



Explosion Hazard Evaluation and Determination of the Explosion Parameters for Selected Hydrocarbons C6 – C8

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Abstract: Fire and explosion prevention plays an important role in the running of chemical processes, especially where flammable gases or liquids are present, which may form explosive atmospheres of gas/vapours in air. These include organic solvents such as the hydrocarbons C6 – C8. It is necessary to know the properties of these substances and the volume of an explosive atmosphere. Determination of these can identify and assess the risk of explosion, and zones in areas where there are or may occur explosive atmospheres. Information on explosion limits are also important in safety data sheets. In this study a research methodology is compared with previous studies and signals guidelines for explosion protection and prevention of explosions. The aim of this work was to determine the experimental explosion characteristics like LEL, UEL, p_{\max} and $(dp/dt)_{\max}$ for selected hydrocarbons. The investigations were carried out in accordance with EN 1839 by method b and EN 15967. The studies were conducted in a closed, spherical, acid-proof vessel of 20 dm³ internal volume.

Keywords: explosion limits, lower explosion limit (LEL), upper explosion limit (UEL), maximum explosion pressure (p_{\max}), maximum rate of pressure rise ($(dp/dt)_{\max}$)

Introduction

Fire and explosion prevention is an important issue in the managing of chemical processes, especially where flammable gases or liquids are present

which may form explosive atmospheres of gas/vapours in air. Chemical mixtures are useful for industrial processes, but their potential toxicity and flammability might lead to serious harm to people and the environment [1, 7]. In recent years the number of industrial accidents caused by fire and explosion has increased all over the world [8]. Therefore, it is important to emphasize the significance of flammability hazards. Such an important problem as chemical safety in many plants is neglected or ignored. It is necessary to know the physicochemical properties of the chemical substances in order to prevent accidents.

The determination of explosion parameters can help to provide specific and important information on properties related to explosions [2]. According to EN 1127-1, a proper explosion hazard analysis should include data such as combustion properties e.g.: lower explosion limit (LEL), upper explosion limit (UEL) and explosion behaviour e.g.: maximum explosion overpressure (p_{\max}), maximum rate of explosion pressure rise ($(dp/dt)_{\max}$) [14]. The likelihood of the occurrence of a hazardous explosive atmosphere depends on: the degree of dispersion, the presence and concentration of flammable substances and the volume of explosive atmosphere. There are many possible ignition sources e.g.: flames and hot gases, hot surfaces, mechanically generated sparks, electrical apparatus, exothermic reactions. The amount of combustible material in the atmosphere should be reduced by the limitation of its concentration or by adding an inert component. The equipment which contains the flammable substances should keep the chemicals in an enclosed system at all times [14]. In the past, many explosion properties have been studied using different research methods. The flammability characteristics of hydrocarbons can describe by formulae [3]. The LEL depends only upon the number of carbon atoms in the chain. The UEL depends on the number of hydrogen atoms present on the chain. The formulae for paraffinic hydrocarbons, olefins and their isomers are shown in Table 1.

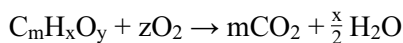
Table 1. Lower and Upper Explosion Limits formulae [3]

Compound	Formula	
	LEL [mol.%]	UEL [mol.%]
Paraffinic hydrocarbons and olefins	$\frac{6}{nC} + 0.2$	$\frac{60}{nH} + \frac{nC}{20} + 2.2$
Isomers of hydrocarbons	$\frac{6}{nC} + 0.1$	$\frac{60}{nH} + 2.3$

Notes: nC = number of carbon atoms; nH = number of hydrogen atoms

Another theoretical method to calculate the explosion limits is presented

below. This is based on reaction stoichiometry [11].



$$z = m + \frac{x}{4} - \frac{y}{2}$$

$$C_{st} = \frac{100}{1 + \frac{z}{0.21}} \quad LEL = 0.55C_{st} \quad UEL = 3.50C_{st}$$

where C_{st} is volume % flammable substance in air.

An alternative method is a correlation between the explosion limits and the heat of combustion. This was used for organic compounds containing carbon, hydrogen, oxygen, nitrogen and sulfur. This correlation is shown below [11].

$$LEL = -\frac{3.42}{\Delta H_c} + 0.569\Delta H_c + 0.0538\Delta H_c^2 + 1.20$$

$$UEL = 6.30\Delta H_c + 0.567\Delta H_c^2 + 23.5$$

where LEL and UEL are volume % flammable substance in air and ΔH_c is in 10^3 kJ/mol.

