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# Identifying Hazardous Conditions for Rapid Compression Scenarios of Chemically Unstable Gases in Industrial Scaled Pipes

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The polymeric industry handles Tetrafluoroethylene (TFE) as basic material for polymer (PTFE) and co-polymer (PCTFE) production. As a chemically unstable gas, it can react in an explosive way, without the presence of any other gases. Once initiated such an exothermic reaction can propagate through the pipe system of a plant and might lead to massive damages and/or fatalities. Especially after maintenance parts of the pipe systems can be filled with TFE, nitrogen or air at pressures up to atmospheric conditions whereas connected parts of pipes might still contain TFE at operating pressure state. Many of the regarding pipes are separated by ball valves, which allow a fast opening procedure. Thereby fast compression of the gas can occur and lead to a massive temperature increase which might induce unwanted reactions. Former tests in laboratory scale described by Meyer (2009) allowed an ignition of a TFE/air system by rapid compression only for a set of sharp defined boundary conditions. First tests in the lower industrial scale were done by Ferrero et al. (2013), where an ignition at typical industrial operating conditions was initiated. The results of the tests indicated that the critical achievable compression temperatures strongly depend on the setup and therefore on the pipe diameter as well. Therefore the necessity of further tests has been pointed out. The original setup presented by Ferrero (2013), which represents the smallest typical industrial size with an inner diameter of 1.125", was modified to withstand an explosive decomposition reaction and to avoid a deflagration to detonation transition. Different safety concepts as burst discs and time controlled cut-off valves had been tested and evaluated to optimize the experimental setup for reproducible test conditions. This allowed the systematic investigation of the rapid compression of TFE–systems for the first time in the described scale without serious damages after an ignition. In the donor pipe always TFE at high pressure and in the receiving pipe TFE, nitrogen or air were present at an absolute pressure ranging from 500 Pa to atmospheric pressure.
The scope was to generate a "hazard diagram" in which the ignition probability in dependence of donor (high) pressure and the receiving (low) pressure is shown. Hazardous conditions can easily be determined. A reference method for the maximum achievable temperatures of non-reacting gas systems was created using an air/air-system. Thus reactive TFE-systems could be evaluated regarding additional exothermic effects. The final hazard diagram demonstrates that there is no sharp limit between a "safe" state and an "ignition" for a TFE/air-system. Rather a transition range exists, which decreases with rising donor pressure. An increased temperature in this range, sometimes combined with small pressure peaks in the profile, indicates first partial restricted reactions near the end flange. The more it gets closer to the "ignition" transition the more traces like soot or undefined solid fractions were found. A TFE/nitrogen- and a TFE/TFE-system could not be ignited at all. A description of the experimental tests as well as a detailed explanation of the hazard diagram will be presented.

## 1. Introduction

One of the main causes of accidents in chemical plants processing tetrafloroethylene (TFE) is rapid compression (Reza and Christiansen, 2007). TFE belongs to the small group of decomposable gases. These gases can react in an explosive way even without the presence of any oxidator. Therefore handling of TFE requires high demands on the process industry especially regarding safety issues.

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Local heating of TFE can lead to a decomposition reaction as described by Kluge (2012). Here TFE decays into tetrafluoromethane and carbon black. The regarding reaction equation is shown in Eq. (1) showing the high possible energy release (Duus, 1955) which once triggered can proceed as a self-propagating reacting. Especially in pipes and large volumes at elevated conditions of pressure and/or temperature this can lead to heavy damages of equipment, instrumentations and machineries up to the complete destruction of TFE containing pipes and vessels. One open question was whether a rapid compression can initiate such a reaction.

$$C_2F_4 \Rightarrow CF_4 + C \qquad \Delta H_R = -257 \text{ kJ/mol} \qquad \text{Eq. (1)}$$

Besides the decomposition reaction, a dimerization reaction forming octafluorocyclobutane (OFCB) out of two TFE molecules can already start from temperatures of about 200 °C, according to Eq. (2). Due to the second order characteristic of the reaction order the reaction rate increases with increasing pressure and temperature (Lacher et al., 1952; Babenko et al., 1993).

