FIRE SAFETY CHARACTERISTICS OF NATURAL GAS WITH HYDROGEN ADMIXTURE

***Matěj Mašín*[1]*, Daniel Maxa*[1]*, Jan Karl*[2]*, Martin Stukbauer*[3]**

[1]*Department of Sustainable Fuels and Green Chemistry, University of Chemistry and Technology, Prague*
[2]*Technical Institute of Fire Protection of the Czech Republic, Písková 808/42, Prague*
[3]*CEPS, a.s. Belnická 628, Jesenice, Czech Republic*
Daniel.Maxa@vscht.cz

The increasing pressure to decarbonise energy production leads to the need to use low or zero carbon fuels or energy carriers. One of the promising fuels of the future is hydrogen, which is carbon-free if renewable energy sources are used for its production. However, the capacity for hydrogen production is currently insufficient to make it applicable on a large scale. Adding hydrogen to natural gas allows for a reduced carbon footprint without costly modifications to pipeline distribution network. However, changing the composition of gas in transport and distribution facilities requires a thorough assessment of the impact on operational safety. Fire safety of flammable mixtures is commonly assessed on the basis of explosive limits and other parameters. Although methods are available to calculate these parameters based on the composition of the mixtures being evaluated, the final safety assessment should rely on actual measured values. The scope of this work is to determine the explosion limits of natural gas from the transit system and changes in the limits caused by the addition of hydrogen at the concentration levels of 10% and 20% (v/v). Obtained experimental results were further compared with theoretically calculated values. Attention was also paid to the change in maximum explosion pressure, maximum pressure rise rate and oxygen concentration limits (LOC). As a result, valuable data on the expansion of the explosion limits of natural gas after the addition of hydrogen are presented.

Key words: fire safety, natural gas, hydrogen, explosion limit, limiting oxygen concentration

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1. Introduction

Fire safety is extremely important in the transport, storage and processing of flammable liquids, gases and chemicals [1]. Basic parameters describing the flammability of substances and their mixtures have been well described in the past. These are mainly the lower and upper explosive limits (LFL, UFL) describing the range of concentrations at which a substance in a mixture with air is capable of combustion or explosion. Methods for estimating flammability limits of mixtures were well established [2,3]. Most of them are based on the well-known formula of Le Chatelier [4,5]. These methods were then widely applied in practice, particularly for mixtures of hydrocarbons in oil and gas industry [6-8]. Other approaches leading to simple calculation methods found also their application, such as the use of heat of combustion in Lloyd's rule [9]. In recent years, more sophisticated approaches for calculation of flammability limits were suggested, based on basic descriptions of ignition and flame propagation phenomena [10]. Calculated adiabatic flame temperature (CAFT) methods giving empirically estimated values are the most cited, which use the energy balance of the fuel-oxidizer reaction system [11,12]. QSPR (quantitative structure-relationship between properties) approach uses multivariate regression of the data set of compounds with known flammability limits to obtain a correlation between molecular structure and flammability limits [13].

Parameters describing the dynamics of the reactions taking place may then be important for engineering practice. These include the burning rate, the maximum explosion pressure in a closed container and the rate at which it is reached. Limiting the fire hazard in technical and industrial applications can be achieved by inerting using a gas that does not react with either oxygen or the components of the flammable mixture [14]. The parameter used to evaluate inerting is the limiting oxygen concentration (LOC), which is the highest possible oxygen concentration at which a mixture with any ratio of fuel to inerting agent is non-combustible [15]. As with the estimation of explosion limits for mixtures of combustibles and air, flammability assessment procedures have been developed and experimentally validated for mixtures of combustibles, air and inert substances [16-19].

The object of this work is to obtain data on explosion limits, explosion pressures and oxygen concentration limits in a system containing natural gas, hydrogen, air and nitrogen as an inert agent. The data obtained were then compared with those calculated by various estimation methods.

2. Experimental

2.1. Material and samples

- Natural gas sampled at the pipeline control station (January 2023)
- Natural gas with 10 % and 20 % hydrogen (the preparation procedure is described in Chapter 2.2)
- Hydrogen with a purity of > 99,9995 %
- Air (nitrogen+/oxygen mixture in the ratio of 79:21)
- Nitrogen

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2.2. Preparation of samples containing hydrogen and analysis of the samples

A piping and pressure measurement system of the test equipment used for explosivity measurements (see Chapter 2.3) was used to prepare the mixtures. The amount of hydrogen added to the pressure vessel was controlled by increasing the total pressure to match the partial pressure of hydrogen in the desired mixture.

