Laminar Flame Propagation in Rich Ethane-Air-Inert Mixtures

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The laminar flame propagation in rich and stoichiometric ethane-air mixtures diluted with N_2 or CO_2 was studied at ambient initial pressure and various mixture compositions. The normal burning velocities obtained from experimental pressure-time records of the early stage of combustion in a closed spherical vessel with central ignition were compared with those obtained by numerical modelling of 1D flames. For all mixtures the adiabatic flames temperatures were computed assuming that chemical equilibrium is reached in the flame front. The overall activation energy of ethane oxidation in rich flames has been determined using the temperature dependence of normal burning velocity.

Keywords: combustion, rich ethane-air mixtures, normal burning velocity, inert additive, activation energy

Ethane is one of the main components of natural gas, used nowadays as an alternative clean fuel in the power generation industry, material synthesis, and automotive propulsion. Ethane itself is used in the chemical industry for production of ethylene by steam cracking or as a refrigerant in cryogenic systems. It is also a by-product during some operations involving the refinery of oil and coal-carbonization. Bound to these applications, the combustion characteristics of ethane with air are important for prediction of engines and/or combustors performances in various conditions as well as for combustion of accidentally formed flammable mixtures. In many cases the combustion of ethane-air mixtures takes place in the presence of various amounts of inert gases: in engines, exhaust gases (CO_2, H_2O and N_2) may be present due to a poor evacuation of cylinders; in plants or storage facilities, the dilution of ethane-air with inert additives is required for the safe handling of these flammable mixtures. Addition of inert gases results in the decrease of flame temperature, normal burning velocity and propagation speed; in confined explosions the inerting of a flammable mixture is accompanied by the decrease of maximum explosion pressure and of maximum pressure rise rate. Among propagation properties of flames supported by flammable mixtures, the normal burning velocity is a key parameter, influenced by the reaction rate in the flame front and by the thermophysical properties of the flammable mixture. Accurate values of the normal burning velocity are required for validation of detailed reaction mechanisms, for the design and efficient control of practical combustion systems or for the design of active protection devices (vents) of confined explosions.

The flame laminar propagation of ethane-air mixtures was extensively studied and reference values of experimental normal burning velocity were recently discussed, in comparison with burning velocities obtained by detailed numerical modelling [1-4]. Various methods have been used, based on measurements with stationary flames [1,2] or non-stationary expanding spherical flames [3,4]. For ethane-air-inert mixtures less data are available, most of them focused on combustion of lean ethane-air mixtures, in connection to ethane occurrence in natural gas, extensively used as alternative fuel [5-7]. Konnov [6,7] used the heat flux method to determine the stretch-corrected burning velocities of ethane–oxygen-inert mixtures (inert = N_2, Ar or CO_2) using flames stabilized on a perforated plate burner at ambient initial pressure. Additional experiments were conducted by adding H_2 to lean C_2H_6/air flames and by diluting those mixtures by either He or N_2, in order to vary the flame temperature. The results were compared with data from a detailed C/H/N/O reaction mechanism for the combustion of small hydrocarbons. On the other hand, the combustion of rich fuel-air mixtures raises additional problems derived from the incomplete oxidation and formation of different pollutants. The presence of inert gases lowers the flame temperature, normal burning velocity and changes the burned gas composition.

In the present paper the normal burning velocities of rich and stoichiometric ethane-air mixtures diluted with various amounts of N_2 or CO_2 are reported, based on pressure-time measurements in a spherical vessel with central ignition. The experiments were made at ambient initial pressure and temperature using ethane/air mixtures with various equivalence ratios. The obtained normal burning velocities were examined in comparison with computed values obtained from the kinetic modeling of laminar premixed flames. The influence of nature and amount of inert additive were discussed for both experimental and computed normal burning velocities.

Experimental part

Experiments were made in a spherical closed vessel (V = 0.52 L) with central ignition by 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 pressure evolution during explosion was measured with a piezoelectric pressure transducer type Kistler 601A connected to a Charge Amplifier type Kistler 5001SN whose signals were recorded with an acquisition data system TestLab™ Tektronix 2505. Data acquisition was made at 7000 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 flammable mixture was admitted and allowed to become quiescent. Other details were previously given [8-10].

