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OVERALL ACTIVATION ENERGY OF PROPANE-AIR COMBUSTION IN LAMINAR FLAMES

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abstract: The overall activation energy of propane oxidation in laminar flames was evaluated from normal burning velocities characteristic for the flame propagation in preheated or diluted propane-air mixtures, using various correlations between the normal burning velocity and the average flame temperature. The burning velocities were obtained both from experimental measurements on spherically propagating flames and from detailed kinetic modeling of flame propagation. The experiments used a near-stoichiometric propane-air mixture ($[C_3H_8]$ = 4.08 vol.%) and were made in a spherical closed vessel, at various initial temperatures (298-423 K). The modeling was made by means of INSFLA package, based on a comprehensive mechanism valid for gas-phase oxidation of C_1-C_4 hydrocarbons (53 chemical species and 592 elementary reactions).

key words: laminar flames; spherical vessel; propane; overall activation energy.

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Introduction

The modern society depends in a large extent on the energy obtained from the controlled combustion of the fossil fuels. An important part of the necessary energy, both for industry and for domestic use, is obtained from combustion of gases, usually hydrocarbons. In certain conditions, the combustion of hydrocarbons can take place as an explosion, whose evolution is due to a fast energy release, accumulating in the system due to a slow dissipation rate. The problem of gaseous explosive mixtures of fuels with air, in particular of hydrocarbons, raises the interest towards the safe storage, processing and transport of gases or flammable liquids, especially in the chemical and petrochemical industry.

Fundamental research in this field is focused on theoretical aspects of kinetics and thermodynamics of combustion reactions in different conditions (deflagration or detonation; isobaric or isochoric propagation etc) [1÷6].

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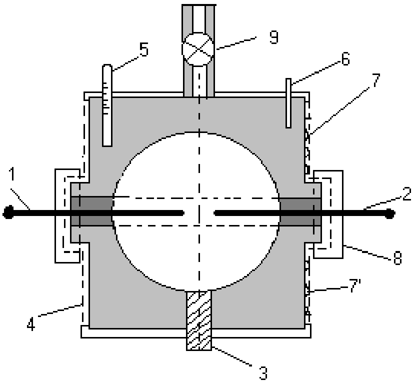
The objective of the present paper is to evaluate the overall activation energy of propane gas-phase oxidation in flames, using the normal burning velocity of propane-air – a characteristic parameter of propagation process, directly influenced by the reaction rate in the flame front. For this purpose, the experimental and computed burning velocities of a near-stoichiometric propane-air mixture with variable initial temperature are examined in correlation with the average flame front temperatures.

The overall activation energy is an important parameter, characterizing the dependency of normal burning velocity on temperature of fuel-air mixture. It is obtained by assuming a simple one-step kinetics of fuel oxidation, valid over a restricted range of pressure and temperature. The overall activation energy and the overall reaction order are required as input data for Computational Fluid Dynamics modeling of flame propagation in closed and vented vessels and for design of venting systems [7].

Experimental procedure

Experiments were made in a thermostated spherical closed vessel ($V = 0.52$ L), electrically heated, with central ignition; its temperature was adjusted (± 1^0C) using an AEM 1RT96 controller and monitored by a K-type thermocouple. Ignition was made with inductive-capacitive sparks produced between stainless steel electrodes. The spark gap of constant width 3.5 mm was located in the geometrical centre of the spherical vessel. The scheme of the combustion vessel is given in Fig. 1.



1,2 - electrodes
3 - pressure transducer
4,8 - thermal isolation
5 - thermometer
6 - thermocouple
7,7’ - heating resistors
9 - admission / evacuation valve

Fig. 1 *Combustion vessel.*

The combustion vessel is equipped with an ionization probe for monitoring the flame front position. The pressure evolution during explosion was measured with a piezoelectric pressure transducer type Kistler 601A mounted in a special adapter, maintained at (25 ± 1^0C) 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 TestLab^{TM} Tektronix 2505. Data acquisition was made at 5000 signals per second using an acquisition card Tektronix type AA1.

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. Other details were previously given [8,9].

The 4.08 vol.% C_3H_8-air mixture was obtained in a 10 L storage cylinder using the partial pressures method, at a total pressure of 4 bar and used 48 h after mixing. Propane (99.99%) (SIAD Italy) was used without further purification.

Computing program

The normal burning velocities of propane-air mixture were computed by means of the program INSFLA, developed by Warnatz and coworkers [10] for kinetic modeling of fuel-air flames in various conditions. A premixed laminar free flame was considered, assuming radiative energy losses and a mechanism CH_4-C_4 (53 chemical species, 592 elementary reactions). The runs were performed for a near-stoichiometric propane-air mixture ($[C_3H_8]$ = 4.08 vol.%) and mixtures diluted with N_2 or CO_2 at initial pressure p_0 = 1 bar and various initial temperatures T_0 within 298-420 K.

