



OVERALL ACTIVATION PARAMETERS OF PROPANE OXIDATION IN FLAMES FROM NORMAL BURNING VELOCITIES

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The normal burning velocities for the deflagration of propane-air mixtures were determined from pressure-time records, in experiments performed in a spherical vessel with central ignition at total initial pressures between 0.3 and 1.3 bar, initial temperatures within 298 and 423 K and different equivalence ratios ϕ between 0.69 and 1.58. The normal burning velocities were obtained also by kinetic modeling of the corresponding laminar flames, using an extended mechanism (53 chemical species, 592 elementary reactions) and including radiative energy losses. The overall activation parameters of propane oxidation in flames (reaction orders and activation energies) were calculated from normal burning velocity variation with initial pressure and average temperature of the flame front of preheated propane-air gaseous mixtures. The overall activation energies obtained from both calculated and experimental burning velocities are discussed and compared with other reported data.

INTRODUCTION

The increasing concern over fossil fuel shortage and air pollution brings an increasing number of studies on alternative fuels around the world community. Propane, which is a major component of the liquefied petroleum gas (LPG), has a good air-fuel mixing potential due to its low boiling temperature. Propane can be liquefied under a moderate pressure, and this makes onboard storage and handling easier.¹ In addition, its combustion in engines is characterized by low hydrocarbons and CO emissions. Nowadays a great number of domestic combustors and vehicles around the world utilize propane or LPG as cheap, alternative fuels. The analysis and prediction of engines and/or combustors performances require their combustion characteristics in various conditions. Among them, the normal burning velocity is a key parameter characteristic for explosion propagation in deflagration regime, directly influenced by the reaction rate in the flame front. As a first approximation the reaction rate variation with the total pressure and with the local temperature can be expressed by an empirical, Arrhenius type, rate law containing two overall parameters: the overall

reaction order and the overall activation energy. They are obtained under the assumption of a simple one-step kinetics of fuel oxidation, valid over a restricted range of pressure and flame temperature variation. In fact, the kinetics of hydrocarbon oxidation in flames is much more complicated and it is usually described by a set of hundreds of elementary reactions. However, the overall reaction order and overall activation energy are important to characterize from kinetic point of view the dependency of normal burning velocity on pressure and temperature of fuel-air mixtures.

The normal burning velocity can be determined using stationary flames, by means of burner method or non-stationary flames, using the closed bomb method or the tube method. The bomb method allows evaluation of the normal burning velocity from $p(t)$ curves and can be utilized for evaluation of normal burning velocity at different initial conditions (pressure and/or temperature).

Analysis of the normal burning velocity variation with total initial pressure in experiments at constant initial temperature allows determination of overall reaction orders, while analysis of normal burning velocity variation with flame temperature, at constant initial pressure, allows the determination

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of the overall activation energy. The overall kinetic parameters are basic data for Computational Fluid Dynamics modeling of flame propagation in various conditions and for design of venting systems of enclosures where accidental explosions may occur.^{2,3}

EXPERIMENTAL

The experimental set-up was designed to allow experiments at various total initial pressures within 0.3-1.3 bar and various initial temperatures within 298-423 K.

The experiments were performed in a thermostated spherical explosion vessel (volume $V = 0.52$ L) with central ignition, equipped with an ionization probe for monitoring the flame front position. The combustion vessel was electrically heated; its temperature was adjusted ($\pm 1^\circ\text{C}$) using an AEM 1RT96 controller and monitored by a K-type thermocouple. The pressure evolution during explosion was measured with a piezoelectric pressure transducer type Kistler 601A mounted in a special adapter, maintained at ($25 \pm 1^\circ\text{C}$) by a water jacket. The piezoelectric pressure transducer was connected to a Charge Amplifier type Kistler 5001SN whose signals were recorded with an acquisition data system TestLabTM Tektronix 2505. Data acquisition was made at 5000 signals per second using an acquisition card Tektronix type AA1.

Ignition was made with inductive-capacitive sparks produced between stainless steel electrodes and having limited discharge energy in order to avoid the disturbances of the ignition nucleus. The spark gap of constant width 3.5 mm was located in the geometrical centre of the spherical vessel.

