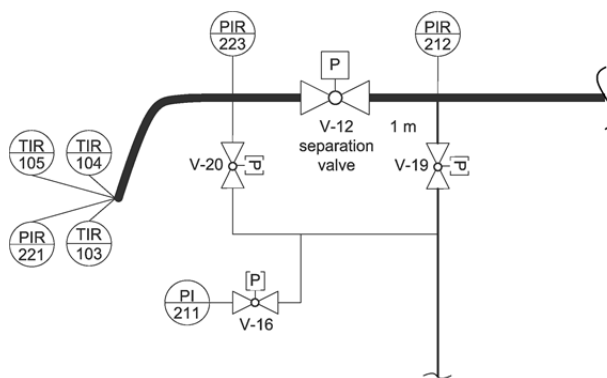


Figure 2: Experimental setup showing the elbow receiving section with an inner diameter of 28 mm and a bending radius of about 230 mm.

3. Results

Figure 3 depicts the hazard diagram based on the one already reported for 28 mm pipes by Kluge et al. (2016). The black line is based upon compression tests with TFE in the donor section of the 28 mm pipe. This data is reported by Ferrero et al. (2017) as 'warning line'. For this experimental set-up, above the line the initial conditions are expected to be safe, below the line, they are known to be hazardous.

The present contribution gives a comparison of hazardous conditions in different geometries. In a sequence of initial tests only air was filled in both pipe sections of a 63 mm pipe. The various grey shaded areas in Fig. 3 belong to those air-air tests with comparable compression temperatures reached. They are separated by grey lines belonging to identical compression temperatures (isotherms).

The test result of TFE after compression and reaction (if any) in the donor pipe can be categorised as listed; the symbols used for the list are the same ones that are used in Fig. 3:

- "safe situations", i.e. temperatures at the end flange are comparable to tests with an air-air system, or below. No reaction identified from the temperature record.
- ▲ "slow reaction", i.e. temperatures at the end flange are higher than in comparable air-air tests, partial reactions occur, oligomerisation, polymerisation and decomposition can lead to a contamination of the gas in the pipe. Soot could be produced from the decomposition reaction. The main reactions last for up to a minute but for this experimental setup, the burst disc stays intact. The region in the hazard diagram where slow reactions occur is a transition region (Ferrero et al., 2017).
- "ignition", i.e. decomposition reaction is initiated and propagates through the pipe. This is accompanied with high temperature rise ($T > 1000$ °C) at the end flange and a pressure increase sufficient to rupture the burst disc.

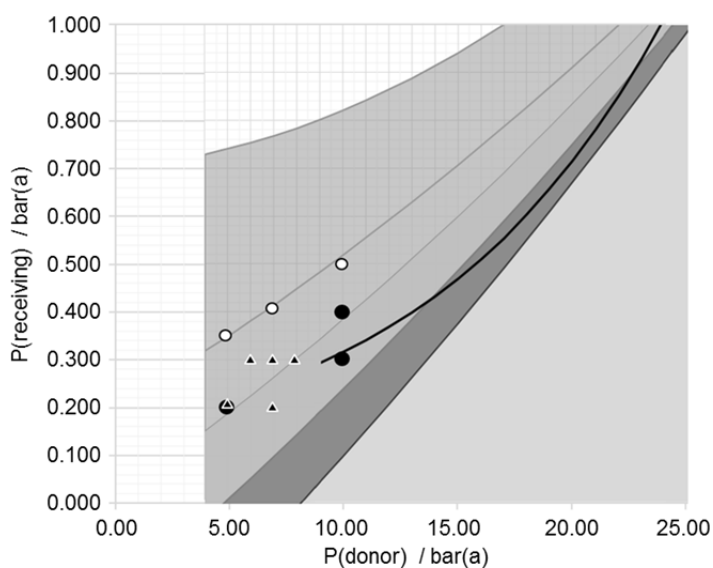


Figure 3: Hazard Diagram; comparison of results from straight pipes with an inner diameter of 28 mm (black line) and 63 mm (grey shaded areas and symbols).

Initial conditions of $P(\text{donor}) = 20.00 \text{ bar(a)}$ and $P(\text{receiving}) = 1.000 \text{ bar(a)}$, i.e. atmospheric pressure, according to the diagram depicted in Fig. 3 are believed to be safe starting conditions for these experimental setups. However, experience in TFE industrial facilities indicates that these conditions may have led to TFE decompositions (Ferrero et al., 2017). This starting point had been tested several times in the 28 mm straight pipe. It is located clearly above the black line. In the 63 mm pipe there is no validated experimental proof that this is safe, but the point characterising this condition is above the second isothermal compression temperature line with the white dots on it. Thus, no explosion is expected in the experiment, neither in case of the 28 mm pipe nor in the 63 mm pipe. In the modified experimental setup according to Fig. 2, the 28 mm pipe with the 90° elbow, these initial test conditions led to explosion with opening of the rupture disc. This more complicated geometry is closer to the reality of production facilities and supports the conclusions in some industrial accidents that these conditions lead to a decomposition.