The resulting gas mixture was collected in sampling bags (Tedlar) for the analysis of the main components using a gas chromatograph (HP 6890) equipped with two analytical channels. The first channel (capillary column, Supelco Al_2O_3/KCl 50 m × 530 µm × 4 µm; flame ionisation detector) was used for the analysis of C_1-C_7 hydrocarbons. The second channel with packed pre-column, HayeSep Q 0,9 m × 3,2 mm, 80/100 mesh; capillary column 1, HP PLOT Q 30 m × 530 µm × 40 µm; capillary column 2, HP PLOT Molsieves 5A (30 m × 530 µm, 50 µm film) and TCD detector was used for the analysis of permanent gases. The carrier gas (He) flow rates, the oven temperature program (70 °C for 7 min, then increasing to 90 °C at 10 °C.min^{-1}, then to 220 °C at 20 °C/min, then constant temperature for 7 min) and the valve switching times were optimized to allow complete gas analysis in less than 20 min.

2.3. Test apparatus

The measurements were carried out in equipment compliant with EN 1839, method B [20]. The pressure autoclave is a spherical vessel with a volume of 10 dm^3, a minimum wall thickness of 25 mm and an internal diameter of 270 mm. The vessel was fitted with a circular lid attached to the flange of the vessel body. This flange joint was sealed with a trapezoidal graphite gasket.

A sketch of the device is shown in Figure 1. The test vessel was equipped with two thermocouples (one in the upper hemisphere and one in the lower hemisphere) and one pressure sensor (Kistler) with a range of 0-2000 bar. The initiation was carried out by means of a resistance ignition coil (Kanthal), which was located in the lower part of the device and its tightness was ensured by Teflon tape. The ignition energy was calculated to be in range of 10-20 J, The device was also equipped with a diaphragm pump for mixing the contents of the vessel, and isolation valves to ensure that the pump and piping were disconnected from the explosion.

Gas distribution lines are grouped into a filling panel. This is further used for filling, depressurization, evacuation, and flushing of the test vessel and piping systems. Up to 6 gas source inputs to the filling panel and subsequently one output leading to the test vessel are available. All inputs are equipped with check valves, pressure gauges, shut-off valves, pressure relief valves, and a system of self-closing quick couplings. A set of measuring sensors for accurate pressure determination in various ranges and a main shut-off valve for complete closure of the test vessel are installed before the test vessel.

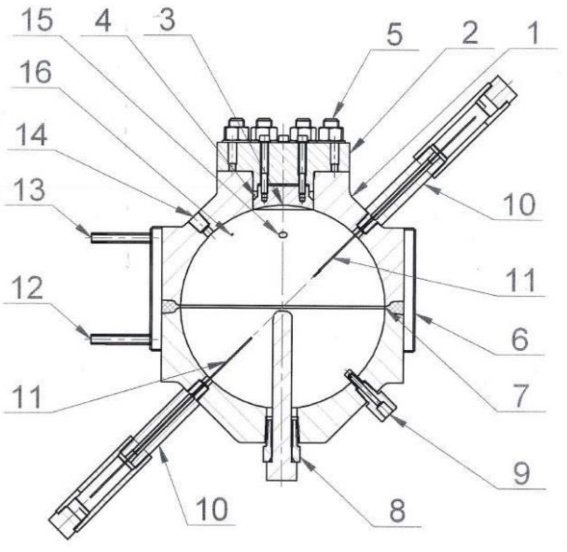


Fig. 1: Explosion vessel
Body (1), lid (2), inner cap (3), graphite seal (4), screw (5), duplicator/double jacket (6), weld (7), initiating electrode (8), special nozzle (9), thermowell (10), thermocouple (11), heating medium inlet (12), heating medium outlet (13), rupture disk (14), HPLC pump connection fitting (15), explosion pressure sensor (16)

2.4. Procedure for determining explosion limits

The measurements were carried out according to the standard procedure set out in EN 1839 [20]. The standard mentions two possible methods of performance, method B (determination in spherical or cylindrical test vessels) was followed. The standard defines an explosive mixture as one for which the explosion overpressure measured during the test is equal to or greater than the sum of the overpressure generated by the initiating source in air and (5 ± 0,1) % of the initial pressure.

The internal methodology of Technical Institute of Fire Protection of the Czech Republic No. 37-14 [21] is based on the above-mentioned standard but defines a different criterion for determining an explosion, which is an increase in temperature inside the test vessel by at least 50 °C compared to the initial temperature. The reason for this criterion is small pressure changes near the explosion limits. Both methods define the lower explosion limit (LEL) as the highest concentration of flammable substance at which no explosion occurs in repeated measurements. The upper explosion limit (UEL) is defined as the lowest concentration of flammable substance at which no explosion occurs in repeated determinations.

Before the actual test, the apparatus was assembled, properly sealed, and tightness was verified by a standardized method. The apparatus was then evacuated to the technological limit of the available vacuum pump (less than 0.03 bar residual pressure). Individual components were then filled into the autoclave through the filling panel in the following order: flammable substance, inert (if used), and air.

The concentrations of individual components in the autoclave were determined based on their partial pressures in the mixture. After mixing the sample, the circulation pump was turned on to ensure sample homogeneity, and after it was turned off, the apparatus was left to stabilize, and all valves were closed. Subsequently, the measurement recording was started, and the melting wire was initiated from the control panel.