$$C_2F_4 \Leftrightarrow 0.5\ c - C_4F_8 \qquad \Delta H_R = -103 \text{ kJ/mol} \qquad \text{Eq. (2)}$$

Just as the decomposition reaction the dimerization reaction is also exothermal and can act as a promoter of the explosive decomposition due to the heat generated.
A possible scenario susceptible to ignition of TFE due to rapid compression is depicted in **Errore. L'origine riferimento non è stata trovata.**. There two sections of a pipeline are shown which are separated by a ball valve. The left section contains TFE at high pressure (HP), while in the right section a gas at low pressure (LP) is present. This gas could be either TFE (process gas) or nitrogen (purge gas) at very low pressure after an evacuation process or even air at pressures up to 1 bar absolute, due to leakages in the low pressure pipe or after maintenance or repair procedures. When now rapidly open the connecting valve a pressure discontinuity is formed generating a shock wave which compresses and thereby heats the gas present in the low pressure section almost instantaneously. At the end of the low pressure section, which can be represented by a closed valve for example, the shock wave will be reflected which might generated a further increase in pressure and temperature. Thus would be the behavior in an ideal theoretical case.
Even if the opening process of the high speed valve (HSV) is very fast it is not a really adiabatic compression but rather a rapid compression. Nevertheless the compression process is still sufficient fast enough to produce a high temperature increase which can initiate the dimerization and the decomposition reactions of TFE under certain initial conditions.

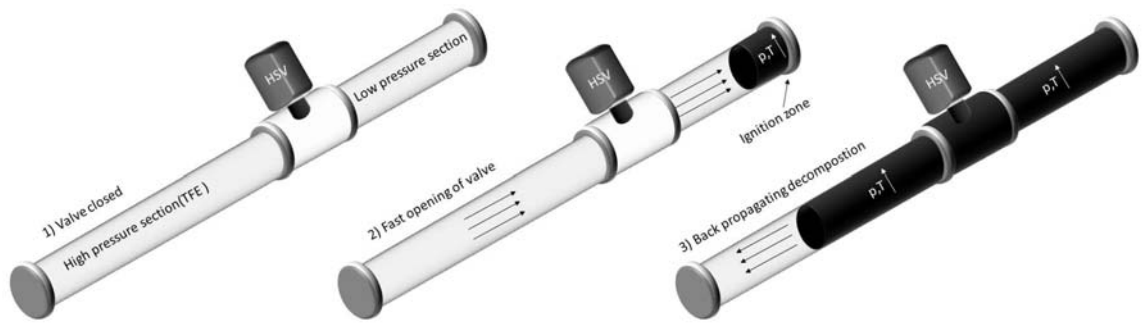


*Figure 1 Ignition scenario in TFE containing pipe sections*

For more detailed information about basics of the shock wave theory it is referred to Lamnaouer and McMillan, (2004). In practice the described scenario of can occur during start-up procedures or after repair or maintenance works and is therefore of high technical interest. While shock pressure scenarios for other decomposable gases as for example acetylene have been already investigated experimentally (Lietze, 2002), no literature was found so far on tests dealing with the ignition of TFE induced by rapid or adiabatic compression.
Within the framework of a research project funded by the Association of Plastic Manufacturers in Europe (PlasticEurope), an experimental study was performed with the aim of better understanding the hazardous conditions required for the occurrence of TFE ignition caused by rapid compression processes.

Therefore several different parameters were varied during the experimental tests, namely volume and geometry of the high pressure section as well as the length of the low pressure section and the initial pressure ratio between the sections.
Furthermore, numerical simulations with FEM and FVM based CFD-models for the rapid and adiabatic compression processes were performed, in order to support the experimental findings. A comprehensive model description and the extensive results will be presented in a separate publication.
The data base produces by the current research activities will lead to a better understanding of possible hazardous conditions for rapid compression scenarios which might lead to an unwanted initiation of the decomposition reaction of TFE in industrial plants. Thus the results will directly help to increase the safety of such TFE processing facilities.

