NUMERICAL STUDY OF DILUENT INFLUENCE ON BURNING VELOCITY OF ACETYLENE-AIR MIXTURES

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In the present paper, the numerical study of 1-D adiabatic laminar premixed flames of acetylene-air and acetylene-air-diluent (stoichiometric acetylene-air mixtures containing various amounts of Ar, N_2 or CO_2) was carried out at room temperature and atmospheric pressure, using two software packages (INSFLA, based on Warnatz mechanism and COSILAB, based on GRI mechanism). The kinetic modelling provides the normal burning velocities and the profiles of temperature and heat release rate across the flame front. For the stoichiometric acetylene-air mixture, the burning velocities computed with GRI mechanism agree well with experimental values from literature while the burning velocities computed with the Warnatz mechanism are underestimated. Dilution by increasing amounts of diluents determines the decrease of burning velocity, of maximum flame temperature and of heat release rate, determined by decrease of overall reaction rate between fuel and oxidant in the reaction zone and of heat and mass transfer rates between the burnt and unburnt gases.

INTRODUCTION

The acetylene combustion with air or oxygen has a considerable chemical and industrial interest and importance. The high enthalpy of formation of acetylene determined by the presence of the triple C≡C bond results in flame temperatures higher than those normally obtained from other hydrocarbon fuels; therefore acetylene is widely used in industrial welding and cutting and also in other applications where high temperature flames are required, such as photometry and atomic absorption.[1] The combustion reactions of acetylene are of wider significance, since acetylene is formed as an intermediate in the combustion of fuel-rich mixtures of other hydrocarbons and plays an important role in soot formation.[2] Knowledge of acetylene combustion is important also with respect to industrial hazards presented during acetylene manufacture and its wide using for chemical synthesis. This is particularly so since acetylene is capable of sustaining a self-decomposition flame, while in mixture with oxygen it readily detonates.[3] The laminar burning velocities for acetylene-air mixtures are also substantially higher than those of any other hydrocarbon mixture for the same equivalence ratio.[4, 5]

Among characteristic propagation parameters, the normal burning velocities are key properties for modelling the turbulent combustion, optimization of internal combustion engines and the design and construction of venting devices. Reliable values of burning velocities for gaseous acetylene-air mixtures are found in literature, from various measurements on premixed flames, under stationary or non-stationary conditions.[6-12] The burning velocities of acetylene with air over lean to rich fuel concentrations, at various initial pressures between 0.5 and 20 atm were measured by means of the spherical bomb technique.[6-8] For the stoichiometric mixture at ambient initial pressure and temperature, burning velocities ranging within 125 cm/s [6] and 135 cm/s [8] were reported. Other

measurements on outwardly propagating spherical flames in a constant-pressure chamber [9] for various equivalence ratios and pressures up to 5 atm, confirmed the previously found burning velocity (125 cm/s) for the stoichiometric mixture at 1 bar. Slightly higher burning velocities of acetylene-air, for mixtures with an equivalence ratio between 1.1 and 1.3 were found by measurements with the burner technique, using moist acetylene-air mixtures (0.3 vol.% H_2O (vap)) at 1 bar:[10] the authors found S_u =144 cm/s for the stoichiometric mixture and S_u =154 cm/s for the most reactive mixture (equivalence ratio φ = 1.2). In this case, the burning velocity was determined by direct photographic records; improved measurements based on Schlieren records of flames stabilized over a Bunsen burner delivered S_u =155 cm/s for the stoichiometric mixture and S_u =168 cm/s for the most reactive mixture (equivalence ratio φ = 1.25) at ambient initial conditions.[11] Recent measurements on acetylene-air mixtures at ambient initial conditions were made with the counter-flow twin flames technique;[12] the burning velocity of the unstretched flame in the stoichiometric mixture was found to be S_u =135 cm/s.

The fuel/air ratio, as well as the addition of inert diluents, strongly affects both the kinetics and thermodynamics of the combustion process and consequently the observable properties like the burning velocity, thus being used in many practical applications. The dilution effects on the burning velocity of fuel/air mixtures are frequently studied using Ar, N_2 and CO_2 gases having quite different physical and chemical properties.