2.5. Procedure for Determining Maximum Explosion Pressure

In the case of determining the maximum explosion pressure, the same technological equipment was used in the same arrangement, and the measurements were carried out in the same order. The monitored parameter was the difference between the maximum and initial pressure. These values were read from the record of pressure course during the explosion. The concentrations of flammable substance for determining the maximum explosion pressure were chosen in the vicinity of the stoichiometric composition of the mixture.

2.6. Procedure for Determining Limiting Oxygen Concentration

The limiting oxygen concentration is the highest oxygen concentration at which no explosion occurs at any concentration of flammable substance. The experimental procedure was identical to the procedure for determining the lower and upper explosion limits. In the case of the limiting concentration, the proportions of individual components were chosen so that the concentration of flammable substance was equal to the lower explosion limit. The oxygen content was then gradually reduced by replacing the oxidizer with an inert gas (nitrogen) until no explosion occurred.

2.7. Calculations of explosion limits

2.7.1 Calculation of explosion limits of a gaseous mixture according to Le-Chatelier

The Le-Chatelier equation is used as a suitable calculation method for estimating the explosive range, in which the input data are the explosive limits of the pure mixture components together and their concentrations. Several basic assumptions must be met for the method to be applicable:

- Pure substances must have similar adiabatic heating (adiabatic flame temperature)
- Pure substances must have similar combustion kinetics
- Products must have constant heat capacities

The Le-Chatelier equation is widely used in technical practice and its practical application is anchored in EN 386405 [22]. This method provides a more accurate estimate than the Lloyd's rule (see Chapter 2.7.2) and its variants for the lower and upper limits, including the inclusion of inert gas effects, are described by equations (1), (2) and (3):

$$L_1(h,d) = \frac{100}{\sum_{i=1}^{i} \frac{y_i}{L_i(h,d)}} \qquad (1)$$

where L_1(h,d) denotes the explosive limit of the mixture without inert gases, yi denotes the concentration of component i in the combustible gas and L_i(h,d) denotes the explosive limit of pure substance i. All values in (% vol.).

$$L_2(h,d) = \frac{100}{\sum_{i=1}^{i} \frac{y_i}{L_i(h,d)} + \frac{n}{100}} \qquad (2)$$

where L_2(h,d) denotes the explosive limits of flammable gases in a mixture with air or oxygen and a small inert content (up to 10 % vol.) and n is the sum of the concentrations of the inert components in (% vol.).

$$L_3(h,d) = L_1(h,d) \cdot \frac{100 \cdot \left(1 + \frac{n}{100-n}\right)}{100 + L_1(h,d) \cdot \frac{n}{100-n}} \qquad (3)$$

where L_3(h,d) denotes the explosive limits of flammable gases mixed with air or oxygen with an inert gas content greater than 10 % vol.

2.7.2 Lloyd's Rule

The Lloyd's rule is used to empirically estimate the explosive limits from the composition of the substance and is based on the calculation of the stoichiometric composition of the combustible agent in the air mixture, which is based on the general combustion equation (4). From this equation, the stoichiometric concentration of the combustible agent is then calculated from equations (5) and (6) according to Zabetakis [7]:

$$C_nH_mO_\lambda F_k + \left(n + \frac{m-k-2\lambda}{4}\right) O_2 \rightarrow n\,CO_2 + \left(\frac{m-k}{2}\right) H_2O + k\,HF \qquad (4)$$

$$C_{st} = \frac{n_{fuel}}{n_{fuel} + n_{air}} \cdot 100 \qquad (5)$$

$$C_{st} = \frac{100}{1 + \frac{1}{0.21} \cdot \left(n + \frac{m-k-2\lambda}{4}\right)} \qquad (6)$$

where C_{st} is the stoichiometric concentration, n_{fuel} is the quantity of fuel (mol), n_{air} is the quantity of air (mol) and 0.21 is the oxygen content of the air.

Based on the stoichiometric concentration of the combustible agent, the upper and lower explosive limits can then be estimated according to relations (7) and (8):

$$UEL = 3{,}5 \cdot C_{st} \qquad (7)$$

$$LEL = 0{,}55 \cdot C_{st} \qquad (8)$$

where UEL is the upper explosive limit in (% mol. or vol.) and LEL is the lower limit (% mol. or vol.), the coefficients were defined by Zabetakis [7] and Tong [24].

2.7.3 Calculation of the explosive limits of a pure substance from the carbon and hydrogen content

Shimy [25] uses equations (9) and (10) for the calculation, for the lower explosive limit he works with the thesis that the lower explosive limit of hydrocarbons depends only on the number of carbon atoms and therefore does not depend on the number of hydrogen atoms s in the structure. Whereas for the upper explosive limit he already accounts for the primary effect of the hydrogens present in the chain. From the equations for each hydrocarbon group, those that provide an estimate of the limits for paraffinic hydrocarbons and olefins have been selected:

$$\mathrm{LEL} = \frac{6}{\mathrm{nC}} + 0.2 \qquad (9)$$

$$\mathrm{UEL} = \frac{60}{\mathrm{nH}} + \frac{\mathrm{nC}}{20} + 2.2 \qquad (10)$$

where nC is the number of carbons in the structure and nH is the number of hydrogens in the structure.