Ethane-air mixtures were prepared in a 10 L storage cylinder using the partial pressure method, at a total

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Dedicated to the 150th aniversary of the Romanian Academy pressure of 4 bar and used after 48 h. C_2H_6-air-inert mixtures were prepared in the combustion vessel by adding the inert gas with various partial pressures to C_2H_6-air mixtures of known composition and allowed 30 min. to become quiescent.

Ethane (99.99%), N_2 (99.99%), and CO_2 (99.99%) (SIAD Italy) were used without further purification.

Computing programs

The adiabatic flame temperature and the end mole number of ethane-air and ethane-air-inert isobaric combustion were calculated using the program ECHIMAD [11], assuming that the thermodynamic equilibrium is reached within the flame. The program is based on a general algorithm for computing the equilibrium composition of products for fuel-oxygen gaseous mixtures by minimizing the free energy of the system. The heat capacities, the standard enthalpies of formation at 298 K and the standard entropies at 298 K were taken from literature [12,13]. Other details were previously given [11,14].

The kinetic modeling of one-dimensional, premixed laminar free flames was made with the package INSFLA, developed by Warnatz and Maas [15,16]. INSFLA was run using the Warnatz mechanism CH4-C4 considering 53 chemical species and 592 elementary reactions, assuming radiative losses during flame propagation. Updated values of rate coefficients for the rate-limiting reactions were taken from Heghes [17].

Results and discussions

The normal burning velocities have been widely determined from pressure-time measurements during explosions in closed vessels after making suitable corrections of the temperature gradients in the burned and the unburned gas and by taking into account the flame stretch after ignition [2,3,18-21]. The advantage of determining the normal burning velocity using such method is that, from a single test, burning velocities can be calculated over wide temperature and pressure ranges. The approach is recommended if the equations used for the determination of the burning velocities are valid throughout the range of pressure variation during the process. A simpler way to determine the normal burning velocity by experiments in a closed vessel was to restrict the examination of flame propagation just to the early stage [18], when the temperature variation in both unburned and burned gas is small and can be neglected. This simple procedure is based on the relationship between the pressure increase in the early stage of flame propagation, Δp, and the time from ignition, t [22]:

$$\Delta p = kt^3 \qquad (1)$$

where k, the cubic law constant, is dependent on the initial composition, pressure and temperature of the flammable mixture. The law was considered valid only for a pressure increase $\Delta_p \le p_0$, whose duration is taken as *the early stage* of the process. The coefficient k was determined for each experiment by a nonlinear regression method, applied to a relationship of the form:

$$\Delta p = a + k(t - c)^3 \qquad (2)$$

where a and c are corrections of pressure and time, meant to eliminate the signal shift of the pressure transducer and any possible delay in signal triggering.

The normal burning velocity S_u was correlated with the cubic law constant k assuming that the compression of unburned gas ahead of the flame front is adiabatic [18]:

$$S_u = R\left[\frac{k}{p_0 E^2 (E-1)\gamma_u}\right]^{1/3} \qquad (3)$$

where R is the radius of the explosion vessel, E is the expansion coefficient of the flammable mixture at the initial pressure p_0 and γ_u is the adiabatic compression coefficient of the unburned gas. The expansion coefficient E is defined as the ratio of unburnt to burnt gas densities across the flame front:

$$E = \frac{\rho_u}{\bar{\rho}_b} = \left(\frac{T_{f,p}}{T_0}\right)\left(\frac{n_e}{n_0}\right) \qquad (4)$$

where ρ_u is the unburnt gas density, $\bar{\rho}_b$ is the average burnt gas density, $T_{f,p}$ is the adiabatic flame temperature of isobaric combustion, T_0 is the initial temperature, n_e is the end (final) number of moles and n_0 is the initial number of moles. The expansion coefficient can be computed for any flammable mixture using the adiabatic flame temperature of the isobaric combustion and the end mole number as obtained from equilibrium computations.

