Initial Pressure and Mixture Composition Influence on LPG-air Confined Explosions

DOMNINA RAZUS[1*], VENERA BRINZEA[1], MARIA MITU[1], DUMITRU OANCEA[2]

[1] "Ilie Murgulescu" Institute of Physical Chemistry, 202 Spl. Independentei, 060021, Bucharest, Romania

[2] University of Bucharest, Department of Physical Chemistry, 4-12 Regina Elisabeta Blvd., 030018, Bucharest, Romania

Values of some characteristic parameters of confined explosions for LPG (Liquefied Petroleum Gas)-air quiescent mixtures are examined in correlation with the initial pressure of fuel-air mixture and fuel/air ratio. The explosion pressures, the explosion times and the maximum rates of pressure rise were obtained from experiments made at ambient initial temperature in two closed vessels with central ignition: a spherical vessel (V = 0.52 L) and a cylindrical vessel (V = 1.12 L; diameter/height = 1.5) using mixtures with variable fuel content ([LPG] = 2.50 – 6.15 vol.%), at total initial pressures within 0.3 - 1.3 bar. For LPG – air at ambient initial temperature and pressure, the adiabatic explosion pressures and the flame temperatures of isochoric and isobaric combustion were calculated, assuming that chemical equilibrium is reached. The calculated and measured explosion pressures of LPG-air mixtures are compared and discussed taking into account the heat losses during explosion propagation in the two closed vessels.

Keywords: LPG (Liquefied Petroleum Gas), closed vessels, explosion pressure, explosion time, rate of pressure rise

Collections of data characterizing explosions of pure and mixed fuels are of great interest for various human activities dealing with energy and/or chemicals production and engine propulsion. Recent documents and databases issued by OSHA (Occupational Health and Safety Administration from USA), NFPA (National Fire Protection Administration from USA) or BAM (Federal Institute for Material Research and Testing from Berlin, Germany) enlist characteristic values of flammability limits, minimum ignition energies, burning velocities and explosion pressures in standard closed vessels. Usually, information is given for pure fuels in oxygen or air, at ambient initial conditions, sometimes in the presence of various additives. It is interesting, however, to characterize fuel-air mixtures by means of flammability properties at non-standard ranges of initial temperature and pressure. The recently developed EU project entitled SAFEKINEX [1] aims at measuring and reporting values of explosion indices at initial temperatures and pressures higher than ambient, in order to improve safety recommendations for various chemical processes. Several publications issued from this project report data on methane-air, propene-oxygen and propene-air [2] and n-butane-oxygen mixtures [3] both at ambient initial conditions and at elevated temperatures and pressures. Other recent data, measured in a 2.56 L cylindrical vessel with central ignition [4] refer to propane- and LPG-air mixtures with variable initial composition, pressure and temperature. Besides values of several flammability characteristics of closed vessel combustion (maximum explosion pressure, maximum rate of pressure rise, time to maximum pressure, time to maximum rate of pressure rise, ignition delay, severity factor), this paper reports laminar burning velocities of these mixtures determined from *p(t)* records during flame propagation, using several models of flame propagation. For all flammability parameters, the dependencies on initial pressure, temperature and equivalence ratio are given both as diagrams and fit equations, able to be used for comparison with other sets of data.

It is important to notice the interest towards LPG-air explosions, in various conditions. Indeed, LPG is among the extensively used fuels, both as feed for domestic stoves and as alternative fuel for automotive engines [5, 6]. The composition of LPG varies according to the origin country and manufacturer, e.g. from approx. 70 vol.% propane and 30 vol.% butane (a blend used in India [7]), to approx.12 vol.% propane and 87 vol.% butane (a Romanian blend [8]). In order to use correct values of the explosion characteristic parameters, it is necessary to examine each commercial blend. For a LPG mixture manufactured in Romania, several characteristic parameters of explosion propagation in two closed vessels for LPG-air mixtures were recently reported [8]: explosion pressures, explosion times and maximum rates of pressure rise. These values were examined against literature data on LPG combustion in closed vessels [4, 7] and compared to data referring to propane-air and n-butane-air, obtained in identical conditions [9, 10].