Unfortunately, most of these methods are theoretical calculations or are incompatible with current criteria. Hence, an investigation of flammability properties is needed to provide chemical safety.

Experimental apparatus and method

The test stand is shown in Figure 1. It was designed and constructed by firm ANKO. The stand consists of a spherical, acid-proof, steel test vessel of 20 dm³ internal volume plus auxiliaries (pressure and temperature sensors, vacuum pump, cooling system, stirrer, computer). The test vessel was designed to use the bomb method – method “b” in EN 1839 [12]. Using this vessel it is possible to measure the explosion pressures up to 16 bar and to work to a maximum temperature of 150 °C. The ignition source is a fusing wire, placed at the center of the test vessel. An igniter releases 10-20 J of energy. The device initiating the measurement is established in accordance with EN 1839.



Figure 1. Test stand for determining the explosion parameters of gases and vapours.

The tests are carried out in several steps. At the beginning, the pressure in the test vessel is reduced to below 10 mbar. The sample is then injected into the vessel at low pressure. Next, air is loaded into the vessel up to the atmospheric pressure. Afterwards, the mixture in the vessel is stirred for 3 minutes. After the mixture has stabilized without stirring for 3 minutes, the mixture is ignited and the data from the pressure sensor are processed by the computer and displayed on the screen. After the explosion, the vessel is purged with the air, opened and cleaned.

The aim of this work was to determine the experimental explosion characteristics, such as the lower explosion limit (LEL), the upper explosion limit, the maximum explosion pressure (p_{\max}) and the maximum rate of pressure

rise ($(dp/dt)_{\max}$). The determinations for cyclohexane, 1-hexene, n-heptane and isooctane were carried out at atmospheric pressure and normal oxygen concentration (21 vol.%). A temperature of 100 °C was selected optimally for all of the substances analyzed. The temperature of the process should be at least 25 K higher than the boiling point of the tested substance [12]. The determinations of the lower and upper explosion limits were performed in accordance with EN 1839. The determinations of the maximum explosion pressure and the maximum rate of pressure rise were carried out in accordance with EN 15967 [13].

Results and Discussion

Lower explosion limit and upper explosion limit for cyclohexane, 1-hexene and n-heptane

By definition a mixture is not burnt when its concentration is lower than the LEL or is not combustible when its concentration is above the UEL. So, the mixture is explosive only when its concentration is between the explosion limits (the so-called explosive range) [11].

Figures 2-4 show the graphs of the pressure – mole fraction of cyclohexane, 1-hexene and n-heptane. These display the attempted determination of the lower and upper explosion limits and the relationship between the explosion pressure for the three different hydrocarbons. As can be seen in these graphs, values of the explosion limits are similar. Only the upper explosion limit of 1-hexene (9.1 mol.%) is slightly higher than the other two substances. Our experimental values for the LEL and UEL for the substances analyzed were determined and are shown in Table 2 below. The UELs are more difficult to determine experimentally [10]. Fortunately, the use of higher process temperatures allowed the results presented in this study to be obtained. Several tests were carried out in order to obtain satisfactory results.

Table 2. Explosion limits for different hydrocarbons at 100 °C and atmospheric pressure in a 20-L-Apparatus according to EN 1839

Name of substance	LEL [mol.%]	UEL [mol.%]
cyclohexane	0.9	8.0
1-hexene	1.0	9.1
n-heptane	0.7	8.2