Before each test, the combustion vessel was evacuated down to 0.5 mbar and the explosive mixture was admitted and allowed 30 min. to become quiescent and thermally equilibrated.

The propane-air mixtures with fuel concentration between 2.80 and 6.22 vol.% were obtained by partial pressures method, at a total pressure of 4 bar and used after 48 h after mixing. Propane (99.99%) (SIAD Italy) was used without further purification.

Other details on the experimental set-up and procedure were previously given.^{4,5}

COMPUTING PROGRAM

The laminar burning velocities of propane-air were computed by the program INSFLA, developed by Warnatz, Maas and coworkers⁶ for kinetic modeling of fuel-air flames in various conditions. A premixed laminar free flame was considered, assuming radiative energy losses and a mechanism $\text{CH}_4\text{-C}_4$ (53 chemical species, 592 elementary reactions). Updated values of several rate coefficients, for the rate-limiting reactions in propane-air oxidation were taken from Heghes.⁷ The runs were performed for the isobaric combustion of propane-air mixtures at 1 bar initial pressure and various initial temperatures within 300-500 K. The program delivered also the temperature and chemical species profiles in the flame front.

EVALUATION OF $p(t)$ DIAGRAMS

The normal burning velocities of propane-air gaseous mixtures with variable fuel/ O_2 ratio were determined from experiments on explosions in the spherical vessel with central ignition, at initial temperatures within 298 and 423 K and initial pressures p_0 within 0.3 and 1.3 bar. Records of pressure variation Δp during explosions were used to determine the normal burning velocities using the cubic law of pressure rise versus time during the early stage of propagation⁸ ($\Delta p \leq p_0$) as illustrated in Figure 1.

The normal burning velocity of a gaseous mixture at initial pressure p_0 was calculated assuming an isothermal compression of the unburned gas during the early stage of propagation as:⁸

$$S_u = R \left(\frac{k^*}{\Delta p_{\max}} \right)^{1/3} \left(\frac{p_0}{p_{\max}} \right)^{2/3} \quad (1)$$

where R is the spherical vessel radius, k^* is the coefficient of the cubic law of pressure rise in the early stage of flame propagation, Δp_{\max} is the maximum pressure rise during explosion; $p_{\max} = p_0 + \Delta p_{\max}$. As input values for equation (1), we used the experimental values of Δp_{\max} and p_{\max} from the recorded $p(t)$ diagrams. The coefficient k^* , characteristic for the early stage of combustion, given originally by equation:⁹

$$\Delta p = kt^3 \quad (2)$$

was determined for each experiment by an improved method using a nonlinear regression, applied to an equation of the form:

$$\Delta p = a + k^*(t - b)^3 \quad (3)$$

where a and b are pressure and time corrections respectively, meant to eliminate the signal shift of pressure transducer and any possible delay in signal recording.⁸

The significance of the coefficient k^* was thoroughly discussed in literature⁹ and it was related with the normal burning velocity S_u , the initial pressure p_0 and the vessel volume V_0 through:

$$\Delta p = K p_0 \frac{S_u^3 t^3}{V_0} \quad (4)$$

where K is a dimensionless constant dependent on initial composition, pressure and temperature of the explosive mixture. It can be calculated using

simplifying assumptions regarding the compression of the unreacted gas during the early stage of the process. The isothermal and adiabatic compression

assumptions lead to similar values of S_u . However the first assumption is simpler and was consequently adopted for obtaining the equation (1).