In the present work, a closer examination of initial pressure influence on explosion pressures and maximum rates of pressure rise is made, for data measured in two closed vessels and for LPG-air mixtures of various initial concentrations. In addition, values of adiabatic flame temperatures and adiabatic explosion pressures for LPG-air mixtures at ambient initial temperature and pressure are given. The comparison of calculated and measured explosion pressures reveals the extent of heat losses appearing during explosion propagation in the two closed vessels, depending on fuel/air ratio and on geometrical characteristics of the vessel. LPG is a blend used in Romania, purchased from Arpechim-Pitesti plant. Mixtures with variable content of LPG, within 2.50 vol.% and 6.15 vol.% were studied, at total initial pressures between 0.3 and 1.3 bar and ambient initial temperature.

Experimental part

A schematic drawing of the experimental set-up is given in figure 1.

Experiments were made in two stainless steel vessels with different geometry: vessel **S** – a spherical vessel with

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[*] *email : drazus@icf.ro*

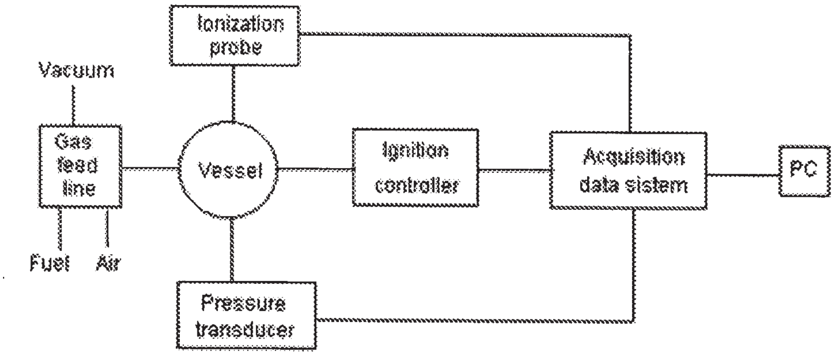

Fig. 1. Scheme of the set-up used for studies of gaseous explosions in closed vessels

the radius R = 5 cm and vessel **C** – a cylinder with height h = 15 cm and diameter Φ = 10 cm. Explosion ignition was made by inductive-capacitive electric sparks (energy within 2 - 5 mJ, duration: approximately 1 ms) produced between stainless steel electrodes with rounded tips. The spark gap, positioned in the geometrical centre of each vessel, was 3.5 mm.

Explosions were monitored by means of a piezolectric pressure transducer (Kistler 601A), connected to a Charge Amplifier (Kistler 5001N) and an ionization probe with the tip mounted 3 mm far from wall, in every explosion vessel. The signals from the Charge Amplifier and from the ionization probe amplifier were recorded with a Tektronix acquisition data system (TestLab 2505, acquisition card 25AA1) at 5000 signals/s.

The fuel-air mixtures were prepared in a stainless steel cylinder at a total pressure of 4 bar by partial pressure method and used 48 h after mixing the components. A vacuum and gas-feed line, tight at pressures from 0.5 mbar to 1.5 bar, connects the vacuum pump, the gas cylinders with fuel and air, the metallic cylinder for mixture storage and the explosion vessels. The vacuum pump maintained a vacuum of 0.5 mbar in the explosion vessel, after each experiment.

The experimental procedure consisted of evacuating the combustion vessel down to 0.5 mbar; the fuel-air mixture was then introduced, allowed to become quiescent and ignited. More details were recently given [8, 10].

LPG contained 12 vol.% propane, 62.6 vol.% n-butane, 24.4 vol.% i-butane, 1 vol.% pentane. The examined mixtures had LPG concentration between 2.50 and 6.15 vol.%, within the flammability limits of LPG-air mixture (1.8 - 8.9 vol.% [7]).

