



Research paper / Praca doświadczalna

Examination of the explosive limits of flammable liquid vapours at various temperatures *Badanie granic wybuchowości par cieczy palnych w różnych temperaturach początkowych*

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Abstract: The article contains the results of experimental tests on the explosive limits of methanol, ethanol and 1-butanol vapours at 40, 60, 80, 100 and 120 °C. The tests were conducted in accordance with method B of PN-EN 1839 standard. Additionally, the article presents an overview of the current knowledge regarding methods for determining the explosive limits for the safe transport and storage of flammable liquids.

Streszczenie: Artykuł zawiera wyniki badań doświadczalnych granic wybuchowości par metanolu, etanolu oraz 1-butanolu w temperaturach początkowych 40, 60, 80, 100 oraz 120 °C. Badania przeprowadzono według metody B opisananej w standardzie PN-EN 1839. Dodatkowo, w treści artykułu przedstawiono przegląd stanu dotychczasowej wiedzy w zakresie metod określania granic wybuchowości na potrzeby bezpieczeństwa w transporcie i w magazynowaniu ciekłych substancji palnych.

Keywords: flammability limits

Słowa kluczowe: granice wybuchowości

1. Review of the current knowledge

Over the years, it has been experimentally proven that there are specific mixture and temperature ranges which define the flammable area limits of vapours. It has been observed that these also depend on the physical conditions and the methodology of the experiments. Research concerning explosive limits has been conducted for many years and the results can be found in the relevant literature. In 1952, Coward and Jones [1] proposed the first definition and method for determining explosive limits. They proposed that the determinations be carried out in a vertical test tube with an internal diameter of approx. 50 mm and a length of approx. 1.5 m, closed at the top and open at the bottom, with connection to the atmosphere. The movement of a flame along the length of the pipe was the criterion for the occurrence of ignition. The proposed apparatus was not thermally stabilised, therefore its use was limited to only testing the explosive limits of liquids which showed the ability to evaporate at room temperature. In [1], the authors also showed that some substances, e.g. halogens,

are resistant to the standard testing procedure. The work by Coward and Jones was the basis for the development of the German DIN 52649 standard, where the use of a cylindrical, glass, vertical tank with a length of 300 mm and an internal diameter of 60 mm, in which the ignition is spark-initiated by electrodes located above the bottom surface of the tank, is assumed. In 1965, Zabetakis [2] proposed a modification of the equipment, which allowed the testing of explosive limits at temperatures up to 230 °C. In addition, Zabetakis observed that the pipe diameter affected the test results. Increasing the temperature twofold resulted in a lowering of the upper explosive limit and was not related to the lower explosive limit. A test set-up for testing explosion limits was constructed and standardised in 1972, and designated in American standards as *American Society for Testing and Materials* (ASTM) E-681, commissioned by Kodak. It consisted of a spherical tank with a capacity of 5 dm³, thermally stabilised to a temperature of 1500 K, equipped with a magnetic stirrer and an ignition system located below the center of the tank. In 1986, Schrodter published the results of his research [3], which extended Zabetakis's efforts. Subsequently, in 2001, Arnalods *et al.* [4] worked on the experimental determination of explosive limits at lowered pressures. They showed a strong dependence of the pressure on the upper explosive limit, and weaker dependence on the lower limit when testing methanol, heptane, toluene and acetone at pressures below 1.2 bar. In 2007, van den Schoor *et al.* [5] used 4 different available numerical methods to calculate the upper explosive limit of flammable mixtures at different pressures up to 10 bar and at temperatures up to 200 °C. They used three mechanisms of chemical reaction kinetics for which the calculated outcomes were compared with results of experimental studies found in literature. It was noticed that for pressures close to ambient, the models performed well. For pressures significantly higher than ambient, the discrepancy between the results is large. In the numerical codes, too much emphasis was placed on the dependence of explosive limits on the pressure and too little on their temperature dependence. The literature review showed gaps in knowledge concerning the testing of explosive limits at elevated temperatures. These deficiencies can effectively hinder the design of explosion protection systems, as well as being the source of faults during the design of industrial facilities [6, 7].

