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INVESTIGATION OF LAMINAR FLAME PROPAGATION OF THE MOST HAZARDOUS CONFINED METHANE/AIR MIXTURE USING PRESSURE-TIME RECORDS IN A SMALL VESSEL

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ABSTRACT

The study of flame propagation in closed vessels, a subject of increasing consequence for safety measures designed to minimize the risks of explosion hazards, requires either complex equipment or high level computational effort. Simple methods to evaluate the explosivity parameters like maximum explosion pressure, maximum rate of pressure rise, time to peak explosion pressure, burning velocity, flame speed, even for mixtures with unknown nature and composition, are profitable at least for a preliminary stage. The paper describes such a method based on an elementary analysis of the cubic law of pressure rise during early stages of flame propagation. The validity of the method, previously proved and reported for spherical vessels, is now extended for a symmetrical cylindrical vessel of small volume (0.17 L) for the 10% methane/air mixture, known as the most explosive one. The results are in agreement with literature data.

Keywords: methane/air, deflagration, pressure-time variation, burning velocity, flame speed.

1. INTRODUCTION

Methane is a widespread compound encountered in many natural, domestic and industrial processes. Its oxidation with gaseous oxygen from air, either as such or mixed with other

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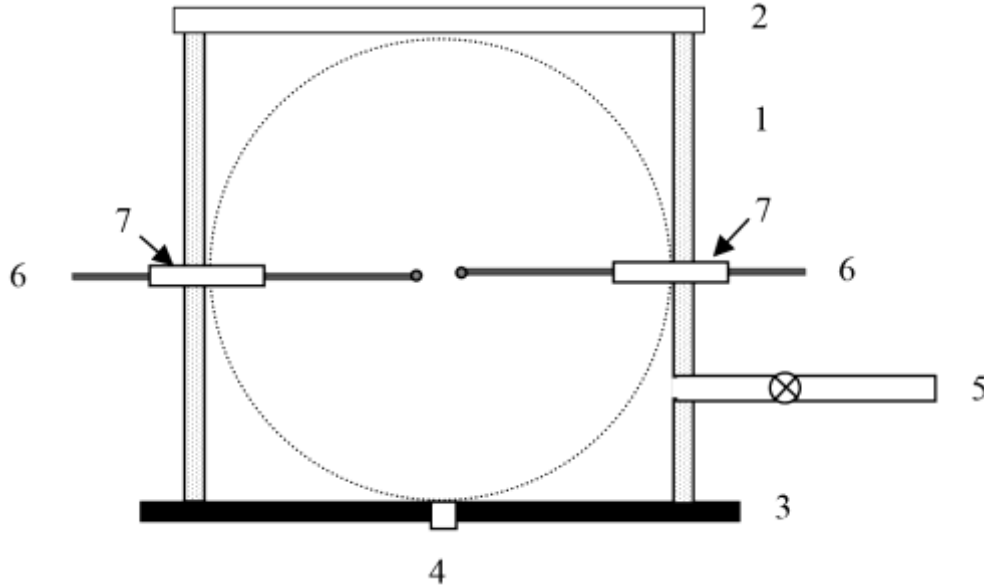
fuels, is an exothermic process frequently used as a source of heat or energy. At the same time, within some concentration limits, the methane/air mixtures are hazardous systems, being able to sustain explosions, either as deflagrations or as detonations, thus requiring severe safety norms to protect the people and the environment. The flammability limits of CH₄ in air range between 5 and 15% in normal conditions [1]. Within this range, the main deflagration properties exhibit extremes (maxima or minima) which define the most explosive mixture. Properties like the maximum explosion pressure, maximum rate of pressure rise, deflagration index, burning velocity and flame speed are situated on maxima, while the quenching distance, minimum ignition energy and time necessary to reach the peak pressure are situated on minima. For methane/air mixtures, the most explosive composition is approximately 10%, slightly higher than the stoichiometric one (9.5%). For safety reasons, the evaluation of the explosivity parameters for the most explosive mixture is of the first importance, although the whole explosivity range is of relevance for a complete characterization of this hazardous system. In this paper we present several aspects of flame propagation as laminar deflagration of this mixture in a small explosion vessel and compare the results with the available literature data. There are numerous experimental and computational methods [2,3] able to provide data on flame propagation. Among these, the analysis of pressure evolution during the flame propagation in relatively large spherical vessels with central ignition proved to be a highly informative and productive method [4-7]. The method can be extended even for easier available small vessels with lower symmetry, especially for cylindrical vessels with diameter equal to height, as will be shown subsequently. From the pressure-time curves recorded during the flame propagation with central ignition in such a vessel, the following relevant properties can be evaluated: maximum explosion pressure, maximum rate of pressure rise, time necessary to reach the peak pressure, quasi-adiabatic pressure rise, burning velocity, flame speed, as well as several derived properties.