## 2. Experimental Setup

All the tests regarding the rapid compression investigation were performed on the BAM Test Site Technical Safety (TTS). The setup was installed on a special test ground surrounded by a protective barrier and was remote controlled from a separate control room (“control zone”). The present setup within the barrier (“hazard zone”) is depicted in Figure 2. It is subdivided in a high pressure part (HP or donor pipe) and a low pressure part (LP or receiving pipe), both connected by a high speed ball valve (HSV), which internal diameter is equal to the pipes.

### 2.1 Testing site – hazard zone

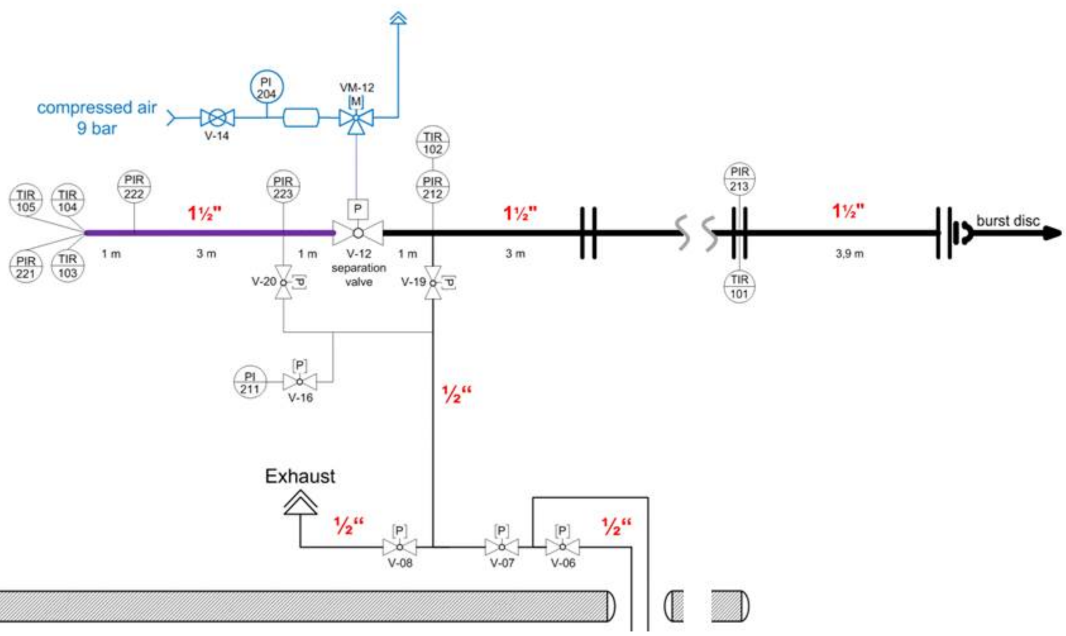


*Figure 2: Experimental setup – left: receiving pipe (5 m), right: donor pipe (22 m) connected by a high speed ball valve (HSV) – V-12*

The high pressure part consists of a 19-m-BASF pipe with a pressure resistance up to PN 325 bar and an inner diameter of d = 3 cm. The complete length of 19 m consists of 5 sections connected by bolted joints and a lens gasket. At one end a burst disk was installed with venting in flow direction. The burst disk consists of an 88-µm-brass-foil (CuSn), which is clamped between lens gasket and last flange.
An additional thermocouple and pressure transducer near the burst disc were installed for monitoring the initial conditions. The opposite end of the BASF-pipe was adapted to a 4-m-Swagelok-pipe (d = 1.125”). The high and low pressure sections could be separately evacuated, purged and filled. The high speed ball valve (Swagelok 67 series) had an equivalent inner diameter as the Swagelok pipes, for a non-restricted flow regime at opened state. The ball valve is powered by an electro-pneumatic actuator. The air supply is switched by an electromagnetic valve (VM-12, Figure 2) triggering the electronic measurement recording. An additional buffering vessel was installed near the actuator, to reduce the opening time. An inductive limit switch was used to determine the time for the opening process. With approximate 10 bara compressed air supply an opening time between 100 ms to 110 ms could be archived. In industrial plants high pressure shut-off devices

are switched with minimum opening times, to avoid rapid compression phenomena. The present justification hence simulates a “worst case scenario” for opening procedure, which can also be possible at manual operation procedures of a ball valve.

