Pressure Evolution during Confined Deflagration of n-Butane/Air Mixtures

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The peak pressures p_{max}, the maximum rates of pressure rise $(dp/dt)_{max}$ and the times necessary to reach the peak pressure θ_{max} of n-butane-air deflagrations in two closed vessels with central ignition (a spherical vessel of 5 cm diameter and a cylindrical vessel with height h = 15 cm and diameter Φ = 10 cm) are reported, for mixtures with variable fuel content (2.3 – 5.7 vol.%) and initial pressures p_0 = 0.4 - 1.2 bar, at ambient initial temperature. Adiabatic values of explosion pressures, calculated for all mixtures at p_0 = 1 bar and T_0 = 298 K, are examined against experimental values of explosion pressures observed in the two vessels. The deflagration index K_G, characteristic to deflagrations in vessels with volume V and central ignition, is calculated as $K_G = (dp/dt)_{max} \cdot \sqrt[3]{V}$ and examined against composition of flammable mixtures. All characteristic parameters of the closed vessel combustion of n-butane-air mixtures have extreme values in the concentration range 3.8 - 4.2 vol.% (equivalence ratio 1.1 - 1.2). The obtained results are discussed in connection with mixture composition and pressure.

Keywords: combustion, deflagration, n-butane, explosion pressure, maximum rate of pressure rise

Numerous studies were focused on flammability characteristics of fuel-air mixtures in closed vessels, with the purpose of determining the parameters that describe the evolution of their explosion in confined conditions. These parameters, namely the peak pressure (or maximum explosion pressure), the time necessary to reach the peak pressure, the maximum rate of pressure rise and the severity factor are the most important characteristics of combustion dynamics in deflagration regime, necessary for safety assessment in various conditions, scaling explosions in chemical reactors and design of safety devices [1-3]. Lower alkanes and their mixed blends were thus studied, due to their frequent use as fuels of industrial, transportation or domestic use: methane [4-13], landfill gas or biogas (LFG) [14], propane [1, 2, 6, 9, 10, 15-17], liquefied petroleum gas (LPG) [18-20]. The flammable mixtures were frequently characterized by the peak pressures and rates of pressure rise, necessary also in further studies on burning velocity evaluation in unsteady conditions [21-27]. Few quantitative data on flammability characteristics of *n*-butane-O_2 or *n*-butane-air mixtures in closed vessels are reported: the extreme values of explosion pressures and rates of pressure rise [2, 10, 15] and the induction periods of autoignition, at high pressures and temperatures [28, 29]. As *n*-butane is widely used either pure or mixed with propane, as domestic fuel, it is important to determine the values of its flammability parameters over the entire flammability range and to examine the pressure influence upon the closed vessel combustion of these mixtures.

The present paper reports data on explosive combustion of *n*-butane-air mixtures, obtained in two closed vessels with central ignition: a spherical vessel (volume V = 0.52 L) and a cylindrical vessel (V = 1.12 L). Mixtures with variable content of n-butane, within 2.3 and 5.7 vol.% were studied, at total initial pressures between 0.4 and 1.2 bar and ambient initial temperature. The experimental values of explosion pressures are examined in comparison with adiabatic explosion pressures, calculated for isochoric combustion after assuming the chemical equilibrium is reached throughout the flame front.

Experimental part

Experiments were performed in two closed vessels with central ignition: spherical vessel ***S*** (radius R = 5 cm) and cylindrical vessel ***C*** (height h = 15 cm and diameter Φ = 10 cm). Ignition was made with inductive-capacitive sparks produced between stainless steel electrodes by a standard automotive induction coil. The pressure variation during explosion, in both vessels ***S*** and ***C***, was recorded with piezoelectric pressure transducers (Kistler 601A), connected to Charge Amplifiers (Kistler 5001N). The signal was recorded and stored by a digital acquisition data system Tektronix TestLab 2505, usually at 5.000 signals per s. An ionization probe mounted in equatorial position of each vessel, with the tip at various distances from the wall, allowed the detection of flame front position.

Other characteristics of the experimental set-up were previously given [21-24, 27].

The explosive mixtures were obtained by partial pressure method, in 10 L steel cylinders, at 4 bar total pressure. Such mixtures were used for extensive measurements of pressure-time variation, in experiments at various initial pressures. In addition, several fuel-air mixtures with a high fuel content ("primary mixtures") were prepared (e.g. 10 vol.%) in storage vessels. "Secondary mixtures" were obtained from the "primary mixtures" directly in the explosion vessel, using adequate partial pressures of primary mixture and air. This procedure allowed an increased number of experiments, usually at ambient initial pressure.