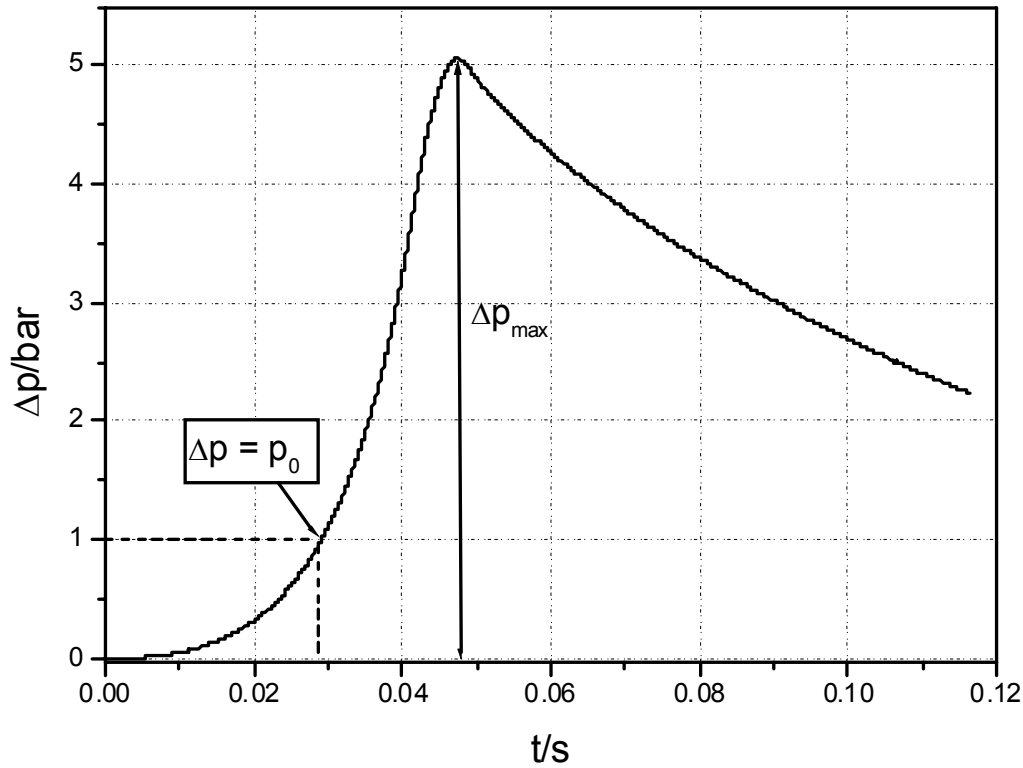


Fig. 1 – Pressure variation during explosion of a rich C_3H_8 -air mixture (6.22 vol.%), at $p_0 = 1$ bar and $T_0 = 423$ K.

RESULTS AND DISCUSSION

The normal burning velocity depends on both microscopic and macroscopic properties of any fuel-air mixture. The available experimental techniques allow its measurement at various gas pressures and temperatures and the results can be utilized to evaluate other valuable properties on the basis of simpler or more detailed models. Among these properties, the overall kinetic parameters are very useful from both theoretical and practical points of view.

Thus, the analysis of the normal burning velocity variation with pressure allows the calculation of the baric coefficient β of burning velocity, defined as:

$$S_u = S_{u,ref} \left(\frac{p}{p_{ref}} \right)^\beta \quad (5)$$

where: $S_{u,ref}$ is the normal burning velocity in reference conditions (at $p = p_{ref}$).

The overall reaction orders n can be obtained from the baric coefficients with the relationship:

$$n = 2(\beta + 1) \quad (6)$$

assuming a simplified one-step kinetic model.¹⁰

Equation (6) is a simplified equation derived from the Semenov burning velocity equation,¹¹ assuming that the term involving the pressure dependence of flame temperature has a very small value and can be neglected:

$$n = 2(\beta + 1) - \left(r' + \frac{E_a}{RT_f} \right) \frac{\partial \ln T_f}{\partial \ln p} \quad (7)$$

where: E_a is the overall activation energy; T_f is the temperature of flame front; $r' = 1.5$ is a constant parameter, lumping into a single value all temperature dependencies of preexponential factors of Semenov equation; R is the universal gas constant. This method is simpler and more reliable as compared to the alternative method implying the measurements of the normal burning velocity at

constant flame temperature and variable composition through addition of inert gas.¹²

Examples of baric coefficients and overall reaction orders for C₃H₈-air mixtures at different

initial temperatures are given in Table 1. The baric coefficients were calculated by non-linear regression analysis of S_u versus p data.

