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Study of the spontaneous ignition of stoichiometric tetrafluoroethylene–air mixtures at elevated pressures

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The Ignition Temperature (IT) of stoichiometric tetrafluoroethylene–air mixtures on hot walls was determined in a 3-dm^3-reactor. Tests at elevated pressure conditions were performed, namely at 5, 15 and 25 bar(a), showing a decrease of the IT with the initial pressure. Furthermore, the measured ignition temperatures of stoichiometric tetrafluoroethylene–air mixtures were lower than the ignition temperatures required for the decomposition pure tetrafluoroethylene (Minimum Ignition Temperature of Decomposition, MITD) reported in previous works.

Equations from the Semenov thermal explosion theory on spontaneous ignition were used to identify approximate combustion kinetics of tetrafluoroethylene from the experimental results. The determined kinetics was used for the prediction of the IT of stoichiometric tetrafluoroethylene-air by simplified calculation methods. A very good agreement with the experimental results was observed.

1. Introduction

Industrial plants processing tetrafluoroethylene (TFE) have to face with the hazardous properties of this gas. TFE is in fact a flammable gas, meaning it can build explosive atmospheres in mixture with air. The combustion reaction can be expressed as follows (Reza & Christiansen, 2007):

$$C_2F_4 + O_2 \Rightarrow 2COF_2 \quad \Delta H_R = -628 \mathrm{kJ/mol} \tag{1}$$

Furthermore, TFE is rated as a chemically unstable gas, since it can decompose into tetrafluoromethane and carbon black (soot) without the presence of an oxidizer. The explosive decomposition of TFE is reported in Eq. (2) (Duus, 1955).

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

Within the causes which could trigger one of the two shown explosive reactions we account for sparks, hot surfaces and adiabatic compression heat by premature polymerisation. Accidents involving TFE can lead to equipment/building damage, injuries and even casualties (Reza & Christiansen, 2007) and are therefore of extreme interest. The current study focuses on the spontaneous ignition induced by contact with hot surfaces. It is known (Babenko, Lisochkin, & Poznyak, 1993; Matula, 1968) that hot surfaces may promote the occurrence of the exothermic dimerization of TFE to form octafluorocyclobutane (OFCB), expressed by Eq. (3). TFE dimerization is noticeable from temperature of about 200 °C and the reaction rate is the higher the pressure and/or temperature (Babenko et al., 1993; Lacher, Tompkin, & Park, 1952).

$$C_2F_4 \Leftrightarrow 0.5c - C_4F_8 \quad \Delta H_R = -103 \mathrm{kJ/mol} \tag{3}$$

The TFE dimerization induced by hot surfaces can act as a pre-reaction which could finally turn into the explosive decomposition (Ferrero, Beckmann-Kluge, Spoormaker, & Schröder, 2012).

Up to now, the TFE combustion kinetics at elevated pressure is not known. Furthermore, it has not been yet systematically studied if, in presence of air, during the contact of TFE on hot surfaces, the dimerization reaction in Eq. (3) will be responsible for triggering the explosive decomposition in Eq. (2) or if the combustion reaction will be the predominant mechanism leading to ignition.

Therefore, ignition tests with stoichiometric TFE–air mixtures were performed in a small scale vessel (volume 3 dm^3) at elevated initial pressures, namely 5, 15 and 25 bar(a). Here the Ignition Temperature (IT) of the mixture was assessed. The IT is here defined as the lowest temperature of a hot surface, in this case the vessel walls, where the stoichiometric TFE–air mixture experiences an ignition. The IT resembles the standard Auto Ignition Temperature

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(AIT) 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 at atmospheric conditions (ASTM E 659-78, 2005; DIN EN 14522, 2005). Nonetheless, the IT used in the current work refers to a specific mixture under pressures which exceed standard conditions.

In order to assess the effect of the presence of air on the ignition behaviour, the ignition temperatures for the stoichiometric TFE–air mixture (IT) registered in the current experiments were compared to the ignition temperatures of pure TFE (MITD) from previous works (BAM, 2005; Beckmann-Kluge, Ferrero, Schröder, Acikalin, & Steinbach, 2010; Ferrero et al., 2012). Here the MITD is the Minimum Ignition Temperature of Decomposition, defined as the lowest temperature of a hot surface, in this case 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.

Furthermore, the experimental results achieved were used for the determination of simplified kinetics for the combustion of TFE in stoichiometric proportions with air at elevated pressure. The determined kinetics was then used in simplified calculation methods here developed for the predictions of the ignition temperatures of stoichiometric TFE–air (IT).

In the current paper the experimental setup and procedures employed are described. Thereafter, a short theoretical background on the calculation methods is given. Finally, the experimental results are discussed and compared with the predictions of the calculation methods employed.

