Dedicated to the memory of
Professor Eugen Segal (1933-2013)

PHYSICO-CHEMICAL PARAMETERS
OF C2 HYDROCARBON-AIR FLAMES RESULTED FROM COMPUTED
# AND MEASURED LAMINAR BURNING VELOCITIES

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Computed burning velocities of C_2H_6-air, C_2H_4-air and C_2H_2-air stoichiometric flames with variable initial pressure and temperature obtained by a detailed numerical modeling are compared to those measured or previously reported burning velocities obtained from transient pressure-time records during explosions in spherical vessels with central ignition. Correlations in the form of $S_u/S_{u,ref} = (p/p_{ref})^\nu (T_u/T_{u,ref})^\mu$ describe well the burning velocity dependence on pressure and temperature of all mixtures, for both experimental and computed data. The baric coefficient, **ν**, was further used for calculation of the overall reaction order, **n**, found to vary within 1.3 and 1.8 for the examined hydrocarbons. The burning velocity dependence on the average flame temperature was used to calculate the overall activation energy of the oxidation, **E_a**, specific for each flame. The change of flame initial conditions (pressure and temperature) was found to determine important changes of the flame thickness, the heat release rate and the mass fraction of radical intermediates. Linear correlations were found between the burning velocities of each C2 hydrocarbon and the sum of peak mass fractions of main radical species, $x_{rad} = x_H + x_{OH} + x_O$, for flames propagating either at the same initial temperature and various initial pressures or at the same initial pressure and various initial temperatures.
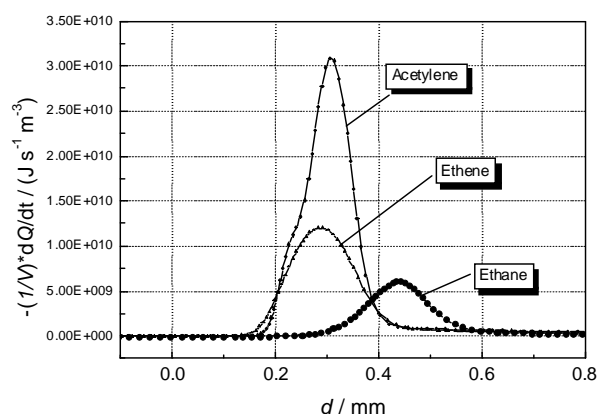
INTRODUCTION

Combustion of C2 hydrocarbons in air is a main topic of basic and applied studies. Basic research is focused on chemical and physical processes occurring during heat release and its transfer from the flame, in connection to fuel structure and combustion conditions.[1,2] The C2 hydrocarbons are intermediates in the oxidation of any hydrocarbon; this is an additional reason for fundamental studies, performed in various conditions: in premixed or diffusion flames

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anchored on burners, in shock tubes or in enclosures (open or vented) under various thermal regimes (low-, medium- or high-temperature flames) in conjunction with modeling experiments.[3-7] Comparison of experimental and predicted parameters such as the normal burning velocity of premixed plane unstretched flames or the profiles of various species concentrations have been used to develop and test detailed kinetic models. For C1-C4 alkane-air flames, the mechanisms developed by Warnatz,[2] Davis,[5] Ranzi,[7] Konnov[8] and Law[9] have been able to predict flame structure and its characteristic parameters for different reactor types (high-pressure flow reactors, shock-tubes) over wide ranges of temperatures, pressures, and equivalence ratios. The interest for this topic is determined also by technological uses of these fuels: C_2H_6 as component of natural gas, used nowadays as domestic fuel and as alternative fuel for IC engines; C_2H_4 as precursor of important materials (ethylene oxide or polyethylene); C_2H_2 as precursor (e.g. acrylic acid) or for generating high temperatures used in metal cutting and welding. The explosive combustion of C2 hydrocarbons was extensively studied in order to ensure safe conditions for their use and for increasing their thermal efficiency.[10-14]

The deflagration parameters characteristic for the ignition and propagation of C2 hydrocarbon-air flames follow a common trend and reveal the differences in reactivity of ethane, ethene and acetylene. In respect to this, the burning velocities are the most relevant as they depend on the overall reaction rate in the flame. A set of relevant data on premixed flames of C2 hydrocarbons with air at ambient initial conditions is given in Table 1.

