EXPLOSION PRESSURES OF CONFINED DEFLAGRATIONS PROPAGATING IN STOICHIOMETRIC GASEOUS MIXTURES OF LOWER ALKANES WITH AIR

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abstract: An experimental study on maximum explosion pressure in closed vessel deflagration of stoichiometric gaseous mixtures, for various initial pressures within $0.3 - 1.2$ bar and ambient initial temperature is reported. Explosion pressures and explosion times of stoichiometric methane-, ethane- and propane-air mixtures were measured in a spherical vessel and in two cylindrical vessels with different diameter/height ratios. The measured explosion pressures are examined in comparison with the adiabatic explosion pressures, computed by assuming chemical equilibrium within the flame front. The influence of initial pressure and heat losses during propagation on explosion pressures and explosion times are discussed for the examined systems. Both measured and calculated explosion pressures are linear functions of total initial pressure, at constant initial temperature and fuel concentration.

key words: explosion pressure; explosion time; alkanes; flammable mixtures.

1. Introduction

Fuel-air mixtures are formed in plants, motors, combustion chambers and are subject to exothermal chemical reactions between fuel and oxygen, running in various explosive regimes: deflagrations or detonations. The evaluation of hazards associated to explosion of such mixtures is an important component of research in this field, based on determination of safety characteristic parameters in various conditions. For deflagrations propagating in closed vessels, the most important safety parameters are the peak (maximum) explosion pressure, the explosion time and the maximum rate of pressure rise [1,2]. The explosion pressures and explosion times are important also for design of safety devices (vents), able to ensure active protection of pressure vessels where flammable mixtures are formed [3]. In

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basic research, the peak explosion pressures are used for validation of propagation wave models and for calculation of the laminar burning velocity in various conditions [4,5].

The present paper reports explosion pressures and explosion times of stoichiometric mixtures of lower alkanes (methane, ethane and propane) with air, measured for various initial pressures within 0.3 – 1.2 bar in three closed vessels with different symetries. The measured peak explosion pressures of fuel-air mixtures are examined in comparison with the calculated adiabatic explosion pressures, obtained by means of two dedicated computing programs.

2. Experimental

Experiments were performed in a spherical vessel S with diameter $\Phi = 5$ cm and two cylindrical vessels: C_1 with height h = 15 cm and $\Phi = 10$ cm; C_2 with h = Φ = 6 cm. Inductive-capacitive sparks produced between stainless steel electrodes in the geometrical centre of each vessel were used as ignition sources. Ionization probes mounted in the equatorial position of vessels, with tips at various distances from the wall, allowed the detection of flame front position.

Measuring systems: The transient pressure during explosions was recorded with piezoelectric pressure transducers (Kistler 601A) connected to Charge Amplifiers (Kistler 5001SN) and an acquisition data system TestLab[TM] Tektronix 2505 (acquisition card type AA1) at 10^4 signals/s.

Examined systems: stoichiometric CH_4-, C_2H_6-, C_3H_8-air mixtures at initial pressures between 0.3 and 1.3 bar and ambient initial temperature. The fuel-air mixtures were obtained by partial pressures method, at a total pressure of 4 bar and used after 48 h after mixing. Methane (99.99%), ethane (99.99%) and propane (99.99%) (SIAD Italy) were used without further purification.

Other details on the experimental set-up and procedure were previously given [6,7].

Computing programs

Adiabatic flame temperatures and adiabatic explosion pressures of fuel-air mixtures at various initial pressures were calculated with the program ECHIMAD [8], 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) and assuming the thermodynamic equilibrium is reached in the flame. The heat capacities (expressed as $c_p = f(T)$ polynomials), standard enthalpies of formation at 298 K and standard entropies at 298 K were taken from reference sources [9,10]. The adiabatic flame temperatures and adiabatic explosion pressures of stoichiometric alkane-air mixtures were computed also by means of the package COSILAB, taking into account 38 compounds (15 compounds identical to those listed above and 23 additional compounds: HO_2; H_2O_2; CH; CH_2; CH_3; HCO; CH_2O; CH_2OH; NO_2; N_2O; CH_3O; CH_3OH; C_2H; C_2H_3; C_2H_4; C_2H_5; C_2H_6; HCCO; CH_2CO; HCCOH; C_3H_7; CH_2CHO; CH_3CHO). In this case, the thermodynamic data were taken from JANAF tables [11].