The low pressure part (LP or receiving section), in Figure 2 left side, consists of a 5-m-Swagelok pipes (d = 1.125”) and a special constructed end flange. The pipe is sectional constructed and allows variable LP length. In the pipe connectors a piezoelectric pressure transducer is fitted nearly flush with the inner wall. The end flange was equipped with a piezoelectric pressure transducer (end surface) and three thermocouples. Up to three piezoelectric pressure transducers were installed in the receiving section along the pipe for recording the propagating compression wave. Thereby conclusions to the wave speed and applicability of theoretical approaches (shock wave theory) were possible.

The end flange, depicted in Figure 3, has an inner length of 0.1 m. The 1-mm-thermocouples measuring the compression temperature were modified by stripping the first 7 mm leaving only the two welded wire endings with a diameter of d = 160 µm. Thus the thermal inertia could be reduced. Tests concerning the response characteristics of uncoated thermocouples were made by Meyer (2009). The tips of the thermocouples are positioned in the pipe middle axis, in distances of 10, 20 and 30 mm from the end surface. By using this design it was also possible to identify the hottest region within the compression zone.

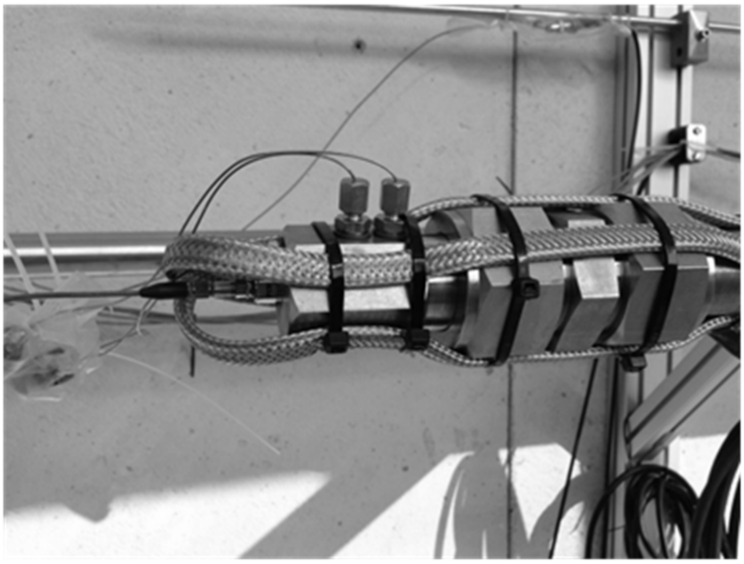

*Figure 3 special constructed end flange with one piezoelectric pressure transducer (end surface) and three thermocouples in distance of 10 mm, 20 mm and 30 mm from the end surface*

The setup can be heated by 8 separate heating cycles to perform tests at elevated temperatures and avoid condensing TFE at elevated pressure. All remote controlled valves are powered by compressed air.

### 2.2 Control zone

In the control zone the gas supply units (compressed air, TFE, Nitrogen), compressor (Maximator), vacuum pump and measurement instrumentation are positioned. Also the pipes in the “control zone” were heat able. In the inlet pipe system analog pressure indicators are installed to monitor system pressure conditions for over pressure (steady connection) and under pressure (manually connectable). The ball valves for connecting the vacuum pump and a by-pass valve for flushing the setup with compressed air are manually. The initial test conditions based on industrial operation parameters, thereby the LP-section related to practice mainly between 0.01 bara and 1 bara and HP-section up to 30 bara.