Results and discussions

The normal burning velocity was evaluated either from pressure-time records, obtained in a closed spherical vessel with central ignition using the cubic law of pressure rise versus time in the early stage of propagation ($p_0 \leq p \leq 2p_0$) [11], or from computations, based upon a comprehensive reaction scheme [12].

The overall activation energy of flame propagation E_a of preheated propane-air mixtures was calculated according to a modified Arrhenius type equation [13,14]:

$$\ln S_u = Const. - \frac{E_a}{2R\overline{T_f}} \tag{1}$$

where: S_u is the normal burning velocity, $\overline{T_f}$ is the average flame temperature and R is the universal gas constant.

The average flame temperature can be expressed as [15]:

$$\overline{T_f} = T_0 + 0.74\ \ T_f - T_0 \tag{2}$$

where: T_0 is the initial temperature and T_f is the maximum temperature in the flame front, determined from computed temperature profiles.

In Table 1 the experimental and computed normal burning velocities ($S_{u,exp}$ and $S_{u,calc}$) at various initial temperatures together with the maximum temperatures in the flame front and average flame temperatures are given.

In Fig. 2 the experimental and computed normal burning velocities of the near-stoichiometric propane-air mixture are plotted versus the reciprocal average flame temperature. The linear plots have close values of their slopes and the corresponding overall activation energies agree well with literature data referring to a stoichiometric propane-air mixture, as seen from Table 2.

Table 1 Normal burning velocities, maximum temperatures in the flame front and average flame temperatures of a 4.08 vol.% C_3H_8-air, at p_0 = 1 bar

T_0 (K)	$S_{u,exp}$ (cm/s)	$S_{u,calc}$ (cm/s)	T_f (K)	$\overline{T_f}$ (K)
298	38.86	35.10	2302.5	1781.3
333	47.86	42.75	2331.4	1811.8
363	53.72	50.12	2339.0	1825.2
393	61.23	56.58	2352.2	1842.8
423	69.53	66.62	2380.8	1871.8

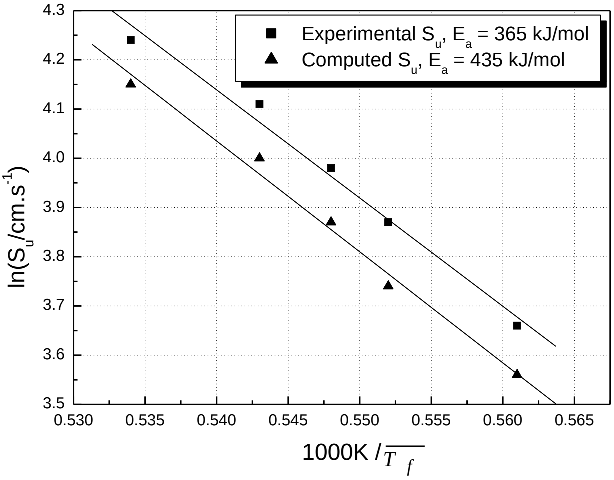


Fig. 2 *Normal burning velocity variation with average flame temperature*

Table 2 Activation energies calculated with eq. (1); present data and data from literature

[Reference]	Equivalence ratio φ	$-\frac{E_a}{2R\overline{T_f}}$	E_a (kJ/mol)
Present data	1.01	22.98	365
Kuehl [16]	1.00	29.32	487
Hill [17]	1.00	26.02	432
Zhao [18]	1.00	27.09	451
Metghalchi [19]	1.00	24.13	401

The overall activation energy of flame propagation for the examined C_3H_8-air mixture was obtained also using the maximum temperature in the flame front T_f in eq. (1) instead of average flame temperature, together with experimental and computed burning velocities. The calculated overall activation energies (E_a = 705 kJ/mol from experimental values of S_u

and E_a = 782 kJ/mol from computed S_u) are quite high as compared to that obtained using the average flame temperature, as already reported for C_3H_6-air mixtures [20].

From the two sets of values, those calculated by means of average flame temperature are more reliable, because the combustion reaction occurs only in a restricted zone of the flame front, characterized by the average flame temperature.