3. Results and discussion

3.1. Composition of used gaseous samples

The hydrocarbon composition of the sample with hydrogen is always relatively equivalent to the composition without hydrogen. The sample contains a greater amount of higher hydrocarbons compared to natural gas from a transit pipeline in the past.

Tab 1 Composition of tested mixtures (% mol.)

Component	Natural gas	NG + 10 % H_2	NG + 20 % H_2
Methane	89,537	80,807	70,734
Ethane	5,604	5,057	4,427
Propane	1,008	0,910	0,797
i-Butane	0,144	0,130	0,114
n-Butane	0,132	0,119	0,105
2,2-dimethylpropane	0,002	0,002	0,002
i-Pentane	0,028	0,025	0,022
n-Pentane	0,019	0,017	0,015
2,2-dimethylbutane	0,002	0,002	0,002
Cyclopentane	0,002	0,002	0,002
2,3-dimethylbutane	0,002	0,002	0,002
2-methylpentane	0,006	0,005	0,005
3-methylpentane	0,004	0,004	0,003
Hexane	0,004	0,004	0,003
Methylcyclopentane	0,006	0,005	0,005
Benzene	0,002	0,002	0,002
Cyklohexane	0,006	0,005	0,005
Nitrogen	2,076	1,874	1,640
Carbon dioxide	1,416	1,278	1,119
Hydrogen	0,000	9,750	21,000
Total	100,000	100,000	100,000

3.2. Explosion limits

3.2.1 Explosion limits of natural gas

A record of the tests carried out with different concentrations of the starting mixture is given in Tables 2 and 3. It gives the partial pressures of the combustible, the total pressure, the initial temperature, the combustible content and the test result. The explosive limit in this case is between (4,76 ± 0,32) % mol. and (16,62 ± 0,33) % mol.

Tab. 2 Measurement of LEL

Exp. No.	p_{fuel} (kPa)	p_{total} (kPa)	T_{init} (°C)	y_{fuel} (% mol.)	Explosion
1	4.8	100.8	16.1	4.82	+
2	4.8	102	16.5	4.76	-
3	5	106.3	16.7	4.76	-
4	4.7	99.8	15.5	4.76	-

Tab. 3 Measurement of UEL

Exp. No.	p_{fuel} (kPa)	p_{total} (kPa)	T_{init} (°C)	y_{fuel} (% mol.)	Explosion
1	16.8	103.1	16.5	16.49	+
2	16.3	99.1	16.5	16.64	-
3	16.4	99.9	16.7	16.61	-
4	16.8	102.3	16.9	16.62	-

3.2.2 Explosion limits of natural gas with hydrogen (9,75 % mol.)

A record of the tests carried out with different concentrations of natural gas with hydrogen is given in Tables 4 and 5. The flammability limit in this case is between (4,74 ± 0,80) % mol. and (17,20 ± 0,80) % mol. These measured values correspond to the theoretical assumption of a broadening of the explosive limits due to the addition of hydrogen, which has a wider explosive limit.

Tab. 4 Measurement of LEL

Exp. No.	p_{fuel} (kPa)	p_{total} (kPa)	T_{init} (°C)	y (% mol.)	Explosion
1	4.8	100	18.9	4.86	+
2	4.7	100.2	18.4	4.75	-
3	4.6	98.2	18.6	4.74	-
4	4.6	98.2	19.3	4.74	-

Tab. 5 Measurement of UEL

Exp. No.	p_{fuel} (kPa)	p_{total} (kPa)	T_{init} (°C)	y (% mol.)	Explosion
1	16.9	100.2	19.5	17.06	+
2	17.1	100.5	19.7	17.21	-
3	17.0	100.1	19.7	17.18	-
4	17.0	100.0	18.9	17.20	-

3.2.3 Explosive limits of natural gas with hydrogen (21,0 % mol.)

The record of the tests performed with different concentrations of natural gas with hydrogen is given in Tables 6 and 7. The flammability limit in this case is between (4,64 ± 0,33) % mol. and (20,37 ± 0,35) % mol. These measured values are consistent with the theoretical assumption of a further extension of the explosive limits.

