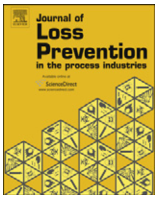
Journal of Loss Prevention in the Process Industries 25 (2012) 1010–1017

Contents lists available at SciVerse ScienceDirect

Journal of Loss Prevention in the Process Industries

journal homepage: www.elsevier.com/locate/jlp



Analysis of the self-heating process of tetrafluoroethylene in a 100-dm^3-reactor

Fabio Ferrero [a,*], Robert Zeps [a], Martin Beckmann-Kluge [a], Volkmar Schröder [a], Tom Spoormaker [b]

[a] *BAM Federal Institute for Materials Research and Testing, Unter den Eichen, 87, 12205 Berlin, Germany*
[b] *PlasticsEurope Fluoropolymers TFE Safety Task Force DuPont de Nemours (Nederland) B.V., Baanhoekweg 22, 3313 LA Dordrecht, The Netherlands*

ARTICLE INFO

Article history:
Received 27 April 2012
Received in revised form
4 June 2012
Accepted 4 June 2012

Keywords:
Tetrafluoroethylene
Decomposition
Self-ignition
Large-scale reactor

ABSTRACT

There is a lack of data on the self-ignition behaviour of tetrafluoroethylene in industrial sized equipment. Therefore, a facility was designed and constructed for the determination of the Minimum Ignition Temperature of Decomposition of tetrafluoroethylene in a cylindrical reactor with a volume of 100 dm^3. Tests with initial pressures of 5 and 10 bar(a) were performed. The Minimum Ignition Temperature of Decomposition of tetrafluoroethylene was observed to decrease with the initial pressure, in agreement with previous experiments with small scale cylindrical vessels. This paper describes the test set-up und gives an overview of the achieved experimental results. In particular the effect of the reactor orientation (vertical or horizontal) is discussed. Furthermore, simplified equations from the Semenov thermal explosion theory are used to attempt extrapolations of previous and current data on the Minimum Ignition Temperature of Decomposition of tetrafluoroethylene to other vessel volumes or initial pressures. Moreover, the experimental data are plotted together against the heated volume to heated surface ratio, which should provide a better extrapolation to other vessel dimensions by taking into account that the efficiency of the dispersion of the heat generated by the reaction is different for two reactors with the same volume but different diameter. Finally, simplified methods for predicting the Minimum Ignition Temperature of Decomposition of tetrafluoroethylene presented previously by the authors are validated for large scale reactors with the experimental data collected within the current work.

1. Introduction

The main industrial application of tetrafluoroethylene (TFE, chemical formula C_2F_4) is as monomer in the production of polytetrafluoroethylene (PTFE), sold under various brand names, like Teflon® resin by DuPont. The process leading to the formation of PTFE is a polymerisation, which normally occurs in large reactors as a liquid phase reaction. Under certain circumstances the gas phase -mainly composed of TFE- above the liquid may undergo a self-heating, which might turn into a runaway reaction leading to the decomposition of TFE into tetrafluoromethane and carbon black. This decomposition is strongly exothermal and may result in the vessel rupture with consequent economical and even human losses.

Equation (1) shows the dimerisation reaction: from temperatures of about 200 °C TFE is converted to octafluorocyclobutane (OFCB, chemical formula C_4F_8). The higher the pressure and/or temperature the faster OFCB is formed (Babenko, Lisochkin, & Poznyak, 1993; Lacher, Tompkin, & Park, 1952).

$$C_2F_4 \Leftrightarrow 0.5c - C_4F_8 \quad \Delta H_R = -103\,\text{kJ/mol} \tag{1}$$

During the industrial production of PTFE the equilibrium might be shifted in the forward direction, thus energy is released. This would generate the above-mentioned self-heating of TFE, producing local high temperatures, at which the decomposition to carbon black (soot) and tetrafluoromethane, described by equation (2), could occur. TFE decomposition has an explosive behaviour (Duus, 1955) and can therefore lead to serious accidents (Daikin Industries LTD., 2004; Reza & Christiansen, 2007).

