

# EXPERIMENTS ON THE UPPER EXPLOSION LIMITS OF GASEOUS ALKANES-OXYGEN MIXTURES AT ELEVATED CONDITIONS OF T AND P IN A SPHERICAL VESSEL

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## **Summary**

*This experimental work has been completed in the Institute of Heat Engineering Laboratories of Warsaw University of Technology. The article reports on the explosion pressure data and the influence of chosen physical parameters on the value of the Upper Explosive Limit (UEL) of gaseous alkanes-oxygen mixtures. Such explosion behavior data of common gases for different initial conditions are essential for a quantitative risk assessment in many industrial environments. A number of higher alkanes-oxygen mixtures were examined (up to n-butane). Summarized research data is presented in the paper. All the presented data have been obtained from the experiments conducted in a 2.3 dm<sup>3</sup> spherical, steel vessel. Exploding wire was used as the mean of ignition source. It released about 0.1 J energy each time. The pressure histories in the combustion vessel have been recorded by means of piezoelectric pressure transducer. The influence of the increased initial temperatures of the tested mixtures on their value of UEL was investigated in the range of 20°C up to 200°C. Further experiments on the influence of elevated pressure, as well as the position of the ignition source, were carried out too. The experiments allowed the authors to find a distinct dependencies in the values of obtained UEL under elevated conditions of pressure and temperature.*

**Keywords:** *Flammability, Explosive limits, Flammability limits, Elevated conditions, Explosion pressure*

## **1. INTRODUCTION**

The upper explosion limits (UEL) data of common gases such as gaseous alkanes in their mixtures with air and oxygen at elevated conditions are essential for a factual risk assessment. Many industrial processes involve the mixing of these flammable gases with oxygen at standard and elevated conditions [1]. Mixtures of light alkanes and oxygen can be converted into many useful products (such as acetylene) by partial combustion (oxidation) in excess of fuel at moderate conditions of temperature and pressure. The flammability limits for all commonly used gaseous fuels, including those used in experiments here, are rather well documented in the literature.

However, the data available almost always applies to ambient temperature and pressure conditions, Thus, despite the fact of extensive research on explosibility limits have been carried out for nearly 200 years now, there is only limited data on the influence of pressure and temperature on upper explosion limits even common gaseous fuels[2].

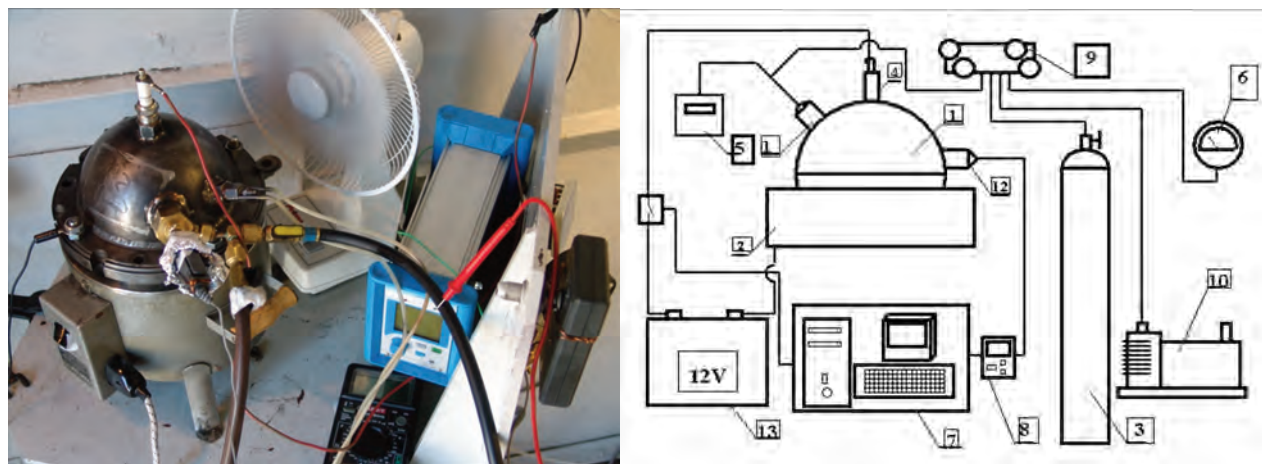
The determination of the UEL is more difficult compared to the lower explosion limit (LEL). The UEL value changes significantly over a wide range to higher fuel composition with pressure and temperature [3]. Various research explosion centers have published explosion limits values which often differ quite significantly from each other [4,5,6]