Several comprehensive kinetic models for the combustion of unsaturated hydrocarbons were reported in literature.[13-17] Their validation was made by comparison between the computed and measured values of a few global parameters, such as the normal burning velocity and/or the ignition delay and ignition temperature, for the examined fuels under extensive variations of their state parameters. Among them, the models developed by Warnatz *et al.*[13, 18-20] for flames of C1-C4 hydrocarbons and by the Gas Research Institute[17] for natural gas-air flames were considered adequate and were tested for acetylene-air and acetylene-air-inert flames. The computed burning velocities of the stoichiometric acetylene-air and acetylene-air-inert mixtures with various dilution degrees will be discussed in comparison with available literature data. The results will be compared with those computed for other fuel-air-diluent systems, in order to correlate the observed burning velocity variation with physical and/or chemical factors.

COMPUTER PROGRAMS AND DATA EVALUATION

The kinetic modelling of acetylene-air and acetylene-air-diluent flames was made with packages INSFLA, developed by Warnatz and coworkers[20] and COSILAB version 3.0.3, developed by Rogg and Peters.[21] One-dimensional, premixed laminar free flames were considered, assuming the mechanism CH_4-C_4 (53 chemical species and 592 elementary reactions) with updated values of rate coefficients for the rate-limiting reactions in acetylene-air oxidation as reported by Heghes.[22] Another mechanism taken into account was the GRI mechanism – version 3.0 (53 chemical species and 325 elementary reactions).

The input data were taken from thermodynamic and molecular databases of Sandia National Laboratories, USA, according to the international standard (format for CHEMKIN).

RESULTS AND DISCUSSION

The kinetic modelling of flame propagating in gaseous acetylene-air and acetylene-air-diluent mixtures of given initial composition, pressure and temperature provides the laminar burning velocity S_u and the profiles of the volumetric rate of heat release, dQ/dt, of temperature and of concentration for all chemical species taken into account, describing the flame structure. The modelling refers to stable one-dimensional (1-D) laminar, premixed free flames.

A set of results obtained for the stoichiometric acetylene-air flame ([C_2H_2] = 4.02 vol. %) diluted with various amounts of CO_2 at ambient initial conditions are given in Fig. 1, where normal burning velocities computed by the two mechanisms (Warnatz and GRI, respectively) are plotted against diluent concentration. A good agreement between literature data referring to the stoichiometric acetylene-air mixture [6, 8-10] is found for the burning velocities computed by means of the GRI mechanism; comparatively, the burning velocities computed with the Warnatz mechanism are lower at any diluent concentration.

The normal burning velocities of the stoichiometric acetylene-air mixture in the presence of various diluents, at ambient initial conditions, are drawn in Fig. 2. As expected, CO_2 dilution has the highest influence on burning velocities, since CO_2

has a larger influence on mixture heat capacity and on heat dissipation rate in comparison with nitrogen and argon.

This effect was already observed for stoichiometric ethylene-air and propylene-air mixtures, for computed and measured burning velocities, as well.[23, 24] Similar dependencies were obtained for both mechanisms used in the present computations, at various initial pressures between 1 and 5 bar.