3. Results and discussions

The pressure-time records during the explosion of a stoichiometric methane-air mixture in the three explosion vessels are presented in Fig. 1. The highest explosion pressure is reached in the spherical vessel S; in this case, the pressure increases smoothly and an inflection point is observed. In cylindrical vessels C_1 and C_2, the inflection point appears much earlier, at the moment when the flame reaches the nearest wall and the heat losses from the burned gas to vessel wall become important. In these two vessels, the heat losses reach higher values in comparison with the spherical vessel, resulting in smaller measured peak explosion pressures. The explosion times are strongly dependent on the volume and form: 27 ms in vessel C_2, 32 ms in vessel S, 55 ms in vessel C_1. A specific shape of the $p(t)$ curve is recorded in vessel C_1: a fast pressure increase until the inflection point is reached, followed by a much slower process characterizing the propagation of flame distorted by the asymmetry of this vessel (h / Φ = 1.5).
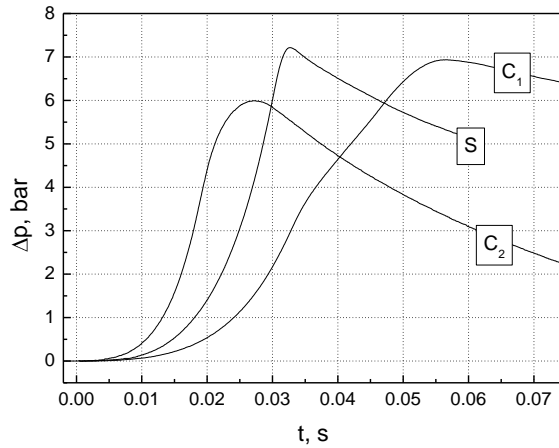

Fig. 1 *Pressure evolution during confined explosions of the stoichiometric CH_4-air mixture in vessels S, C_1 and C_2, at ambient initial conditions.*

For all studied flammable mixtures linear correlations between the peak (maximum) explosion pressure and the initial pressure were found, as seen in Fig. 2. The differences between maximum explosion pressures for fuels with various carbon numbers are quite small at initial pressures smaller than 0.5 bar and can be observed only at higher initial pressures. Such linear correlations were found for the examined flammable mixtures in all explosion vessels.

From the analysis of the heat balance during the explosion propagation in a closed vessel a correlation between the end (final) explosion pressure p_e and the initial pressure p_0 was derived [12]:

$$p_e = p_0\left(\xi + \frac{r_1}{v_l} \cdot \frac{\Delta_c U^{'}}{\overline{C}_{e,v}T_0}\right) - q_{tr}\frac{\gamma_e - 1}{V_0} = k_{a,v} \cdot p_0 - q_{tr}\frac{\gamma_e - 1}{V_0} \qquad (1)$$

where $\xi = n_e/n_0$ is the molar ratio of combustion, n_0 is the initial number of moles, n_e is the number of moles at the end of combustion, $r_l = n_l/n_0$ is the volume fraction of each reactant component, v_l is the stoichiometric coefficient of the limiting component of the mixture (the component with a concentration lower than the stoichiometric one), $\Delta_c U'$ is the average molar heat of combustion taking into account the endothermic reaction (at constant volume and T_0), $\overline{C}_{e,v}$ is the molar heat capacity of the end mixture at constant volume, averaged for the end components and for the temperature range T_0 to $\overline{T_f}$, q_{tr} is heat transferred to the cell before the end of combustion, γ_e is the adiabatic compression coefficient of the end products. Equation (1) was further expressed as a simpler correlation, where $k_{a,V}$ is the adiabatic coefficient of pressure rise during explosions.
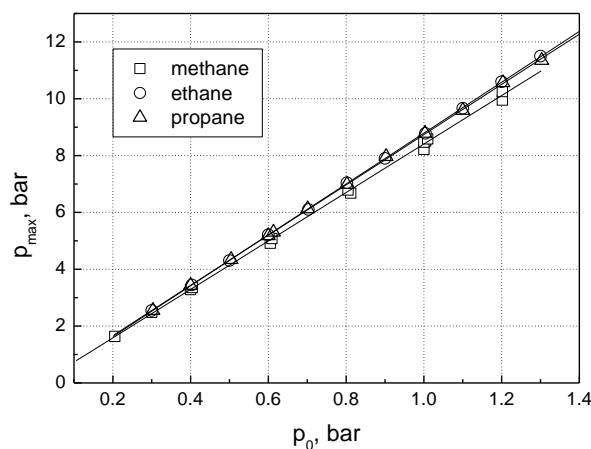
Fig. 2 *Maximum explosion pressures of stoichiometric fuel-air mixtures measured in vessel S at various initial pressures*

