ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2016, *61*(4-5), 299-305

Dedicated to Professor Alexandru T. Balaban on the occasion of his 85th anniversary

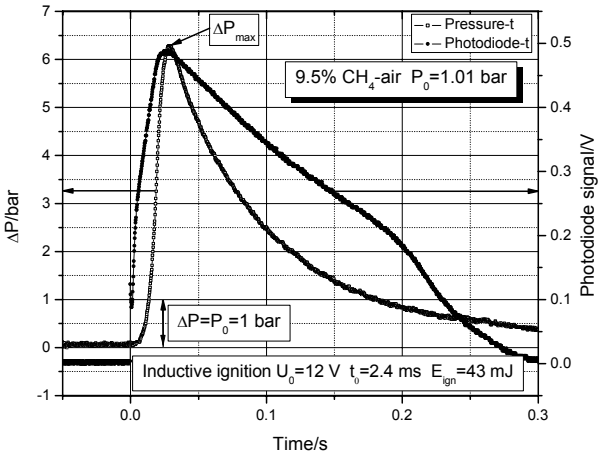
SPARK IGNITION AND PROPAGATION PROPERTIES OF METHANE-AIR MIXTURES FROM EARLY STAGES OF PRESSURE HISTORY

Maria PRODAN,[a] Maria MITU,[b] Domnina RAZUS[b] and Dumitru OANCEA[a,*]

[a] Department of Physical Chemistry, University of Bucharest, 4-12 Bd. Elisabeta, 030018 Bucharest, Roumania
[b] "Ilie Murgulescu" Institute of Physical Chemistry, Roumanian Academy, 202 Spl. Independenței, 060021 Bucharest, Roumania

Received November 13, 2015

The early stages of pressure-time history during propagation of laminar flames in closed vessels contain valuable information on the formation and development of the flame kernel initiated by an electric spark. Assuming the validity of the cubic law of pressure increase, when the unburned gas temperature remains roughly constant, the best fit analysis of the pressure-time curves proved the existence of a necessary time correction. Considered initially as an adjustable parameter, its physical significance as an ignition delay period was advanced and confirmed by parallel measurements of intensity of the emitted radiation using a photodiode. The pressure-time curves for lean, stoichiometric and rich methane-air mixtures were recorded and analyzed. From the early stages of pressure-time history, when the pressure increase is equal to or less than the initial pressure, the ignition delay periods and normal burning velocities were evaluated and discussed. Their pressure dependences provided plausible overall reaction orders.



INTRODUCTION

The spark ignition and propagation of laminar flames in stagnant fuel-air mixtures are presently active research topics implying both fundamental and practical aspects of combustion. The recent experimental and theoretical achievements referring, on the one hand, to the high-speed imaging[1] (laser-induced fluorescence, infrared emission, schlieren and shadowgraphy etc.) and, on the other, to numerical methods using detailed kinetics and fluid dynamics,[2, 3] allowed a more advanced understanding of the mechanisms that govern the flame formation and propagation. Considering only the spark ignition, the initial high temperature channel resulted from the electric discharge induces the formation of a flame kernel which grows until it reaches a critical size necessary for the subsequent propagation. This stage is strongly dependent on the spark characteristics, electrodes configuration and flammable gas properties. If the spark stores at