A set of representative data obtained in the present computations for stoichiometric acetylene-air mixture diluted with 10% diluent, is given in Table 1, together with data characteristic of the stoichiometric acetylene-air mixture at ambient initial conditions: the maximum flame-front temperature (T_{max}), the flame front width (d_{fl}) and the normal burning velocity (S_u). Both data sets confirm the decrease of the maximum flame temperatures and burning velocities and the increase of flame front width of acetylene-air flames in the presence of diluents.
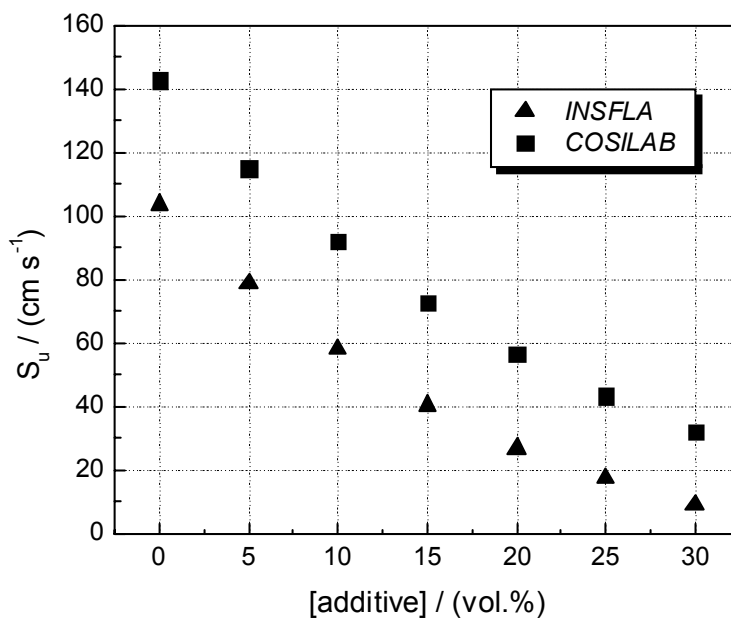
Fig. 1 – Computed normal burning velocities
for stoichiometric C_2H_2-air-CO_2 mixtures at p_0 = 1 bar and T_0 = 298 K.
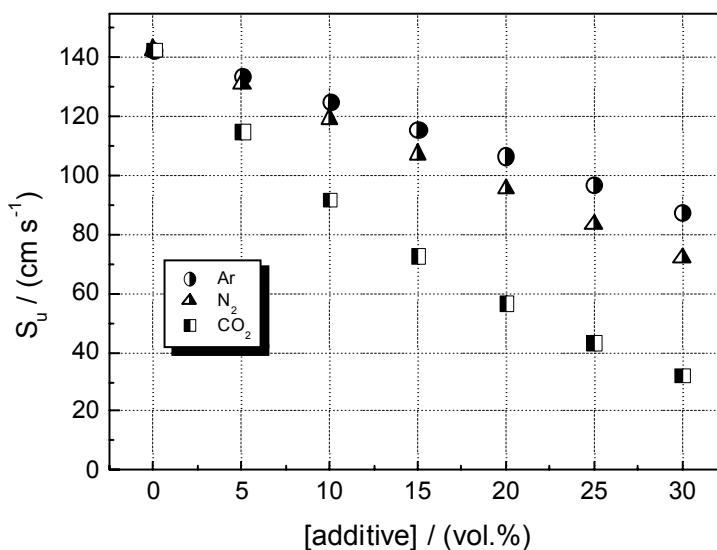
Fig. 2 – Computed burning velocities using GRI mechanism
for stoichiometric acetylene-air mixtures diluted with various diluents.

Table 1

Characteristic parameters of the stoichiometric acetylene-air and acetylene-air-10% diluent flames
at ambient pressure and temperature

	INSFLA				COSILAB			
	no diluent	argon	nitrogen	carbon dioxide	no diluent	argon	nitrogen	carbon dioxide
T_{max} / K	2569.6	2507.1	2472.9	2371.5	2125.0	2053.3	2020.9	1935.0
d_{fl} / mm	0.449	0.512	0.542	0.654	-	-	-	-
S_u / (cm s^{-1})	103.7	87.10	80.79	57.99	142.76	125.13	119.23	92.10

Significant differences are revealed between data obtained with the two mechanisms, determined by adopting different reaction routes; they are maintained even for the relative (normalized) flame front temperatures, defined as $T_{max,rel} = T_{max}/T_{max}^0$ (where T_{max} is the temperature of fuel-air-diluent flame and T_{max}^0 is the temperature of fuel-air flame without diluent) and for the relative burning velocities, defined as $S_{u,rel} = S_u/S_u^0$ (S_u is the burning velocity of fuel-air-diluent mixture and S_u^0 is the burning velocity of fuel-air mixture without diluent). Taking into account the better agreement between burning velocities of acetylene-air computed with GRI mechanism and the reference data from literature, we will discuss only results computed by means of this mechanism.

Comparison of relative burning velocities computed for stoichiometric C_2H_2-air and stoichiometric C_3H_8-air mixtures in the presence of various diluents reveals systematic differences between the two fuels. For each examined diluent,

the relative burning velocities of C_3H_8-air-diluent are lower in comparison with burning velocities of C_2H_2-air-diluent, as seen in Fig. 3. Identical dependencies were obtained for the relative flame front temperatures, proving that dilution effect is influenced not only by diluent nature and concentration but also by the combustion heat of examined fuels.