2. EXPERIMENTAL METHOD/MODEL

The gaseous mixture containing 10% methane in air was prepared in a stainless steel cylinder at 4 bar total pressure by partial pressure method using methane 99.99% purity from SIAD and used 24 h after mixing. The ignition was initiated by high voltage inductive sparks between 1.5 mm diameter stainless steel electrodes with rounded tips within a spark gap of 2 mm. The ignition energy (0.09 J) was higher than the minimum ignition energy (0.29 mJ) ensuring a safe ignition without important induced turbulence. The pressure variation during the explosion process was monitored with a Kistler piezoelectric pressure transducer type 601A coupled with a charge amplifier type 5011B and recorded using a Tektronix TDS 210 oscilloscope. Details on the experimental procedure were given elsewhere [2,3].

The experiments were carried out in a cylindrical explosion vessel with diameter equal to height: $\Phi = h = 6$ cm ($V_0 = 1.70 \cdot 10^{-4}$ m³ and with a radius of the equivalent spherical volume $R^* = 0.03434$ m) given in Figure 1.

Figure 1: Explosion vessel: 1-vessel body; 2-transparent top cover; 3-bottom cover; 4-pressure transducer; 5-feeding/evacuation pipe with tap; 6-high voltage electrodes; 7-electric insulation (the inscribed sphere with $r_1 = 0.03$ m is outlined inside the vessel)



3. RESULTS AND DISCUSSIONS

A typical pressure-time record, “1”, and its derivative dP/dt , “2”, are given in Figure 2 for a mixture at $P_0 = 1$ bar and $T_0 = 298$ K. The maximum pressure rise, ΔP_{\max} , and the time to peak pressure, θ_{\max} , are measured directly on the recorded diagram. The derivative dP/dt is obtained by numerical derivation of curve ΔP - t , using a previous smoothing through polynomial interpolation followed by the Savitzky-Golay derivative algorithm with a 5% smoothing level. The early stage of pressure evolution was considered for $\Delta P \leq P_0$, when the compression of the unreacted gas was sufficiently small to approximate its temperature equal to the initial temperature. A user defined function of the cubic form was fitted on the resulted curve.

Similar measurements were carried out for different initial pressures. The results are given in Table 1.

According to several previous analyses of data for similar systems [8-10], ΔP_{\max} is related to the heat released during explosion, while $(dP/dt)_{\max}$ and θ_{\max} depend also on the rate of this process. Within the explored pressure range both $P_{\max} = P_0 + \Delta P_{\max}$ and $(dP/dt)_{\max}$ are linear functions on P_0 :

$$P_{\max} = a \cdot P_0 + b \quad (1)$$

$$(dP/dt)_{\max} = \alpha \cdot P_0 + \beta \quad (2)$$

while θ_{\max} slightly increases with initial pressure according to a third power law:

$$\theta_{\max} = a' + b' \cdot P_0^3 \quad (3)$$

Figure 2: Illustration of the experimental pressure-time curve, ΔP -t, its calculated derivative (dP/dt) -t and resulted characteristic parameters ΔP_{\max} , $(dP/dt)_{\max}$, θ_{\max} . The initial pressure rise for $\Delta P \leq P_0$ is shown in the lower left side