Tab. 6 Measurement of LEL

Exp. No.	p_{fuel} (kPa)	p_{total} (kPa)	T_{init} (°C)	y (% mol.)	Explosion
1	4.6	97.3	24.1	4.78	+
2	4.7	102.3	22.3	4.65	-
3	4.6	99.9	22.5	4.66	-
4	4.5	98.6	22.8	4.62	-

Tab. 7 Measurement of UEL

Exp. No.	p_{fuel} (kPa)	p_{total} (kPa)	T_{init} (°C)	y (% mol.)	Explosion
1	20	100	22.7	20.23	+
2	20.2	100.5	24.5	20.34	-
3	20.2	100.3	22.7	20.38	-
4	19.9	98.7	22.8	20.40	-

3.3. Maximum explosion pressure and maximum rate of explosion pressure rise

A record of the tests carried out with different concentrations of the initial mixture is given in Table 8. The maximum explosion pressure was reduced by about 1 bar for the sample with 20 % H_2 compared to the two previous concentrations. Next, Figure 2 shows a comparison of the explosion pressures under different concentrations of natural gas alone and natural gas with hydrogen admixture.

Table 8 Data of maximum pressure and pressure rate

Sample	Max. pressure		Max. pressure rate	
	y (% mol.)	p_{max} (MPa)	y (% mol.)	$(dp/dt)_{max}$ (MPa/s)
Natural gas	10.64	0.74	10.13	20
NG + 9.75 H_2	10.08	0.74	10.08	19.9
NG + 21.0 H_2	9.61	0.65	10.13	17

3.4. Limiting oxygen concentration

During the measurement of the limiting oxygen concentration, 4 sample concentration levels were measured, according to which the curves for the LOC were subsequently plotted.

3.4.1 LOC of natural gas without hydrogen admixture

Table 9 shows the tests carried out at different concentrations of the combustible, with the explosion limits below the line to better plot the curve in Figure 3. The highest oxygen concentration for which no explosion occurred under any concentration of combustible is shown in bold. The experiments were measured in the temperature range of 21.3–22.3 °C.

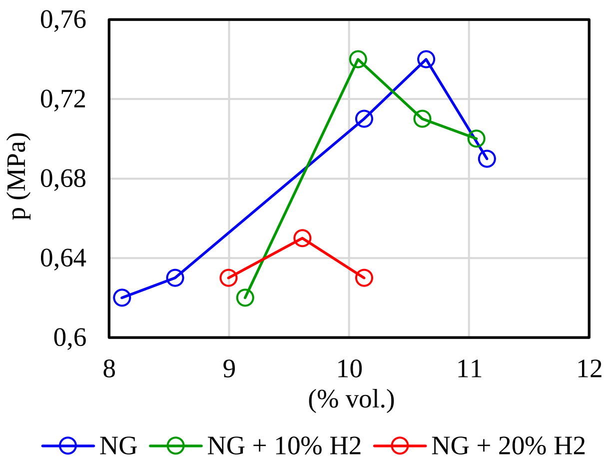


Fig. 2 Dependence of the explosion pressure on the concentration of the combustible in the stoichiometry region

Tab 9 Experimental data for natural gas LOC (% mol)

Fuel	Inerts	Oxygen	Explosion
4.88	82.21	12.91	+
4.90	82.40	12.71	+
4.84	82.90	12.26	+
4.91	83.02	12.07	+
4.88	83.23	11.89	+
4.84	83.49	11.67	+
4.88	83.63	11.48	+
4.87	83.86	11.27	-
5.84	83.47	10.68	-
5.87	83.23	10.90	-
5.89	82.83	11.27	-
5.80	82.52	11.67	+
5.87	82.64	11.50	+
5.38	83.36	11.26	+
5.39	**83.73**	**10.88**	**-**
5.35	83.57	11.08	+
6.87	81.25	11.88	-
6.81	80.76	12.42	+
6.83	80.96	12.20	-
4.59	75.41	20.00	-
16.03	66.46	17.51	-