* Corresponding author: doan@gw-chimie.math.unibuc.ro

least the minimum ignition energy,[2] the formation of the kernel with a critical size able to ensure autonomous propagation requires a finite time known as ignition delay period.[4, 5] The ignition delay has been also detected and measured in many combustion phenomena like those occurring in shock tube or rapid compression experiments and has been used to characterize the kinetics of the overall process.[6] It is different from that used to describe the time development of combustion in diesel or spark ignition engines. Recent numerical studies for spark ignition in quiescent flammable mixtures modeled the ignition and flame propagation using the ignition delay time defined as the time interval between the start of the ignition energy input and the onset of ignition.[2] It is thus expected that relevant experimental results referring to spark ignition delay periods can be obtained if appropriate properties are followed and the necessary information is extracted, as will be shown below from the analysis of the early stages of pressure-time evolution in a closed vessel. The pressure-time history during deflagration of premixed fuel-air flammable mixtures in a closed vessel has been widely used to determine the laminar burning velocities.[7] The procedures and limitations regarding the use of the whole pressure-time curves have been critically analyzed and discussed.[8, 9] A different approach has been recently proposed[10] based on the use of early stages of pressure-time evolution assumed to follow the cubic law, $\Delta P \sim t^3$. To obtain a better fit on the experimental data, the cubic law was put in the form $\Delta P = a + b \cdot (t - c)^3$, where a and c are two adjustable parameters accounting for different random deviation of the curve and b is a parameter related to the burning velocity. The approach was successfully applied to several flammable systems.[11-15] A thorough examination of parameter c resulted from the pressure-time diagrams at different initial pressures for the 10% CH_4-air mixture obtained through spark ignition suggested the possibility that it can represent the associated ignition delay period.[16] In the present paper the normal burning velocities and the ignition delay periods of lean, stoichiometric and rich CH_4-air mixtures were measured using the early stages of pressure evolution in a closed vessel, following the spark ignition. The existence of these ignition delay periods is confirmed by the simultaneous measurements of the emitted radiation from the expanding flame using a photodiode. The obtained curve exhibits a specific pattern during ignition and subsequent propagation.

EXPERIMENTAL METHOD

The gaseous mixture containing 7, 8, 9, 9.5, 11 and 12% methane in air were successively prepared in stainless steel cylinders 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 2.5 mm. The high voltage spark was obtained from an automotive ignition coil. The primary winding, with an inductance L = 9.5 mH, was fed from a source able to give impulses with voltages between U = 12 to 30 V during adjustable time intervals t_0 = 0.5 to 10 ms. The energy stored in the coil is given approximately by $E = U^2 t_0^2/(2L)$ and the discharge time is approximately 1 ms. The spark energy was adjusted to ensure a safe ignition without important induced turbulence. The pressure variation during the explosion 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.[10, 14, 16] The experiments were carried out in a cylindrical stainless steel explosion vessel with diameter equal to height: $\Phi = h$ = 6 cm ($V_0 = 1.70 \cdot 10^{-4}$ m^3 and with a radius of the equivalent spherical volume R^* = 0.0343 m). The pressure transducer was mounted on the lower lid of the vessel. The upper lid was a transparent window with very good transmittance in visible and near infrared spectral region tightly fixed on the main body of the vessel. A photodiode S1223 from Hamatsu Photonics, with spectral response range between 320 and 1100 nm and high speed response up to 30 MHz, was mounted outside the transparent window centered on the spark gap and coupled to the second oscilloscope channel.

COMPUTING PROGRAM

The kinetic modeling of methane-air flames was made with the package COSILAB (version 3.0.3)[17] using the GRI (Gas Research Institute) mechanism version 3.0. This mechanism, where 53 chemical species and 325 elementary reactions are taken into account, is optimized for combustion of natural gas in air. The input data were taken from thermodynamic and molecular databases of Sandia National Laboratories, USA, according to the international standard (format for CHEMKIN). The computations were made for premixed 1D adiabatic laminar free flames of methane-air mixtures at various initial compositions ([CH_4] = 7.0 – 12.0 vol.%; φ = 0.72 – 1.30) and pressures (1 – 10 bar).

RESULTS AND DISCUSSION

The experimental results consist of simultaneous pressure and photodiode signal variations following the spark ignition, exemplified in Fig. 1 for the stoichiometric CH_4-air mixture starting from the initial pressure P_0 = 1.01 bar. The data show that the photodiode signal closely tracks the pressure variation, ΔP.

The pressure-time diagram allows the measurement of ΔP_{max} (and consequently of $P_{max} = \Delta P_{max} + P_0$) and the analysis of the early pressure variation from $\Delta P = 0$ to $\Delta P = P_0$ as illustrated in the lower left side of the figure. Within this range it is assumed that the unburned gas preserves approximately its initial temperature,[10] greatly simplifying the evaluation of the burning velocity, S_u. On the basis of several previous observations, it was shown[10] that the early pressure variation can be described by a cubic law:

$$\Delta P = k \cdot t^3 \tag{1}$$

To account for the inherent experimental data deviations and to obtain better fits of this law on the experimental data, the cubic law was used in the form:

$$\Delta P = a + b \cdot (t - c)^3 \tag{2}$$

with three adjustable parameters a, b and c. In the following, the parameter b will be written as k_3 and parameter c as τ to specify their significances as cubic law constant and ignition delay period, respectively ($\Delta P = a + k_3 \cdot (t - \tau)^3$). An example is illustrated in Fig. 2 where the goodness of fit parameters is also given.