$$C_2F_4 \Rightarrow CF_4 + C \quad \Delta H_R = -257\,\text{kJ/mol} \tag{2}$$

Gases like TFE, which can decompose without the presence of oxygen, are commonly called chemically unstable gases. One way to assess their hazards is by determining the so-called Minimum Ignition Temperature of Decomposition (MITD). This is 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

---

[*] Corresponding author. Tel.: +49 8104 3440; fax: +49 8104 1217.
E-mail address: fabio.ferrero@bam.de (F. Ferrero).

0950-4230/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jlp.2012.06.001

mixture of a flammable gas with air may register an ignition (ASTM E 659-78, 2005 or DIN EN 14522, 2005).

Previous works dealing with the self-ignition of TFE considered experiments at a laboratory scale (Babenko et al., 1993; BAM, 2005; Beckmann-Kluge, Schröder, & Acikalin, 2010; Ferrero, Beckmann-Kluge, Spoormaker, & Schröder, 2012). With the aim of understanding the conditions necessary for TFE decomposition in large scale reactors to occur, tests for the determination of the MITD were performed in a cylindrical vessel with a volume of 100 dm^3. Initial pressures of 5 and 10 bar(a) were analysed. Furthermore, the effect of the vertical or horizontal orientation of the reactor was studied.

The current paper describes the experimental set-up in detail and summarizes the achieved results. The collected data are discussed and compared with findings from previous works with laboratory scale equipment, in order to attempt extrapolations of the MITD of TFE to other test conditions (initial pressures or vessel dimensions). Furthermore, the two simplified approaches for predicting the MITD of TFE presented in a previous work (Ferrero et al., 2012) are validated for large scale reactors with the data collected here. The current paper assumes therefore extreme importance for scaling up the understandings on the self-ignition of TFE to a scale of practical interest.

2. Experimental facility and methods

Fig. 1 shows a schematic view of the experimental facility. The core of the facility is a cylindrical stainless steel vessel (material number 1.4571) with a volume of 100 dm^3 and a pressure resistance of 345 bar(a) at ambient temperature. Stainless steel is generally accepted for the determination of standard safety related characteristics of gases: on the influence of the vessel material on the ignition temperature it is discussed in Andrews, 2005. The dimensions of the reactor were calculated according to the methods proposed in DIN EN 13445-3 (2002) and VDI 2230 (2003) for unfired pressure vessels. In order to operate under safe conditions, tests were performed in an explosion bunker. Up to 12 TFE supply cylinder were located in an external bunker. The operating board as well as the gas supply was run from a separate control room, where also the data acquisition system was located.

The 100-dm^3-vessel was mounted on a special support, which allowed for a complete 360° rotation (see Fig. 2). Therefore, the reactor could be positioned horizontally as well as vertically and the effect of its orientation on the MITD of TFE could be studied. The support was mounted on wheels, so that it could be comfortably moved, when needed. A top view of the reactor can be seen in Fig. 3. For practical purposes a small lid was mounted on each side of the reactor on the corresponding main cap. These lids could be more easily removed for the cleaning of the vessel compared to the large reactors caps.

In order to achieve short filling times of the autoclave (under 40 s), three 50-dm^3-cylinders with a pressure resistance of 300 bar(a) were used to store TFE before the experiment (tank 1–3 in Fig. 1). This was necessary in order to minimize pre-reactions during the fill-up of the vessel. By using this intermediate storage the risk of a back ignition in the original supply cylinders was also avoided. As a further safety measure a flame arrestor was inserted in the pipeline between the reactor and the cylinders for the intermediate storage (see Fig. 1 for the location of the flame arrestor). The flame arrestor consists of a 0.6 m long tube, whose interior is filled with pipes of small diameter. Furthermore, the flame arrestor is equipped with two rupture discs, in order to release the pressure build-up, which originates during the decomposition of TFE. By this device, the possibility of a back reaction towards the intermediate storage is strongly reduced and