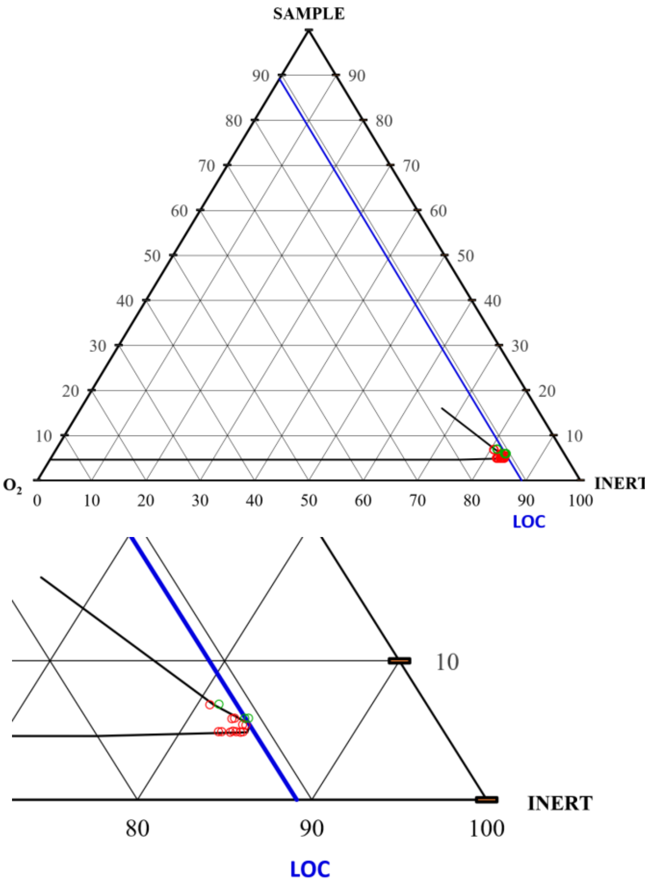


Fig. 3: Ternary diagram of the composition of the combustible-oxygen-inert mixture for natural gas and detailed view of the region with LOC

3.4.2 LOC of natural gas with hydrogen (9.75 % mol.)

Table 10 shows the tests carried out at different concentrations of the combustible, with the explosion limits below the line to better plot the curve in Figure 5. The limiting oxygen concentration is shown in bold. The experiments were measured in the temperature range 19.7–21.2 °C.

Tab 10 Experimental data for LOC measurements (% mol)

Fuel	Inerts	Oxygen	Explosion
4.90	85.49	9.61	-
4.85	85.07	10.08	-
4.91	84.21	10.88	-
4.70	83.43	11.86	-
4.80	82.25	12.95	+
4.73	82.75	12.52	+
4.81	83.02	12.17	+
4.71	83.17	12.12	+
4.69	83.40	11.91	-
6.19	81.91	11.90	+
6.87	81.74	11.39	-
6.85	81.44	11.71	-
6.89	81.16	11.95	-
6.87	80.91	12.22	-
6.86	80.72	12.42	+
8.86	78.50	12.64	-
8.88	77.93	13.19	-
8.79	77.26	13.95	+
8.81	77.74	13.44	+
5.70	83.30	11.01	+
5.85	83.40	10.75	-
5.34	83.91	10.76	+
5.39	84.06	10.55	+
5.34	**84.33**	**10.34**	-
4.59	75.40	20.00	-
16.64	65.97	17.39	-

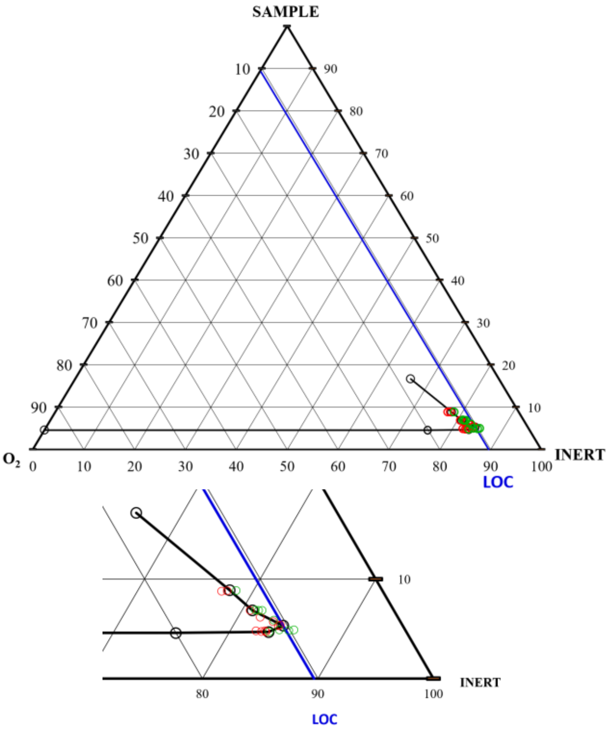


Fig 5 Ternary diagram of the composition of the combustible-oxygen-inert mixture for natural gas with hydrogen (9.75 % mol.) and detailed view of the region with LOC

3.4.3 LOC of natural gas with hydrogen (21.0 % mol.)

Table 11 shows the tests carried out at different concentrations of the combustible, with the explosion limits below the line to better plot the curve in Figure 7. The highest oxygen concentration for which no explosion occurred at any concentration is shown in bold. The experiments were measured in the temperature range 21.8–23.1 °C.

Tab 11 Experimental data for LOC measurements (% mol)

Fuel	Inerts	Oxygen	Explosion
5.05	83.58	11.37	+
4.76	84.36	10.88	-
4.92	83.96	11.12	+
6.04	83.38	10.58	+
5.94	83.67	10.39	-
6.79	82.00	11.21	+
7.01	82.32	10.68	-
6.89	82.21	10.90	+
8.68	79.34	11.98	-
8.85	78.75	12.40	+
8.94	**78.86**	**12.21**	**-**
4.47	75.49	20.03	-
19.55	63.68	16.78	-