Assuming an isothermal compression of the unburned gas in the early stage of flame propagation, the normal burning velocity can be evaluated according to the equation:[10]

$$S_u = R^* \left(\frac{k_3}{\Delta P_{max}} \right)^{1/3} \left(\frac{P_0}{P_{max}} \right)^{2/3} \tag{3}$$

with R^* the radius of the sphere with the same volume as the cylindrical vessel.

The results for the measured and derived properties are given in Table 1.

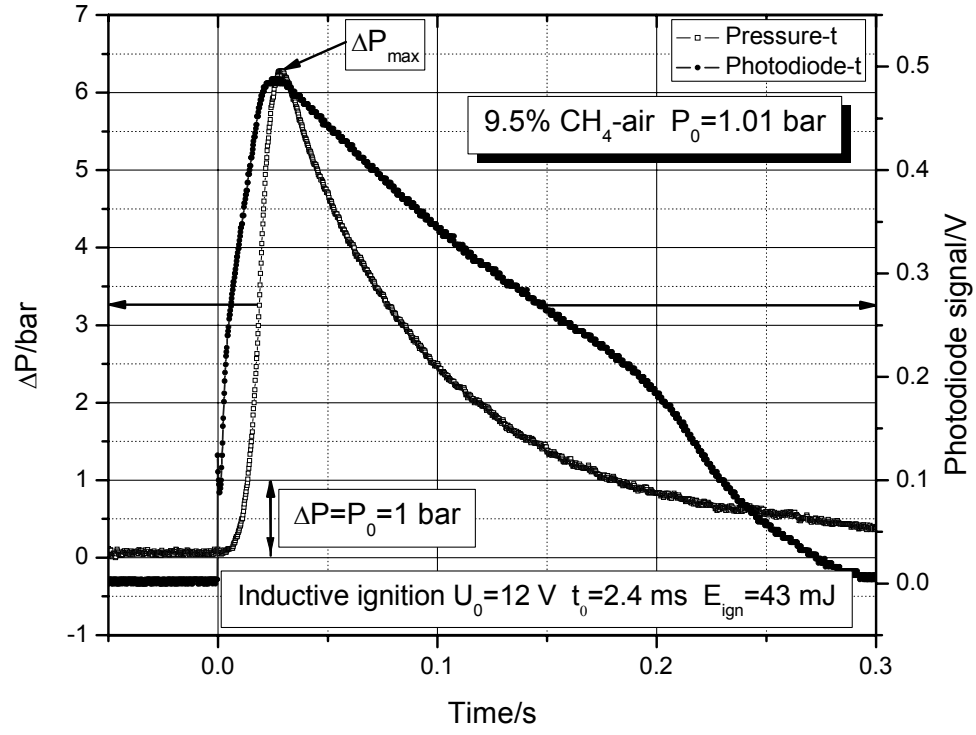


Fig. 1 – Pressure and photodiode signal during laminar propagation of the stoichiometric methane-air mixture.