Table 1

Overall reaction orders of C₃H₈-air mixtures at ambient pressure and various initial temperatures

[C ₃ H ₈] (vol.%)	Equivalence ratio (ϕ)	T ₀ (K)	- β	n
		298	0.224	1.55
		333	0.207	1.59
		363	0.247	1.51
		393	0.269	1.46
		423	0.250	1.50
		298	0.126	1.75
		333	0.171	1.66
		363	0.147	1.71
		393	0.132	1.74
		423	0.143	1.72
5.06	1.27	298	0.206	1.59
		333	0.170	1.66
		363	0.231	1.54
		393	0.193	1.61
		423	0.186	1.63
6.22	1.58	298	0.271	1.46
		333	0.230	1.54
		363	0.224	1.55
		393	0.343	1.31
		423	0.321	1.36

The baric coefficients of burning velocities at 298 K vary within the range -0.13...-0.35, characteristic to all hydrocarbon-air mixtures.¹³⁻¹⁹ At constant fuel concentration, the temperature increase does not influence too much the baric coefficients. Data reported in literature for the most-reactive propane-air mixture ($\phi = 1.05$ -1.10), from measurements made in a constant volume spherical vessel, as well, are: -0.133;¹⁵ -0.170;¹⁶ -0.125;¹⁷ -0.260.¹⁸ The overall reaction orders n range between 1.3 and 1.8 for all examined mixtures. The highest values are determined for near-stoichiometric propane-air mixtures, as already observed for propylene-air mixtures.¹⁹

The data allow also the analysis of the variation of normal burning velocity with initial temperature, at constant initial pressure. The variation of S_u with initial mixture temperature at several initial pressures is illustrated in Figure 2, for a rich propane-air mixture. Similar results were obtained for all examined mixtures.

Since the combustion reaction occurs only within a limited zone of the flame front thickness having a steep temperature gradient, an appropriate

temperature averaging is necessary. The average flame temperature can be approximated as:²⁰

$$\overline{T_f} = T_0 + 0.74(T_f - T_0) \quad (8)$$

where: T_0 – initial temperature, T_f – the maximum temperature in the flame front, determined from computed temperature profile.

From normal burning velocity variation against average flame front temperature, the overall activation energy E_a was calculated according to equation:^{10, 12}

$$\ln S_u = Const. - \frac{E_a}{2RT_f} \quad (9)$$

where: $\overline{T_f}$ - the average flame temperature, R – the universal gas constant.

A set of data referring to a lean C₃H₈-air mixture is given in Figure 3. The activation energies were calculated from the slopes of plots given by eq. (9) as illustrated in Figure 3.

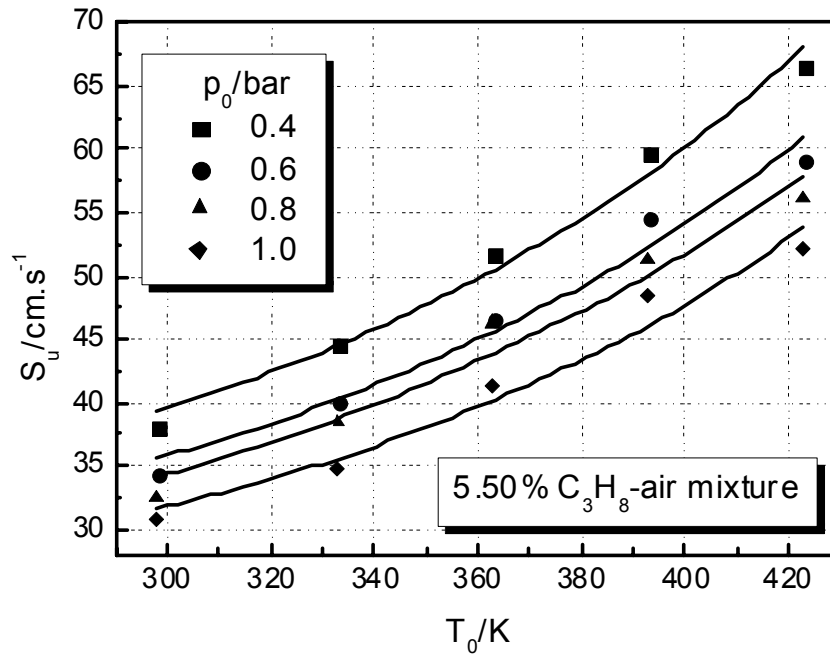


Fig. 2 – The normal burning velocity of a rich propane-air mixture, at various initial pressures and temperatures.