In figure 1 the normal burning velocities of ethane-air mixtures at ambient initial pressure and temperature, obtained from evaluation of flame propagation in the early stage are given together with the normal burning velocities of ethane-air obtained from the numerical modeling of flame propagation using the Warnatz mechanism and those computed from pressure-time records over an extended duration of flame propagation by means of burned gas mass fraction, using a previously described model [4]. The normal burning velocities obtained by numerical modeling match well the present data in the range of lean ethane-air mixtures, but are systematically higher for the stoichiometric and rich ethane-air mixtures. Other researchers reported normal burning velocities of ethane-air from chemical modeling based on GRI-Mech 3.0 mechanism [5,23]. In this case the normal burning velocities of lean ethane-air mixtures were overpredicted by the simulations and a better agreement has been found for rich mixtures.

A comparison of our data referring to the stoichiometric ethane-air mixtures at ambient initial conditions with literature data is given in table 1.

Taking into account the accuracy differences between experimental methods, the present data are close to reported results from literature. They match better the stretch-corrected burning velocities measured for outwardly propagating spherical flames, focused also on the early stage of flame propagation in an enclosure [21].

The normal burning velocities for two ethane-air mixtures in the presence of nitrogen or carbon dioxide, determined by the above-mentioned procedure, are plotted in figures 2(a) and 2(b) against the percent of added inert

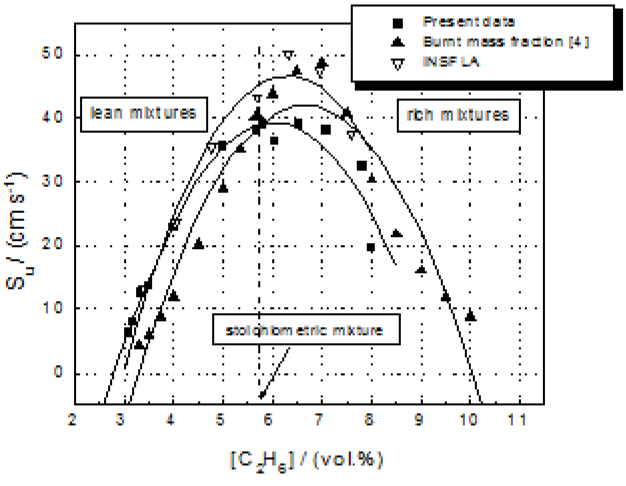

Fig. 1. The normal burning velocity of ethane-air mixtures at T_0 = 298 K and p_0 = 1 bar

Experimental measuring technique	S_u / (cm/s)	Reference
Heat flux measurement on flat flames	40.7	Dyakov et al., 2007 [1]
Counterflow flames; Stagnation flow	40.0	Jomaas et al., 2005 [2]
Spherical vessel, burnt mass fraction calculation	43.4	Mitu et al., 2014 [4]
Cylindrical vessel, flame radius measurements	39.0	Kochar et al., 2011 [21]
Spherical vessel, pressure measurements	38.0	Present results

Table 1
THE NORMAL BURNING VELOCITY OF THE STOICHIOMETRIC ETHANE-AIR MIXTURE AT T_0 = 298 K AND p_0 = 1 BAR, FROM EXPERIMENTAL DATA