2. Test site and research procedure

In order to test the explosive limits of flammable liquid vapours, a test set-up described in the PN-EN 1839 standard [8], consisting of a test chamber, ignition system, mixture preparation device and pressure and temperature measurement systems associated with the apparatus, was used. The test chamber is a 20-litre stainless steel, spherical tank, resistant to high pressures and corrosion by combustion products. Insulation and a temperature stabilisation system allows tests to be conducted at temperatures up to 120 °C. Additionally, the test chamber is equipped with a thermocouple to measure the flame temperature. The ignition system was located in the geometrical centre of the test chamber. Ignition is by the burning of a fuse wire. The data acquisition system consists of a pressure transducer, a signal amplifier and a recording device. Preparation of the mixture is carried out in accordance with the partial pressure method. The test chamber was also equipped with a vacuum pump, a manometer and a mechanical stirrer. A photograph of the test set-up is shown in Fig. 1.



Figure 1. Experimental stand for testing flammability limits of fuel vapors

The testing procedure complies with the PN-EN 1839 [8] standard, but has been optimised to obtain the highest possible homogeneity of the test mixture. Each test was initiated by placing a resistance wire between the electrodes located on the head of the test chamber and closing it tightly. The vacuum pump was subsequently started, which created an atmosphere with pressures in the range of 3 mbar. A specified amount of liquid was poured into the test chamber. Air was then delivered into the chamber and the first mixing of the evaporating liquid was carried out using the stirrer. The next step involved providing additional air to equalise the pressure with ambient and further mixing. Subsequently, the ignition source was activated and the results recorded. The explosion criterion was the pressure increase, in accordance with the requirements of the PN-EN 1839 standard [8].

3. Study results

Three liquids, *i.e.* methanol, ethanol and 2-butanol were tested at various concentrations and at elevated initial temperatures, *i.e.* 40, 60, 80, 100 and 120 °C. Tests for each liquid at a given initial temperature, at a fixed concentration and at a pressure inside the test tank equal to atmospheric pressure were carried out. Figs. 2-4 show the results of the tests.