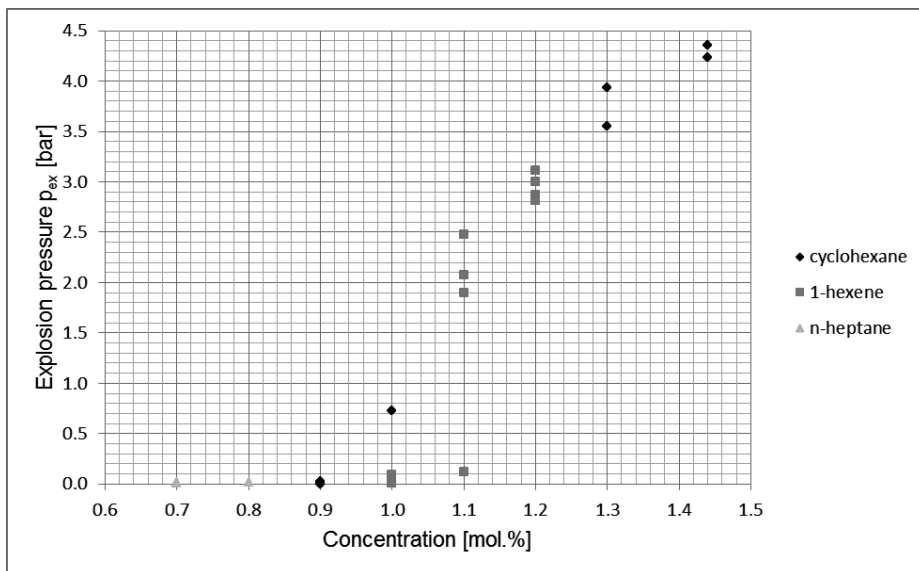


Figure 2. Explosion pressure as a function of vapour concentration – determination of the lower explosion limit.

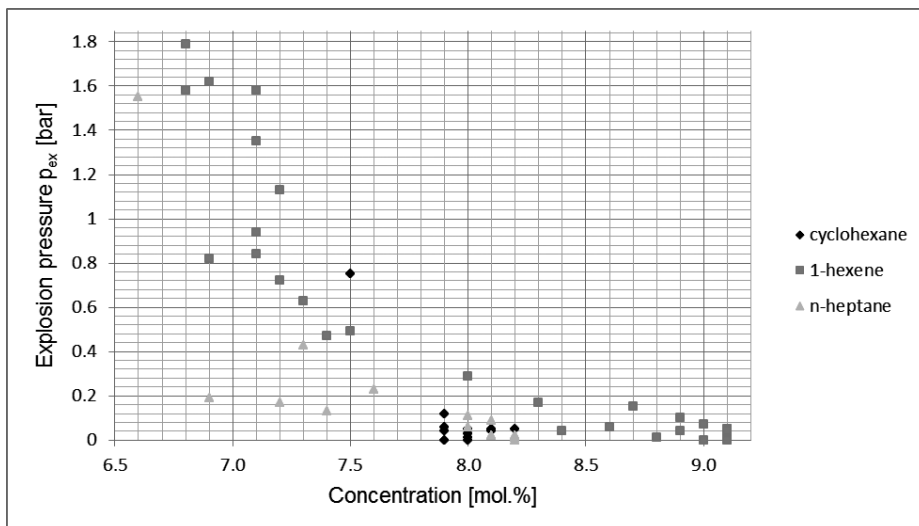


Figure 3. Explosion pressure as a function of vapour concentration – determination of the upper explosion limit.

In addition, Table 3 lists the values of the lower and upper explosion limits from previous references [3, 6]. Differences (lower or higher values) between

the values reported in this work and the previously published values are due to the improved experimental apparatus used here. As mentioned before, other studies used different criteria of explosion [5, 9].

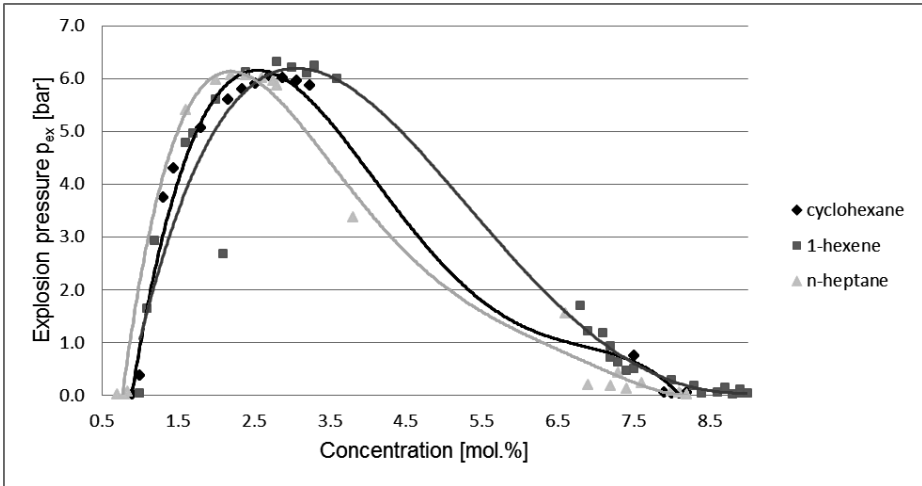


Figure 4. Explosion pressure versus mole % of the substances analyzed at 100 °C and atmospheric pressure.