It can be assumed, without a great error, that $p_{max} = p_e$ especially in the spherical vessel with central ignition; therefore, we may use equation (1) for an interpretation of linear correlations given in Fig. 2.

The influence of the characteristic properties of fuel on the maximum explosion pressure is found in both the coefficient $k_{a,V}$ which depends mainly on the molar combustion heat and the intercept; ξ and $\overline{C}_{e,v}$ are approximately constant for the three examined fuels: ξ varies between 1.003 and 1.005 in fuel-air mixtures; $\overline{C}_{e,v}$ = 43.5÷44.0 J/mol*K for burned gas, containing only CO_2, H_2O and N_2 from combustion of stoichiometric fuel-air mixtures. The heat of combustion increases with the carbon number: 889.5 kJ/mol for methane, 1559.3 kJ/mol for ethane, 2217.8 kJ/mol for propane. Taking into account that r_l for CH_4 is 0.095, for C_2H_6 is 0.057 and for C_3H_8 is 0.040, a slight increase of the global coefficient $k_{a,V}$, from methane to propane is expected. Indeed, this slight increase is observed in data from Table 1, where calculated and measured explosion pressures are given. Table 1 includes data referring to the stoichiometric n-butane-air mixture, previously reported [14]. It can be

observed that adiabatic values of explosion pressures calculated with programs ECHIMAD and COSILAB are very close.

Table 1 Measured and calculated explosion pressures of stoichiometric fuel-air mixtures at $p_0 = 1$ bar and $T_0 = 298$ K.

Fuel	p_{max}^{calc}, bar ECHIMAD	p_{max}^{calc}, bar COSILAB	p_{max}^{exp}, bar (vessel S)
CH_4	8.80	8.68	8.47
C_2H_6	9.19	9.17	8.79
C_3H_8	9.34	9.32	8.74
C_4H_{10} [14]	9.38	9.35	8.93

The parameters of the linear correlations between the measured peak explosion pressures and the initial pressure for the studied mixtures are presented in Table 2, for vessels S, C_1 and C_2. These correlations are useful for the determination of explosion pressures at any initial pressure within the studied range of variation.

**Table 2** Parameters of correlations $p_{max} = a + b \cdot p_0$.

Vessel \ Fuel	CH_4	C_2H_6	C_3H_8
	-a, bar		
S	0.119	0.159	0.104
C_1	0.376	-	0.229
C_2	0.102	-	0.445
	b		
S	8.526	8.950	8.842
C_1	8.294	-	8.414
C_2	7.060	-	7.293

As indicated by equation (1), the influence of the shape and size of the explosion vessel on explosion pressures is found also in the values of intercept a. The variation of the intercept is also influenced by the rate of flame propagation which entails a variation of time of flame contact with the wall of the explosion vessel.

A comparison between the measured and calculated peak explosion pressures of the stoichiometric methane-air mixture is given in Fig. 3, where data calculated by ECHIMAD and COSILAB fit the same linear plot of p_{max} vs. p_0. Measured peak explosion pressures are lower as computed explosion pressures, for all fuels, even in vessel S, where the heat losses during the late stage of flame propagation are much lower as compared to vessels C_1 and C_2. The higher heat losses associated to the asymmetry of the explosion vessel (earlier contact of flame with top and side walls, as compared to central ignition) determine lower explosion pressures, over the whole range of examined initial pressure.

The data of the explosion pressures reported in this paper are close to those reported in the literature, obtained in various explosion vessels. The same peak explosion pressure ($p_{max} = 8.1$ bar) of the most reactive methane-air mixture was obtained in a 5L spherical vessel [2] and in a 20 L spherical vessel [3]. Cashdollar et al. [14] report different values of maximum explosion pressures for methane-air mixtures, depending on the volume of the explosion vessel: 8.3 bar in a 20 L explosion vessel, 8.5 bar in a 120 L explosion vessel, and 7.6 bar in a 25 m^3 explosion vessel. For the most reactive propane-air mixture, the same authors found explosion pressures between 8.8 bar and 9.6 bar in the above mentioned explosion vessels.