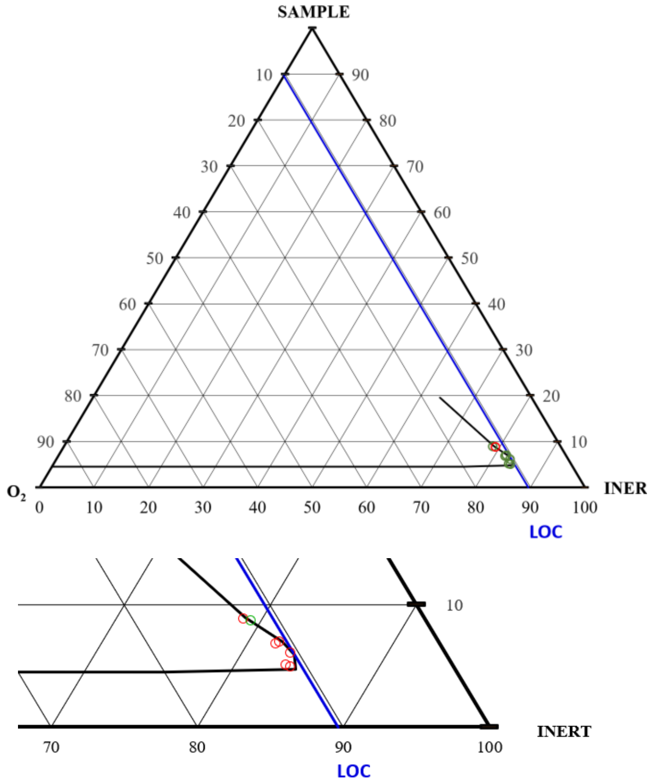


Fig. 7 Ternary diagram of the composition of the combustible-oxygen-inert mixture for natural gas with hydrogen (21 % mol.) and detailed view of the region with LOC

3.5. Comparison of the determined and calculated explosion limits

Tables 12, 13, and 14 compare the different methods for the theoretical calculation with the measured values. For the calculation, apparatus working with the analytical composition of natural gas was used. Considering a total nitrogen and carbon dioxide concentration between 3-4 % mol. The equation according to EN 386405 was not used for mixtures with inert gas content over 10 % mol.

For the natural gas LEL, the Lloyd's rule came closest to the measured value. For the UEL of natural gas, the closest estimate was from a calculation of the carbon and hydrogen abundances.

For the LEL of natural gas with hydrogen admixture, all estimates were about equally close to the measured value, and for the UEL, again the closest estimate was from a calculation from the carbon and hydrogen representation.

Tab 12 Comparison of calculated natural gas explosion limits with experimental results

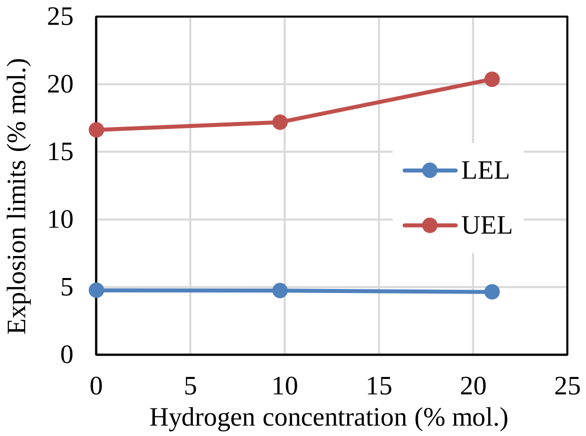
Method	LEL	UEL
ČSN EN 386405	4.2	17.3
ČSN EN 386405 with inerts up to 10 %	4.2	17.2
Lloyd’s rule	4.9	31.3
Carbon/hydrogen abundance	5.7	16.6
Experimental results	4.76 ± 0.32	16.62 ± 0.33

Tab 13 Comparison of calculated gas explosion limits of natural gas with 9.75 % hydrogen with experimental results

Method	LEL	UEL
ČSN EN 386405	4.2	18.7
ČSN EN 386405 with inerts up to 10 %	4.2	18.6
Lloyd’s rule	5.3	33.7
Carbon/hydrogen abundance	6.3	17.4
Experimental results	4.74 ± 0.80	17.20 ± 0.80

Tab 14 Comparison of calculated gas explosion limits of natural gas with 21.0 % hydrogen with experimental results

Method	LEL	UEL
ČSN EN 386405	4.2	20.6
ČSN EN 386405 with inerts up to 10 %	4.2	20.5
Lloyd’s rule	5.8	36.7
Carbon/hydrogen abundance	7.1	18.3
Experimental results	4.64 ± 0.33	20.37 ± 0.35



3.6. Comparison of measured LOC values

The comparison is shown in Table 15. As expected, the required oxygen concentration decreases as the amount of hydrogen in the sample increases, based on the stoichiometric combustion of the samples. For natural gas with 9.75% H_2 admixture, the observed LOC was higher than the value for natural gas without admixture. This could be due to the measurement bias of the lower precision pressure sensor used to determine the LOC for the natural gas with 9.75 % H_2.

