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Research paper / Praca doświadczalna

Effect of inert agents on the flammability parameters of selected gases and organic liquid vapours
Wpływ czynników inertnych na parametry wybuchowości wybranych gazów i par cieczy organicznych

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Abstract: *Flammable substances may form explosive atmospheres when mixed with air. To prevent their formation or minimise the risk of their occurrence, it is necessary to understand the properties of the mixtures of flammable substances and to apprehend the properties characterising the course of a potential explosion. To minimise the risk of a fire or an explosion, a process called inerting is used in which, e.g. nitrogen plays the role of an inert agent. The article discusses the method for testing the flammability limits, the "bomb" method, in accordance with the European standard PN-EN 1839 and the limiting oxygen concentration (LOC) according to the European standard PN-EN 14756. The study shows the influence of inert gas on the flammability range of selected substances: hydrogen, methane, and hexane, which in practice allows the assessment of the explosion hazard of closed and open spaces, the establishment of safe working conditions, and the selection of equipment operating in given explosion hazard zones. The tests were carried out at 25 °C for hydrogen and methane and at 40 °C for hexane, at ambient pressure.*

Streszczenie: *Palne substancje w mieszaninie z powietrzem mogą tworzyć atmosfery wybuchowe. Aby zapobiec ich powstaniu lub zminimalizować ryzyko ich wystąpienia, niezbędne staje się poznanie właściwości mieszanin palnych substancji oraz właściwości charakteryzujących przebieg potencjalnego wybuchu. W celu zminimalizowania ryzyka powstania pożaru lub wybuchu stosuje się proces zwany inertyzacją, w którym rolę czynnika obojętnego może pełnić np. azot. W artykule omówiono metodę badań granic wybuchowości, metodę „bomby", zgodną z normą europejską PN-EN 1839 oraz granicznego stężenia tlenu (GST) według normy europejskiej PN-EN 14756. Praca pokazuje wpływ gazu inertnego na zakres wybuchowości wytypowanych substancji: wodoru, metanu oraz heksanu, co w praktyce pozwala na ocenę zagrożenia wybuchem pomieszczeń oraz przestrzeni zewnętrznych, ustalenie bezpiecznych warunków pracy oraz dobór urządzeń pracujących w odpowiednich strefach zagrożenia wybuchem. Badania zostały przeprowadzone w temperaturze 25 °C dla wodoru i metanu oraz w temperaturze 40 °C dla heksanu, pod ciśnieniem atmosferycznym.*

Keywords: *explosion limits, limiting oxygen concentration, inertization*
Słowa kluczowe: *granice wybuchowości, graniczne stężenie tlenu, inertyzacja*

1. Introduction

An explosion is a violent combustion reaction of a flammable substance in the entire volume of the explosive atmosphere. The presence of an oxidant and a flammable substance, the concentration of which is at least equal to its lower explosive limit (and a source of ignition), is required for an explosion or fire to occur. Each combustible substance has its own explosive range, *i.e.* the range of concentration at which, at a given temperature and pressure, it can explode in a mixture with air. In order to minimise the occurrence of a fire or an explosion, the explosive range of the combustible substance should be limited. A process called inerting is used for that purpose. Inerting involves inserting an inert agent into the mixture of the test substance and air. Examples of inert agents are nitrogen, carbon dioxide and argon. Nitrogen is the most commonly used inert gas due to its advantages. Nitrogen:

– does not require cooling,
– and above all, it is widely available.

The characteristic features of a flammable liquid or gas are determined by carrying out appropriate tests. The paper presents the results of tests on the determination of explosive limits and limiting oxygen concentration for selected substances.

In practice, knowledge about the explosive parameters of gases and liquid vapours enables assessment of the explosion hazards of closed and open spaces, and thus involves the establishment of safe working conditions and selection of equipment used in the zones affected by explosion hazard, designing explosion protection techniques and explosion protection measures.

Explosive limit is divided into lower explosive limit (LEL) and upper explosive limit (UEL). In current literature, the term “flammability limits” is also used, and is synonymous with explosive limits. No-flame transfer (propagation) occurs at concentrations corresponding to explosive limits; that is, LEL is the lowest concentration of flammable substance in a mixture with air, at which ignition is not yet possible. UEL is the highest concentration of flammable substance in a mixture with air, at which ignition is no longer possible. These definitions apply to the experimental data in accordance with EN 1839. Concentrations between the explosive limits form the explosive range (also called flammability range) of the substance.