In the present paper, the experimental and computed burning velocities of flames propagating in the stoichiometric C2 hydrocarbon-air mixtures, together with several important features of the flame structure (rate of heat release, temperature and concentration of the most reactive chemical species) are examined as functions of unburned gas temperature and pressure, aiming at a better understanding of their reactivities. At the same time the correlations found between the burning velocities (experimental and calculated) and the pressure or average temperature of burned gas

allow the calculation of the overall kinetic parameters characteristic for the oxidation of C_2H_6, C_2H_4 and C_2H_2 in flames with air, required in vent design and CFD modeling of flame propagation.

The experimental data consist in the laminar burning velocities S_u of the stoichiometric fuel-air mixtures obtained from pressure-time records of outwardly flames propagating in spherical vessels. The burning velocities of ethane-air, obtained from the burned mass fraction calculated in various moments of flame propagation, have been reported in a previous publication.[15] In the present case, the same $p(t)$ records have been used to determine the burning velocities from the cubic law coefficients of pressure rise, during the early stage of flame propagation in the spherical vessel. The burning velocities of ethene-air, determined from the cubic law coefficients of pressure rise and previously reported[16] have been calculated now from the burned mass fraction in various moments of flame propagation. The burning velocities of acetylene-air have been obtained from the burned mass fraction calculated in various moments of flame propagation in a spherical vessel, as given by Rallis *et al.*[17,18] and from measurements on counterflow flames, as reported by Egolfopoulos *et al.*[3] The experimental burning velocities are compared to burning velocities obtained from the chemical modeling of premixed free one-dimensional laminar fuel-air flames with equivalence ratio φ = 1 at variable initial temperatures (300 - 550 K) and initial pressures (101.3 – 10^3 kPa) performed with a detailed mechanism (GRI-Mech version 3.0) using the COSILAB package.[19] The predictions of chemical modeling (the maximum flame temperature, the heat release rate and the peak concentrations of main reaction intermediates) of these flames are examined as functions on the distance across the flame front and on initial pressure and temperature of fuel-air mixtures. A previous numerical study on ethane-air flames using the GRI 3.0 mechanism (developed for the components of natural gas: C1, C2 and C3 alkanes) delivered the flame structure for mixtures with variable initial composition, pressure and temperature.[20] The same mechanism is now tested for its ability to describe accurately ethylene-air and acetylene-air flames.

Table 1

Characteristic properties of fuel-air flames (stoichiometric fuel/O_2 ratio) at $p_0 = 101.3$ kPa and $T_0 = 300$ K

Property	Fuel C_2H_6	C_2H_4	C_2H_2
Adiabatic flame temperature of isobaric combustion, $T_{f,p}$ / K	2263.4	2368.7	2532.4
Adiabatic flame temperature of isochoric combustion, $T_{f,V}$ / K	2613.8	2719.7	2896.7
Adiabatic explosion pressure, $p_{max,ad}$ / kPa	917	934	969
Normal burning velocity, S_u / (cm s^{-1})	41.7	83.4	142.8

EXPERIMENTAL

The measurements on stoichiometric ethane-air (at $p_0 = 50$-200 kPa and $T_0 = 298$-423 K) and ethylene-air (at $p_0 = 30$-120 kPa and $T_0 = 298$ K) mixtures have been done in a spherical vessel (R = 5 cm) with central ignition using inductive-capacitive sparks. The flammable mixtures have been prepared by partial pressure method in gas cylinders, at 400 kPa total pressure.