Table 3. Literature values of the explosion limits for cyclohexane, 1-hexene and n-heptane [3, 6]

Method	Name of substance	
	LEL [mol.%]	UEL [mol.%]
	cyclohexane	
theoretical calculation	1.25	7.98
in 5 cm diameter tube with upward propagation of flame	1.33	8.35
	1.26	7.75
in 10.2 cm diameter tube with upward propagation of flame	1.33	6.20
5 cm diameter closed tube, 65 cm in length	1.31	4.50
	1-hexene	
theoretical calculation	1.25	7.98
	n-heptane	
theoretical calculation	1.03	6.55
in 5.08 cm diameter tube with upward propagation flame	1.10	6.70
vessel	1.00	6.00

Maximum explosion pressure for cyclohexane, 1-hexene and n-heptane

The maximum explosion pressure as a function of the substance concentration is shown in Figure 5. The maximum explosion pressures of the substances tested are similar but their mole % is different at the maximum pressure. The values of this parameter were not found in previous references. This fact is striking because the maximum explosion pressure gives basic information about the explosion behaviour and should be characterized [13, 14]. In this study, we successfully determined p_{\max} and the results are presented in Table 4.

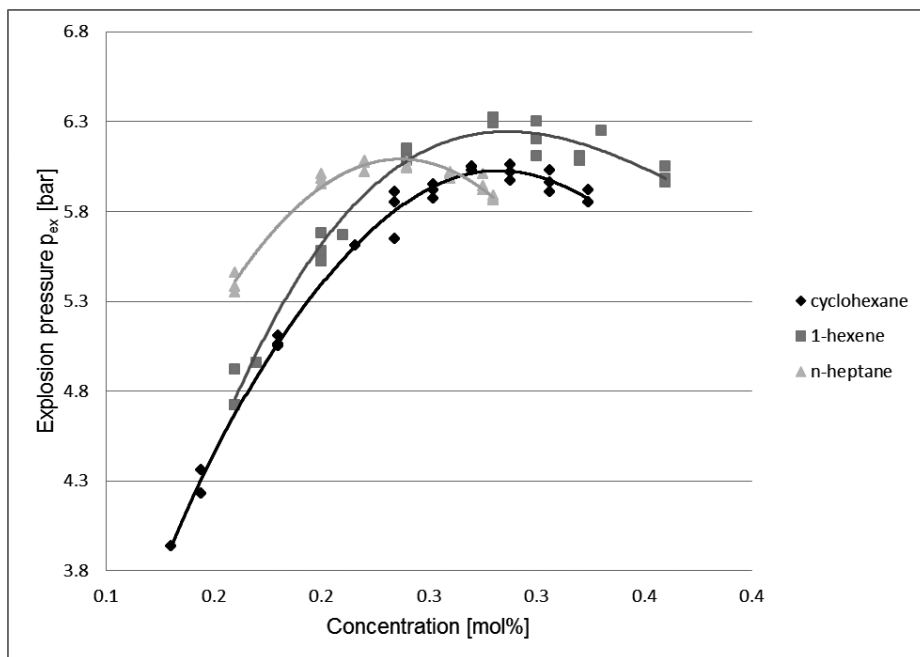


Figure 5. Variation of explosion pressure depending on mole % for the substances analyzed.

Table 4. Maximum explosion pressure and maximum rate of explosion pressure rise for the different hydrocarbons at 100 °C and atmospheric pressure in a 20-L-Apparatus according to EN 15967

Name of substance	p_{\max} [bar]	$(dp/dt)_{\max}$ [bar/s]	K_g [bar·m/s]
cyclohexane	6.1 for 2.7 mol.%	360 for 2.7 mol.%	98
1-hexene	6.3 for 2.8 mol.%	380 for 2.8 mol.%	103
n-heptane	6.1 for 2.2 mol.%	410 for 2.2 mol.%	111

Maximum rate of explosion pressure rise for cyclohexane, 1-hexene and n-heptane

As an example of the data obtained, Figure 6 shows the values of the maximum rate of explosion pressure rise as a function of the sample concentration. The hydrocarbons investigated have similar values of $(dp/dt)_{\max}$ as shown in Table 4 above. This explosion indicator is not commonly used, which is a mistake. Both explosion parameters: p_{\max} and $(dp/dt)_{\max}$ are extremely useful for conducting chemical processes and designing safety measures in industry. The values for $(dp/dt)_{\max}$ depend on the volume and shape of the test vessel. Therefore, a rate of explosion pressure rise should be normalized to a vessel volume of 1 m^3 (K_g) [15]. Comparison of the results for each substance was included in Table 4.