An alternative way to determine the activation energies of flame propagation is the dilution method, when the normal burning velocities are examined against average flame temperature using fuel-air mixtures at constant initial temperature (usually T_0 = 298 K), diluted with various amounts of an inert component. In the present case, the stoichiometric propane-air mixtures diluted with N_2 or CO_2 were examined. Their normal burning velocities calculated by means of INSFLA program were correlated with the average flame temperatures, using the relationship [15]:

$$\ln S_u - \frac{1}{2}\ln \overline{T_f} - \frac{n}{2}\ln Y = Const. - \frac{E_a}{2R\overline{T_f}} \tag{3}$$

where: n is the overall reaction order; Y is the mole fraction of reactive components (fuel + oxidant) in the examined mixture.

Data used in eq. (3) are given in Table 3, assuming that the overall reaction order is 2, for both stoichiometric systems C_3H_8-air-N_2 and C_3H_8-air-CO_2.

Table 3 Burning velocities and flame temperatures of propane-air-inert mixtures, at ambient initial conditions

Inert	[Inert] (vol.%)	Y	T_f (K)	$\overline{T_f}$	S_u (cm/s)
N_2	0	1.00	2307	1785	35.13
	5	0.95	2233	1730	32.23
	10	0.90	2150	1669	30.47
	15	0.85	1997	1555	24.16
	20	0.80	1859	1453	15.54
	30	0.70	1602	1263	2.62
CO_2	0	1.00	2307	1785	35.13
	5	0.95	2187	1696	26.28
	10	0.90	2032	1581	19.54
	15	0.85	1874	1464	13.18
	20	0.80	1706	1340	6.61
	25	0.75	1552	1226	2.05

In Fig. 3 the plots of the left member of eq. (3) against the reciprocal value of average flame temperature, for a stoichiometric propane-air mixture diluted with N_2 and CO_2 are given.

The results obtained from the slopes of linear correlations (3) are: E_a = 171 kJ/mol for C_3H_8-air-N_2 mixture and E_a = 182 kJ/mol for C_3H_8-air-CO_2 mixture. Closer values of overall activation energies for the two systems: E_a = 177 kJ/mol (C_3H_8-air-N_2) and E_a = 186 kJ/mol (C_3H_8-air-CO_2 mixture) were obtained assuming a lower value for the overall reaction order, i.e. n = 1.5. Our data are in good agreement with those reported by Munteanu et al. [21]: E_a = 170 kJ/mol from quenching distances of C_3H_8-air-inert mixtures. Examination of the induction periods for self-ignition of propane in air delivered close values of the overall activation energy: E_a = 196 kJ/mol, as reported by Chang and coworkers [22].

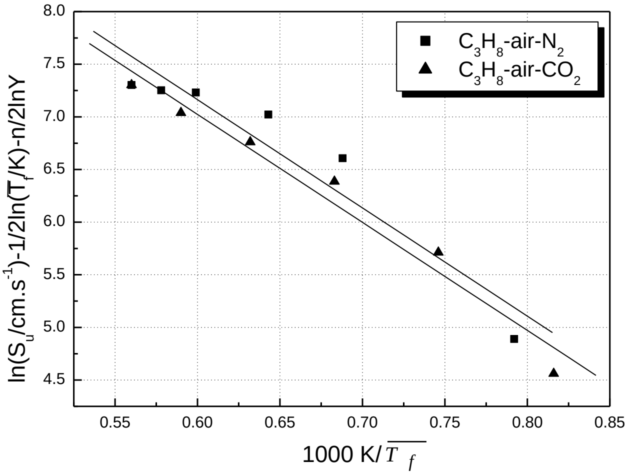


Fig. 3 *Linear correlations describing eq. (3)*

A systematic difference between the overall activation energies from preheating method and dilution method is obtained. Such deviations were found earlier for C_3H_6-air mixtures [23]. These differences can be attributed to the active role of the studied additives.

Conclusions

The overall activation energy of propane oxidation in a flame was obtained for a near-stoichiometric (4.08 vol.%) propane-air mixture by means of preheating method examining the normal burning velocity in correlation either with the average flame temperature $\overline{T_f}$ or with the maximum temperature in the flame front T_f. The overall activation energies for stoichiometric C_3H_8-air-N_2 and C_3H_8-air-CO_2 mixtures were also obtained by means of dilution method. The overall activation energy obtained by means of preheating method (E_a = 365 kJ/mol for C_3H_8-air mixture) is approximately double in comparison with the overall activation energies obtained by means of dilution method (E_a = 171 kJ/mol for C_3H_8-air-N_2 mixture and E_a = 182 kJ/mol for C_3H_8-air-CO_2 mixture) due probably to the active role played by the additives in the process of flame propagation.

A good agreement was found between the overall activation energy computed from experimental values of burning velocities and those from computed burning velocities. The values are also in good agreement with literature data.

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