If the decomposition reaction takes place in a slow reaction mode different observations are made. An irregular creepy noise could be recognized and a significant increase in the gas phase temperature ($> 700 \text{ }^\circ\text{C}$) and in the pressure record is observed. Figure 4 depicts the pressure-time-histories for a single experiment in the 63 mm pipe with a 2.65 m long straight receiving section. In this experimental run, the compression heat leads to a slow decomposition reaction lasting for several seconds. Within the time range from 0.404 to 0.850 s the valve turns from completely closed to fully opened state. Two pressure records are depicted. The sensor in end flange of the receiving section is PIR 226 (compare Fig.1). It starts with a zero line since the piezoelectric pressure sensor does not record the absolute pressure but the dynamic change of the pressure only. Artefactual signals below zero are caused by the reaction heating the sensor's surface. This influences its electrical charge. Pressure signal denoted as PIR 214 is from a piezo resistive pressure sensor and depicts the absolute pressure in the donor pipe. This sensor is not placed side on. Shortly after the opening of the valve has started the pressure drops down when the gas flows from the donor to the receiving section.

After the test is completed the pipe is filled with soot.

From Fig. 4 it can be identified that there is:

- a 50 Hz noise disturbs the pressure signal, probably this is caused by the power supplies of the electric heating of the pipe,
- a regular oscillation (see Fig. 4, within the time range from 8 to 14 s), since the acoustic shock travels from one end of the pipe to the other,
- an irregular oscillation is present (most pronounced within the time range from 4 to 8 s), that is induced by the decomposition reaction taking place.

From the Fourier transformation power spectrum significant frequencies could be derived. Peak values from the power spectrum corresponding to the pressure record depicted in Fig. 4 are listed in Table 1.

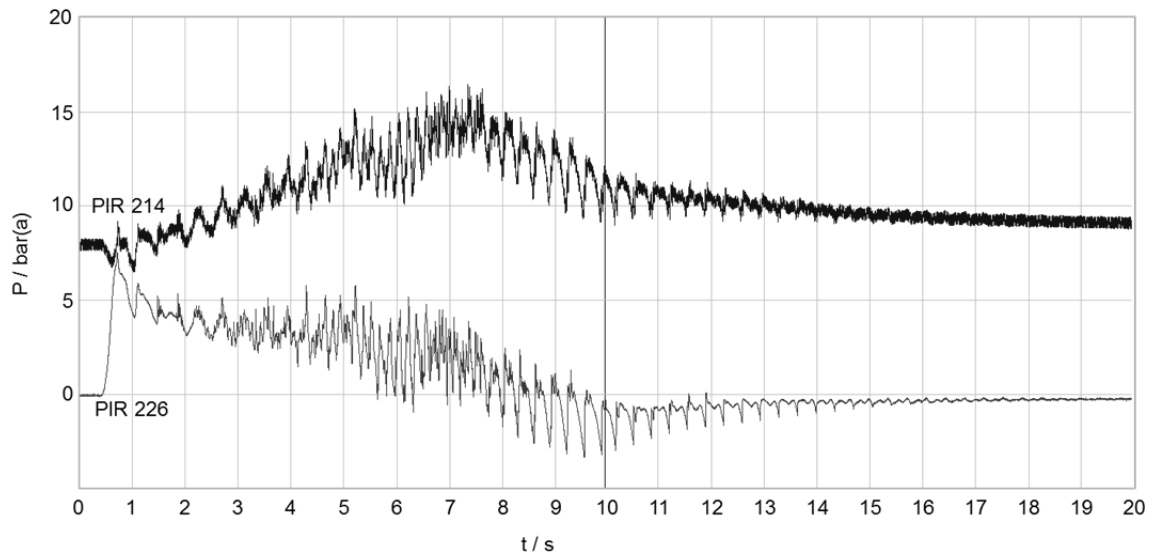


Figure 4: Pressure-time-history, initial conditions: $P(\text{donor}) = 8.00 \text{ bar(a)}$ and $P(\text{receiving}) = 0.300 \text{ bar(a)}$.

Table 1: Results from the Fourier transformation power spectrum analysis, intensity values / 10^3

f / Hz	PIR 214	PIR 226
2.4	67.6	26.3
2.6	60.0	
3.0	48.9	
3.2		13.9
3.4	33.4	
5.6	56.9	
5.8		80.0
6.0	45.0	95.0
6.2	65.8	101.0
6.4	46.9	
6.8		27.5
8.2	14.4	11.3
15.0	4.5	
50	17.6	
3547	1.56	

4. Conclusions

There is a remarkable difference in the hazard diagram for the safe region of pipes of different diameter. As the surface to volume ratio decreases heat transfer becomes smaller at the same time when the total amount of energy released as compression heat is increased. This leads to higher compression temperatures and the gas remains at higher temperatures for a longer time than in the smaller pipes. Figure 3 allows a direct comparison of the diameter influence.