Data evaluation and computing program

The derivatives *(dp/dt)* were obtained after smoothing the experimental *p(t)* data by Savitsky-Golay method, based on least squares quartic polynomial fitting across a moving window within the data. In all cases, we used a 10% smoothing level.

Adiabatic flame temperature, adiabatic explosion pressure and burned gas composition were calculated with the program ECHIMAD [11], taking into account 15 compounds ($C_{graphite}$, O_2, N_2, H_2O, CO, CO_2, H_2, NO, CH_4, C_2H_2, C_3H_8, C_4H_{10}, H, OH and O), assuming that the thermodynamic equilibrium is reached. The program is based on a general algorithm for computing the equilibrium composition of products for fuel-oxidizer gaseous mixtures by determining the minimum of free enthalpy (in isobaric combustion) or free energy (in isochoric combustion). The heat capacities (expressed as $C_p = f(T)$ polynomials), the standard enthalpies of formation at 298 K and the standard entropies at 298 K were taken from [12, 13].

Results and discussion

Typical plots of pressure variation during LPG-air explosions in spherical vessel **S** at various initial pressures are shown in figure 2.

The measured maximum explosion pressures p_{max} are linearly correlated with the initial pressures, p_0, for all LPG-air mixtures and for both vessels. An illustrative diagram is given in figure 3, where several results obtained in vessel **C** are plotted. The coefficients of linear fits are given in Table 1 (data obtained in vessel **S**) and in table 2 (data obtained in vessel **C**). The obtained correlations allow the calculation of peak pressure at any value of initial pressure even beyond the investigated range (as long as the process takes place as a deflagration).

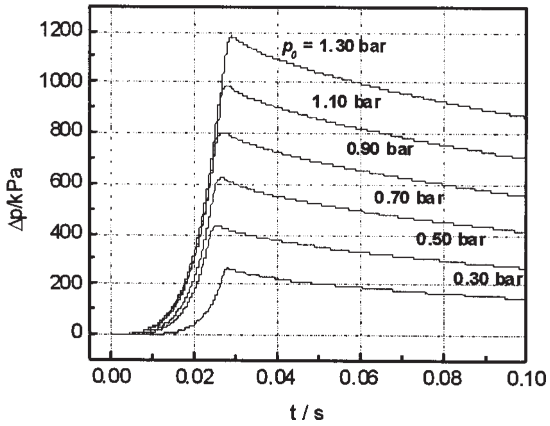

Fig. 2. Pressure-time history during deflagration of quiescent LPG-air mixtures ([LPG] = 4.50 vol.%) in vessel **S**

As shown in a previous paper [16], the intercepts of these correlations depend both on flammable mixture composition and on geometrical characteristics of explosion vessels: volume and height/diameter ratio, which influences mostly the amount of heat losses during explosion propagation. Indeed, for each LPG mixture, the absolute values of intercepts are larger in vessel **C** as compared to vessel **S**, due to larger heat losses in the asymmetrical vessel **C** as compared to vessel **S**. This was already observed for other flammable systems of single fuel-air mixtures [10, 14] and fuel-air-diluent mixtures [17].

The measured explosion pressures of LPG-air in spherical vessel **S** and in cylindrical vessel **C** at ambient initial conditions, together with the adiabatic explosion pressures, are plotted versus LPG concentration in figure 4.

Higher heat losses in asymmetrical vessel **C** as compared to vessel **S** account for the lower peak pressures measured in vessel **C** as compared to vessel **S**. The experimental explosion pressures measured in both vessels **S** and **C** are systematically lower in comparison with adiabatic values; the observed deviations are important especially for lean mixtures.