The measurements were performed at ambient temperature and various total initial pressures within 0.4 and 1.2 bar.

n-Butane (SIAD-Italy), 99.9% was used without further purification.

Computing methods

The calculation of adiabatic explosion pressure, adiabatic flame temperature and burned gas composition in isochoric combustion was made with the program ECHIMAD [30], based on a general algorithm meant to compute the equilibrium composition of products for any

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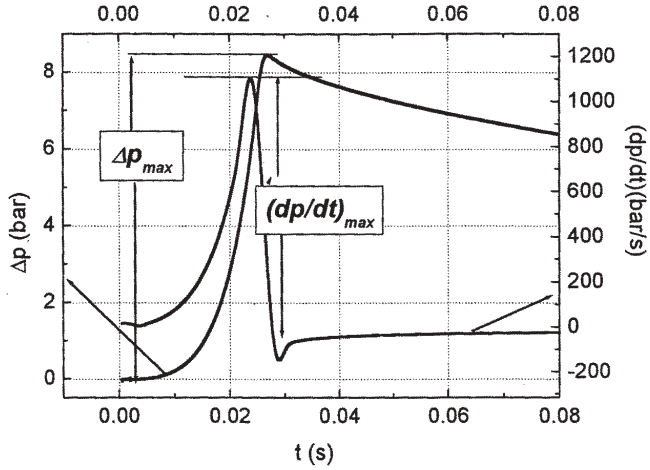

Fig. 1. Variation of pressure and of pressure rise rate during the explosion of a 3.10 vol.% n-C_4H_{10}-air mixture in vessel **S**, at T_0 = 298 K and p_0 = 1 bar

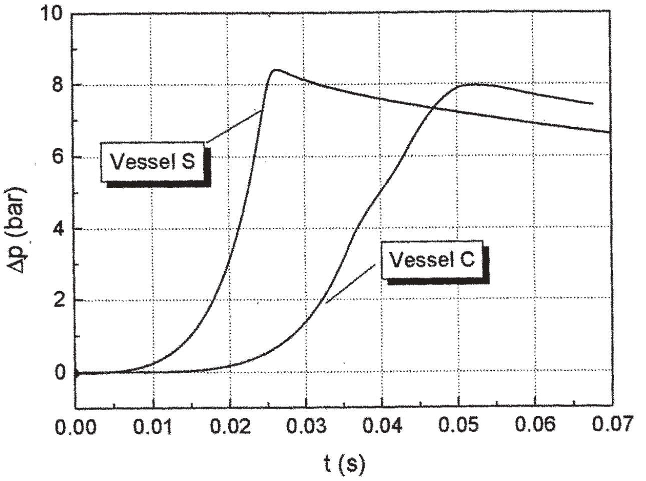

Fig. 2. Pressure-time history of explosions, in vessels **S** and **C**, for a near-stoichiometric n-butane-air mixture ([n-C_4H_{10}] = 3.10 vol.%) at T_0 = 298 K and p_0 = 1 bar

fuel–oxidant gaseous mixture. The algorithm is based on the thermodynamic criterion of chemical equilibrium used by Gibbs. Fifteen compounds (among them one solid compound) were considered as products: $C_{graphite}$, CO_2, CO, H_2O, O_2, N_2, CH_4, C_2H_2, C_2H_4, C_3H_6, H_2, NO, H, OH and O). Their heat capacities (expressed as function of temperature with the form: $C_P = a + b\cdot T + c\cdot T^2 + d\cdot T^{-2}$), the standard enthalpies of formation at 298 K and the standard entropies at 298 K were taken from references [31-32].

A typical *p(t)* diagram recorded during the explosion of a near-stoichiometric n-C_4H_{10}-air mixture ([n-C_4H_{10}] = 3.10 vol.%) in spherical vessel S is shown in figure 1 together with the computed time-derivative. The computation of *(dp/dt)* was made after smoothing the *p(t)* data by Savitzky-Golay method, based on least squares quartic polynomial fitting across a moving window within the data. The method has the advantage of producing a smoothed first derivative without filtering the data. This involves the analysis of 500-700 points within $0 \le t \le \theta_{max}$. In all cases, we used a 10% smoothing level, since a higher value of this level (e.g. 20%) leads to a reduction of both noise and signal.