For the elbow test the situation was different. As the valve opens TFE flows through the elbow filled with air. As the pipe is not straight, more turbulence is generated as the gas flows through the pipe elbow compared to a straight pipe. The consequences of the turbulence should be considered. Firstly, the turbulence acts as a flow restrictor and thus the fluid velocity will be at a slightly slower speed, so the process will be less adiabatic enabling more time for the heat exchange with the walls to take place and thus a lower compression gas temperature will be reached. On the other hand, the turbulence serves for a better mixing of the two gas volumes. When compressing air, this is likely to make the oxidation reaction of TFE another significant pre-reaction to TFE decomposition. Downstream the turbulence inducing installation the mixture is being further compressed. Such a mixture is much more sensitive to compression temperature and thus the decomposition reaction is triggered.

Mild polymerization stabilisation chemicals like alpha-pinene are effective in reducing the unwanted polymerisation but are totally ineffective at stopping a TFE decomposition once initiated. Alpha-pinene is a 'radical scavenger'; this means it can react with an oxygen radical to stop it from initiating polymerisation or more commonly stop the continuing polymerisation of low molecular weight PTFE polymer by removing the reactive radical on the polymer. The radical is stabilised on the alpha-pinene molecule as shown in Fig. 5.

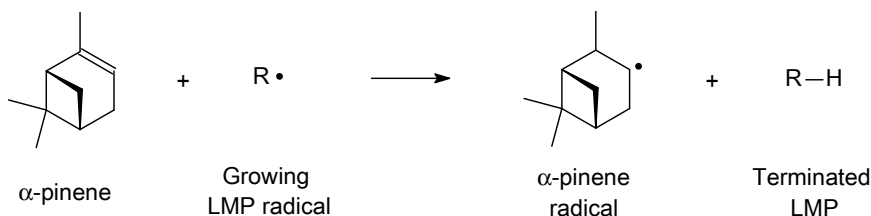


Figure 5: Reaction of alpha-pinene with low molecular weight PTFE polymer (LMP).

In the present contribution initial conditions were investigated that were capable of leading to an explosive decomposition of stabilized TFE in two different tube diameters and in an elbow. It could be confirmed that under specific industrial conditions, compression heat can act as a source of an accident.

The already known "hazard diagram" (donor pressure over receiving pressure) was expanded to pipe diameters of 63 mm. Hazardous initial (pressure) condition(s) were studied.

It has been shown, that below a specific donor pressure no sharp transition between "safe" and "ignition" state exists. In the experiments reported with a donor pressure of 5 to 10 bar(a), a transition range exists, in which the gas system reacts slowly with a pressure generated not sufficient to rupture the burst disc. It could be seen that a self-propagating decomposition reaction can cause damage to pipes and instrumentations especially when it transitions into a detonation. A venting of a pipe system in the case of a deflagrative decomposition is most effective if the burst disc is in line with the propagating reaction. Venting perpendicular to the flow direction of the pipe can even lead to an acceleration of the decomposition reaction and is therefore less effective. Besides the self-propagating reaction, it could be observed that even reactions within the transition region of the hazard diagram might be hazardous, i.e. sometimes a slow reaction occurs, sometimes an ignition to explosion. For the slow reactions, the decomposition reaction can become so slow that the heat generated is insufficient to ignite the fresh TFE through the soot barrier. In this case, the flame is extinguished along the pipe and unreacted TFE remains. In other cases, all the TFE can decompose.

Acknowledgments

The support of this research project by PlasticsEurope TFE Safety Task Force is gratefully acknowledged. The authors also thank Sven Maurice Hyman for his assistance with the experimental explosion testing.

References

- BAM Federal Institute for Materials Research and Testing, 2005, Surface ignition of TFE and TFE-air mixtures, BAM research report, Berlin, Germany.
- Babenko Yul., Lisochkin YaA., Poznyak VI., 1993, Explosion of tetrafluoroethylene during nonisothermal polymerization. *Combustion Explosion and Shockwaves*, Vol 29, 603 – 609.
- Duus HC., 1955, Thermochemical studies on fluorocarbons, *Industrial and Engineering Chemistry*, Vol 47(7), 1445 – 1449.
- Ferrero F., Shenton MJ., Bellucci D., Spoomaker T., 2017, Guide for the Safe Handling of Tetrafluoroethylene, PlasticsEurope AISBL.
- Kluge M., 2012, Experimentelle Bestimmung und Modellierung von sicherheitstechnischen Eigenschaften der Zerfallsreaktion von Tetrafluorethen, PhD Thesis, BAM and TU Berlin, Germany.
- Kluge M., Kreißig M., Liebner C., Spoomaker T., 2016, Identifying hazardous conditions for rapid compression scenarios of chemically unstable gases in industrial scaled pipes, *Chemical Engineering Transactions*, Vol 48, 607 – 612.
- Lietze D., 2002, Zündung von Hochdruck-Acetylen durch adiabatische Verdichtung von Luft, *Chemie Ingenieur Technik*, Vol 74, 126 – 128.
- Meyer R., 2009, Untersuchung des Zündverhaltens des Tetrafluorethens (TFE) durch adiabatische Kompression, Thesis, BAM and TU Berlin, Germany.
- Reza A. Christiansen E., 2007, A case study of a TFE explosion in a PTFE manufacturing facility. *Process Safety Progress*, Vol 26(1), 77 – 82.