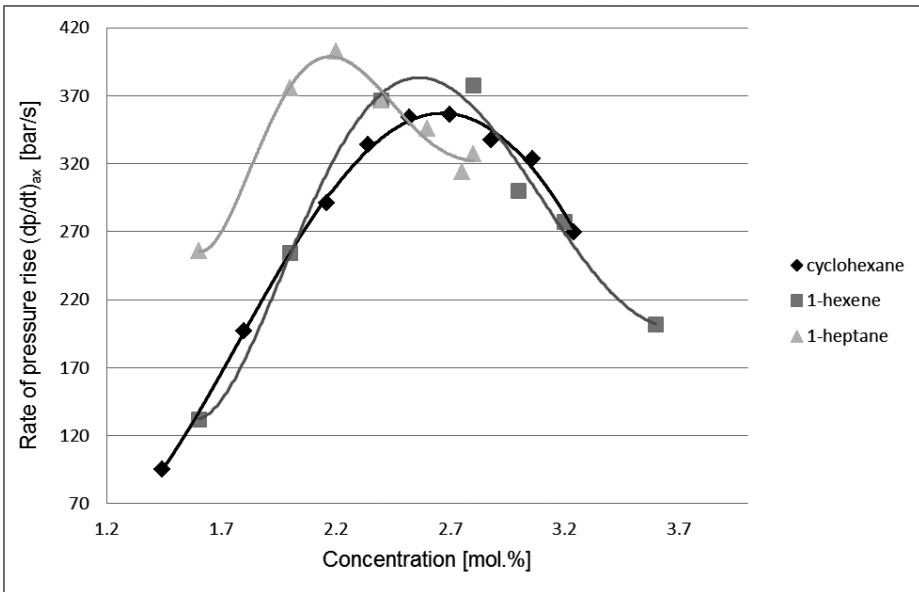


Figure 6. Variation of the rate of the pressure rise depending on mole % for the substances analyzed.

Comparison of explosion parameters of isooctane at elevated temperature and atmospheric pressure

In this study, attempts were made to detect the explosion properties of isooctane. The LEL, UEL, p_{\max} and $(dp/dt)_{\max}$ were experimentally determined. Our experimental values for the explosion parameters were compared with the literature values as shown in Table 5. The previous reference does not specify at which temperature the explosive limits was determined. The values of the LEL

and UEL depend on the temperature so we decided to introduce the temperatures in which our studies were carried out. The agreement between our results and the values in the references is excellent, although there are small differences. This is primarily due to differences in the construction of the experimental set-up and the method of study. Secondly, our investigation was probably carried out at a different temperature. In addition, the maximum explosion pressure was found at 24 °C and 100 °C. For isooctane at 24 °C, p_{\max} is 8.1 bar for 2.00 mol.%, at 100 °C it is 6.0 bar for 1.92 mol.%,. The maximum explosion pressure decreases at higher temperatures.

Table 5. Comparison of explosion limit values for isooctane

Explosion parameters	Literature data [6]	Our experimental results
LEL	0.98 mol.%	0.80 mol.% 24 °C
UEL	6.03 mol.%	5.90 mol.% 60 °C
p_{\max}	–	8.1 bar for 2 mol.% at 24 °C
	–	6.0 bar for 1.92 mol.% at 100 °C
$(dp/dt)_{\max}$	–	330 bar/s for 2.08 mol.% at 100 °C

Conclusions

In previous work, the investigators have studied the explosion parameters in different testing systems and conditions. One of the differences between the earlier results and the present ones is the pressure rise criterion [4]. Knowing only the results of research, such as those given in safety data sheets, we do not know which method was used for their determination. Moreover, the difference between the glass tube method and the bomb method is highly significant because it generates expected differences in the test results. The values of the explosion limits depend on, for example: the length and diameter of the glass tube, the diameter (volume) of a spherical vessel and the type of ignition source [5]. The explosive parameters for the selected hydrocarbons are similar but there are differences between their values at different temperatures. The experimental results of the explosive parameters for cyclohexane, 1-hexene, n-heptane and isooctane can be taken full advantage of in industrial processes in order to make them safer for humans and the environment.

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