The limiting oxygen concentration (LOC) is the maximum oxygen concentration in a mixture of flammable substance with air and inert gas, at which the mixture does not explode. Oxygen is the agent in the combustible substance/air mixture which conditions the flame propagation during a fire/explosion. For this reason, it is very important to reduce the oxygen content in the mixture. Below the LOC, the mixture of flammable substance and air does not generate enough heat to allow the propagation of the flame. In the literature, LOC is often also called the minimum oxygen concentration. This parameter is strictly dependent on the type of combustible material and inert gas. Its value is also influenced by the process conditions, *i.e.* temperature and pressure.

Determination of the explosive limits of gases and liquid vapours is carried out in accordance with the European standard PN-EN 1839 [1], while the determination of LOC is done in accordance with the European standard PN-EN 14756 [2].

2. Apparatus and method

The tests were carried out in accordance with the European standard PN-EN 1839 using the B method (“bombs”) [1]. The test stand, designed by the ANKO enterprise and the Institute of Industrial Organic Chemistry, consists of a spherical tank made from acid-resistant steel with a volume of 20 dm^3 (Fig. 1), pressure and temperature sensors, vacuum pump, cooling system, stirrer and a computer equipped with the Explosion Plotter software. The maximal parameters, at which measurements can be made are: pressure of 16 bar and temperature of 150 °C. The source of ignition is a fuse wire, fixed between two metal electrodes located in the centre of the test tank. Ignition energy is equal to 10-20 J.

During each test, the course of the pressure changes in the test chamber is recorded as a function of time. In the case of liquid combustible substances, the test temperature should be raised to produce an appropriate amount

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of liquid vapour/air mixture. The explosion criterion is in accordance with the provisions of the standard [1] and was equal to 0.06 bar.

Figure 1. Test tank for determining the explosive parameters of gases and liquid vapours

LOC is a value calculated from the limiting air concentration (LAC) determined in the tests. The formula describing this relationship is as follows [2]:

$$LOC = 0.209 \cdot LAC \tag{1}$$

The studies start with the determination of the apex of the explosive area. The explosive limit should be determined with the mole fraction of the test substance being equal to x_{TS} = 1.2 LEL and the variable percentage of air and inert gas. The mole fraction of the inert gas, at which ignition no longer occurs, is described as x_{IN} and the mole fraction of air is described respectively as x_P. After conducting the tests described above, a point is obtained, which corresponds to the apex of the explosive area: $x_{TS} – x_{IN} – x_P$. This result determines further proceedings. The standard [2] presents two procedures for determining LOC – a shortened one and an extended one. The shortened procedure can be used when the LAC is at the apex of the explosive area, which is most common. The extended procedure should be used when the LAC is determined by the tangent on the UEL branch. The criterion for applying a given procedure is:

$$UEL \leq 0.8(100 – x_p) \tag{2}$$

If the inequality is satisfied, the shortened procedure can be used.
In the shortened procedure, only a check of the area around the top of the explosive area is required. This area is checked in order to confirm that LAC matches the designated $x_{TS} – x_{IN} – x_P$. Four tests are then performed with a change in the content of the test substance at a constant x_P. The change in the mole fraction of the test substance depends on the x_{TS} value. Two tests should be conducted above and two below the apex of the explosive area. The explosive limits are subsequently determined with the inert gas concentration equal to $0.8x_{IN}$.
If the inequality (2) is not satisfied, further testing should be conducted in accordance with the extended procedure. Explosive limits are determined along the branch of UEL. The tests should be conducted

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with a constant abundance of inert gas and air. The marked explosive limits are plotted on a ternary diagram and drawn with a curve passing through these points, starting at UEL and ending at $x_{TS} - x_{IN} - x_{P}$. The LAC value specifies the intersection of the tangent to the UEL branch with the air/inert gas axis.
The test results are recorded on a ternary diagram (Fig. 2). Ternary diagrams are used to present ternary systems and relationships which exist between the components of such a system. The vertices of the triangle indicate three substances: the test substance – air – inert gas. The marked area inside the triangle is called the explosive area of the test substance. The black dotted line marks the tangent to the curve, which limits the explosive area at its apex. This line intersects with the base of the triangle and marks LOC.