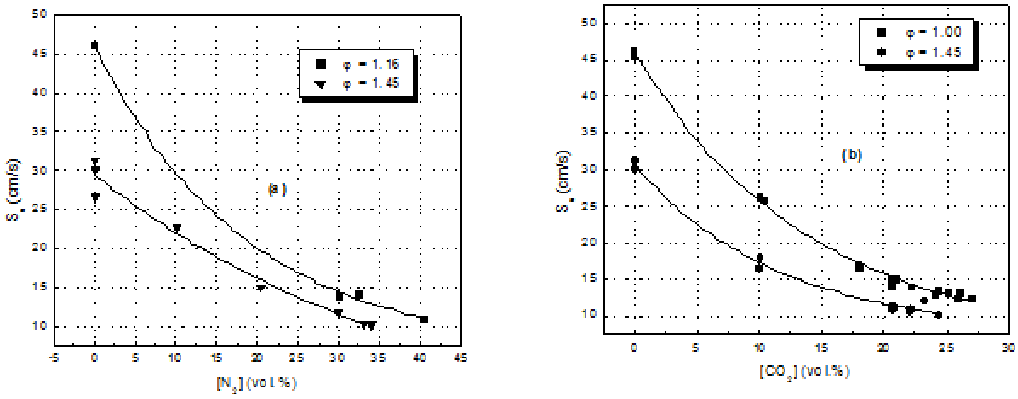

Fig. 2. The normal burning velocities of ethane-air-inert mixtures at ambient initial conditions:
(a) dilution by N_2;
(b) dilution by CO_2

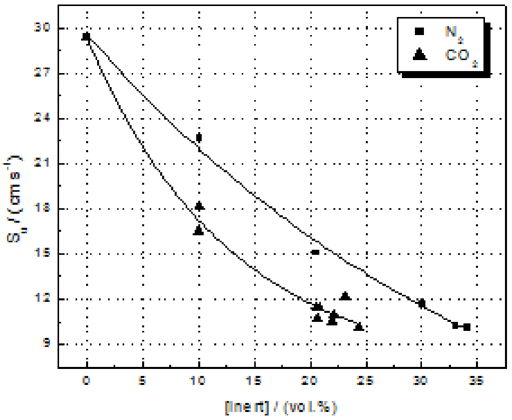

Fig. 3. Experimental normal burning velocities of a rich ethane-air mixture diluted with N_2 or CO_2 ($[C_2H_6]_0$ = 8.0 vol%; φ=1.45)

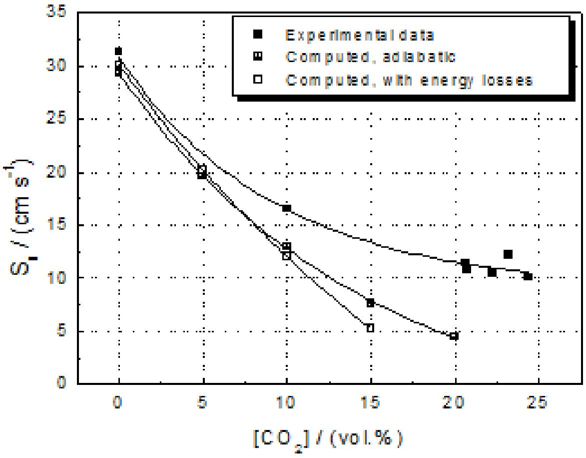

Fig. 4. Experimental and computed normal burning velocities of a rich ethane-air mixture diluted with N_2 or CO_2 ($[C_2H_6]_0$ = 8.0 vol%; φ=1.45)

gas; data are evaluated at p_0 = 1 bar. As expected, progressive dilution leads to the decrease of the normal burning velocity for both additives, determined by the decrease of fuel and oxygen content in the flammable mixture and by the enhanced heat dissipation, determined by the presence of the gaseous additive.

A comparison of normal burning velocities of ethane-air with constant equivalence ratio in the presence of N_2 and CO_2 is shown in figure 3, where the best-fit lines have been drawn. At constant inert concentration, CO_2 has a higher influence on burning velocities, since CO_2 has a larger influence on mixture heat capacity and on heat dissipation rate in comparison with nitrogen. This effect was already observed for stoichiometric propane-air [24] and propylene-air mixtures [25] in the presence of N_2 and CO_2, for computed and measured burning velocities, as well. For both diluents, nonlinear correlations describe the burning velocity variation with the concentration of inert additive, as found by Stone et al. [26] for methane-air-inert mixtures and by Razus and coworkers [25] for propylene-air-inert mixtures.