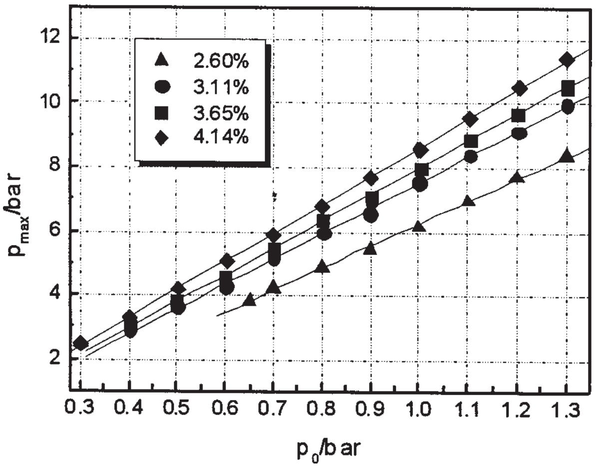

Fig. 3. Maximum explosion pressures measured during deflagration of LPG-air mixtures in cylindrical vessel C with central ignition

The computing program ECHIMAD delivers also the values of adiabatic flame temperatures of isobaric ($T_{fl,p}$) and isochoric combustion ($T_{fl,V}$), which are plotted in figure 5 versus LPG concentration, for mixtures at ambient initial conditions. Important variations of both $T_{fl,p}$ and $T_{fl,V}$ are observed in fuel-rich mixtures ([LPG] > 3.50 vol%) . In contrast to it, the adiabatic explosion pressures decrease quite slowly when fuel concentration increases. Such behaviour was observed for other rich hydrocarbon-air mixtures as well [10, 14], since computation of adiabatic explosion pressure and burned gas composition predicts formation of graphite only at high hydrocarbon concentrations, beyond the soot threshold, in the vicinity of upper flammability limit.

At various initial pressures, different from ambient, the maximum explosion pressures follow a similar pattern as shown in figure 6, where data measured in vessel **S** are plotted.

As recently discussed [8], comparison of our data with results reported by other authors reveals a similar variation when explosion pressures are plotted versus LPG concentration. The observed differences between peak pressures can be assigned both to differences in volume and shape (length to diameter ratio) of explosion vessels and to the different composition of the examined LPG blends. According to our measurements, the highest value of maximum explosion pressure for LPG-air at p_0 = 1 bar

Table 1

COEFFICIENTS OF REGRESSION EQUATIONS $p_{max} = a + b \cdot p_0$; DATA MEASURED IN SPHERICAL VESSEL **S**

[LPG] (vol %)	-a (bar)	b	r^2
2.60	0.322 ± 0.158	7.655 ± 0.146	0.9980
3.11	0.141 ± 0.039	8.887 ± 0.041	0.9990
3.22	0.161 ± 0.039	9.256 ± 0.043	0.9999
3.65	0.235 ± 0.038	9.433 ± 0.042	0.9999
4.14	0.234 ± 0.045	10.204 ± 0.053	0.9998
4.70	0.273 ± 0.046	10.268 ± 0.051	0.9999
5.38	0.201 ± 0.036	10.114 ± 0.040	0.9999
5.70	0.218 ± 0.047	9.859 ± 0.053	0.9998

Table 2

COEFFICIENTS OF REGRESSION EQUATIONS $p_{max} = a + b \cdot p_0$; DATA MEASURED IN CYLINDRICAL VESSEL **C**

[LPG] (vol %)	-a (bar)	b	r^2
2.60	0.769 ± 0.129	7.529 ± 0.139	0.9992
3.11	0.339 ± 0.076	8.575 ± 0.082	0.9997
3.22	0.589 ± 0.106	9.092 ± 0.118	0.9993
3.65	0.418 ± 0.045	9.125 ± 0.046	0.9999
4.14	0.370 ± 0.046	9.768 ± 0.056	0.9998
4.70	0.459 ± 0.033	9.862 ± 0.036	0.9999
5.38	0.385 ± 0.042	9.674 ± 0.049	0.9999
5.70	0.318 ± 0.043	9.246 ± 0.052	0.9998