Measuring systems: piezoelectric pressure transducer (Kistler 601A) + Charge Amplifier (Kistler 5001SN) + acquisition data system TestLab[TM] Tektronix 2505 (acquisition card type AA1), 10^4 signals per second.

Reagents: ethane (99.99%) and ethylene (99.99%) – SIAD Italy. Other details on the experimental set-up and data acquisition were previously given.[21-23]

COMPUTING PROGRAMS

Equilibrium calculations – The adiabatic explosion pressures and the adiabatic flame temperatures have been calculated with the 0-D COSILAB package. The program is based on a general algorithm meant to compute the equilibrium composition of products for any fuel–oxidizer gaseous mixture using the thermodynamic criterion of chemical equilibrium: the minimum of Gibbs energy, at constant temperature and pressure or minimum of Helmholtz energy, at constant temperature and volume. Fifty-three compounds have been considered as combustion products.

Chemical kinetic modeling – The kinetic modeling of laminar fuel-air flames has been performed with 1-D COSILAB package (version 3.0.3)[19] used for the comprehensive simulation of chemically reactive flows including freely propagating adiabatic premixed flames. The GRI (Gas Research Institute) kinetic mechanism version 3.0, using 53 chemical species and 325 elementary reactions has been used, taking the input data from thermodynamic and molecular databases of Sandia National Laboratories, USA, according to the international standard (format for CHEMKIN). The runs were performed for the isobaric combustion of stoichiometric fuel-air mixtures at various initial pressures (101.3 – 10^3 kPa) and temperatures (300 – 550 K).

Data evaluation – The laminar burning velocities of the stoichiometric ethane-air mixture were determined from *p(t)* records by using the cubic law constants of pressure rise, calculated for the early stage of flame propagation in a closed vessel. The procedure has been described in a previous paper.[24] The laminar burning velocities of the stoichiometric ethene-air mixture were determined from *p(t)* records by using the burned mass fraction calculated in various moments of flame propagation, according to the model recently described.[15]

RESULTS AND DISCUSSION

The laminar burning velocities of the examined fuel-air mixtures depend on the initial pressure and temperature: at constant initial composition and temperature, S_u decreases when the initial pressure increases; at constant initial composition and pressure, S_u decreases when the initial temperature increases. In Fig. 1 the laminar burning velocities of the stoichiometric fuel-air mixtures at an unburned mixture temperature (T_u) of 300 K and variable initial pressures computed with GRI mechanism version 3.0 are plotted against the initial pressure together with experimental velocities from several literature sources. It is seen that the measured data for ethane-air agree well with the computed data at all initial pressures, but there are some deviations at pressures between 100 and 500 kPa for ethene-air and acetylene-air flames. It must be observed, however, that experimental data referring to a frequently examined flame such as ethene-air are scattered, as a consequence of unavoidable errors made by the measuring systems. A better agreement between experimental and computed burning velocities is found when the burning velocities at constant initial pressure and variable initial temperature are examined, as shown in Fig. 2. In Figs. 1 and 2, the same trend is observed: at any initial pressure or temperature, the burning velocity varies according to the series $C_2H_2 > C_2H_4 > C_2H_6$. The trend is valid for the adiabatic flame temperatures as well.

The pressure influence on burning velocity was analyzed according to a power-law equation:

$$S_u = S_{u,ref} \left(\frac{p}{p_{ref}} \right)^{\nu} \qquad (1)$$

where $S_{u,ref}$ is the normal burning velocity at reference pressure p_{ref} and ν is the baric coefficient. Choosing p_{ref} = 101.3 kPa, the baric coefficients of normal burning velocities for ethane-air mixtures were calculated by a non-linear regression analysis of S_u = f(p) data. The results obtained from both experimental and computed

burning velocities are given in Table 2 together with the overall reaction orders, n, obtained with the equation:[28]

