The Explosive Decomposition of Tetrafluoroethylene: Large Scale Tests and Simulations

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There is a lack of data on the self-ignition behaviour of tetrafluoroethylene (TFE) in industrial sized equipment. In order to assess the tendency of TFE for decomposition in large scale vessels, , a facility was designed and constructed. Tests were carried out in a cylindrical reactor with a volume of 100 L with initial pressures of 5 and 10 bar(a). The effect of the reactor adjustment (vertical or horizontal) was taken into account. The current work describes the test setup and summarizes the experimental results achieved. Furthermore, this paper reports on a numerical model for the prediction of the self-heating of TFE in closed vessels, which was previously developed for small scale reactors and has been here validated for larger dimensions with the experiments performed in the new facility.

1. Introduction

Tetrafluoroethylene (TFE, chemical formula C_2F_4) finds its main industrial application in the production of polytetrafluoroethylene, better known as Teflon® (brand name by DuPont). The process leading to the formation of polytetrafluoroethylene is usually a liquid-phase polymerisation, performed in heated large reactors under relative high pressures, with a free gas phase mainly composed of TFE above the liquid. Unfortunately, wrong combinations of temperatures and pressures may lead to undesired effects. In fact already from temperatures of about 200 °C TFE starts an exothermic dimerization forming octafluorocyclobutane (OFCB); the higher the pressure and/or temperature the faster the reaction and the more heat is released. Under certain circumstances the energy released can heat up the gas phase to a temperature at which TFE decomposes in carbon black (soot) and tetrafluoromethane. The decomposition, once triggered, runs explosively and can result in the vessel rupture with consequent economical and eventually human losses.

It is therefore extremely important to assess the conditions necessary for the occurrence of TFE decomposition in large scale reactors. For this scope a new facility was designed and realized: the core of the setup is a stainless steel pressure resistant vessel of 100 L in volume. This reactor was used for the determination of the so-called Minimum Temperature of Decomposition (MITD), defined as the lowest temperature of a hot surface, e.g. the vessel walls, at which self ignition for the decomposition of a chemically unstable gas like TFE occurs without the presence of an oxidizer 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 (DIN EN 14522, 2005 or ASTM E 659-78, 2005).Tests with initial pressures of 5 and 10 bar(a) were performed and the effect of the position of the vessel (vertical or horizontal) was analyzed.

Furthermore, a mathematical model to predict the self-heating process of TFE previously developed (see Beckmann-Kluge et al., 2008 and Beckmann-Kluge et al., 2010) was here validated for large scale reactors against the data collected. The model was designed and solved in COMSOL Multiphysics® and includes a scheme of seven reactions. The simulations could reproduce satisfactorily the experimentally determined MITD. Therefore the model is suitable for assessing the self-heating behaviour of TFE in industrial sized plants and can be extrapolated to other scenarios.

The current paper gives a short description of the experimental setup, then summarises the test results and finally gives an overview of the performed simulations.