The comparison between experimental and computed burning velocities with the Warnatz mechanism showed a satisfactory match for ethane-air; for ethane-air diluted with N_2 or CO_2 important differences are observed. A set of data referring to a rich ethane-air mixture diluted with CO_2 is shown in figure 4, where the experimental burning velocities are plotted against [CO_2] together with the computed burning velocities under assumption of adiabatic or non-adiabatic propagation (influenced by radiative energy losses); here, the best-fit lines were drawn for all data sets. The computed burning velocities are lower in comparison to the experimental burning velocities, at all concentrations of added CO_2. In experiments, the flame propagation was observed even at large amounts of added CO_2 (between 20 and 25 vol%) whereas computations predicted limit burning velocities (5 cm/s) already at [CO_2] = 15 vol% (propagation with energy loss) or 20 vol.% (adiabatic propagation). The same variations have been observed for nitrogen-diluted ethane-air mixtures. For these rich mixtures approaching the upper explosion limit, the chemical modelling of flame propagation has to be made with more specific chemical mechanisms, taking into account the fuel pyrolysis to polyaromatic hydrocarbons and the formation of soot.

Good correlations have been found between the experimental burning velocities and the adiabatic flame temperatures for both inert additives, as shown in Fig. 5(a)

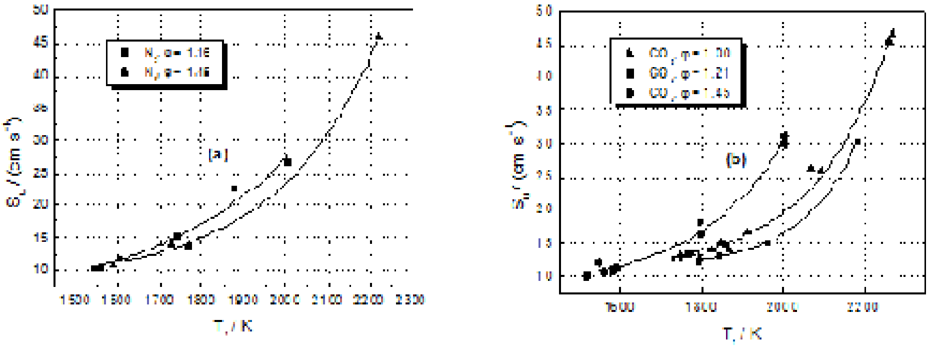

Fig. 5. Correlation between the experimental normal burning velocities and adiabatic flame temperatures for stoichiometric and rich ethane-air-diluent mixtures: (a) C_2H_6-air-N_2; (b) C_2H_6-air-CO_2

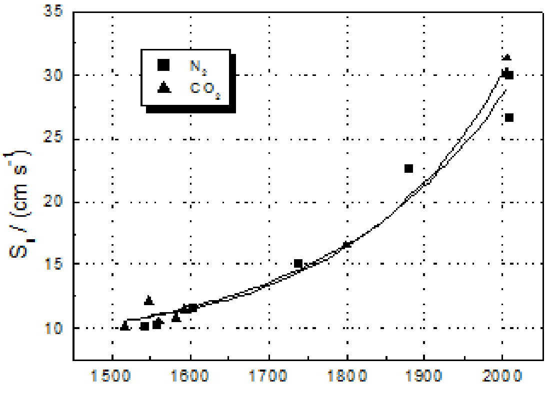

Fig. 6. Correlation between the experimental normal burning velocities and the adiabatic flame temperatures for a rich ethane-air mixture diluted with inert gases ($[C_2H_6]_0$ = 8.0 vol%; φ=1.45)

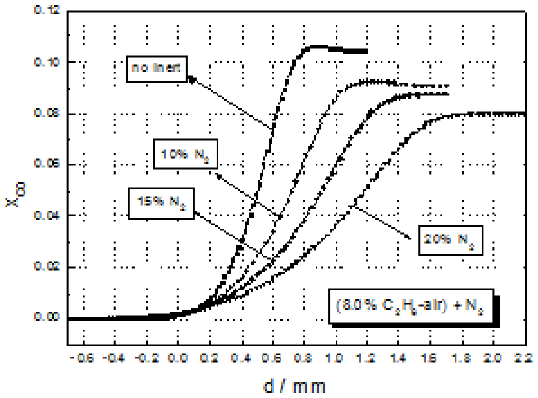

Fig. 7. Profiles of CO mass fraction in flames of a rich ethane-air mixture diluted with nitrogen