The report presents the explosion pressure data for four gaseous alkanes homologues-oxygen mixtures; i.e. methane, ethane, propane and n-butane (all at the upper flammable limit) at both; standard and elevated conditions of pressure and temperature. All the presented data have been obtained from the experiments conducted in the steel spherical explosion vessel of 2,3 dm<sup>3</sup> volume, equipped with external heating/cooling system. The initial temperatures of the examined mixtures have oscillated from 20°C up to 200°C and the initial pressures varied from 1 been 6 bar for methane and ethane.

The pressure histories in the combustion vessel have been recorded by means of special pressure transducer with additional cooling system. The effects of higher initial temperature or pressure of the mixture on the pressure curves have also been investigated and qualitatively analyzed. The effect of the ignition position on the explosion pressure history has been explored as well. The results are plotted as functions of time, with respect to the ignition configuration, temperature and pressure.

## 2. THE RESEARCH STAND

The experimental set-up consist of following parts: spherical steel vessel, fusing wire ignition system, data acquisition system with pressure transducer, amplifier, acquisition card and a computer, bottle with mixture and vacuum pump. To control the initial conditions i.e., pressure and temperature, electronic precise manometer and a type K thermocouple were used. The pressure transducer (together with cooling system) used in this research was manufactured by Kistler.



**Fig. 1. Photography of the experimental test stand and its schematic diagram**

Location of the ignition was changeable, that is was inserted in the center or on the bottom of the vessel in order to evaluate its position on the course of oxidation process.

A general view of the research stand and its schematic diagram is presented in Fig. 1. The explosion vessel (1) was placed on hemispherical electrical heater (2). The ignition system were assembled at the top of the vessel (4), and connected via cable with the battery (13) as well as with the data acquisition system and computer (7). Piezoelectric pressure transducer (12) was mounted in the vessel wall and connected to the amplifier (8), and then to the computer (7). The

thermocouple was also placed in the vessel close to the wall (5). The same valve was used to fill vessel with fresh mixture and evacuate the products.

### 3. EXPERIMENTAL PROCEDURE

Before each experiment the vessel was evacuated by vacuum pump and then filled with test mixture. The gas mixture was allowed to come to rest by waiting at least 5 min. before executing each test. All the test mixtures were prepared at least one day in advance, by using the partial pressure method. The stand for mixtures preparation was equipped with steel bottles, a vacuum pump and a set of precise manometers of high reading accuracy. The first step of the experimental procedure was evacuating the test chamber and then filling it in with the appropriate mixture, then preheating the test vessel containing the mixture to the required temperature, igniting the quiescent test mixture and recording the explosion overpressure inside the chamber. The test mixture was considered as an explosive one, if the measured explosion overpressure was equal to (or greater) than the overpressure formed by the ignition source itself (signal at the level of the reading resolution of the instruments), and exceeded 7% of the initial mixture pressure.

During tests the composition of all mixtures was continuously increased until no ignition was observed (lack of pressure rise). The mixtures were ignited by an exploding wire (aluchrome resistance wire, 0,2 mm diameter), with average energy ignition estimated  $\sim 0,1$  J. The ignition source must be of sufficient energy to guarantee ignition, otherwise the property under investigation would be that of the limiting ignition energy and not of explosibility. Two positions of ignition were utilized during the research; centre and the bottom of the vessel. The limits were evaluated for initial pressure and temperature varied from 1 to 5 bar, and from 20°C to 200°C respectively. The pressure data were measured by water-cooled Kistler piezoelectric pressure transducer mounted in one of the side walls of the vessel. The data acquisition system was used to record all experimental data. The initial pressure of the mixture in the vessel was measured with high accuracy digital pressure manometer. The initial temperature of mixture was controlled by a K-type thermocouple located almost in the centre of the vessel. The temperature of the vessel was controlled by means of special electric heaters. The top half of the vessel was covered with an insulating material.