2. Experimental facility

The core of the facility was a cylindrical stainless steel vessel with a volume of 100 L and a pressure resistance of 345 bar(a) at ambient temperature. The vessel was mounted on a special support, which allowed for a complete 360° rotation (see Figure 1). Therefore, the reactor could be positioned horizontally as well as vertically and the effect of the orientation on the MITD of TFE could be studied.
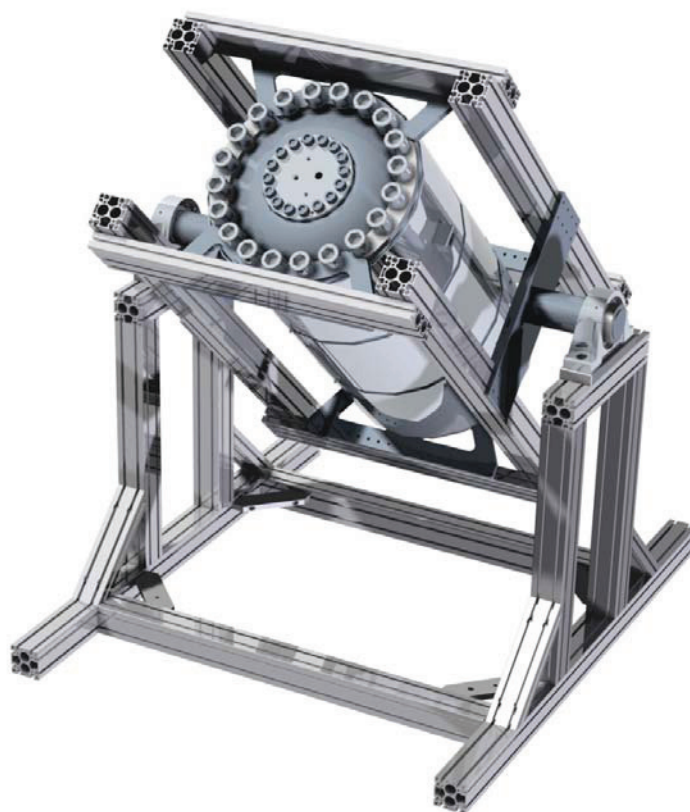

Figure 1: 3D-CAD view of the 100-L-vessel mounted on the support

In order to operate under safe conditions, tests were performed in an explosion bunker. Up to 12 TFE supply cylinders were located in an external bunker. The operating board as well as the gas supply was operated from a separate control room, where also the data acquisition system was located. Three 50-L-cylinders with a pressure resistance of 300 bar(a) were used to store TFE for the experiment, in order to achieve short filling times of the autoclave (under 40 s) and therefore minimize pre-reactions during the fill-up of the vessel. Furthermore, by using this intermediate storage the risk of a back ignition in the original supply cylinders was avoided. As a further safety measure a flame arrestor was inserted in the pipeline between the reactor and the cylinders for the intermediate storage. To achieve the required pressures for the filling of the intermediate storage cylinders, a compressed air-driven compressor (company: Maximator) was employed. A vacuum pump (company: Edwards) was used to partially or completely evacuate the facility, when required.

The reactor was brought to the desired temperature by means of three heating jackets. The temperature was recorded by one platinum resistance thermometer Pt-100 for each heating jacket and regulated by means of a self-made controller. The temperature inside the reactor was measured by three 1.5-mm-NiCr/NiAl-thermocouples (K type). Piezoresistive transducers (company Keller, type PA-10) were used to measure the pressure in the reactor, in the intermediate storage cylinders, in the flame arrestor and in the pipeline between the gas supply cylinders and the compressor. The temperature and pressure signals were sent to an A/D-converter (company Jet Systemtechnik GmbH, type MCL-USB, 16 channels 12 Bit A/D, overall sampling rate 500 kHz), so that the signals could be checked in real-time and stored as digital data.

After a successful leak test of the system, the intermediate storage cylinders were brought to the pressure required for the filling of the reactor by means of the compressor. Once the reactor had reached the desired temperature, the data acquisition was started and TFE was let from the storage cylinders over to the autoclave through the flame arrestor. After the 100-L-vessel was filled at the test pressure, the supply valves were closed and the flame arrestor was then discharged to atmospheric pressure (for protection of the buffer vessel from back reaction). The temperature and pressure curves in the vessel were real-time checked and the criterion for the onset of the decomposition was the appearance of temperature and pressure peaks in the reactor within 30 minutes. In order to determine the MITD of TFE for a defined initial pressure, the reactor wall temperature was varied in ±10 K steps, as to find the lowest temperature at which an ignition occurred. It was mandatory to validate a non-ignition with three tests with the same wall temperature. More detailed information on the experimental facility and methods is given in Ferrero et al. (2012b).