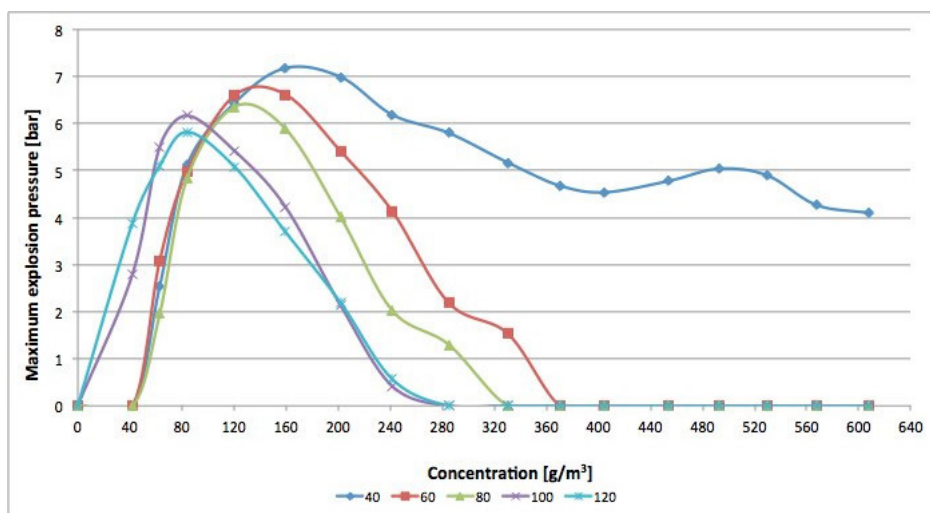


Figure 2. Flammability limits for ethanol at elevated temperatures

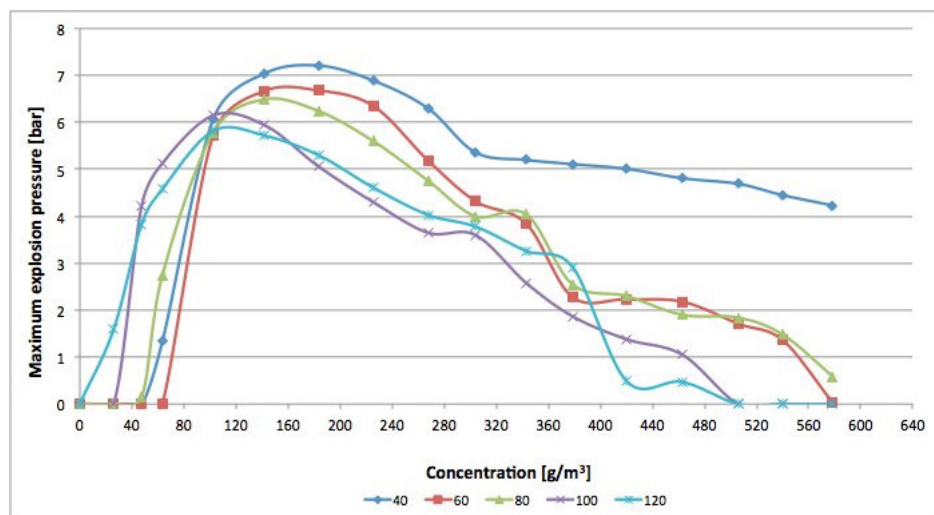


Figure 3. Flammability limits for methanol at elevated temperatures

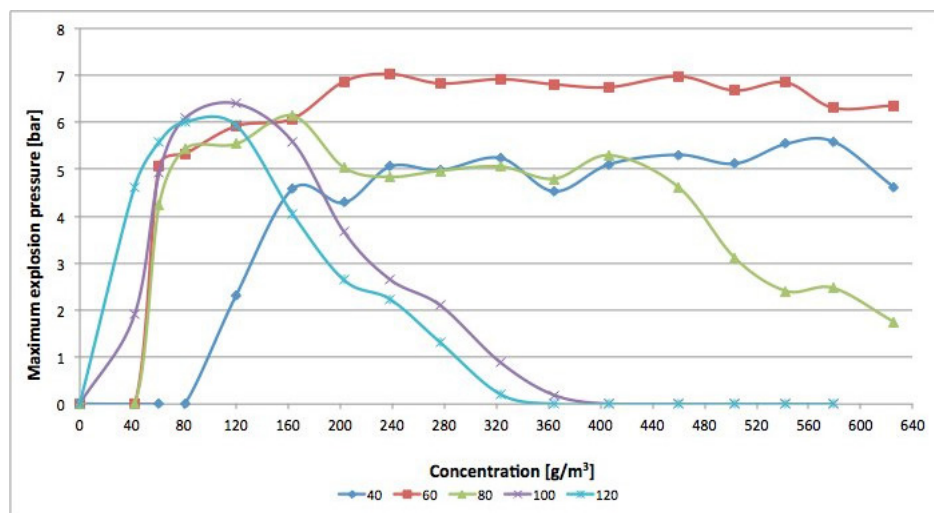


Figure 4. Flammability limits for 1-butanol at elevated temperatures

4. Summary and conclusions

In the case of ethanol, it is clearly seen that an increase in the initial temperature during liquid evaporation reduces its ability to form an explosive mixture with air. When the temperature changed from 40 to 60 °C, an upper explosion limit was observed at 330 g·m⁻³. In the case of methanol, a drop in pressure increase was noted as the temperature increased. For a concentration of 540 g·m⁻³, a change in temperature from 40 to 60 °C caused a five-fold decrease in the pressure increase. In turn, 1-butanol seems to be hardly susceptible to temperature changes. The results show that the lower limit drops as temperature increases. For 1-butanol, the lower explosion limit is approximately 40 g·m⁻³ at 60 and 80 °C, while at 40 °C it is only 20 g·m⁻³.

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