Results and Discussion

The diagram of pressure variation during explosions of a n-C_4H_{10}-air near-stoichiometric mixture ([n-C_4H_{10}] = 3.10 vol.%) in the two explosion vessels is given in figure 2, for experiments performed at ambient initial pressure and temperature. The corresponding rates of pressure rise versus time from ignition are plotted in figure 1 (spherical vessel) and in figure 3 (cylindrical vessel), overlaid on *p(t)* records.

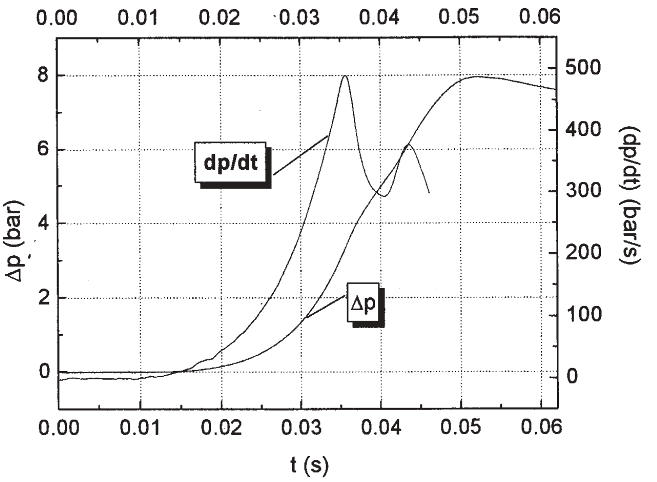

Fig. 3. Variation of pressure and of pressure rise rate during the explosion of a 3.10 vol.% n-C_4H_{10}-air mixture in vessel C, at T_0 = 298 K and p_0 = 1 bar

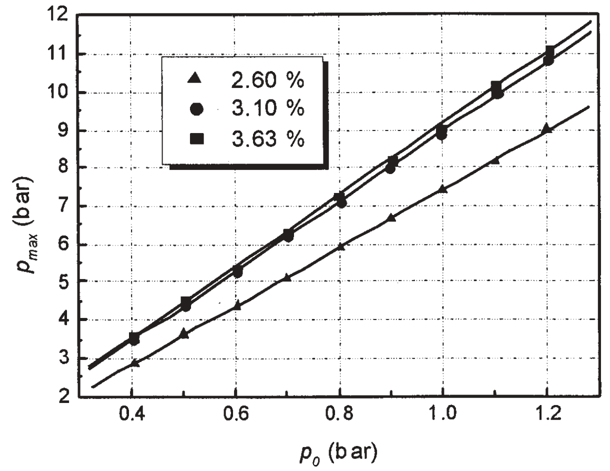

Fig. 4. Maximum (peak) explosion pressures measured in spherical vessel **S**, for n-butane-air mixtures with variable fuel content

For all n-butane-air examined mixtures, the peak (maximum) explosion pressure p_{max} depends linearly on p_0, the total initial pressure:

$$p_{\max} = a + b \cdot p_0 \qquad (1)$$

Several typical plots are given in figure 4, for experiments made in the spherical vessel; a similar variation was observed for measurements in cylindrical vessel *C*. Values of the intercept "*a*" and of slope "*b*" for such correlations are given in table 1 (data obtained in the spherical vessel) and table 2 (data obtained in the cylindrical vessel), together with r_n, the correlation coefficient of the linear dependencies.

Such equations are very useful for evaluation of maximum explosion pressure reached from any initial pressure p_0 from the examined range or even beyond this range, as long as combustion is propagating as a deflagration (subsonic propagation velocity) [22].

A comparison between the maximum explosion pressures measured in the two enclosures used in the present work is given in figure 5. Important differences are observed between the results obtained for spherical and cylindrical vessel. Indeed, an early contact of the burnt, hot gas with the closest cylindrical wall in vessel **C** determines higher heat losses during combustion as

Table 1

SLOPE AND INTERCEPT OF p_{max} vs. p_0 LINEAR REGRESSIONS; SPHERICAL VESSEL **S**

No.	$[C_4H_{10}]$ (vol.%)	Equivalence ratio φ	-a (bar)	b	r_n
1	2.59	0.823	0.194	7.605	0.9999
2	3.10	0.990	0.197	9.129	0.9999
3	3.25	1.040	0.260	9.288	0.9998
4	3.63	1.166	0.210	9.342	0.9997
5	3.64	1.170	0.058	9.221	0.9999
6	4.14	1.337	0.061	9.240	0.9993
7	4.66	1.513	0.185	9.121	0.9999
8	4.67	1.516	0.172	8.798	0.9997