The described setup is the final construction design resulting out of an intense modification process. With the setup several tests with a 5-m-receiving pipe and a 0.1-m-receiving pipe were performed.

## 3. Experimental procedure for TFE (HP) and air (LP) in a 5 m receiving pipe

After leak tightness was ensured the setup was heated up homogenously. The setup was evacuated with the HSV opened, otherwise air could store in the enclosed bore of the ball. For filling the LP-section up to the initial test pressure (air) the HSV was closed and the LP-inlet was used. Afterwards the HP-section was filled with TFE using the Maximator compressor. After preparing the HP-section the inlet pipes were evacuated and all valves were closed. After the gas was homogeneously heated the test starts by opening the HSV. Recorded parameters were:

- 3 temperatures from thermocouples in the end flange (t = 4 s at 10 kHz)
- Up to 3 piezo-electric pressure transducer signals (t = 1 s at 500 kHz)
- Opening time of high speed ball valve (t = 4 s at 10 kHz)

Test results can be:

- "safe" - temperatures in the end flange are comparable to tests with an air/air system, or below.
- "pre-reaction" - temperatures in the end flange are higher than in comparable air/air tests, partial restricted reaction, probable contamination in the pipe
- "ignition" - initiated decomposition reaction propagation through the pipe, accompanied with high temperature rise (T > 1000°C) in the end flange, leading to a burst disk rupture

In case of no reaction ("safe") the HSV (V-12) was closed and the receiving pipe was vented, flushed with compressed air several times, evacuated and refilled to initial low pressure. Now the HP-section was re-pressurized with TFE. The inlet pipes were evacuated and the next test could be performed. In tests with LP length of 0.1m the complete setup has to be discharged, evacuated and filled again.

For induced self-propagating decomposition reaction ("ignition") the burst disk was ruptured and the setup got vented this way. In case of no rupture ("pre-reaction"), pipes were vented through the exhaust. Because the decomposition reaction of TFE is attended by soot production, the setup has to be cleaned by compressed air flushing. The end flange was removed and flushed with compressed air several times and mechanically cleaned as well. The setup was reconstructed, re-heated and leak tightness had to be ensured.

## 4. Results

The first aim of the study was to induce a decomposition reaction of TFE by a rapid compression at industrial conditions. At first a large number of pre-tests with an air/air system and different setup configurations and initial conditions were performed. This data base was used to validate the setup and subsequently to classify results of TFE/air-tests regarding reactivity. In the pre-tests a dependency of the compression temperature from the equilibrium pressure was determined. The tests with a TFE/air system were performed with a 5-m-receiving-pipe at initial temperature of $T_i$ = 35 °C and different pressure levels (HP and LP). The result of each determined pressure condition was plotted in a diagram. A "hazard diagram" (Figure 4), valid only for the present setup, was created for the TFE/air system.