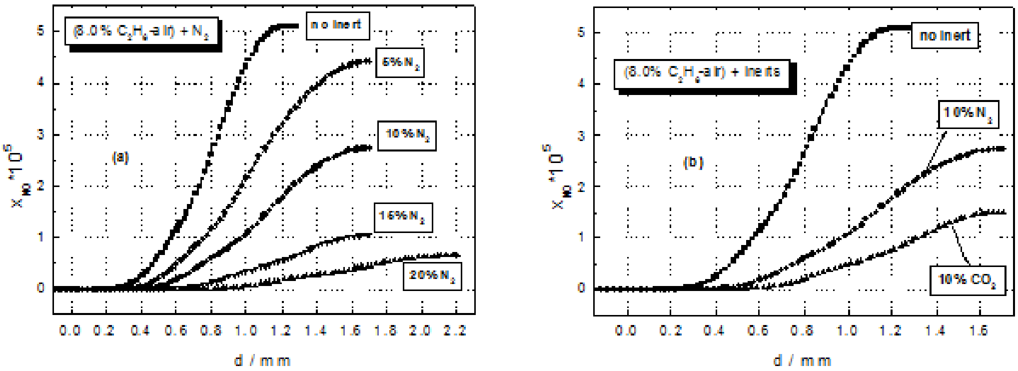

Fig. 8. Profiles of NO mass fraction in flames of a rich ethane-air mixture diluted with: (a) nitrogen; (b) nitrogen and carbon dioxide

for nitrogen-diluted mixtures and in figure 5(b) for CO_2-diluted mixtures. Such correlations were found by Dong et al. [5] for nitrogen- or helium-diluted stoichiometric ethane-air mixtures using burning velocities computed with GRI-Mech 3.0 mechanism. In case of a rich ethane-air mixture, the experimental burning velocities of nitrogen- and carbon dioxide-diluted mixtures, plotted in figure 6, lay approximately on the same graph. This result confirms that the main influence of CO_2 on laminar burning velocity is thermal: it changes the heat capacity of the mixture, thus the flame temperature and the reaction rate, accordingly.

Inert gas influence on fuel-air combustion was studied also in connection to EGR (Exhaust Gas Recirculation) technique meant to lower combustion instabilities of flames and to reduce the pollutant emissions (CO, NO_x) [27] of CH_4-air flames. In a similar way, inert addition to ethane-air flames results in the decrease of CO and NO concentrations, as shown in figure 7 and figure 8 (a,b) by the concentration profiles of CO and NO in the flame front of rich C_2H_6-air-inert mixtures. The observed variations are assigned to the decrease of flame temperature across each flame, determined by the decrease of fuel concentration in the flammable mixture and by the presence of inert gas as a heat sink. The CO_2 dissociation in flames results in an additional decrease of flame temperature and a larger variation of NO mass fraction, in comparison with N_2-dilued flammable mixtures.

The correlation of normal burning velocities with the flame temperatures illustrated by data in figure 5 and 6 can be further used to evaluate the overall activation energy of the combustion process. It results by examining the normal burning velocities against the average flame temperature of the flame front (T_f) using the relationship of Burke [28] for fuel-oxidant-inert gaseous mixtures:

$$\ln S_u - \frac{1}{2}\ln \overline{T_f} - \frac{n}{2}\ln Y = Const - \frac{E_a}{2R\overline{T_f}} \qquad (5)$$

where Y is the mole fraction of reactive components (fuel + oxidant) in the examined mixture and n is the overall reaction order. The average temperature was calculated with the relationship [28]:

$$\overline{T_f} = T_0 + 0.74\cdot\left(T_{f,p} - T_0\right) \qquad (6)$$

A set of data referring to a rich ethane-air mixture (8% C_2H_6) diluted with N_2 or CO_2 is given in table 2 after assuming an overall reaction order n = 2 for both C_2H_6-air-N_2 and C_2H_6-air-CO_2 systems.