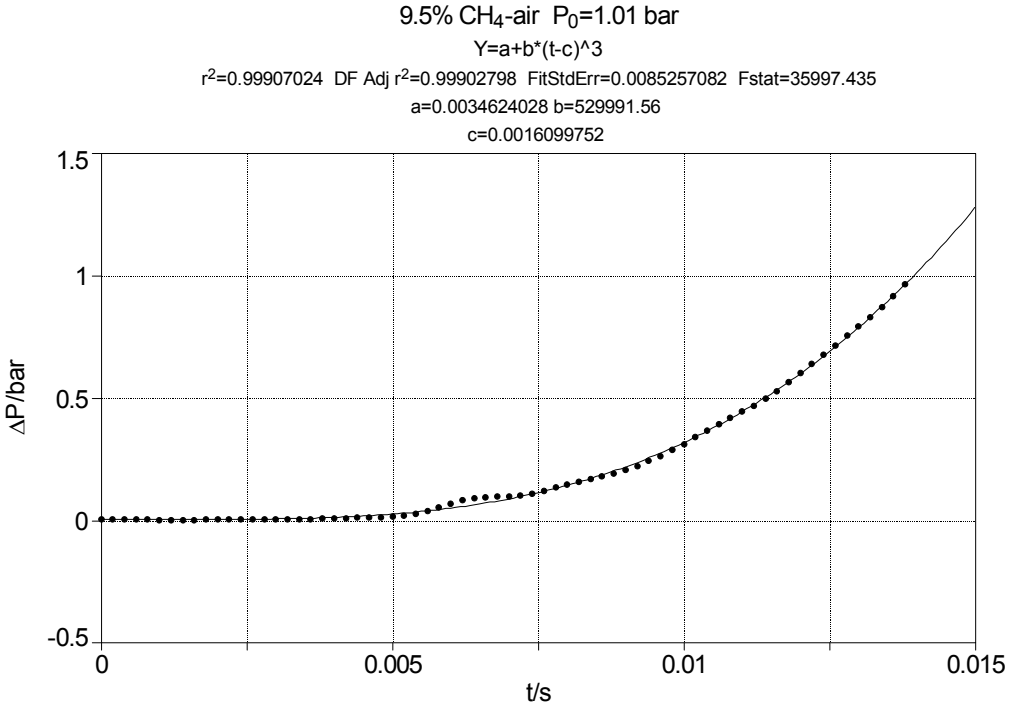


Fig. 2 – Pressure variation during the early stages of flame propagation for the stoichiometric methane-air mixture at P_0 = 1.01 bar.

Table 1

Measured and derived laminar combustion properties for a lean (7%), stoichiometric (9.5%) and a rich (11%) methane-air mixtures

%CH_4	P_0/bar	P_{max}/bar	k_3/(bar/s^3)	τ/s	S_u/(m/s)
	0.40	2.212	37813	0.00544	0.302
	0.60	3.290	40559	0.00234	0.273
	0.80	4.420	41594	0.00170	0.248
	1.01	5.661	42950	0.00154	0.317
	1.10	6.165	43194	-	0.317
7.0	1.20	-	-	0.00152	-
	1.30	7.217	34068	0.00151	0.319
	1.40	7.765	35003	0.00113	0.319
	1.50	8.405	32877	0.00075	0.317
	0.40	2.787	253096	0.005046	0.446
	0.60	4.277	376141	0.002065	0.434
	0.80	5.737	479026	0.001559	0.417
	1.01	7.238	538963	0.001210	0.409
9.5	1.10	8.027	542488	0.000986	0.391
	1.20	8.780	551739	0.001090	0.380
	1.30	9.484	557149	0.000866	0.373
	1.40	10.276	546071	0.000726	0.359
	1.5	11.020	576028	0.000623	0.357
	0.40	2.916	215375	0.005260	0.403
	0.60	4.273	342101	0.002920	0.421
	0.80	5.659	414655	0.002100	0.410
	1.01	7.278	423045	0.001490	0.375
11.0	1.10	7.920	464098	0.001394	0.376
	1.20	8.737	451573	0.001293	0.358
	1.30	9.243	420783	0.001204	0.349
	1.40	10.243	482436	0.001273	0.346
	1.50	10.950	505566	0.001032	0.344