2. Experimental setup and procedure

The tests were performed in a special bunker at the BAM Test Site Technical Safety in Horstwalde, about 60 km S from Berlin, Germany. Due to the high initial pressures required, standard methods (ASTM E 659-78, 2005; DIN EN 14522, 2005) could not be employed and a special setup was required. Fig. 1 shows a schematic drawing of the experimental facility. As to operate under safe conditions, tests were performed in an explosion bunker, which can withstand a 1.5 kg TNT detonation blast. The operating board as well as the gas supply was remotely operated from a barricaded room, where also the data acquisition system was located. The test substances (TFE and air) were stored in cylinders, which were located in a skeleton container placed in a separate bunker. TFE was in the stabilized form with α-pinene, which stops polymerisation reaction by radical catching at normal storage temperatures, but does hardly affects its ignition properties, as shown in BAM (2005).

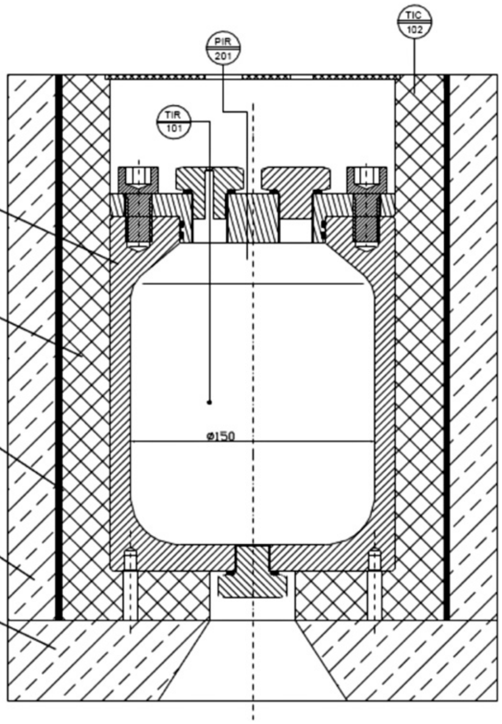

Fig. 2. Sectional view of the ignition vessel: 1) steel vessel walls – 2) aluminium coat – 3) heating jacket – 4) insulation – 5) base plate.

A cylindrical stainless steel mixing vessel with a volume of 6 dm^3 was used to create and to homogenize the stoichiometric TFE–air mixtures by a built-in stirrer. According to Eq. (1) a stoichiometric mixture is composed from ca. 17.5% TFE in air, considering that oxygen is the only air component participating to the

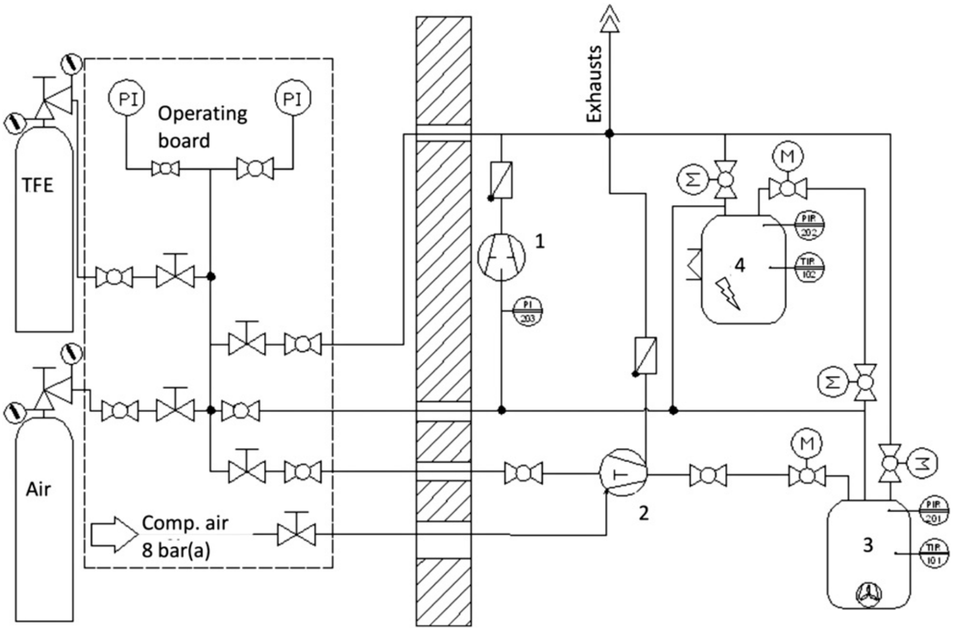

Fig. 1. Schematic view of the experimental setup: 1) vacuum pump – 2) compressed air-driven compressor – 3) mixing vessel (6 dm^3) – 4) heated ignition vessel (3 dm^3).