Table 2

SLOPE AND INTERCEPT OF p_{max} vs. p_0 LINEAR REGRESSIONS; CYLINDRICAL VESSEL **C**

No.	$[C_4H_{10}]$ (vol.%)	Equivalence ratio φ	-a (bar)	b	r_n
1	3.10	0.990	0.383	8.851	0.9999
2	3.25	1.040	0.359	8.905	0.9999
3	3.63	1.166	0.369	9.010	0.9999
4	4.13	1.333	0.528	8.295	0.9997
5	4.67	1.516	0.494	8.634	0.9999

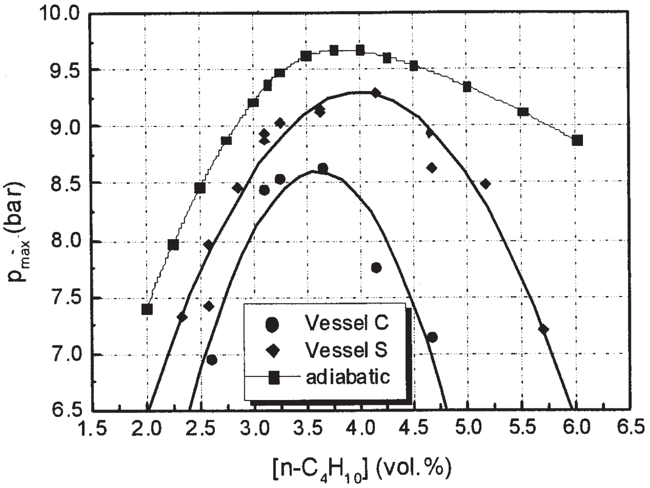

Fig. 5. Experimental and adiabatic explosion pressures of *n*-butane-air mixtures at ambient initial temperature and pressure

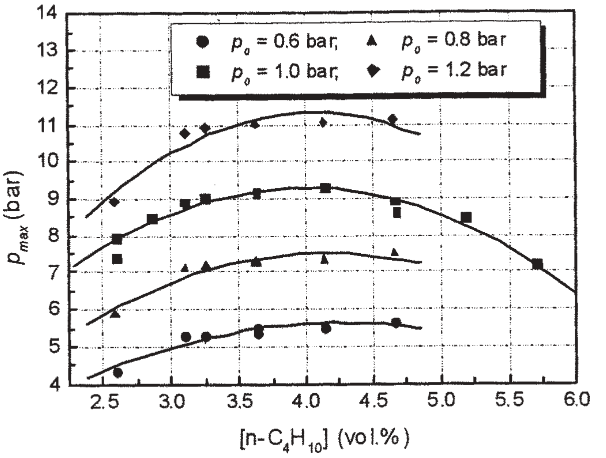

Fig. 6. Measured peak pressures for *n*-C_4H_{10}-air mixtures at variable initial pressure and composition

compared to vessel **S**. Smaller explosion pressures are thus recorded in asymmetrical vessels as compared to symmetrical ones, even if the volume of vessel **C** is approximately double as compared to vessel **S**. Figure 5 contains also the adiabatic explosion pressures computed for *n*-butane-air mixtures at p_0 = 1 bar and T_0 = 298 K, versus n-butane concentration. As expected, the adiabatic explosion pressures are higher than measured ones, both in the cylindrical and in the spherical vessel. The adiabatic explosion pressures are quite high in the concentration range from 4.5 to 6.0 vol.% and decrease very smoothly when fuel concentration increases, approaching the upper flammability limit. This behaviour was observed for all rich hydrocarbon-air mixtures, since computation of adiabatic flame temperature, pressure and composition predicts formation of $C_{graphite}$ only at high hydrocarbon concentration, far beyond the soot threshold [13, 23].

Similar graphs are given in Figure 6, where peak explosion pressures reached at explosions in spherical vessel S at various initial pressures are plotted versus fuel content. Such data are available for cylindrical vessel C as well and follow the same trend, when plotted against *n*-butane concentration.