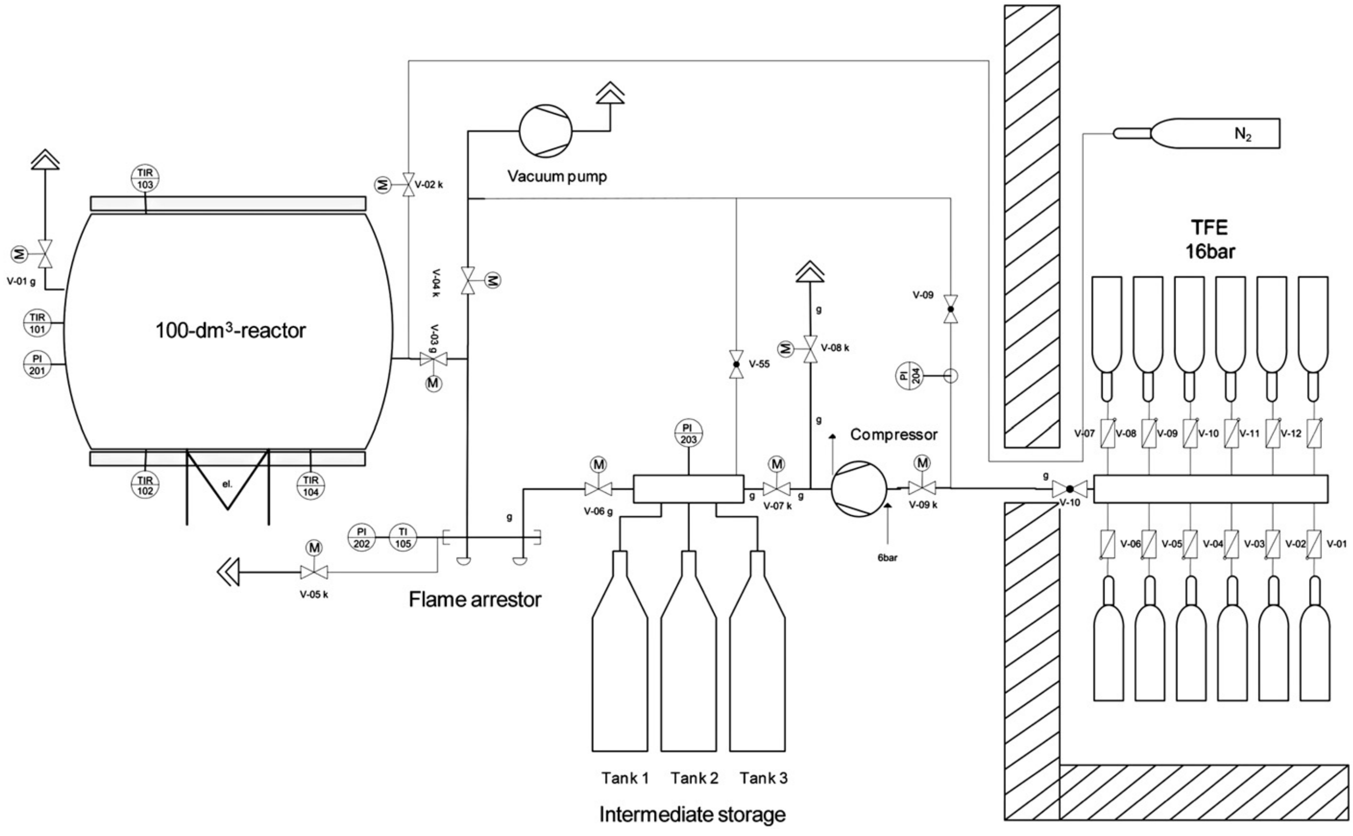


Fig. 1. Schematic view of the experimental facility.