Additional information on diluent influence on C_2H_2-air flames is obtained from heat release rates, computed for atmospheric flames, plotted in Fig. 4. The decrease of heat release rates by dilution is determined mostly by the diminution of acetylene and oxygen concentrations and of the amount of evolved heat, able to sustain the flame propagation. The typical examples are acetylene-air-N_2 and the acetylene-air-Ar mixtures (the upper plots in Fig. 4). In addition, dilution by CO_2 maintains the diminution of fuel content, adding the specific influence of this diluent: its ability to dissociate and to dissipate heat by radiation. However, the effect of carbon dioxide dissociation is less important when diluent amount is increased because the flame temperature is lower and does not support an extensive dissociation.[25]
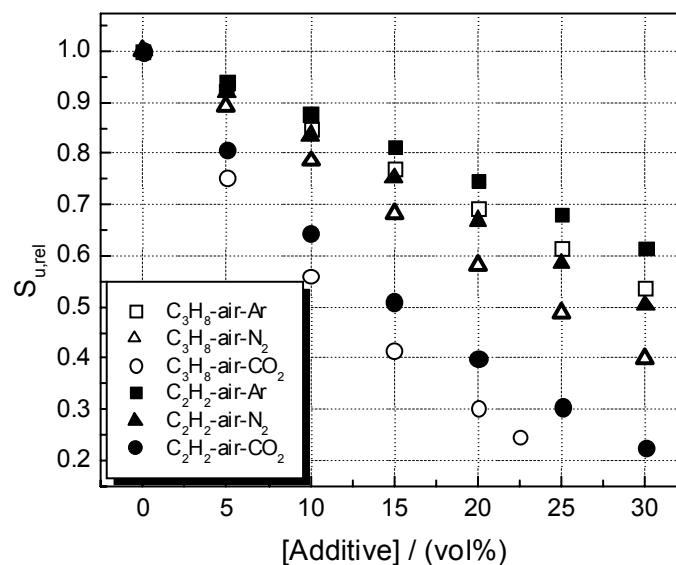

Fig. 3 – Relative burning velocities of C_2H_2-air-diluent and C_3H_8-air-diluent mixtures
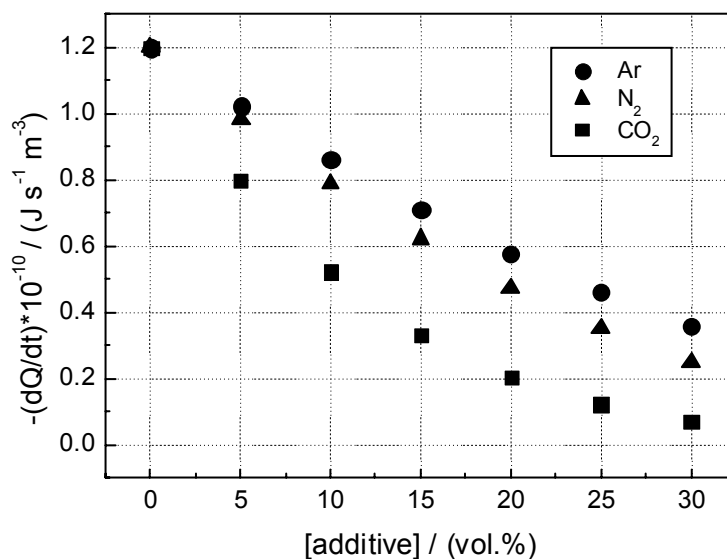at $p_0 = 1$ bar and $T_0 = 293$K, computed with GRI mechanism.

Fig. 4 – Heat release rate from acetylene-air-diluent flames,
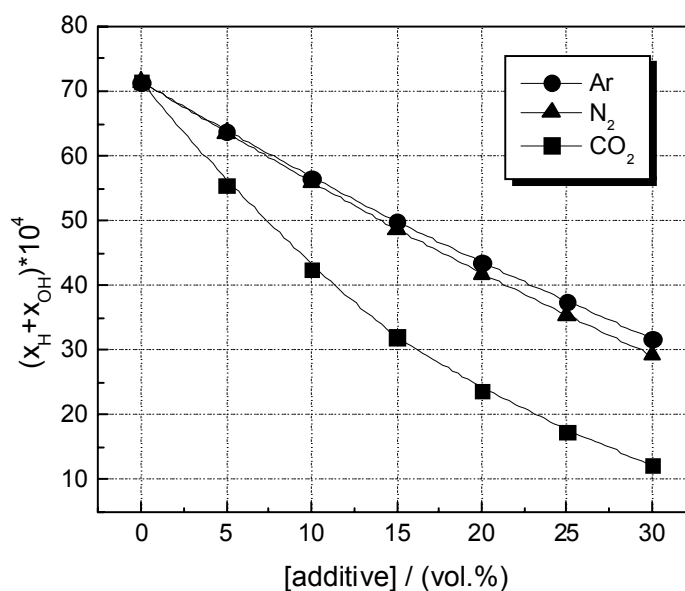at $p_0 = 1$ bar and $T_0 = 298$ K.