The comparison of the present data with the few results available from literature shows a good agreement, within experimental errors. The highest reported peak explosion pressure for *n*-butane-air mixtures is p_{max} = 9.4 bar, measured in a 20 L spherical vessel with electric sparks central ignition (released energy E = 10 J)[10], according

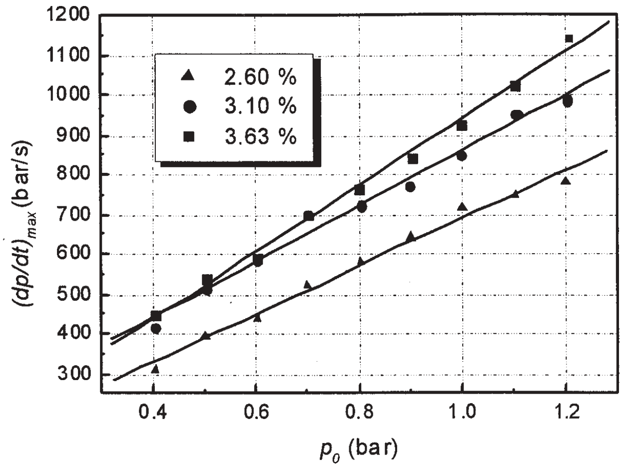

Fig. 7. Maximum rates of pressure rise reached during explosions in spherical vessel **S**, for n-butane-air mixtures with variable fuel content

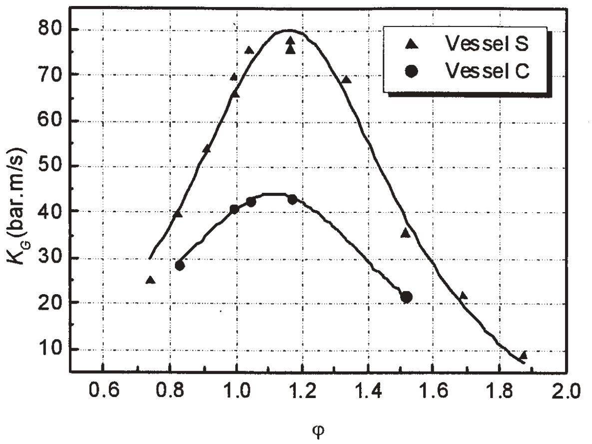

Fig. 8. Deflagration index K_G of *n*-butane-air explosions in vessels S and **C**, for mixtures with variable fuel content, at p_0 = 1 bar

Table 3

SLOPE AND INTERCEPT OF $(dp/dt)_{max}$ vs. p_0 LINEAR REGRESSIONS; SPHERICAL VESSEL **S**

No.	$[C_4H_{10}]$ (vol.%)	α (bar/s)	β (s^{-1})	r_n
1	2.59	87.8	604.6	0.9932
2	3.10	161.0	701.4	0.9930
3	3.25	125.1	814.9	0.9985
4	3.63	102.9	839.4	0.9974
5	3.64	18.9	948.7	0.9985
6	4.14	22.3	837.1	0.9963
7	4.66	-0.6	575.5	0.9946
8	4.67	-0.4	442.6	0.9919

Table 4

SLOPE AND INTERCEPT OF $(dp/dt)_{max}$ vs. p_0 LINEAR REGRESSIONS; CYLINDRICAL VESSEL **C**

No.	$[C_4H_{10}]$ (vol.%)	α (bar/s)	β (s^{-1})	r_n
1	2.59	44.5	226.1	0.9874
2	3.10	51.5	335.0	0.9970
3	3.25	56.3	346.1	0.9936
4	3.63	30.6	380.6	0.9952
5	4.67	-33.4	239.3	0.9944

to the recommendations from EU Standard 13673-1 [4]. Maisey reports 7.68 bar as the highest value for p_{max} [15] from measurements made in a 5 L spherical vessel, but his data were measured at 65° C and cannot be subject to a direct comparison. Other measurements in an identical vessel (sphere, V = 5 L, central ignition) indicate 9.0 bar as the highest value of p_{max} [1].

The maximum rate of pressure rise versus initial pressure at constant fuel concentration shows a linear correlation for all examined systems [22]:

$$\left(\frac{dp}{dt}\right)_{\max} = \alpha + \beta \cdot p_0 \qquad (2)$$

Results referring to explosions of three *n*-butane-air mixtures in vessel **S** are plotted in figure 7. Values of α, β and r_n for the mentioned linear correlations are given in table 3 (data for spherical vessel **S**) and table 4 (data for cylindrical vessel **C**).