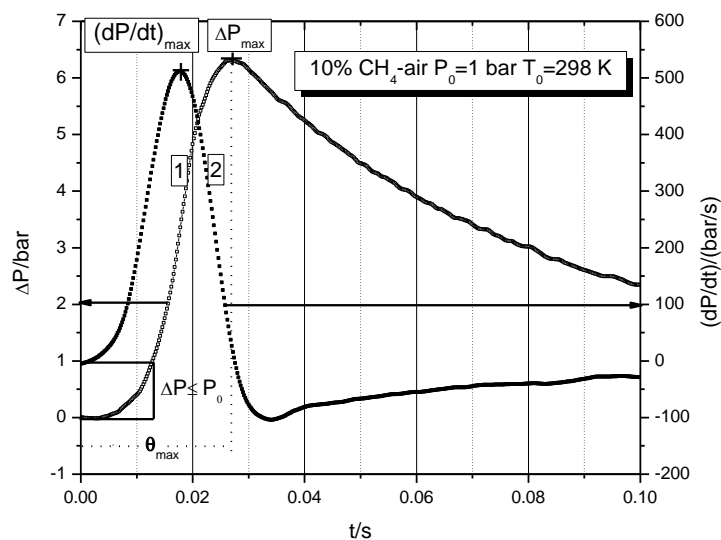


Table 1: Characteristic parameters of pressure evolution for initial pressures, P_0 , of 10% CH_4/air mixture

P_0 (bar)	ΔP_{\max} (bar)	$(dP/dt)_{\max}$ (bar/s)	θ_{\max} (s)
1.50	9.328	690.9	0.0299
1.40	8.795	665.7	0.0299
1.30	8.070	620.0	0.0287
1.20	7.518	591.7	0.0279
1.10	6.967	556.0	0.0269
1.01	6.293	510.7	0.0265
0.80	5.067	423.6	0.0261
0.60	3.716	327.1	0.0259
0.40	2.446	228.3	0.0253

The following results were obtained from the data in Table 1, with the corresponding coefficients of determination, r^2 :

$$\begin{aligned}
 P_{\max} &= (7.271 \pm 0.058) \cdot P_0 - (0.023 \pm 0.063) & r^2 &= 0.999 \\
 (dP/dt)_{\max} &= (423 \pm 12) \cdot P_0 + (74.7 \pm 13) & r^2 &= 0.994 \\
 \theta_{\max} &= (0.0253 \pm 0.0002) + (0.00148 \pm 0.00010) \cdot P_0^3 & r^2 &= 0.966
 \end{aligned}$$

The slope $a = dP_{\max}/dP_0 = 7.271$ represents a good approximation for the quasi-adiabatic pressure rise [8,9]. It can be compared with other measured data (8.3 in a 20 L vessel [1], 7.0 in a 4.2 L vessel [11]) and with the calculated adiabatic value (8.897 using codes described in [12,13]). On the other hand, the maximum rate of pressure rise and the time necessary to reach the peak pressure are significantly more dependent on vessel volume and form, as well as on the power of the ignition source.

It has been observed long ago that during initial stage of the flame propagation the pressure rise is proportional with the third power of time:

$$\Delta P = k_3 \cdot t^3 \quad (4)$$

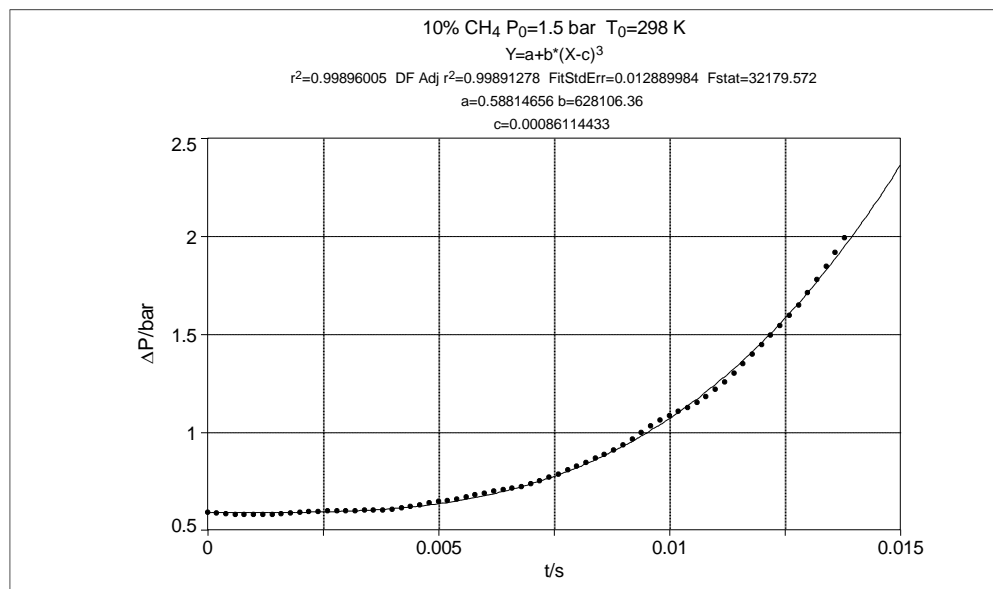
where k_3 is related to the normal burning velocity, S_u , measured with reference to the unburned gas.

Due to inherent displacements of both abscissa and ordinate during the pressure-time recording, an improved correlation equation with three adjustable parameters proved to fit better the experimental data for $\Delta P \leq P_0$ [2]:

$$\Delta P = a_0 + k_3 \cdot (t - \tau)^3 \quad (5)$$

An example is given in Figure 3:

Figure 3: Illustration of the third power law for initial pressure rise of 10% CH₄/air mixture



Two simplified models have been used to give a physical significance of constant k_3 [2]. The isothermal model, more convenient for our calculations, assumes that during this initial period the unburned gas preserves its initial temperature, T_0 , leading to [2]:

$$S_u = R^* \cdot (k_3 / \Delta P_{\max})^{1/3} \cdot (P_0 / P_{\max})^{2/3} \quad (6)$$

Table 2: Normal burning velocities, S_u and flame speeds, S_s evaluated with the third power law (6)

P_0 (bar)	$k_3 \cdot 10^{-5}$ (bar/s)	τ (ms)	ΔP_{\max} (bar)	S_u (m/s)	E_0	S_s (m/s)
1.50	6.74	1.00	9.328	0.383	7.490	2.86
1.40	6.94	1.09	8.795	0.377	7.487	2.82
1.30	6.70	1.17	8.070	0.402	7.483	3.04
1.20	6.16	1.35	7.518	0.398	7.479	3.01
1.10	7.48	1.41	6.967	0.432	7.740	3.23
1.01	6.69	1.50	6.293	0.435	7.470	3.25
0.80	5.36	1.83	5.067	0.430	7.455	3.21
0.60	4.61	3.03	3.716	0.460	7.440	3.42
0.40	3.28	4.40	2.446	0.475	7.403	3.52

The results are given in Table 2 together with the flame speed, S_s , evaluated as $S_s = E_0 \cdot S_u$, where E_0 is the expansion ratio at constant pressure. The flame speed represents the flame front displacement relative to the fix vessel walls. The expansion ratio, E_0 , was approximated as the ratio of the flame temperature, $T_{f,p}$ at constant pressure, and initial temperature $T_0 = 298$ K, neglecting in this case the change in the mole number as a result of combustion. The flame temperatures were calculated using the codes described in [12,13]. The result $S_u = 0.435$ m/s at $P_0 = 1.01$ bar is in good agreement with literature data, 0.36 - 0.45 m/s compiled by [4,5] or measured for both stretched and un-stretched flames of methane/air mixtures [14]. In the above calculations, ΔP_{\max} and consequently P_{\max} are evaluated from experimentally recorded pressure-time curves, implying significant heat losses. An alternative approach relies on the following calculations: $P'_{\max} = a \cdot P_0$ or $(P_{\max})_{ad} = (\Delta P_{\max})_{ad} \cdot P_0$ and $\Delta P_{\max} = P_{\max} - P_0$. For $P_0 = 1.01$ bar the results are given in Table 3:

Table 3: Propagation parameters at $P_0 = 1.01$ bar and $T_0 = 298$ K using different data sources

Source	P_{\max} (bar)	ΔP_{\max} (bar)	S_u (m/s)	S_s (m/s)
Experimental	7.303	6.293	0.435	3.25
$a = dP_{\max}/dP_0$ (7.271)	7.344	6.334	0.433	3.24
$(\Delta P_{\max})_{ad}$ (8.897)	8.986	7.976	0.350	2.62

It can be observed that the differences between experimental and quasi-adiabatic data are negligible, while for adiabatic data significantly lower values are obtained for the burning velocity (and consequently for the flame speed), but they are still in the range of the reported data in literature. There are no sound reasons to state which result is the best one but, for safety applications, the highest value of S_u is preferable.

Within the range of the experimental error, there is a systematic increase of S_u and also of S_s , when the initial pressure decreases. This is usually rationalized with a power law:

$$S_u = S_{u,0} \cdot (P/P_{ref})^\nu \quad (7)$$

where P_{ref} is the reference pressure, taken usually as $P_{ref} = 1$ bar, and ν is the baric coefficient of normal burning velocity. The linear regression $\ln(S_u)$ against $\ln(P/P_{ref})$ gives $\nu = -0.166 \pm 0.027$ which is in the range -0.13 to -0.30 , reported for many hydrocarbon/air mixtures [15]. This parameter can be used to evaluate an overall reaction order n_r , assuming that the reaction rate, r_R , is given by a kinetic equation of factorized form:

$$r_R = k_0 \cdot (P/P_{ref})^{n_r} \cdot \exp(-E_a/RT) \quad (8)$$

where k_0 is a proportionality constant and E_a is the overall activation energy. In isothermal condition, the reaction order can be evaluated using the relationship [16]:

$$n_r = 2(1 + \nu) \quad (9)$$

and obtaining $n_r = 1.67$, in accord with similar data for other hydrocarbon/air mixtures [15].

The adjustable parameter τ in the correlation equation (5) has the significance of an induction period meant as the time needed from ignition to the time when a significant pressure increase can be detected. The existence of an induction period for an electric spark ignition was recently substantiated through a numerical study of this process using detailed chemical kinetics [17]. The results indicate induction periods around 1.5 ms, similar with those reported in Table 2. If a kinetic equation of the form (8) is assumed, then, in isothermal conditions the induction period is given by:

$$\tau = k^* \cdot (P/P_{ref})^{-n_r} \quad (10)$$

The linear regression $\ln(\tau)$ versus $\ln(P/P_{ref})$ gives $n_r = 1.130 \pm 0.044$, a figure slightly different from that obtained with equation (9), an acceptable result taking into account the use of two different models based on different assumptions.

4. CONCLUSIONS

The analysis of pressure-time variation during laminar deflagration of the most explosive methane/air mixture in a small cylindrical laboratory vessel with diameter equal to height ($V_0 = 0.17$ L) provided valuable parameters necessary for safety design of equipment working in explosive atmospheres. The primary analysis gave the maximum explosion pressure, maximum rate of pressure rise and time to peak pressure. A recently proposed method for the processing of pressure variation during the initial stage of the flame propagation in large spherical vessels was successfully used even in this case to obtain reliable values for the burning velocity, flame speed and ignition period. The required necessary information is not dependent on the specific properties of the explosive mixture, rendering the method applicable to explosive systems of unknown nature and composition.

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