### 4. EXPERIMENTAL RESULTS

The increase of the initial mixture temperature causes a significant increase of the upper explosion limit in the case of all investigated mixtures. The change of that explosion limit versus the initial temperature of the mixture can be approximated by means of a linear function. Similarly, the increase of the initial mixture pressure causes a significant widening of the UEL, especially in the case of ethane-oxygen mixtures.

**Table 1. Qualitative results of the flammability of methane-oxygen mixtures in the spherical vessel of 2,3 dm<sup>3</sup> volume and central position of ignition source**

UFL %[v/v]		55	56	57	58	59	60	61	62	63	64	65	66	67	68
1bar	20°C	↔	↔	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
1bar	50°C	↑	↑	↔	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
1bar	100°C	↑	↑	↔	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
1bar	150°C	↑	↑	↔	↔	↔	↔	↓	↓	↓	↓	↓	↓	↓	↓
1bar	200°C	↑	↑	↑	↔	↔	↔	↓	↓	↓	↓	↓	↓	↓	↓
20°C	2bar	↑	↔	↔	↑	↔	↔	↔	↓	↓	↓	↓	↓	↓	↓
20°C	3bar	↑	↑	↑	↑	↑	↔	↔	↔	↔	↓	↓	↓	↓	↓
20°C	4bar	↑	↑	↑	↑	↑	↑	↔	↔	↔	↔	↓	↓	↓	↓
20°C	5bar	↑	↑	↑	↑	↑	↑	↑	↑	↔	↔	↔	↓	↓	↓
20°C	6bar	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↔	↔	↔	↓

↑ flammable, ↓ non-flammable, ↔ the ignition occurred only once during 3 repetitions

The table 1 presents bulk results on the upper flammability limit of methane-oxygen mixtures

at elevated conditions of temperature and pressure (separately). The results are plotted as functions of molar percentage methane content, with respect to the pressure and temperature conditions. It can be seen that the upper explosibility limit increases along with the increase of the initial temperature/pressure of the methane-oxygen mixture. It was also found, that the upper explosion limit of methane-oxygen mixture does not depend on the residual time within investigated initial conditions of pressure and temperature.

The UFL values for gaseous alkanes in their mixtures with oxygen at ambient conditions are given in the table 2. In the tables 3 and 4 the values of UFL at elevated conditions are presented, together with their graphical interpretation in the figure 3.

**Table 2. The UFL measured in the spherical vessel of 2,3 dm<sup>3</sup>, central position of ignition source, 20°C**

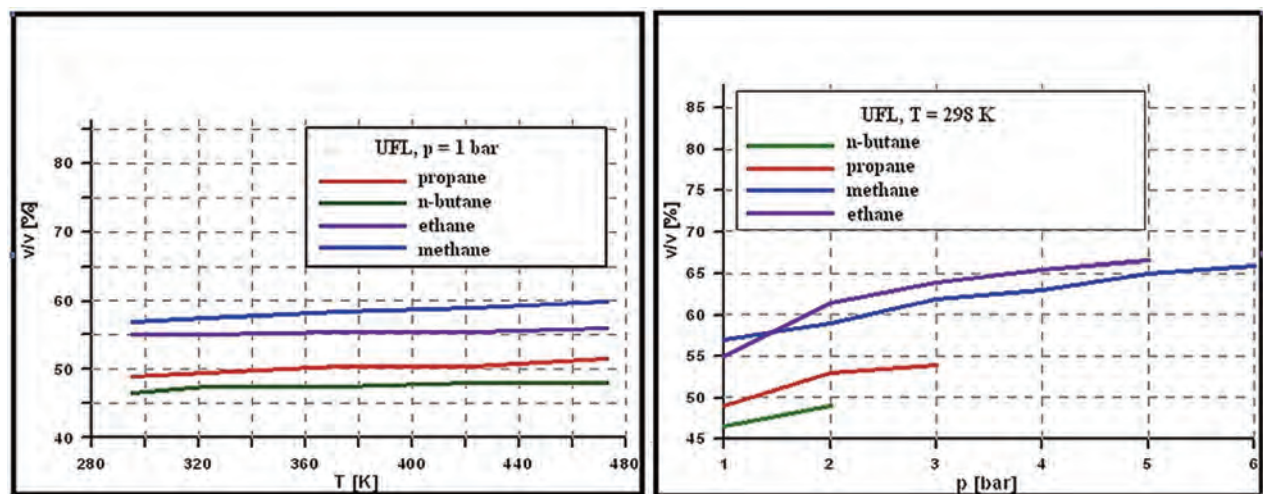
	methane	ethane	propane	n-butane
GGW [% v/v]	57	55	50	49