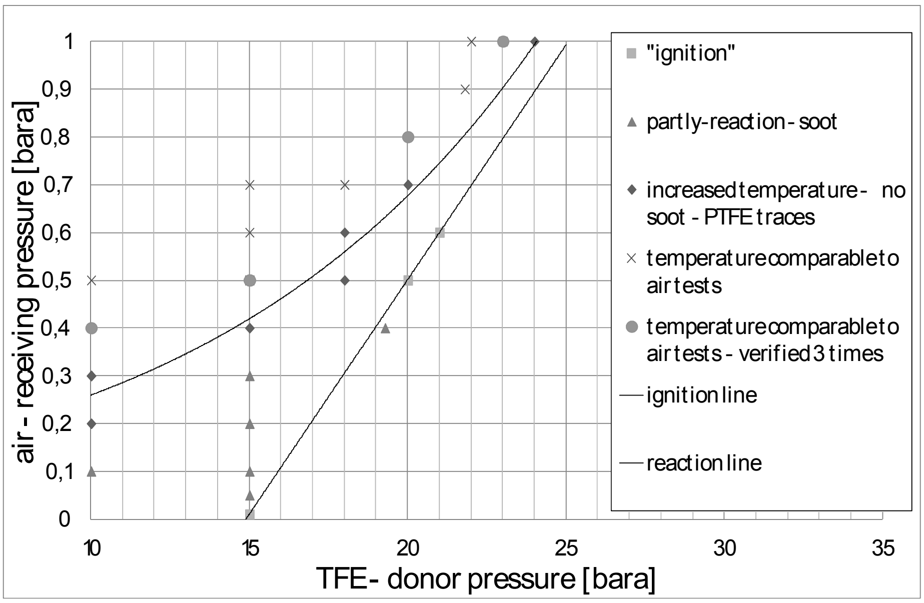


*Figure 4 : „Hazard diagram" for rapid compression processes of a TFE/air-system in a 5-m-receiving-pipe*

With increasing donor pressure the critical receiving pressure for "ignition" rises. In the "hazard diagram" Figure 4 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. In some tests the differential temperature was less than 50 K. The closer the tested pressure conditions shifts to those of the ”ignition line” the more obvious became the temperature peaks due to reactions.
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. For nitrogen and TFE as receiving gas no noticeable reaction could be initiated. Tests were performed at conditions, which leads to an “ignition” in the TFE/air system. In TFE/TFE and TFE/nitrogen tests no additional temperature rise in comparison to the air/air system appears. In tests with a 0.1 m receiving pipe no critical compression temperature with an air/air system in a practical relevant pressure range could be reached. In a single test with a TFE/air system ($T_i$ = 35 °C, $p_d$ = 26 bara and $p_l$ = 0.1 bara) a maximum compression temperature of Tc = 61°C was measured.

## 5. Conclusions

For the first time an explosion resistant setup at common industrial conditions was developed, in which a self-propagating decomposition reaction of TFE could be induced by a rapid compression. It could be confirmed that under specific industrial conditions a rapid compression can act as a source of an accident.
In the presented setup a systematic investigation with a 5-m-receiving pipe was done. As a main result a “hazard diagram” (donor pressure over receiving pressure) was created, in which hazardous (pressure) condition(s) can be visualized.
It has been shown, that below a specific donor pressure no sharp transition between “safe” and “ignition” state exists. With increasing donor pressure a transition range occurs, in which the gas system can partly react. 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. The decomposition reaction can be extinguished along the pipe. Damages inside the pipe can hardly be estimated from the outside than. 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.
The presented hazard diagram can be taken for a first approximation if hazardous conditions are possible for a specific pressure ratio within a plant-installation.
In gas systems without oxygen (TFE/nitrogen and TFE/TFE) reactions could not be initiated within the investigated pressure (and temperature) range and the presented setup.

### References

BAM Federal Institute for Materials Research and Testing. 2005, Surface ignition of TFE and TFE-air mixtures. Research report

Babenko YuI. Lisochkin YaA. Poznyak VI., 1993, Explosion of tetrafluoroethylene during nonisothermal polymerization. Combust Explo Shock+; 29:603-9.

Duus HC., 1955, Thermochemical studies on fluorocarbons. Ind Eng Chem; 47(7):1445-9.

Ferrero, F. ; Meyer, R.;,Beckmann-Kluge, M., Schröder, V.; Spoormaker, T.; 2013, Journal of Loss Prevention in the Process Industries, Volume 26, Issue 1, Pages 177–185

Kluge, M, 2012, PhD Thesis, Experimentelle Bestimmung und Modellierung von sicherheitstechnischen Eigenschaften der Zerfallsreaktion von Tetrafluorethen, TU Berlin, Germany

Lietze D., 2002, Zündung von Hochdruck-Acetylen durch adiabatische Verdichtung von Luft. Chem Ing Tech; 74:126-8 (in German).

Meyer R., 2009, Untersuchung des Zündverhaltens des Tetrafluorethens (TFE) durch adiabatische Kompression. Thesis. BAM Federal Institute for Materials Research and Testing. Berlin. Germany

Reza A. Christiansen E., 2007, A case study of a TFE explosion in a PTFE manufacturing facility. Process Saf Prog 2007;26(1):77-82.