Other sets of data on closed-vessel explosions of ethane-air and propane-air mixtures obtained in various explosion vessels are reported in literature [2,3,16-19].
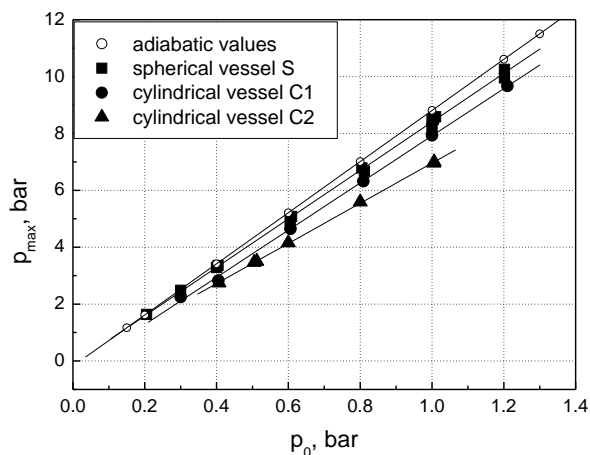
Fig. 3 *Explosion pressures of the stoichiometric CH_4-air mixture at $T_0 = 298$ K and various initial pressures.*

The explosion times, θ_{max}, are strongly influenced by the burning velocity of flammable mixtures and by the volume and shape of explosion vessel (i.e. the volume of flammable mixture). A typical variation of measured explosion times is shown in Fig. 4 for the stoichiometric methane-air mixture. At constant fuel concentration and constant initial pressure, the lowest explosion times are reached in vessel C_2 ($V_{C2} = 0.16$ L) and the highest in vessel C_1 ($V_{C1} = 1.12$ L). The variation of the initial pressure in the examined range (0.3 – 1.2 bar) has little influence on explosion times characteristic for vessels S and C_2.
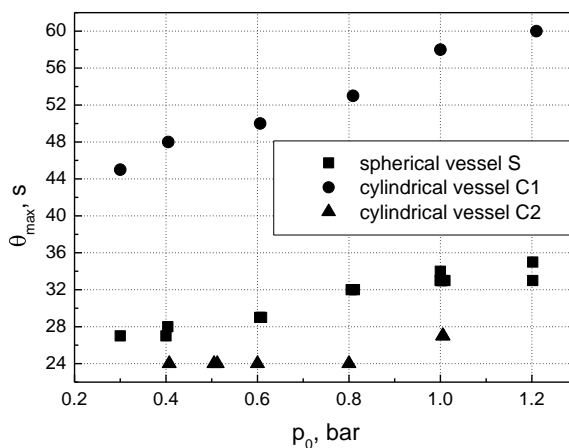
Fig. 4 *The time to peak pressure for the stoichiometric methane-air mixture at $T_0 = 298$ K.*

4. Conclusions

In closed vessels with central ignition, the characteristic parameters of confined explosions, p_{max} and θ_{max} are influenced by the nature and concentration of fuel, by the total initial pressure (at constant composition) and by the shape and volume of the explosion vessel.

For all examined fuel-air mixtures, linear correlations are found between the peak explosion pressure and the total initial pressure of flammable mixture. The slope and intercept of such correlations depend on volume and asymmetry ratio of explosion vessel. These correlations are useful for the determination of explosion pressures at any initial pressure in the studied range of variation.

Measured peak explosion pressures are lower as compared to computed explosion pressures for all fuels even in vessel S, where the heat losses during the late stage of flame propagation are much lower as compared to vessels C_1 and C_2. The higher heat losses associated to the asymmetry of the explosion vessel (earlier contact of flame with top and side walls, as compared to central ignition) determine lower explosion pressures, over the whole range of examined initial pressure.

The data of the explosion pressures reported in this paper are within the range of literature data, obtained in various explosion vessels having different volumes and geometries.

The time necessary to reach the peak pressure depends on vessels volume and shape as well as on fuel nature. Over a restricted range of initial pressure, it has a constant value for each fuel composition and each explosion vessel.

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