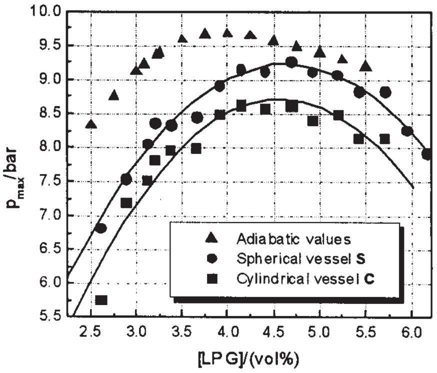

Fig. 4. Maximum explosion pressures, calculated and measured, for LPG-air mixtures with various concentrations

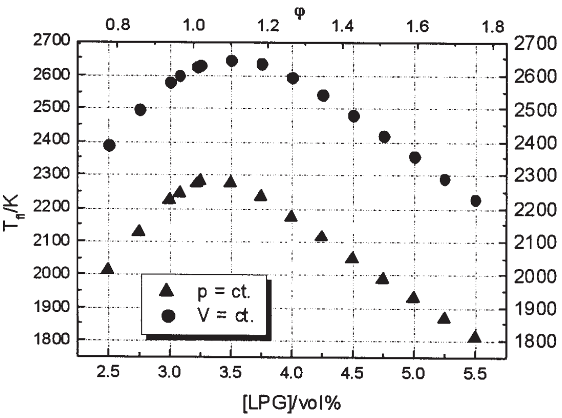

Fig. 5. Adiabatic flame temperatures of LPG-air mixtures, at p_0 = 1 bar and T_0 = 298 K

and T_0 = 298 K were p_{max} = 9.3 bar, recorded in vessel **S** and p_{max} = 8.6 bar in vessel **C** having a volume V = 1.12 L. Compared to this, Huzayyn et al. [4] reported the highest value of explosion pressure as 8.0 bar from measurements in a cylindrical vessel of volume V = 2.56 L and central ignition; Oh and coworkers reported p_{max} = 6.8 bar from measurements in a cylindrical vessel with V = 270 L with side ignition [15].

The maximum rates of pressure rise for deflagrations in vessels **S** and **C** follow similar trends when examined against initial pressure and LPG concentration. The corresponding data are given in figure 7 and 8 and in tables 3 and 4.

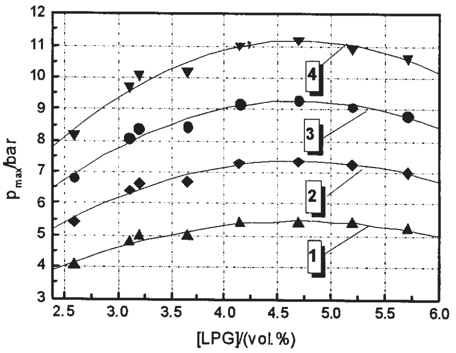

Fig. 6. The variation of peak pressures measured in vessel **S** against fuel content, at various initial pressures: (1) p_0 = 0.6 bar; (2) p_0 = 0.8 bar; (3) p_0 = 1 bar; (4) p_0 = 1.2 bar

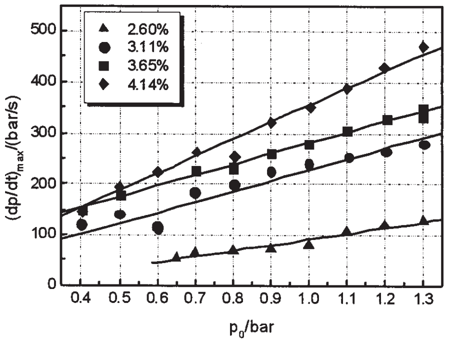

Fig. 7. Maximum rates of pressure rise measured during deflagration of LPG-air mixtures in cylindrical vessel **C**

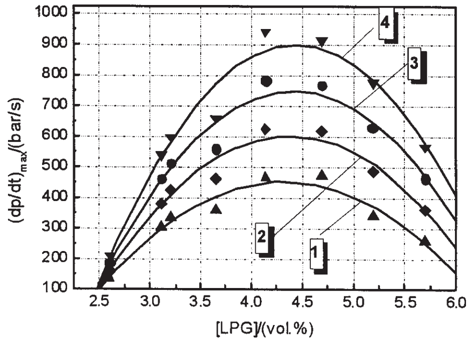

Fig. 8.The variation of maximum rates of pressure rise against fuel content in vessel **S**, at various initial pressures: (1) p_0 = 0.6 bar; (2) p_0 = 0.8 bar; (3) p_0 = 1 bar; (4) p_0 = 1.2 bar