Tab 15 Oxygen concentration limits for natural gas and hydrogen mixtures

Sample	y_{fuel} (% mol)	LOC (% mol)
Natural gas	5.39	10.88
NG + 9.75 H_2	5.34	10.34
NG + 21.0 H_2	5.94	10.39

3.7. Effect of hydrogen content on explosion pressures

Table 16 shows the experiments with predetermined concentrations of hydrogen in the mixture with air (composition 79 % N_2, 21 % O_2). Figure 10 shows the dependence of the maximum explosion pressure on the hydrogen concentration. Fig. 11 shows the dependence of the maximum pressure rise rate on the hydrogen concentration.

Tab 16 Hydrogen experimental data

Test No.	p_{H2} (kPa)	p_{init} (kPa)	T_{init} (°C)	y_{H2} (% mol)	p_{max} (MPa)	$(dp/dt)_{max}$ (MPa/s)
1	10	100	24.4	10.12	0.29	4.6
2	19.59	100.4	23.2	19.74	0.71	51.5
3	30.3	100.9	24.5	30.38	0.84	82.5
4	34.9	99.7	22.4	35.42	0.83	163.8
5	39.9	99.7	25.1	40.49	0.83	200.4
6	50.6	102.1	25.6	50.14	0.72	136.3
7	59.5	99.3	26	60.62	0.5	47.1
8	70.6	101	26.2	70.72	0.36	12.7

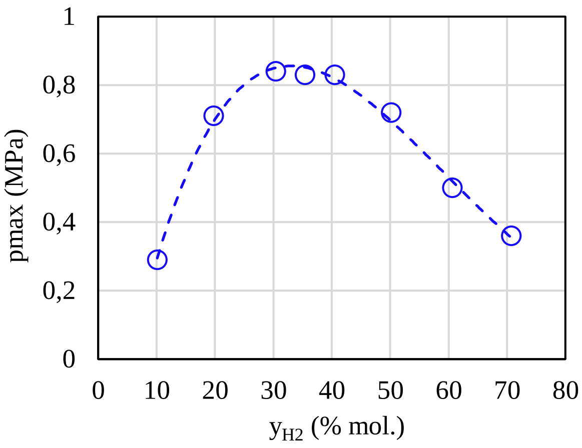


Fig. 10 Dependence of maximum explosion pressure on hydrogen concentration

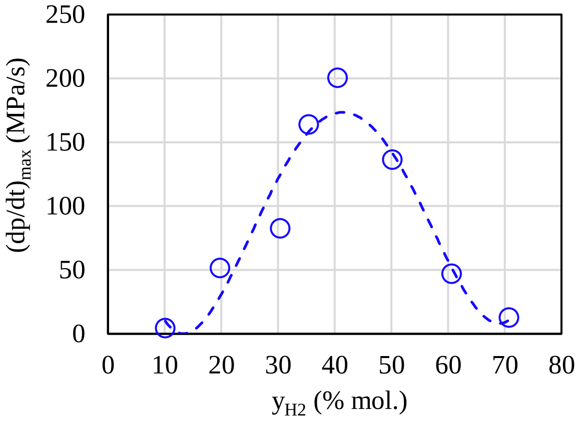


Fig. 11 Dependence of the maximum rate of explosion pressure rise on the hydrogen concentration

4. Conclusions

The addition of hydrogen to the natural gas resulted in the expected expansion of the explosive limits of the mixture. The theoretical calculation of the explosion limits of the tested mixtures based on EN 386405 provides in all cases a 'pessimistic' estimate and its application to these mixtures is therefore possible and safe. The maximum explosion pressure for natural gas and natural gas with hydrogen admixture of 9.75 % mol. remained practically unchanged, while for the sample with 21 % mol. hydrogen, there was a slight decrease.

Although the addition of hydrogen to the natural gas resulted in a gradual expansion of the flammability region of the sample between the LEL and UEL, the downward trend in the limiting oxygen concentration was less pronounced, contrary to expectations. The observed LOC for the sample with a mean hydrogen concentration of 9.75 % was even slightly higher than that of pure natural gas, but this difference was at the limit of the measurement error. The maximum explosion pressure was in the range of 30-40 % mol. of the combustible in the tested mixture, and the maximum rate of pressure rise at 40 % mol.

Mixed results were obtained in terms of theoretical calculations. The Lloyd's rule was identified as the most appropriate theoretical calculation for the LEL NG, followed by calculations based on the standard below. The Lloyd's rule could fit for LEL, but for UEL almost twice the concentration was obtained compared to the experimental values. For mixtures containing hydrogen, the closest calculation was obtained from EN 386405 [22]. The more hydrogen was present in the mixture, the closer the results of the calculation based on the standard were to the experimental values. It is worth noting that all experimental values were part of the theoretical range of explosive limits for the mixture calculated from the standard - in the case of a quick calculation to ensure safety, the standard can be used to determine theoretical values and maintain environmental safety.

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