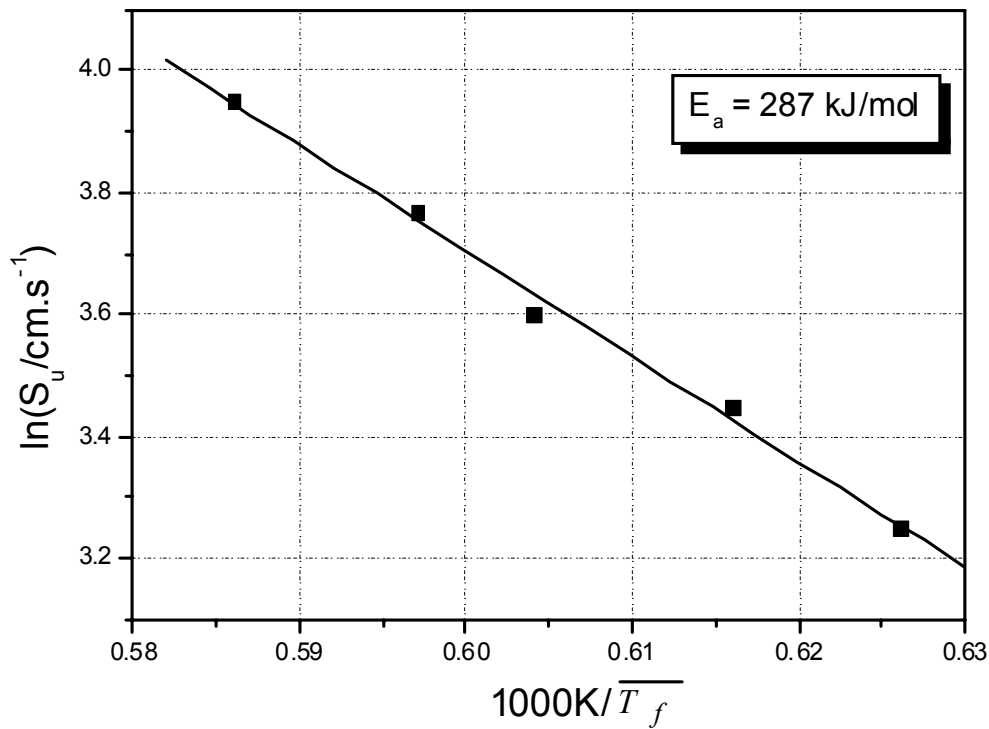


Fig. 3 – Normal burning velocity variation with average flame temperature of a lean propane-air mixture ($[C_3H_8] = 3.15$ vol.%), at ambient initial pressure.

The overall activation energy of the complex combustion reactions occurring within the flame front is expected to be strongly dependent on the mixture composition. To verify this dependence, the data obtained for propane-air mixtures at ambient initial pressure are plotted against the

equivalence ratio in Figure 4, using both measured and computed values of normal burning velocities. The large differences between these values indicate that the oxidation reaction of a hydrocarbon is not suitably described by a simple kinetics, applied to a one step reaction.