**Table 3. The influence of mixture initial pressure on the UFL**

pressure [bar]	methane	ethane	propane	n-butane
1	57	55	50	49
2	59	61,5	51	52
3	62	64	53	
4	63	65,5	54	
5	65	66		
6	66	66,5		

**Table 4. The influence of mixture initial temperature on the UFL**

temperature [°C]	methane	ethane	propane	n-butane
20	57	55	50	49
50	57,5	55	50,5	49
100	58,5	55,5	51,5	49,5
150	59	55,5	51,5	49,5
200	60,5	56	52,5	50

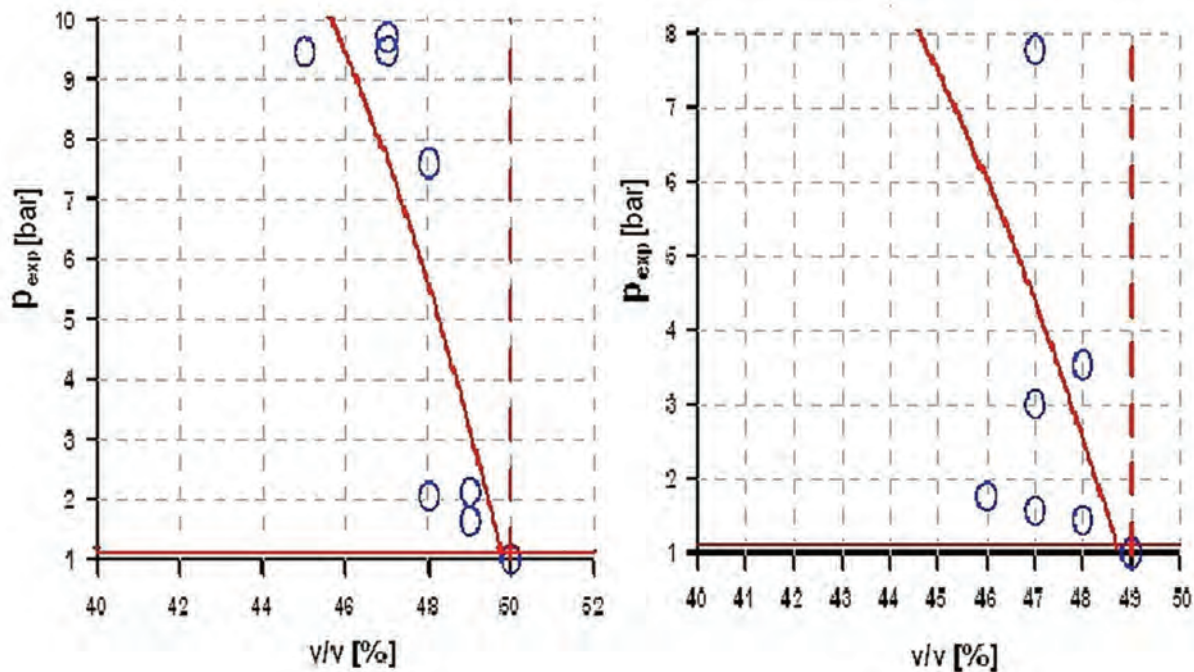


**Fig. 2. The influence of elevated temperature and pressure on the UFL value**

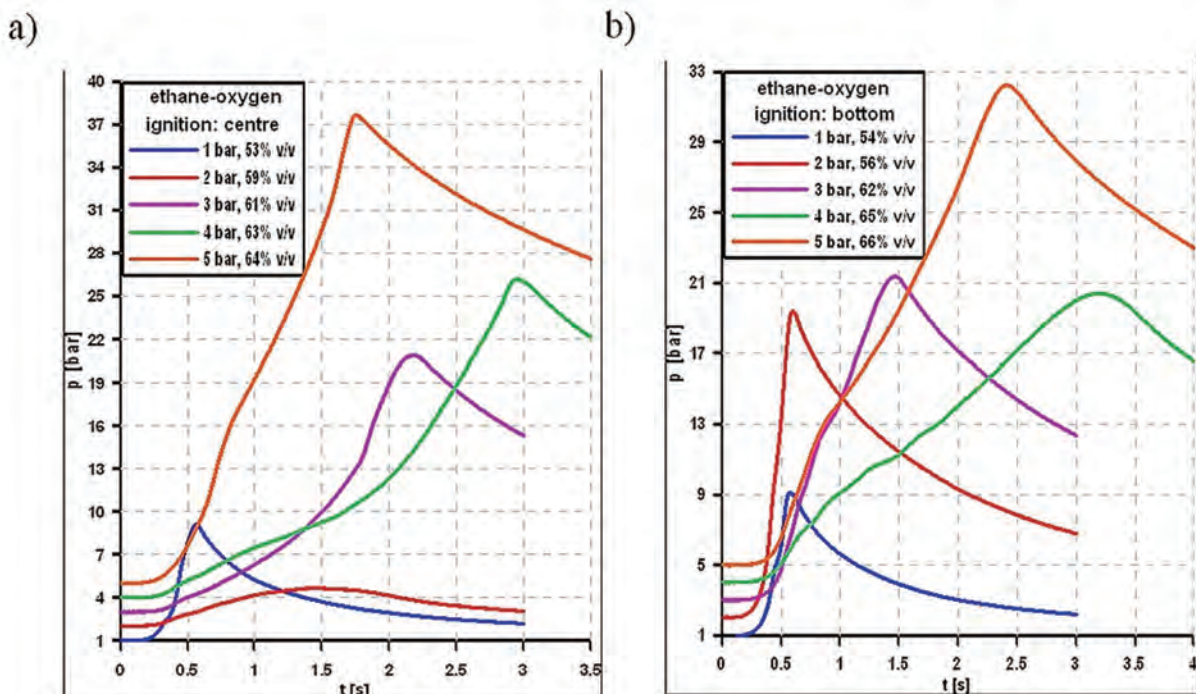
## 5. DISCUSSION

The obtained values of the UFL are the consequence of many experimental measurements. The

7% initial pressure rise was used as a criterion of the UEL (Fig. 4). Experiments on the ignition of extremely fuel-rich methane, ethane propane and n-butane –oxygen mixtures in the 2,3 dm<sup>3</sup> spherical vessel at elevated initial pressure (up to 6 bar) and temperature (473 K) reveal significant influence of the ignition position on the maximum explosion pressure. Direct results of pressure course versus time for the examined mixtures in the UFL regime are shown in Fig. 5.