$$n = 2(\nu + 1) \qquad (2)$$

Reference values of baric coefficients between -0.32 and -0.10 referring to experimental burning velocities at ambient initial temperature have been found for various stoichiometric fuel-air mixtures.[3,26,29] The corresponding overall reaction orders range between 1.36 and 1.80.
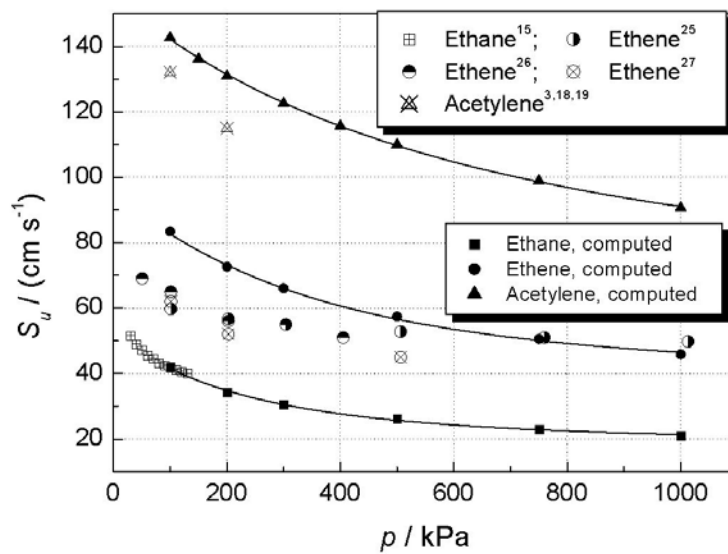

Fig. 1 – Experimental and computed burning velocities for stoichiometric fuel-air flames at T_0 = 300 K; the lines are best fit correlations for computed S_u vs. p.
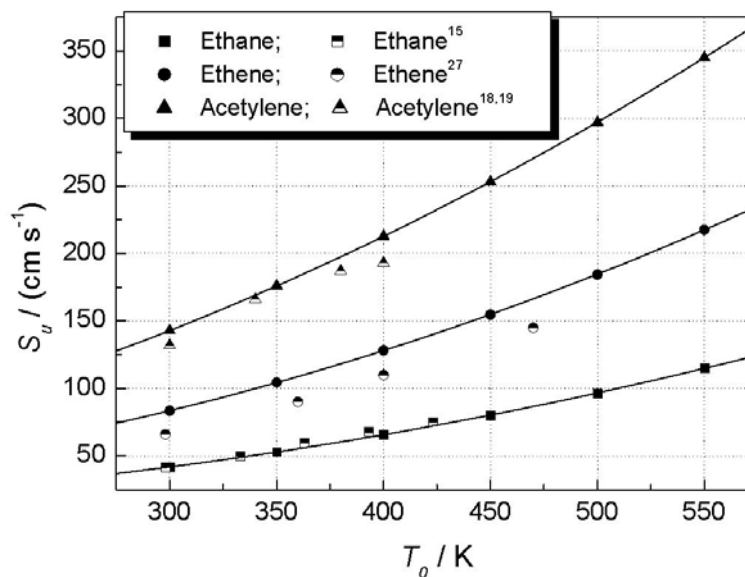

Fig. 2 – Experimental and computed burning velocities for stoichiometric fuel-air flames at p_0 = 101.3 kPa; the lines are best fit correlations for computed S_u vs. T_0.