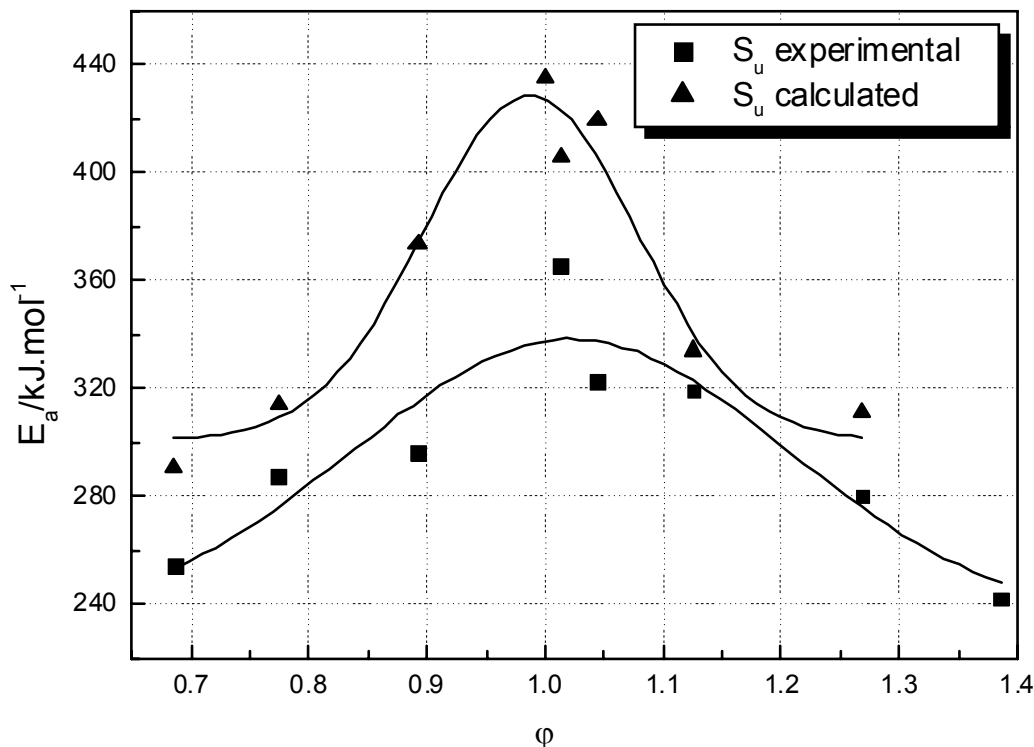


Fig. 4 – Overall activation energies of preheated C_3H_8 -air mixtures from experimental and computed values of normal burning velocities.

The overall activation energies, from both experimental and computed burning velocities, depend on fuel concentration, reaching a maximum at near stoichiometric composition. A similar behavior was observed for CH_4 -air²¹ and C_3H_6 -air mixtures.¹² The overall activation energies from experimental values of burning velocities are lower as compared to the values obtained from computed burning velocities. Other models of determining the overall activation energy from burning velocity variation (e.g. S_u versus flame front temperature instead of average flame temperature) give a better agreement between the two sets of values.¹²

The overall activation energies of propane oxidation calculated from experimental burning velocities increase from $\cong 254$ kJ/mol for a lean (2.80 vol.%) C_3H_8 -air mixture to $\cong 365$ kJ/mol for a near-stoichiometric (4.08 vol.%) C_3H_8 -air mixture. Other values reported for the overall activation energy of propane-air mixtures are: $E_a = 170$ kJ/mol from quenching distances,²² obtained for stoichiometric propane-air mixtures diluted with excess air, $E_a = 196$ kJ/mol from the dependence of the induction period of self-ignition on flame temperature.²³ Using a similar analysis of propane-air normal burning velocities as a function of average flame temperature, Metghalchi and Keck¹⁶ found $E_a = 401$ kJ/mol for a stoichiometric mixture.

The overall activation energies of propane oxidation have typical values for oxidation of hydrocarbons in flames.^{12, 24} Thus, the overall activation energy of propylene oxidation in air, obtained from the normal burning velocities of stoichiometric mixture is $E_a = 177$ kJ/mol (by means of preheating method)¹⁹ or $E_a = 207$ kJ/mol (by means of dilution method, in systems containing CO_2).²⁵

CONCLUSIONS

This paper presents data referring to the overall kinetic parameters of propane combustion in laminar flame. The overall reaction rate was examined through the normal burning velocity, obtained from pressure-time records, in experiments performed in a spherical vessel. The overall activation parameters of the propane oxidation in a flame (reaction order and activation energy) were calculated from normal burning velocity variation with initial pressure and average temperature of the flame front, using preheated gaseous mixtures. Such values, for the range of initial pressures between 0.3-1.3 bar, propane concentration within 2.80-6.22 vol.% and initial temperatures between 298 and 423 K, were

obtained from experimental and computed normal burning velocities and were found in good agreement with literature data, obtained by other techniques. The overall reaction orders range between 1.3 and 1.8 while the overall activation energies range between 254 kJ/mol for a lean (2.80 vol.%) C₃H₈-air mixture to 365 kJ/mol for a near-stoichiometric (4.08 vol.%) C₃H₈-air mixture. The overall activation energies of fuel-air mixtures at ambient initial pressure reach a maximum in near-stoichiometric mixtures; in such mixtures, the overall reaction orders exhibit also maximum values, for all examined initial temperatures.

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