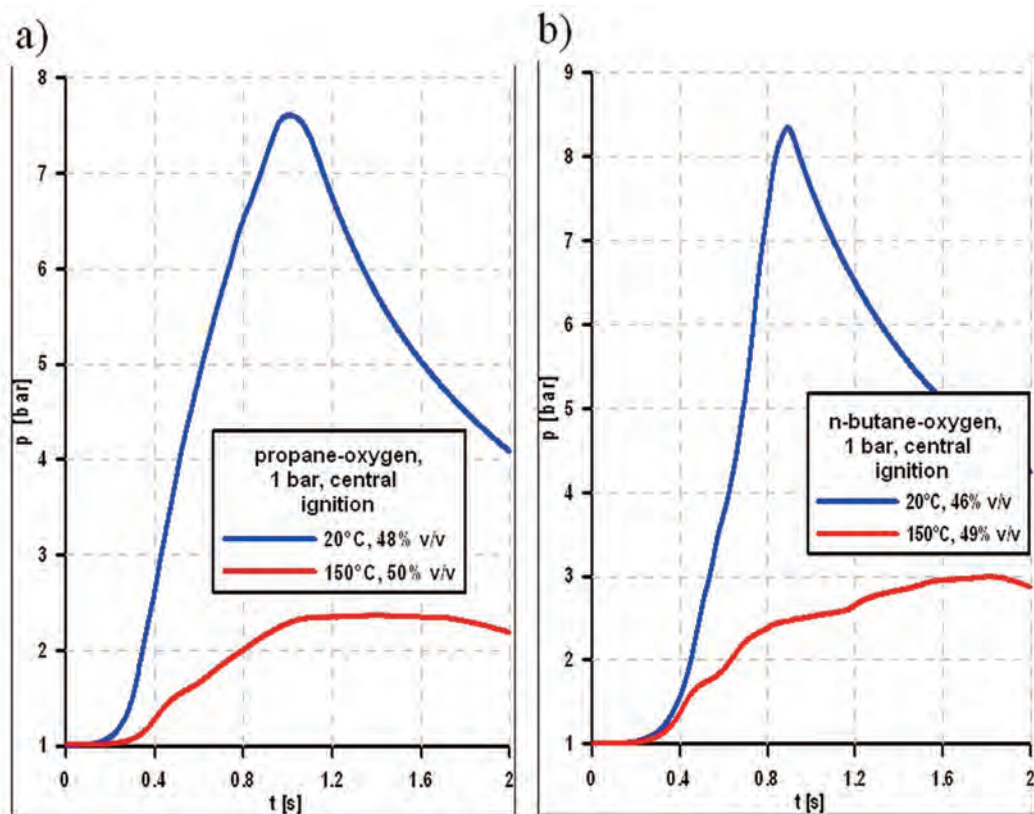


**Fig. 3. The UEL approximation of propane-oxygen (left) and n-butane-oxygen (right) mixtures; 2,3 dm<sup>3</sup> vessel, 20°C, 1 bar, central ignition, 7% criterion**



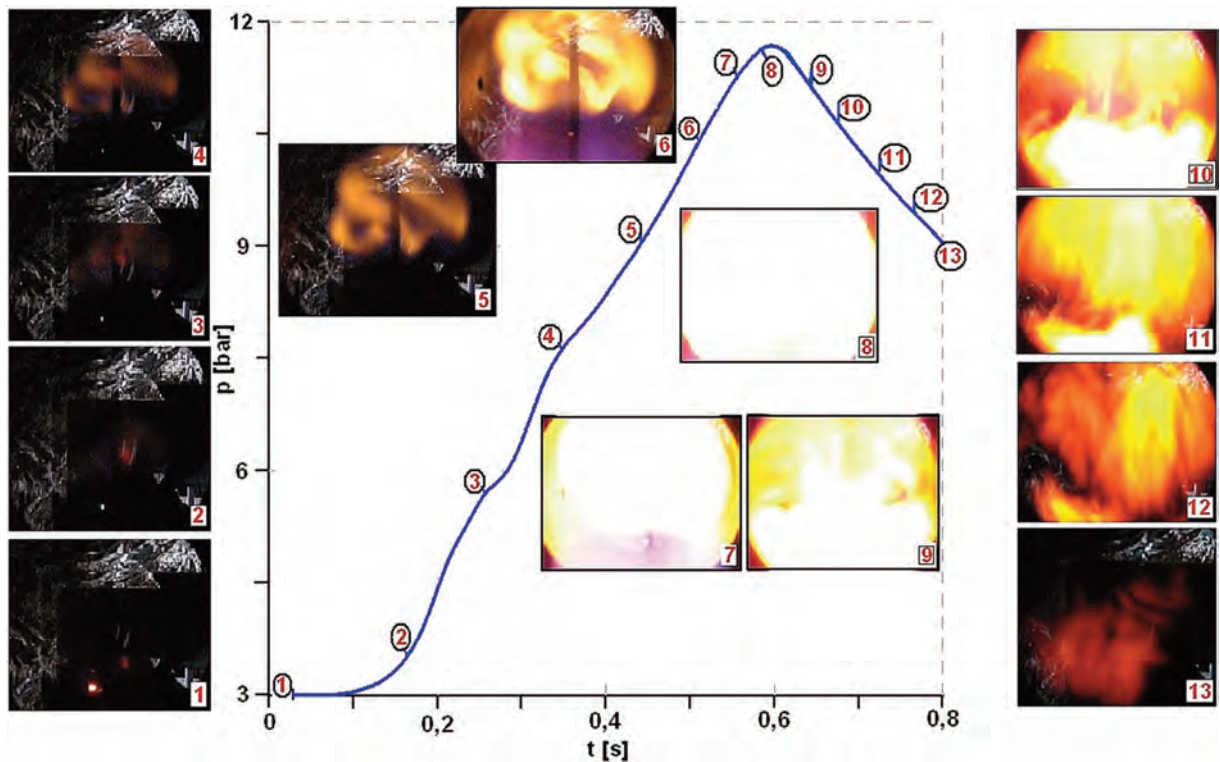
**Fig. 4. The comparison of pressure rise for 5 different initial pressures for 2 ignition positions; 2,3 dm<sup>3</sup> vessel, 20°C**