A comparison between data from tables 3 and 4 indicates higher values of $(dp/dt)_{max}$ in the spherical enclosure as compared to the cylindrical one, for all examined concentrations. An identical behaviour was reported for propylene-air explosions in vessels **S** and **C** [33]. The heat losses, more intensive in the vessel with Φ < h as compared to the spherical vessel, account for this variation.

The maximum rates of pressure rise recorded in explosions at ambient initial pressure were used to calculate the deflagration index K_G (or the "severity factor"), by means of equation:

Table 5

EXTREME VALUES OF FLAMMABILITY PARAMETERS FOR EXPLOSIONS OF *n*-BUTANE-AIR MIXTURES IN TWO CLOSED VESSELS, AT p_0 = 1 bar AND T_0 = 298K

	Vessel S	Vessel C	Concentration range where extreme values of flammability parameters are observed
p_{max} / bar	9.25	8.60	3.6 – 4.3 vol.%
$(dp/dt)_{max}$ / (bar.s^{-1})	970	412	
θ_{max} /ms	23	42	

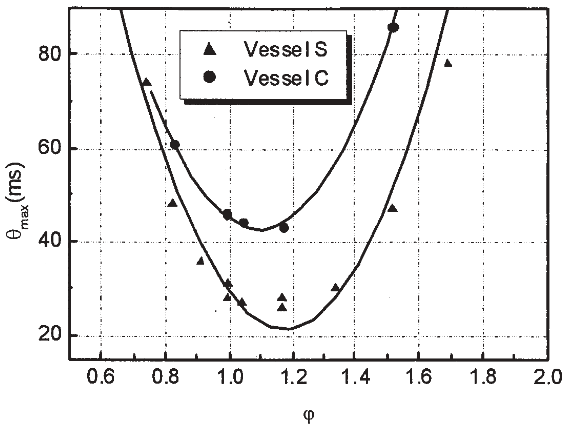

Fig. 9. Time necessary to reach the peak pressure in vessels **S** and **C**, for mixtures with variable fuel content, at p_0 = 1 bar

$$K_G = \left(\frac{dp}{dt}\right)_{\max} \cdot \sqrt[3]{V} \qquad (3)$$

where *V* is the volume of the explosion vessel. The deflagration index calculated for the two explosion vessels **S** and **C** are plotted in figure 8 against the equivalence ratio of *n*-butane-air mixtures.

Even if vessel C has approximately twice the volume of vessel **S**, the corresponding values of the deflagration index K_G are inferior for all fuel/oxidant ratios. Indeed, the heat losses which start earlier in an elongated vessel and have important values before reaching the peak explosion pressure afford a “milder” explosive combustion as compared to symmetrical vessel **S**. The highest value of the deflagration index is K_G = 80 bar.m/s , very close to the value reported by Bartknecht [1]: K_G = 92 bar.m/s, from data measured in a 5 L spherical vessel with central ignition.

The highest values of peak explosion pressures, maximum rates of pressure rise and deflagration indexes of *n*-butane-air mixtures are observed for [*n*-C_4H_{10}] = 3.6 - 4.3 vol.%, in the range of rich mixtures (φ = 1.1 -1.2). In this concentration range, the lowest values of θ_{max} (the time from ignition till the peak pressure) are recorded, for both explosion vessels (fig. 9).

The compact information concerning the explosive combustion of *n*-butane with air in closed vessels is given in table 5.

Conclusions

Prevention of fires and accidental gas explosions requires knowledge of combustion characteristics (peak pressure, maximum rate of pressure rise, deflagration index) of combustible gases and vapours likely to be encountered under various condition of use.

In explosions of quiescent mixtures in the spherical vessel with central ignition, both peak pressures and maximum rates of pressure rise are linear functions on total initial pressure, at constant initial temperature and fuel/oxygen ratio. The slope and intercept of found correlations are influenced by the amount of heat losses from the burned gas to the vessel. The obtained correlations allow the calculation of peak pressure or of maximum rate of pressure rise at any value of initial pressure - important aspect of safety recommendations for ambient conditions different from standard.

The maximum rates of pressure rise and deflagration index of *n*-butane-air explosion in both enclosures have maxima at concentrations higher than stoichiometric one.

The reported measurements, made with a spherical vessel different from the EU standard (recommending a 20 L sphere), provide useful results concerning explosion evolution in n-butane-air systems. They might be also useful for scaling explosions in chemical reactors and for design of safety (venting) devices.

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