3. Mathematical Model

The mathematical model for the prediction of the self-heating process of TFE in closed vessel was developed and solved with the COMSOL Multiphysics® and has been described in detail in Beckmann-Kluge et al., 2008 and Beckmann-Kluge et al., 2010, to which we refer for better understanding. The original model was developed for small scale reactors and is here validated against the experimental data collected in the 100-L-vessel. The model solved three application modes of the *Chemical Engineering Module* of COMSOL Multiphysics®:

- the non-isothermal flow mode was used to describe the free convection caused by the volume forces generated by different densities due to the exothermic dimerization reaction. This model solved the impulse equation and the corresponding continuity equation;

- the convection and conduction mode was used to model the heat transfer resulting from the extended reaction net. Beside the exothermic dimerization reaction of TFE into OFCB and the endothermic back reaction, five additional reactions were considered, as shown in Figure 2. The dimerization reaction is main responsible for the initial self-heating of TFE and has to experience a runaway, in order for decomposition reaction to be triggered. Due to lacking kinetic data, the decomposition itself is not included in the model, but this is not necessary to assess if the system will undergo an ignition;

- the convection and diffusion mode was used to model the mass balance by linking the reaction kinetics.
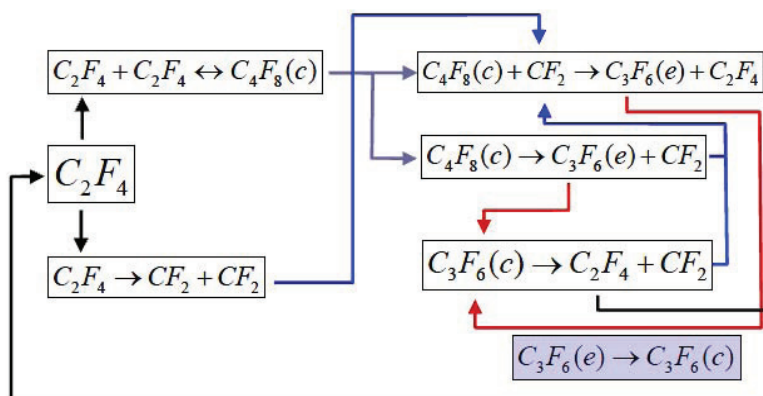

Figure 2: extended reaction net, based on the work of Bauer and Javanovic (1998)

The axial symmetry of the 100-L-autoclave made it possible to perform 2D computations to reduce computing time. After an extensive study of the mesh influence on the model outputs, fine triangular elements were chosen for a total degree of freedom of 150123.

4. Results and discussion

4.1 Test results

During the filling of the reactor with TFE the thermocouples registered lower values than the wall temperature, due to the incoming of cold gas. Since the TFE supply to the vessel was stopped the moment the data acquisition system registered the set pressure, a higher amount of gas than required was filled. Therefore, considering the gas at the set temperature the real initial pressure in the autoclave would be actually higher than the set pressure. Since TFE behaves as in ideal gas at high temperatures, the ideal gas law was used to determine the real initial pressure. This led to real initial pressures of about 6 and 11 bar(a) for set pressures of 5 and 10 bar(a), respectively.

The typical signals recorded in a test without the onset of an ignition are presented in Figure 3a) (initial conditions: set pressure of 5 bar(a), real pressure 6.18 bar(a), temperature: 250 °C). The pressure first increased due to heating of the incoming cold gas, then dropped due to the reduction in the number of moles caused by the dimerisation of TFE into OFCB. The heat produced by the dimerisation was dispersed to the surrounding and therefore no ignition occurred. For higher wall temperatures the energy released by the dimerization exceeded the heat losses and the decomposition of TFE was initiated, as shown in Figure 3b). This picture refers to a test with a set pressure of 5 bar(a) and real pressure of 6.22 bar(a) with a wall temperature of 260 °C. Here the peaks in the temperature and pressure curves due to the exothermal release by the decomposition are clearly visible.