Table 2

Baric coefficients of normal burning velocity and overall reaction orders for stoichiometric fuel-air mixtures at 300 K

Fuel	$-\nu$		n	
	from exp. S_u	from computed S_u	from exp. S_u	from computed S_u
C_2H_6	0.320 ± 0.031 [15]	0.287 ± 0.011 [20]	1.36	1.43
C_2H_4	0.094 ± 0.009 [16]	0.233 ± 0.010	1.81	1.53
C_2H_2	0.177 [17]	0.196 ± 0.013	1.65	1.61

Table 3

Thermal coefficients of normal burning velocities and overall activation energies for stoichiometric fuel-air mixtures at 101.3 kPa

Fuel	μ		E_a / (kJ mol^{-1})	
	from exp. S_u	from computed S_u	from exp. S_u	from computed S_u
C_2H_6	1.53 ± 0.04	1.59 ± 0.02	358 ± 10	383 ± 5
C_2H_4	1.65 ± 0.05	1.58 ± 0.03	400 ± 20	416 ± 5
C_2H_2	1.28 ± 0.03	1.46 ± 0.02	486 ± 71	464 ± 10

In a similar way, the temperature influence on burning velocity was examined according to a power-law equation:

$$S_u = S_{u,ref} \left(\frac{T}{T_{ref}} \right)^\mu \qquad (3)$$

where $S_{u,ref}$ is the normal burning velocity at reference temperature T_{ref} and μ is the thermal coefficient. Using $T_{ref} = 300$ K, the thermal coefficients of normal burning velocities for ethane-air mixtures were calculated by a non-linear regression analysis of $S_u = f(T)$ data. The results are given in Table 3, together with the overall activation energies E_a of fuel-oxygen reactions in flames, calculated according to equation:[9]

$$S_u = ct \cdot e^{-E_a / 2R\overline{T_b}} \qquad (4)$$

Here, $\overline{T_b}$ is the average flame temperature, calculated as: [30]

$$\overline{T_b} = T_0 + 0.74 \cdot (T_b - T_0) \qquad (5)$$

Close values of the activation energy were obtained from experimental and computed burning velocities. The overall activation energies of ethane oxidation match well $E_a = 365$ kJ mol^{-1} reported by Brinzea *et al.*[31] for stoichiometric propane-air flames, but exceed the activation energy found for ethane-air flames by Taylor (210 kJ mol^{-1}).[32] In a similar way, the present activation energies of ethene oxidation are much higher as compared to the activation energy of propene oxidation in the presence of N_2 or CO_2 reported by Razus et al. (145-200 kJ mol^{-1}).[33] Comparing the three fuels, the overall activation

energies of their oxidation with air increase as their flame temperatures increase.

The flame structure is characterized by several important parameters: the flame temperature, the rate of heat release and the concentrations of chemical species. Their profiles, examined as functions on the distance across the flame front, can be further used to determine the flame front width (the flame thickness). For the examined flames, the computed profiles of temperature and heat release rate are shown in Fig. 3 and 4. At constant initial conditions, a steeper increase of temperature profile (Fig. 3) and increasing peak values of heat release rate (Fig. 4) are observed by examining ethane-air, ethene-air and acetylene-air flames.

The flame thickness δ was calculated from temperature profile as the ratio of the maximum temperature difference and the maximum slope of the temperature profile:[34]

$$\delta = \frac{T_b - T_u}{(dT / dx)_{max}} \qquad (3)$$

where T_b is the peak temperature in the flame front and T_u is the temperature of the unburned gas. The influence of pressure and temperature on flame width of stoichiometric ethane-air, ethene-air and acetylene-air flames is shown in Figs. 5 and 6.