Fig. 5 – Total mass fractions of H and OH in the flame front of the stoichiometric acetylene-air mixtures
diluted with various amounts of Ar, N_2 and CO_2 at $p_0 = 1$ bar and $T_0 = 298$ K.

The diluent influence upon flame propagation is observed also by examination of the total mass fraction of H and OH radicals, the chain carriers that influence most significantly the fuel consumption reaction.[20] In Fig. 5, a plot of the total mass fractions of H and OH against diluent concentration is given. The decrease of the mass fractions of examined radicals with dilution is larger in flames diluted with carbon dioxide, as compared to flames diluted by nitrogen or argon.

Good correlations were found between the normal burning velocities and the maximum flame

temperatures for all examined diluents, as seen from Fig. 6. In the range of high flame temperatures, data laye practically on the same plot; they differentiate in the low temperatures range. Similar dependencies were found for many other systems: C_2H_4-O_2-N_2 [24] and CH_4-O_2-N_2-CO_2 or H_2-O_2-N_2-CO_2 where oxygen-enriched air was used, with different enrichment factors.[26]

The correlation of normal burning velocities with flame temperatures, illustrated by data in Fig. 6, can be used to evaluate the overall activation energy of the combustion process.
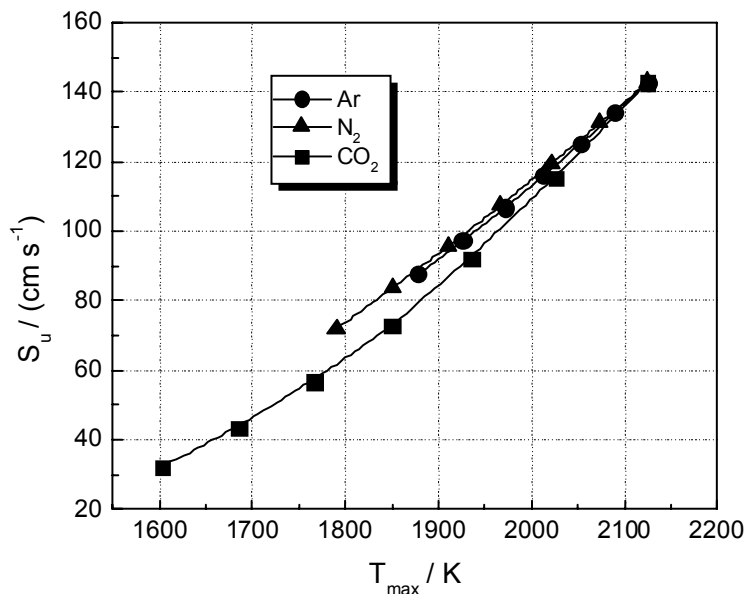
Fig. 6 – Correlation between the normal burning velocities and maximum flame temperatures
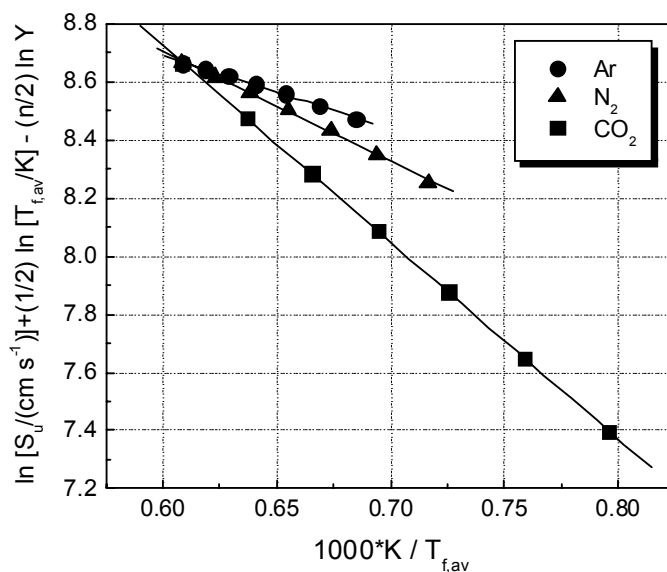for acetylene-air-diluent mixtures, obtained by GRI mechanism.