The examination of the early variation of the photodiode signal confirmed the significance of parameter τ from equation (2) as an ignition delay period. The suggestive pattern is illustrated in Fig. 3 for the 11% methane-air mixture at two initial pressures. The peak signal appearing at the

beginning results from the spark which was also used as the trigger signal. The beginning of the first steep quasi-linear increase appears to be localized close to the end of the ignition delay period. Significant differences between the signals obtained for two different pressures confirm the existence of a critical period necessary for the formation of the flame kernel. Moreover, the variation of the ignition delay period with initial pressure of a certain mixture follows the same trend as that found for shock tube or rapid compression experiments. If the overall reaction rate r_R is of the Arrhenius type:

$$r_R = k_0 \cdot (P / P_{ref})^{n_r} \cdot exp(-E_a / RT) \qquad (4)$$

with n_r the overal reaction order and other symbols having the usual meanings, then, in isothermal conditions, the induction period is given by an equation of the form:

$$\tau = k^* \cdot (P / P_{ref})^{-n_r} \qquad (5)$$

All the data of the type given in Table 1 fit satisfactorily equation (5) and the resulted overall reaction orders given in Table 2 are in agreement with other results reported for laminar combustion.

Additional substantiation of the reported data concerning the ignition delay periods is provided by the comparison between measured and calculated values, illustrated in Fig. 4. The calculated values were taken from a numerical study on the spark ignition characteristics of methane–air mixtures using detailed chemical kinetics[2] and are in very good accord with our data in terms of both size and their variation with mixture composition. Some limitations of the described procedure originate in the inherent fluctuations accompanying the spark discharges which are reflected in important scattering of data. Several experiments are necessary for each set of operational parameters in order to identify the real trend. The relatively long discharge time associated with an inductive spark (<1 ms) can also interfere with the flame kernel growth. The future use of capacitive sparks will remove this possible limitation.

For all investigated mixtures the experimental normal burning velocities S_u were evaluated using the equation (3) and given in Table 2 where the calculated values were also added. The agreement is good enough if some other literature data are taken into account. For the stoichiometric mixture the reported experimental data vary between 0.329[18] and 0.400[7, 19] m/s, thus covering both experimental and calculated values in Table 2.

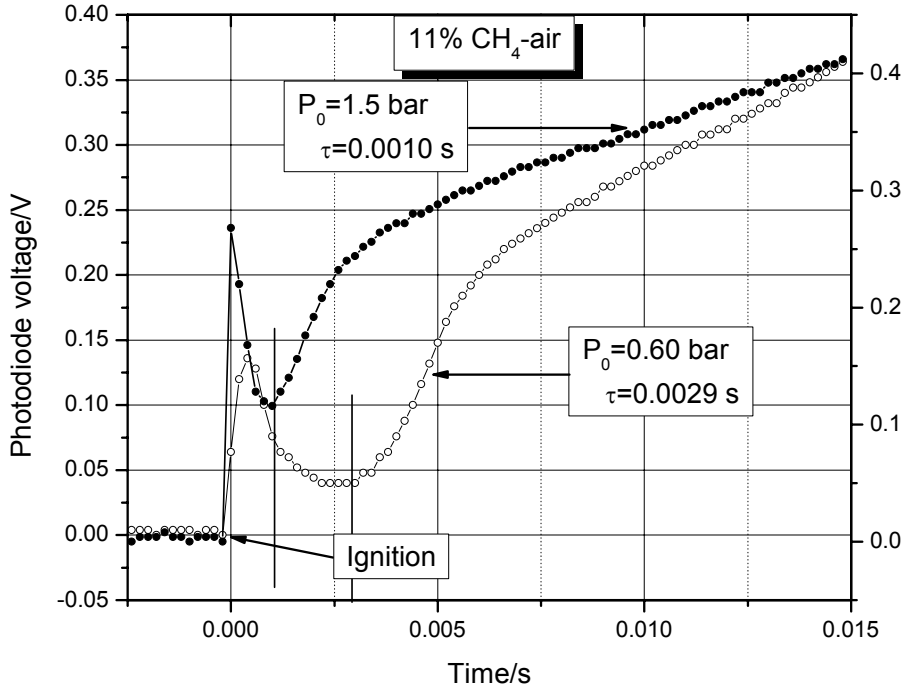


Fig. 3 – Early variations of photodiode signal for the 11% methane-air mixture at two initial pressures (the given ignition delay periods, τ, are obtained from the pressure variation using the cubic law of pressure increase).