As shown in Figs. 5 and 6, the flame thickness of all flames decreases as the initial pressure or temperature increase. These dependencies are indirectly confirmed by examining the variation of the quenching distances of deflagrations as functions of pressure and temperature, since a constant ratio was found between the flame thickness and the quenching distance of deflagrations for various fuel-air mixtures.[34]
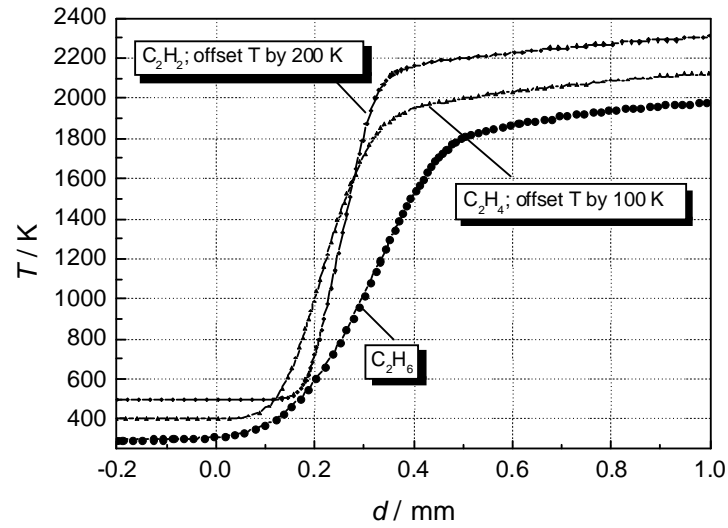
Fig. 3 – Computed temperature profiles of stoichiometric fuel-air flames at p_0 = 101.3 kPa and T_0 = 300 K.
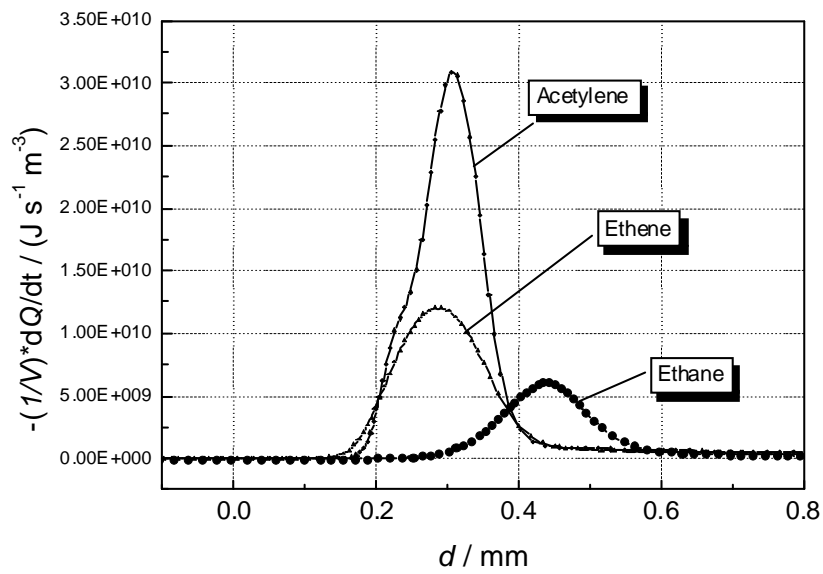

Fig. 4 – Computed profiles of volumetric heat release rates for stoichiometric fuel-air flames at p_0 = 101.3 kPa and T_0 = 300 K.
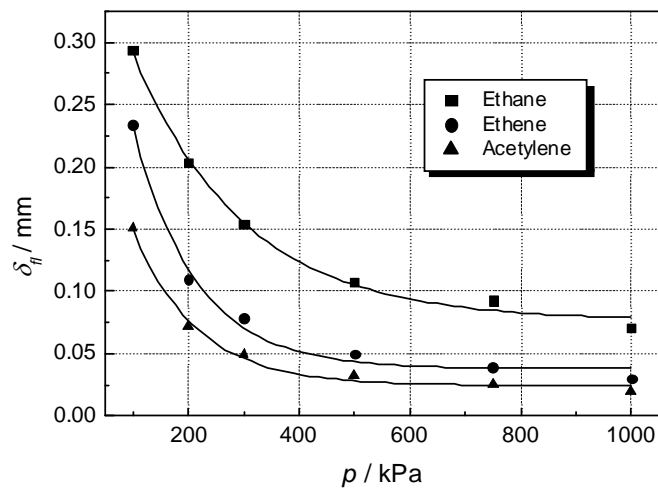