For each LPG-air mixture, at constant initial pressure, the maximum rates of pressure rise obtained in spherical vessel **S** are approximately two times higher as compared

Table 3
COEFFICIENTS OF REGRESSION EQUATIONS $(dp/dt)_{max} = \alpha + \beta \cdot p_0$;
DATA MEASURED IN SPHERICAL VESSEL **S**

[LPG] (vol %)	α (bar. s^{-1})	β (s^{-1})	r^2
2.60	89.94 ± 11.10	140.99 ± 10.21	0.9772
3.11	153.96 ± 36.92	441.01 ± 39.25	0.9662
3.22	172.24 ± 28.20	486.68 ± 31.39	0.9838
3.65	173.36 ± 15.17	553.89 ± 16.89	0.9963
4.14	165.75 ± 52.31	868.53 ± 60.66	0.9777
4.70	194.96 ± 9.09	816.29 ± 9.94	0.9995
5.38	53.07 ± 34.88	802.62 ± 38.79	0.9908
5.70	58.89 ± 21.22	564.43 ± 23.61	0.9931

Table 4
COEFFICIENTS OF REGRESSION EQUATIONS $(dp/dt)_{max} = \alpha+\beta \cdot p_0$; DATA MEASURED IN CYLINDRICAL VESSEL **C**

[LPG] (vol %)	α (bar. s^{-1})	β (s^{-1})	r^2
2.60	-23.25 ± 11.98	124.15 ± 12.20	0.9722
3.11	60.76 ± 7.53	196.27 ± 8.14	0.9940
3.22	-12.54 ± 24.56	288.65 ± 27.32	0.9660
3.65	77.28 ±8.05	232.24 ± 8.31	0.9949
4.14	47.63 ± 5.16	385.79 ± 6.14	0.9989
4.70	37.65 ± 10.61	396.56 ± 11.80	0.9965
5.38	2.97 ± 5.55	354.44 ± 6.44	0.9985
5.70	-13.350 ± 10.219	273.018 ± 12.573	0.9896

to those obtained in cylindrical vessel **C**. Comparison of maximum rates of pressure rise reached in vessel **C** during experiments at ambient initial pressure to literature data shows a good agreement with data reported from experiments in a 2.46 L cylindrical vessel with a height/diameter ratio = 1.05 [4]. In both cylindrical vessels, the heat losses start earlier as compared to spherical vessel and reach important values much before combustion is finished. Accordingly, the rate of heat release is much lower, leading to a “milder” explosive combustion and to lower rates of pressure rise.

Examination of times necessary to reach the peak pressure shows that they are not influenced by the initial pressure, within the range of investigated values. They depend only on fuel content, on the volume of explosion vessel and on the position of the initiation source (central or side ignition).

Conclusions

In explosions of quiescent LPG-air mixtures in two closed vessels of different geometry with central ignition, the peak pressures are linear functions on total initial pressure, at constant initial temperature and fuel/oxygen ratio. The intercept of found correlations are influenced by the amount of heat losses from the burned gas to the vessel. Linear correlations were also found between the maximum rates of pressure rise and initial pressure, in both vessels. The obtained correlations allow the calculation of peak pressure or of maximum rate of pressure rise at any value of initial pressure, even beyond the investigated range, which is important in formulating safety recommendations for conditions characteristic to industrial plants or storage vessels. The data reveal that a lower symmetry of the explosion vessel results in the mitigation of explosion.

The measured and calculated peak pressures of LPG-air have maximum values at LPG concentrations higher than stoichiometric, at each examined initial pressure. The same is observed for the variation of maximum rates of pressure rise recorded in the two enclosures, versus LPG concentration, at each initial pressure within the examined range.

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