Table 1 presents the values of MITD of TFE collected during the current experimental campaign. The results show that the MITD of TFE decreases with increasing initial pressure, in agreement with previous lab scale tests (BAM, 2005; Beckmann-Kluge et al., 2010; Ferrero et al., 2012a). The data sets from the current and previous works have been used as input for to extrapolation to other vessel volumes/initial pressure according to the Semenov's simplified theory on spontaneous thermal ignition (see Glassmann, 1987). The results of the extrapolations are presented in Ferrero et al., 2012b.

For what concerns the effect of the reactor alignment, differences in the MITD of TFE of max. 20 K within the pressure range analysed were observed between the vertical and horizontal adjustment. Lower values of MITD were registered with the reactor in the vertical position, probably due to the formation on local hot spots near the vessel top caused by buoyancy of hot reaction gases, which can enhance the initiation of the decomposition. The effect of the reactor arrangement seems to decrease as the initial pressure increases and should be verified with further tests at higher initial pressure.
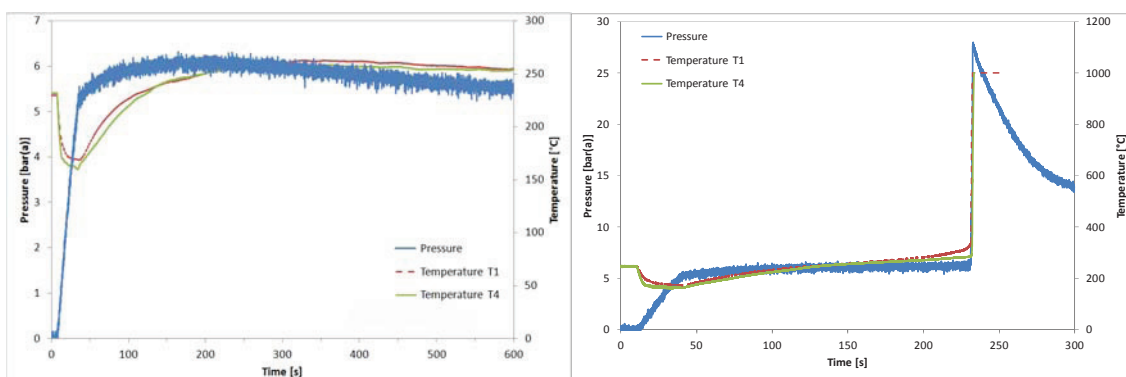

Figure 3: typical temperature and pressure curves in the performed tests: (a) left hand: real initial pressure 6.18 bar(a) and wall temperature of 250 °C (10 K under the MITD) (b) right hand: initial pressure 6.22 bar(a) and wall temperature of 260 °C (MITD). Vessel vertically orientated. Thermocouples: T1 at 10 cm from top cap on the symmetry axis; T4 on the symmetry axis at 1/3 from the bottom cap

Table 1: experimentally determined values of MITD of TFE in the 100-L-vessel

	Vertical Orientation		Horizontal Orientation	
Set pressure [bar(a)]	Real pressure [bar(a)]	MITD [°C]	Real pressure [bar(a)]	MITD [°C]
5	6.22	260	5.71	280
10	10.94	230	11.32	240