Fig. 7 –Variation of normal burning velocities and average flame temperatures, for acetylene-air-diluent mixtures.

The overall activation energy of acetylene-oxygen reaction within the flame front, in the presence of different diluents, was calculated from equation:

$$\ln S_u + \frac{1}{2}\ln T_{fl,av} - \frac{n}{2}\ln Y = const - \frac{E_a}{2R \cdot T_{fl}} \qquad (1)$$

derived by Burke *et al.*[27] for any fuel-oxygen-inert mixture where the flame temperature is varied by dilution. In eq. (1), $T_{fl,av}$ is the average temperature within the flame front, Y is the mole fraction of reactive components (fuel + oxidant) in the

examined mixture and n is the overall reaction order for the reaction between fuel and oxidant. The average flame temperature was calculated with the relationship:[27]

$$T_{fl,av} = T_0 + 0.74 \cdot \left(T_{fl} - T_0\right) \qquad (2)$$

where T_0 is the initial temperature of flammable mixture and T_{fl} is the maximum flame temperature in the flame front. The overall reaction order, n, was considered 2.0, according to data referring to propane-air mixtures.[28] An additional evaluation of the same data used $n = 1.8$, as found for ethylene-air and propylene-air.[23, 24]

Table 2

Activation energies of acetylene oxidation in the presence of various diluents

	Ar	N₂	CO₂
E_a, kJ/mol (based on $n = 2.0$)	41.5 ± 1.1	63.2 ± 1.5	112.7 ± 0.30
E_a, kJ/mol (based on $n = 1.8$)	49.3 ± 1.0	68.3 ± 0.80	115.9 ± 0.30

The plots of the left member of equation (1) (with $n = 2$) against the reciprocal value of average flame temperature, for the stoichiometric acetylene-air mixture diluted with Ar, N₂ and CO₂ are given in Fig. 7. The slopes of the linear correlations gave the overall activation energies.

A typical set of data is given in Table 2. Quite small differences were obtained, for each examined diluent, when the overall reaction order varied from 1.8 to 2.0.

The overall activation energies of acetylene oxidation in flames with O₂, in the presence of diluents, are much lower in comparison with the activation energies of other fuels with oxygen, *e.g.* E_a = 146 kJ/mol for stoichiometric C₃H₆-air-Ar mixtures and 207 kJ/mol for stoichiometric C₃H₆-air-CO₂ mixtures;[29] E_a = 97.2 kJ/mol for C₂H₄-air-N₂, 134.4 kJ/mol for C₂H₄-air-Ar and 158.6 kJ/mol for C₂H₄-air-CO₂.[24] For all fuels, the largest activation energies are calculated for mixtures diluted with CO₂ ; they account for the steeper decrease of burning velocities of fuel-air-CO₂ (in comparison with other fuel-air-diluent mixtures) when CO₂ concentration increases.

CONCLUSIONS

A computational study of flame propagation in stoichiometric acetylene-air-diluent mixtures (diluents: argon, nitrogen, and carbon dioxide, with concentrations between 5-30 vol.%) was performed by using the Warnatz mechanism developed for combustion of C1 - C4 hydrocarbons with air and the GRI mechanism, developed for combustion of natural gas with air. The study provides the burning velocities of examined mixtures at $p_0 = 1$ bar and $T_0 = 298$ K, together with temperature, flame front width, species concentrations and profiles of heat release rate across the flame front. A better agreement between computed and experimental burning velocities was obtained by using GRI mechanism.

A strong influence of the inert diluents on the normal burning velocity, maximum flame temperature, concentration of active radical species and heat release rate in the flame front was observed. Dilution by increasing amounts of diluents determines the decrease of the burning velocity, maximum flame temperature and heat release rate, for all investigated diluents. Among them, CO₂ was found the most efficient, followed by N₂ and Ar. The explanation relies on the larger influence of carbon dioxide on the total heat capacity and heat dissipation rate in comparison to nitrogen and argon. The differentiation of the dilution effect is clearly reflected in the overall activation energies: 41.5 kJ/mol (C₂H₂-air-Ar), 63.2 kJ/mol (C₂H₂-air-N₂) and 112.7 kJ/mol (C₂H₂-air-CO₂), indicating the maximum dilution efficiency of CO₂.

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