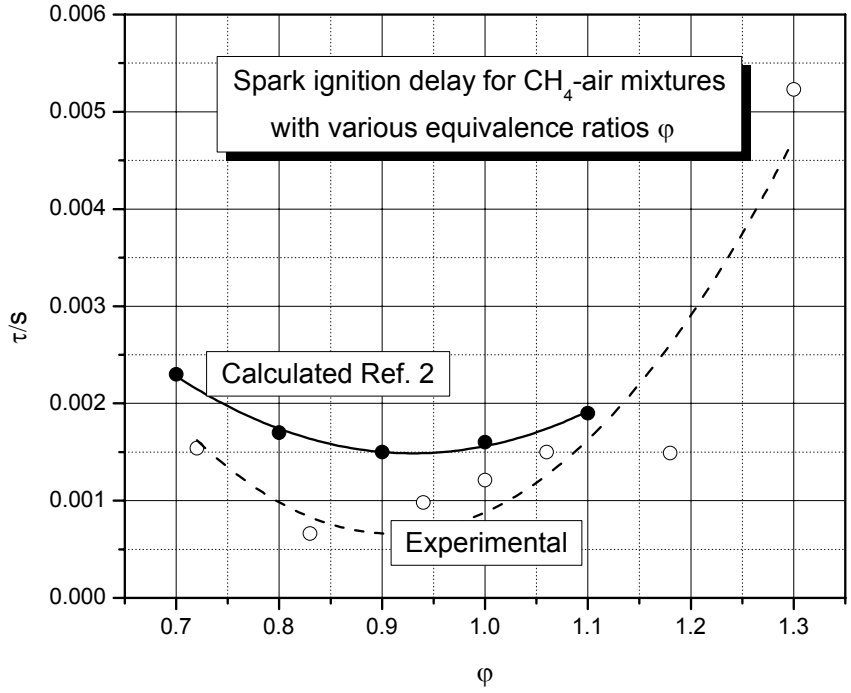


Fig. 4 – Comparison between measured and calculated spark ignition delays for methane-air mixtures with various equivalence ratios.

Table 2

Experimental and calculated normal burning velocities, ignition delay periods at P_0 = 1.01 bar, baric coefficients of normal burning velocity and overall reaction orders resulted from S_u and τ variation with pressure (φ is the equivalence ratio)

% CH_4	φ	$S_{u,0}$/(m/s)$_{exp}$	$S_{u,0}$/(m/s)$_{calc}$	(τ_0/s)	-v	n_r(from v)	n_r(from τ)
7.0	0.72	0.317	0.221	0.00154	-	-	1.33
8.0	0.83	0.341	0.298	0.00066	0.308	1.38	-
9.0	0.94	0.381	0.359	0.00098	0.246	1.51	1.67
9.5	1.00	0.409	0.374	0.001210	0.215	1.57	1.65
10*	1.06	0.435	0.384	0.001500	0.166	1.67	1.13
11	1.18	0.375	0.352	0.001490	0.249	1.50	1.35
12	1.30	0.287	0.246	0.005230	0.271	1.46	-

* Ref. 16

The variation of S_u with the initial pressure is usually rationalized with a power law:

$$S_u = S_{u,0} \cdot (P/P_{ref})^v \quad (6)$$

where P_{ref} is the reference pressure, taken usually as P_{ref} = 1 bar, and v is the baric coefficient of the normal burning velocity. The baric coefficients resulted from the linear regressions ln(S_u) against ln(P/P_{ref}) are also given in Table 2. For the stoichiometric mixtures the obtained value (v = -0.215) is again within the range of the literature data from -0.17[20] to -0.50.[21] Besides its value for prediction of the normal burning velocity within a certain pressure range, the baric coefficient of the normal burning velocity can also be used to evaluate the overall reaction order n_r within the flame, according to equation:[22]

$$n_r = 2(1 + v) \quad (7)$$

The results are in good agreement with those obtained from the pressure variation of the ignition delay periods.