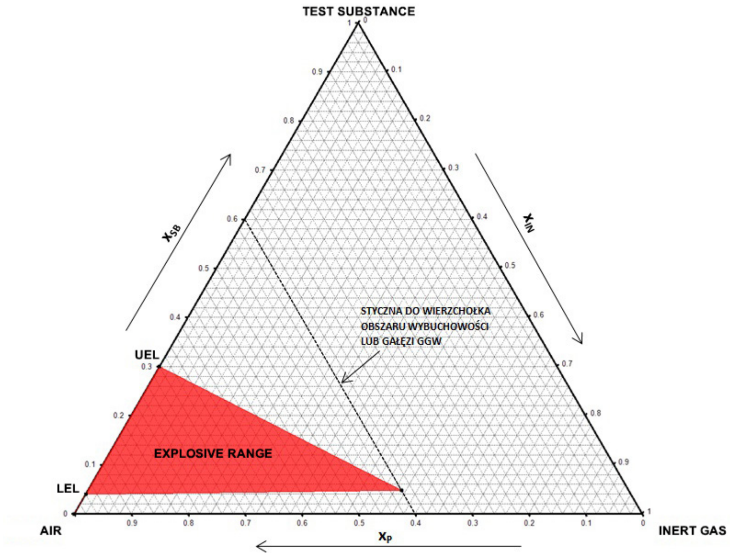

Figure 2. Sample ternary diagram

3. Results

The results of the limiting oxygen concentration tests for gaseous mixtures of hydrogen, methane and hexane are presented below. Due to the use of different standards, testing procedures and apparatus, the obtained results differ from the values given in the literature. The results of the experiments presented below are intended to show how the limiting oxygen concentration is currently determined in accordance with Polish standards.

3.1. Hydrogen

The tests were conducted at a temperature of 25 °C and at ambient pressure. In the course of the study it was found that LEL was equal to 4.0 mol%, while UEL – 78.4 mol%. The results from the determination of explosive limits were the basis for starting the LOC tests. The vertex of the explosive area was determined, for which x_{IN} is equal to 72.5 mol% and x_{P} equals 22.7 mol%. The inequality (2) was not satisfied; therefore, the LAC was determined in accordance with the extended procedure. The results were plotted on a ternary diagram (Fig. 3). The LAC value obtained from the diagram is 17.5%. Using formula (1), the limiting oxygen concentration was calculated. LOC equals 3.7%.

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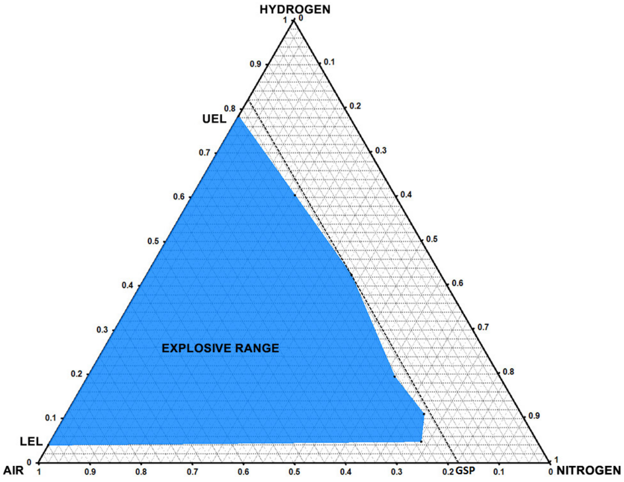

Figure 3. Ternary diagram for hydrogen

3.2. Methane

The tests were conducted at a temperature of 25 °C and at ambient pressure. The tests showed that LEL equals 4.6 mol% and UEL is equal to 17.2 mol%. The procedure was then followed and the vertex of the explosive area was marked. For methane, x_{IN} is equal to 62.5 mol% and x_P is 32.0 mol%. The inequality (2) was satisfied; therefore, the LAC was determined in accordance with the shortened procedure. The obtained LAC is equal to 32%. This result was used in equation (1) and LOC was obtained. The LOC for methane is equal to 6.7%. Figure 4 presents a ternary diagram including the explosion area for methane.