Maximum explosion pressure decreased as initial temperature increased in the case of all investigated mixtures. Examples are presented in Fig. 6. This was probably due to the decrease of the mass of mixture inside the chamber (at given initial pressure).



**Fig. 5. The comparison of the pressure histories in the combustion vessel 2,3 dm<sup>3</sup> for two initial temperatures for central ignition position, 20°C**

At higher initial pressure mixture ignition occurred quite easily but the time of the explosion development lengthened. It means that the higher pressure, the slower flame propagation velocity. When increasing the initial pressure in a rich mixture, the expanding flame ball becomes more irregular in shape (Fig. 7).

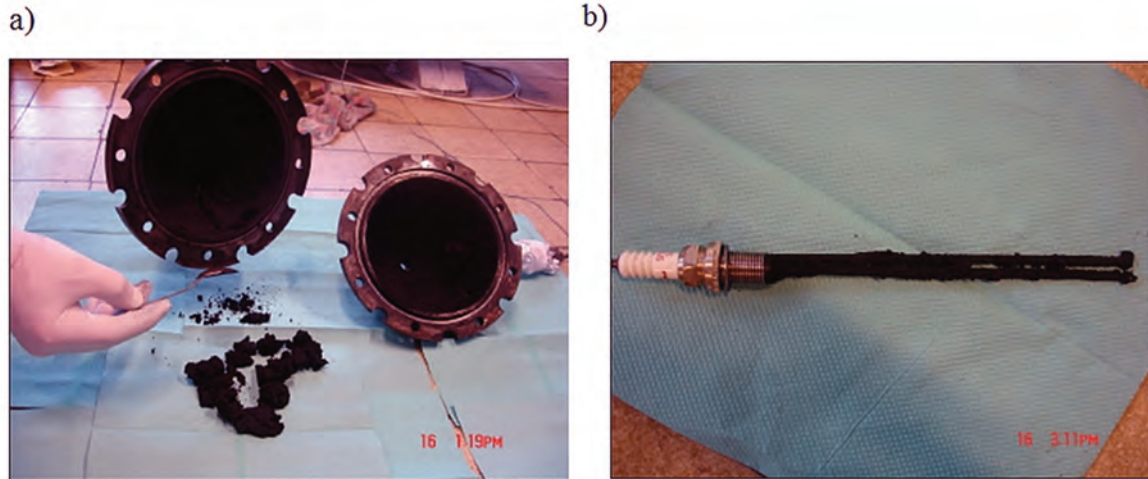


**Fig. 6. Flame propagation in 2,3 dm<sup>3</sup> vessel; 62 mol.% ethane-oxygen mixture, bottom ignition (~ 0,1 J), 20°C, 3 bar**

The experimental results generally show an increase in soot volume fraction with increasing fuel content in the test mixture cases. Besides, it was possible to find the sooting tendency, that can be described as follows;

methane < ethane < propane < n-butane.

In some experimental cases the soot volume fraction was very high, especially at higher pressure and lower temperature (Fig. 8).