Fig. 5 – Computed flame front widths for stoichiometric fuel-air flames at T_0 = 300 K; the lines are best fit correlations for δ vs. p.
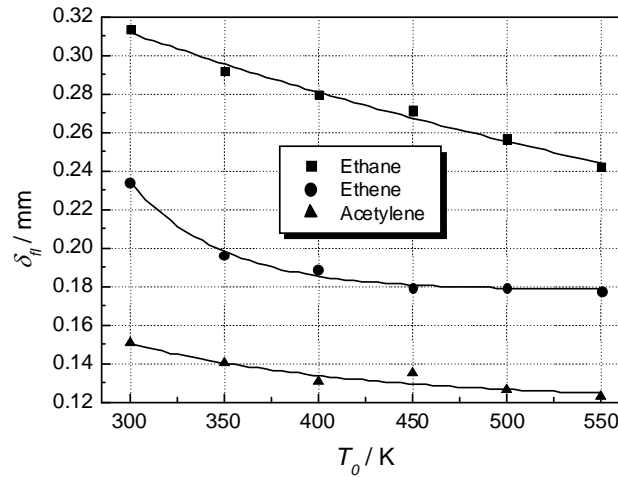
Fig. 6 – Computed flame front widths for stoichiometric fuel-air flames at p_0= 101.3 kPa; the lines are best fit correlations for δ vs T_0.

Another important parameter obtained by chemical modeling of laminar flames, playing a dominant role in flame propagation, is the volumetric rate of heat release. Important increases of the volumetric rates of heat release are obtained when the initial pressure and temperature of fuel-air mixtures increase, as seen from Figs. 7 and 8 where the rates of heat release have been plotted against pressure and temperature.
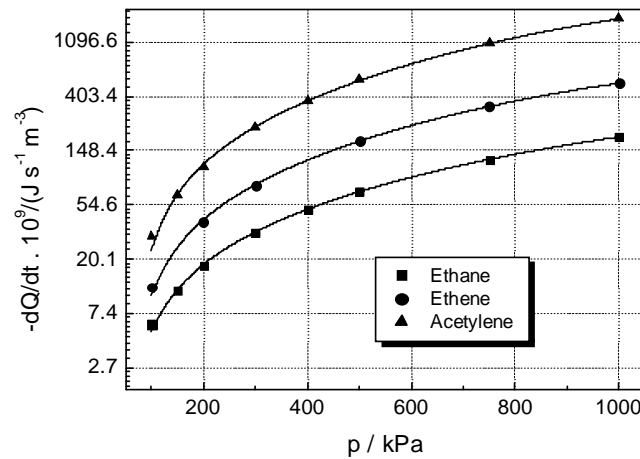

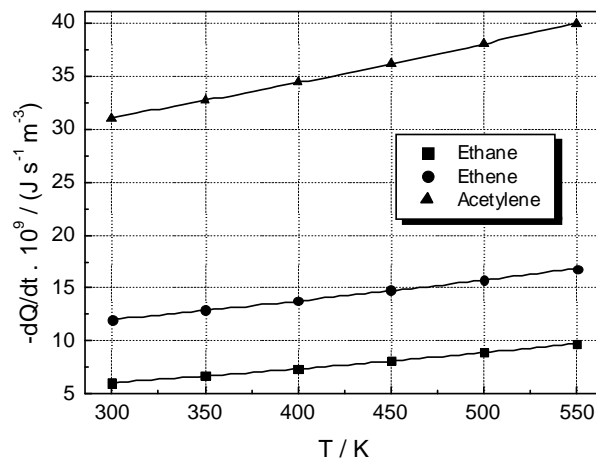Fig. 7 – Volumetric rates of heat release for stoichiometric fuel-air flames at T_0 = 300 K.