CONCLUSIONS

The pressure-time history during deflagration of premixed fuel-air flammable mixtures in closed spherical vessels with central ignition has been widely used to determine the laminar burning velocities using the whole recorded curve and different simpler or more elaborate models, except for early stages when the stretch effects have to be taken into account and for final stages when

important thermal losses become important. In several previous papers it has been proved that the analysis of early stages, relied on the cubic law of pressure rise, provides values of normal burning velocity in agreement with other reliable methods. Since during this period the spherical shape of the flame is maintained even in vessels of lower symmetry, in particular of cylindrical form with diameter equal to height, this methodology was used in this paper to study different methane-air mixtures in such a vessel, with the benefit of using smaller and simpler laboratory equipment. The experimental and calculated burning velocities have similar values with those reported by other researchers. In addition, it was shown that the analytical form of the pressure rise during the early stages includes a measurable parameter identified as the ignition delay period. Simultaneous measurements of the emitted radiation using a photodiode confirmed the existence of such a period. Its magnitude and trend of variation with mixture composition were confirmed by numerical calculations based on detailed kinetics reported in literature. The pressure dependence of both normal burning velocity and ignition delay period provided plausible overall reaction orders.

REFERENCES

1. V. Sick, *Proc. Combust. Inst.,* **2013**, *34*, 3509–3530.
2. J. Han, H. Yamashita and N. Hayashi, *Combust. Flame*, **2010**, *157*, 1414–1421.
3. M.D. Smooke, *Proc. Combust. Inst.*, **2013**, *34*, 65–98.
4. B.L. Salvi and K.A. Subramanian, *Appl. Energ.*, **2015**, *139*, 93–103.
5. K. Dharamshi, A. Pal and A.K. Agarwal, *Int. J. Hyd. Energy*, **2013**, *38*, 10648-10653.
6. C.K. Westbrook, W.J. Pitz, H.C. Curran, J. Boercker and E. Kunrath, *Int. J. Chem. Kinet*. **2001**, *33*, 868–877.
7. A.E. Dahoe and L.P.H. de Goey, *J. Loss Prevent. Proc. Ind.*, **2003**, *16*, 457–478.
8. F.N. Egolfopoulos, N. Hansen, Y. Ju, K. Kohse-Höinghaus, C.K. Law and F. Qi, *Prog. Energy Combust. Sci.*, **2014**, *43*, 36–67.
9. A.N. Lipatnikov, S.S. Shy and W. Li, *Combust. Flame*, **2015**, *16*, 22840–2854.
10. D. Razus, D. Oancea and C. Movileanu, *J. Loss Prevent. Proc. Ind.*, **2006**, *19*, 334–342.
11. D. Razus, D. Oancea, V. Brinzea, M. Mitu and C. Movileanu, *Energy Convers. Manage.*, **2010**, *51*, 2979–2984.
12. D. Razus, V. Brinzea, M. Mitu and D. Oancea, *Energy Fuels*, **2010**, *24*, 1487–1494.
13. C. Movileanu, D. Razus, and D. Oancea, *Energy Fuels*, **2011**, *25*, 2444–2451.
14. D. Razus, V. Brinzea, M. Mitu, C. Movileanu and D. Oancea, *Energy Fuels*, **2012**, *26*, 901−909.
15. M. Mitu , D. Razus, V. Giurcan and D. Oancea, *Fuel*, **2015**, *147*, 27–34.
16. D. Oancea, M. Prodan and D. Razus, *New Front. Chem.*, **2016**, (Former: *Ann. West Univ. Timisoara – Series Chem.*, *25*), *1*, 64–72.
17. Cosilab, version 3.0.3., Rotexo-Softpredict-Cosilab GmbH & Co KG, Bad Zwischenhahn, 2012.
18. P.G. Hill and J. Hung, *Combust. Sci. Technol.*, **1988**, *60*, 7–30.
19. D. Zhu, F. Egolfopoulos, and C.K. Law, *22nd Symp. (Intern.) on Combustion*, **1989**, 1537-1545.
20. F. Cammarota, A. Di Benedetto, V. Di Sarli, E. Salzano and G. Russo, **2009**, *J. Loss Prevent. Proc. Ind.*, *22*, 607–613.
21. G. Andrews and D. Bradley, *Combust. Flame*, **1972**, *19*, 275-288.
22. A.E. Potter Jr. and A.L. Berlad, *Symposium (International) on Combustion*, **1956**, *6*, 27–36.