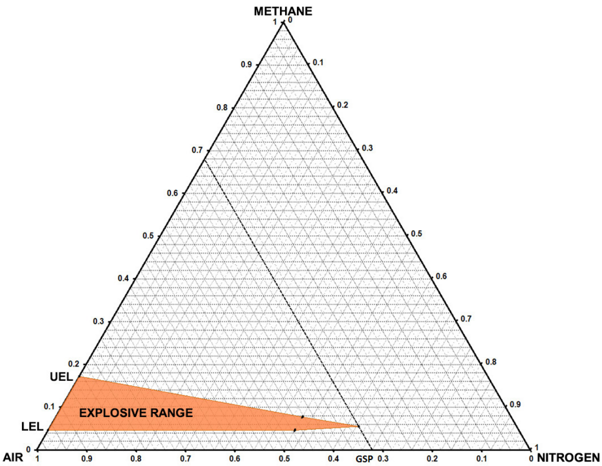

Figure 4. Ternary diagram for methane

3.3. Hexane

The explosive limits of hexane vapours were determined at a temperature of 40 °C and at ambient pressure, and equal: LEL – 1.0 mol%, UEL – 8.8 mol%. x_{IN} was subsequently determined at 61.0 mol%, while x_P was 37.8 mol%. As the inequality (2) was satisfied, the LAC was determined in accordance with the shortened

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procedure. The final results were plotted on a ternary diagram. The obtained LAC is equal to 37.8%. This result was used in equation (1) and LOC was obtained. The LOC of hexane equals 7.9%.

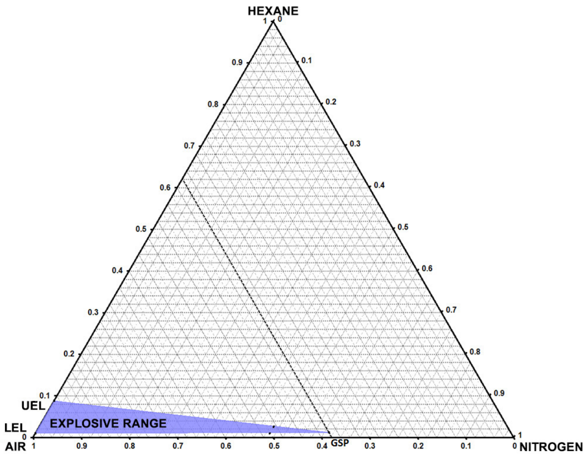

Figure 5. Ternary diagram for hexane

4. Discussion of the results

It should be noted that determination of the limiting oxygen concentration is extremely difficult, time-consuming and labour-intensive. This difficulty primarily results from the intricate provisions of the standard [2]. The guidelines for conducting such tests are ambiguous, and yet in many cases these standards are the basis for testing, for example, hazardous substances for classification purposes. The results for hexane in the standard can be used as an example: the tests on explosive limits were conducted at:

- LEL at room temperature,
- UEL at 40 °C ,
- LOC at 100 °C.

The reason for this difference is not known, as the standards themselves state that all tests should be performed at the same temperature. As mentioned previously, both the explosive limits and the limiting oxygen concentration strictly depend on temperature and pressure. It is worth adding that there are also differences between our test stand and the apparatus presented in other publications (Table 1).

Table 1. Comparison of LOC values for air mixtures of selected substances determined by different methods

Test substance	Research method		
	Experimental values [%]	Data from [2] [%]	Literature data [%]
Hydrogen	3.7	4.4	4.7 [3] 5 [4];
Methane	6.7	–	9.9 [5] 10.7 [3] 12 [4]
Hexane	7.9 (in 40 °C)	8.3 (in 100 °C)	12 [4]

They usually result from the use of different apparatus and varying test conditions (temperature, pressure). The authors of the publication also work with various standards (EN and ASTM), in which the interpretation of the results is completely different. Another dissimilarity involves a different method for producing the vapour-air mixture. This mixture is prepared inside the test tank of the apparatus employed in our study. After conducting a number of tests and comparing the results with the literature data, it was noted that our measuring system yielded wider explosive ranges of the tested substances.

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5. Conclusions

In places with a high risk of the presence of an explosive atmosphere, measures must be taken to mitigate the possible effects of a potential fire or explosion. One of the many approaches to improve safety in this regard is the use of inerting, and the criterion which indicates the extent of safe concentrations of a combustible substance is the limiting oxygen concentration value. The research results presented in the current paper show experimentally determined explosive areas of air mixtures with hydrogen, methane and hexane. The use of nitrogen as the inert gas yielded satisfactory results: the explosive range was narrowed and the explosion pressure was lowered to below the criterion value (0.06 bar).

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