Fig. 8 – Volumetric rates of heat release for stoichiometric fuel-air flames at p_0 = 101.3 kPa.
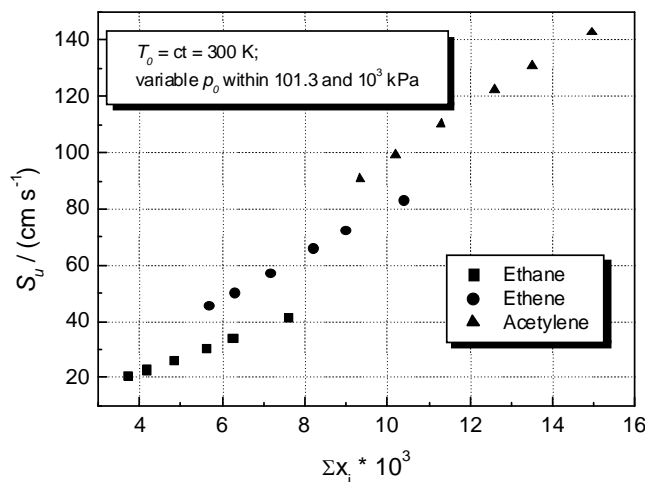
Fig. 9 – Computed burning velocities in correlation with the sum of peak mass fractions of radical species in the flame front; stoichiometric fuel-air flames at T_0 = 300 K.
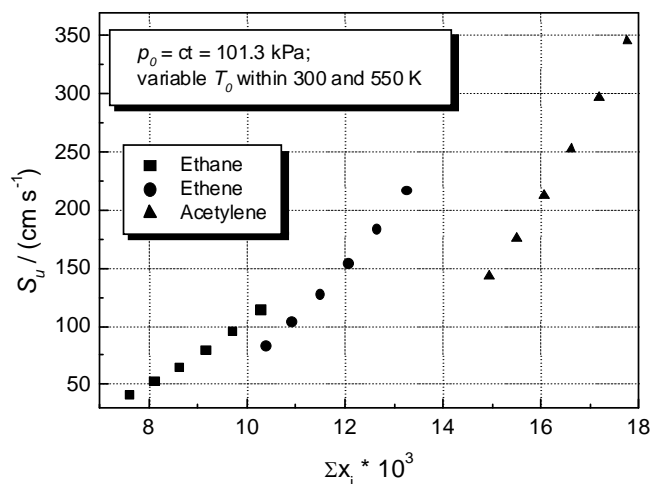

Fig. 10 – Computed burning velocities in correlation with the sum of peak mass fractions of radical species in the flame front; stoichiometric fuel-air flames at p_0 = 101.3 kPa.

The significant role of the active species concentrations in the flame front is shown by the good correlations found between the normal burning velocities and the total concentration of major radical species, either at various initial pressures and constant temperature (Fig. 9) or at various initial temperatures and constant pressure (Fig. 10). Different ranges of variation are observed for peak mass fractions and burning velocities of the examined fuels, but the increase of the peak concentrations of major radical species is accompanied by the increase of the normal burning velocity for all initial conditions.

CONCLUSIONS

The predictive ability of GRI-Mech for the examined flames is excellent for ethane-air over the whole range of initial conditions, but less satisfactory for ethene-air and acetylene-air, especially at pressures within 100 and 500 kPa. For these two fuels, the computed burning velocities are systematically higher than experimental ones. Despite this, the baric and thermal coefficients of burning velocities determined from experimental data are close to those obtained from computed burning velocities.

The large differences of reactivity between the examined fuels are substantiated by the temperature and volumetric heat release rate profiles across flames and by the total peak concentrations of radical species. Faster rates of heat release ($C_2H_2 > C_2H_4 > C_2H_6$) determine higher concentration of radicals, steeper temperature and reactive species profiles, and lower flame widths. The burning velocities

correlate well with the total concentration of active species, for series of data evaluated at constant initial pressure or constant initial temperature. The overall activation energy increases as the adiabatic flame temperature increases.

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