**Fig. 8. The effect of soot formation; propane-oxygen mixture in 2,3 dm<sup>3</sup> vessel, 20°C, 3 bar; a) inside the combustion chamber, b) ignition device**

## 6. CONCLUSIONS

Methane, ethane, propane and n-butane in their rich mixtures with oxygen were examined during the experimental work. Key findings of this part of the research are:

- the upper explosion limits, in the examined range of the mixtures, strongly depend on the initial mixture temperature
- it was also observed that initial pressure has a significant influence on rich explosion limits, especially in the case of ethane-oxygen mixtures
- also the duration time of the explosion at rich limit increases significantly in the case of ethane-oxygen rich mixtures for higher initial pressures
- maximum explosion pressure decreases as initial temperature increases in the case of all investigated mixtures - due to the decrease of the mass of mixture inside the chamber (at given initial pressure)
- the change of the maximum explosion pressure versus initial mixture temperature can be approximated by means of a linear function for all oxygen mixtures
- the change of the upper explosion limit versus initial mixture pressure can be approximated by means of a linear function only for methane, ethane and propane -oxygen mixtures, not for ethane-oxygen mixtures
- lowering the ignition source position leads to easier ignition and higher explosion pressures for near upper limit mixtures, especially those with higher initial pressures – probably due to the fact that in this case more mixture is involved in combustion, and the whole process takes more time

Obtained results of the upper explosion limit for lower gaseous alkanes mixtures with oxygen as a function of initial pressure and temperature might be very useful not only for better understanding of explosive properties of this combustible mixtures but also would contribute to improve the safety conditions in many industry applications. The results of the study indicate that apparently inflammable mixtures can nevertheless become hazardous depending on the initial mixture conditions.

## 7. LITERATURE

- [1] A. Pekalski, E. Terli, J. F. Zevenbergen, S. M. Lemkowitz, and H. J. Pasma, *Combustion Institute Proceedings*, **30**, 1133–1139 (2005).
- [3] L.G. Britton, Two hundred years of flammable limits, *Process Safety Progress*, **21**, 1-11, (2002).
- [4] K. Holtappels, V. Schroeder, A. Kobiera, P. Wolanski, M. Braithwaite, H.J. Pasma, Gas explosion safety characteristics and anomalies at unusual conditions, *Proceedings of the 12th international symposium on loss prevention and safety promotion in the process industries* Edinburgh, UK, (2007).
- [5] K.K. Eltschlager, et al. *Technical Measures for the Investigation and Mitigation of Fugitive Methane Hazards in Areas of Coal Mining* U.S. Department of The Interior Office of Surface Mining, Pittsburgh, 2001.
- [6] D.J. Halliday *Investigation of Natural Gas Explosions* Forensic Science Service Metropolitan Laboratory, London, 2004.
- [7] J. Dwyer, J.G. Hansel, T. Philips *Temperature Influence on the Flammability Limits of Heat Treating Atmospheres* Air Products and Chemicals, Allentown, 2000.

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### **BADANIA GÓRNEJ GRANICY WYBUCHOWOŚCI (GGW) MIESZANIN GAZOWYCH ALKANÓW W TLENIE W NACZYNIU KULISTYM W WARUNKACH PODWYŻSZONEJ TEMPERATURY T ORAZ CIŚNIENIA p**

#### **Streszczenie**

*Przedstawiona praca doświadczalna została wykonana w laboratoriach Instytutu Techniki Ciepłej Politechniki Warszawskiej. Artykuł zawiera wyniki serii pomiarów, których celem było ustalenie wpływu wybranych parametrów fizycznych na wartość ciśnienia wybuchu dla mieszanin gazowych alkanów z tlenem. Dane takie, łącznie z wyznaczoną wartością górnej granicy wybuchowości (GGW) dla poszczególnych mieszanin, mają podstawowe znaczenie dla ustalania odpowiednich norm bezpieczeństwa w przemyśle chemicznym. Badaniom poddano gazowe alkany, a więc metan, etan, propan oraz n-butan. Wyniki, prezentowane w postaci sumarycznych danych (tabel) zostały uzyskane w wyniku przeprowadzenia pomiarów w stalowym naczyniu kulistym o objętości 2,3 dm<sup>3</sup>. Jako źródło zapłonu użyto tzw. eksplodujący drucik (exploding wire), który uwalniał za każdym razem około 0,1 J energii. Przebieg zmian ciśnienia w czasie rejestrowano przy użyciu szybkiego czujnika piezoelektrycznego. Zbadano wpływ temperatury początkowej mieszanin testowych, w zakresie od 20 °C do 200 °C. Przeprowadzono również pomiary w zakresie wzrastającego ciśnienia początkowego mieszanin. Na ich podstawie autorzy wyznaczyli wyraźne zależności GGW od początkowej wartości T oraz p badanych mieszanin.*