4.2 Simulation results

The computed gas temperature distribution at 65 seconds after the filling of TFE in the 100-L-vessel with an initial pressure of 5 bar(a) and wall temperature of 265 °C is presented in Figure 4. Here a local hot zone in the upper part of the reactor is clearly visible. According to this simulation the temperature and pressure of the system further increased with time, meaning the dimerization experienced a runaway and the system did undergo ignition. Computations with different wall temperatures and initial pressures have been performed and the correspondingly determined MITD's were compared with the data collected in the tests. Figure 5 shows the comparison of the experimental and computed MITD of TFE in the 100-L-vessel together with the predictions for a smaller reactor (volume: 3 L). The model shows a good agreement with the test results and is therefore been considered validated for both small and large scale reactors.
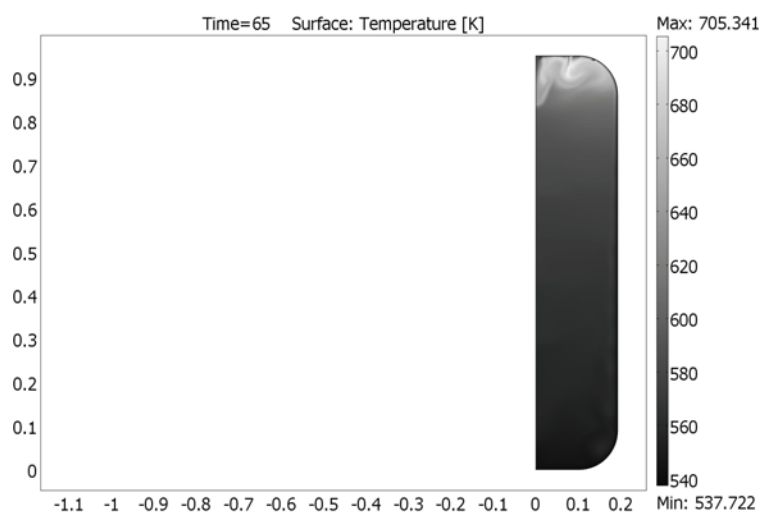

Figure 4: Temperature field in K in the 100-L-vessel after 65 s for an initial pressure of 5 bar(a) and a constant wall temperature of 265 °C (vessel vertically orientated)
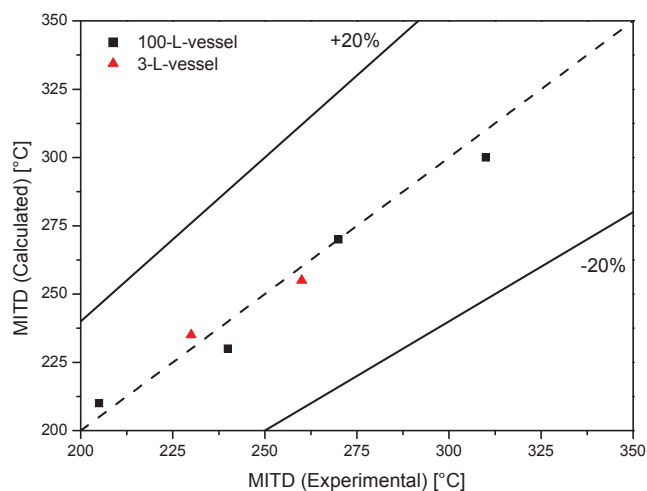

Figure 5: Accuracy of the MITD predictions

Conclusions

Tests for the determination of the Minimum Ignition Temperature of Decomposition (MITD) of tetrafluoroethylene (TFE) have been performed in a large scale reactor with a volume of 100 L. Experiments with initial set pressures of 5 and 10 bar(a) were carried out and the effect of the vessel orientation (vertical or horizontal) was analyzed. The experimental results in the large scale reactors confirmed that the MITD of TFE decreases with increasing initial pressure, as was observed in previous works with lab scale tests. For what concerns the effect of the vessel adjustment, lower MITDs were detected in the tests with a vertical orientation, probably due to the formation of a hot zone under the vessel top in the case of a vertical arrangement, where the dimerization reaction rate and therefore the tendency to ignition can be enhanced. The effect of the reactor arrangement seems to decrease with the initial pressure.

Numerical simulations of the self-heating process in the 100-L-vessel were performed, in order to validate a model previously developed by the authors for small scale reactors against large scale data. The computation of the temperature distribution in the vessel, allowed for the estimation of the MITD of TFE. A comparison between the performed simulations and the experimental results showed good agreement.

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