Table 2
THE NORMAL BURNING VELOCITIES AND AVERAGE FLAME TEMPERATURES OF ETHANE-AIR-INERT MIXTURES (φ = 1.45), AT AMBIENT INITIAL CONDITIONS

Inert	[Inert] (vol%)	Y	$T_{f,p}$ (K)	$\overline{T_f}$	S_u (cm/s)
N_2	0	1.0	2005	1561	19.71
	10	0.9	1879	1468	16.22
	20	0.8	1802	1411	12.88
	30	0.7	1768	1385	9.79
	40	0.6	1587	1252	3.68
CO_2	0	1.0	2005	1561	19.71
	10	0.9	1964	1526	10.21
	20	0.8	1825	1428	9.04
	30	0.7	1750	1372	6.7

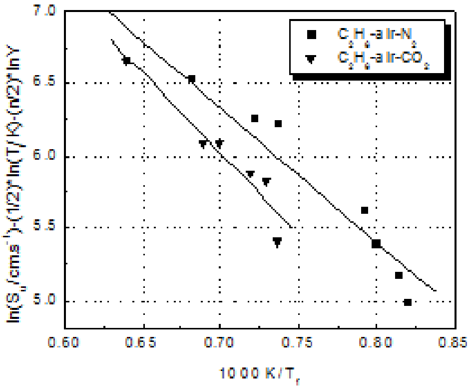

Fig. 9. Linear dependence given by eq. (5) for a rich ethane-air mixture ([C_2H_6]0 8.0 vol%; φ = 1.45)

In figure 9 the plots of the left member of eq. (5) against the reciprocal value of average flame temperature, for the rich ethane-air mixture diluted with N_2 or CO_2 are given. The results obtained from the slopes of linear dependencies (5) are E_a = 155 kJ/mol for C_2H_6-air-N_2 mixture and E_a = 186 kJ/mol for C_2H_6-air-CO_2 mixture. Higher values of the overall activation energy for the two systems: E_a = 165 kJ/mol (C_2H_6-air-N_2) and E_a = 199 kJ/mol (C_2H_6-air-CO_2 mixture) were obtained assuming a lower value for the overall reaction order (n = 1.5). For the stoichiometric ethane-air mixture diluted with CO_2 a similar analysis of data gave E_a = 211 kJ/mol assuming an overall reaction order n = 2.0 and E_a = 221 kJ/mol for an overall reaction order n = 1.5. As already found for preheated ethane-air mixtures [8] the overall activation energy in stoichiometric mixtures is higher in comparison with the overall activation energy characteristic for off-stoichiometric fuel-air and fuel-air-inert mixtures. The present data are close to E_a = 202 kJ/mol, value reported by Munteanu et al. for the combustion of the stoichiometric propane-air mixture in the presence of CO_2 [29] and to E_a = 207 kJ/mol, found by Razus et al. for the combustion of the stoichiometric propylene-air-CO_2 mixture [30].

Conclusions

The normal burning velocities of stoichiometric and rich ethane-air mixtures diluted with various amounts of N_2 or CO_2, based on pressure-time measurements during the early stage of flame propagation in a spherical vessel with central ignition, were reported.

The experimental and computed burning velocities have close values for ethane-air mixtures, but differ in the case of ethane-air-inert mixtures, characterized by lower computed burning velocities in comparison to the experimental ones. These differences can be attributed to the features of the chemical mechanism which should be re-examined especially for rich mixtures by taking into account the fuel pyrolysis to polyaromatic hydrocarbons and soot formation.

The experimental and computed burning velocities dependence on the average adiabatic flame temperature allowed the calculation of the overall activation energy of ethane-oxygen reaction within the flame front. For both stoichiometric and rich mixtures, diluted with inert gases, the overall activation energies are in good agreement with results reported for other fuel-air mixtures.

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