Flammability Limits of Methane/Alkene Mixtures in Air

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The knowledge of alkane/alkene chemical interactions in gaseous mixtures are fundamental for several industrial applications as they represent the main compounds of the pyrolysis gas produced in stream cracking process, or in the oxidative coupling of methane, or even as component of biogas. However, reliable and comprehensive empirical correlations for the estimation of flammability limits for complex fuel mixtures are still to be developed. More in particular, the additivity correlations (e.g. Le Chatelier's rule) are not suitable or uncertain when alkanes are mixed with saturated hydrocarbon species.

In this work, the flammability limits for binary mixtures of ethylene or propylene in air, either pure or in mixture with methane were defined by experimental and numerical analysis. The experimental data were evaluated by means of the heat flux burner method, which is able to reduce the effect of the flame stretching and the related uncertainties. The obtained results were compared with the corresponding experimental data retrieved in the current literature, when available, and with the data calculated by the most common empirical correlations. The data were also compared with numerical estimations obtained by fully validated detailed kinetic model suitable for light compounds oxidative chemistry. To estimate the flammability limits, the limiting laminar burning velocity theory has been adopted. The agreement between experimental data and numerical results was evaluated by means of statistical approach.

1. Introduction

The use of natural gas, mostly composed by methane, for several industrial applications incentives the development of accurate kinetic models and reliable procedures to estimate the main safety parameters suitable for a wide range of conditions. Although extensive studies on these regards were already performed for pure light hydrocarbons in air (Davis and Law, 1998), relatively few studies on fuel mixtures were carried out. Moreover, most of them are focused on the evaluation of hydrogen addition to commonly adopted fuels (Pio and Salzano, 2018a), whereas few data are available for the addition of alkenes to methane (Liu et al., 2010).

In this framework, the laminar burning velocity (S_u) represents an essential parameter for the evaluation of safety and reactivity aspects involving oxidant environment, especially at low temperatures where the alternatives are reduced by technical limitations, e.g. the ignition delay time data. Several experimental systems were developed and currently adopted for the S_u measurement (Ranzi et al., 2012). Among these, the heat flux burner methodology (HFB), as intended by de Goey et al. (1993), is able to determine this value by the interpolation of the unburned gas flowrate with respect to the net heat flux to the burner plate. In the HFB, the adiabatic flat flames are obtained by compensating the heat gained by the burned gas above the plate and the heat losses by the unburned gas below the plate by using with a heating jacket close to the burner head. This technique gives large advantages with respect to other common experimental systems as the counter-flow burners, the spherical bomb and the constant vessel, which require the extrapolations of data in order to obtain unstretched flame data (Bosschaart and De Goey, 2004).

Comprehensive databases for pure hydrocarbons flammability limits exist (e.g. Coward and Jones, 1952). However, their data can be scarce or unavailable for binary or complex fuel mixtures at non-standard temperature and pressure values. Several empirical rules were developed to estimate the effect of fuel

composition at given initial temperature, e.g. Le Chatelier's law, calculated flame temperature at constant volume (CFTV), critical adiabatic flame temperature (CAFT), the Shimy's equation and the limiting laminar burning velocity theory. However, some of these approaches were found to be inadequate for the estimation of the effect of non-hydrocarbons addition on alkanes for a wide range of conditions (Basco et al., 2012; Zaidi et al., 2015). For this reason, additional data and evaluation on the alkanes-alkenes mixtures should be beneficial to evaluate the estimation quality and validity of the cited rules.

In this framework, the laminar burning velocity and flammability limits for binary mixtures of ethylene and propylene in air, either pure or in mixture with methane were investigated by using the HFB technique. Results have been compared with existing literature data, correlations, and numerical results obtained by fully validated detailed kinetic model suitable for light compounds oxidative chemistry.

2. Methods

The S_u with respect to the equivalence ratio (φ, Eq. 1) and alkene addition (R_A, Eq. 2) was experimentally measured by using the heat flux burner and numerically estimated by means of the open source Cantera code (Goodwin, 2003) at an atmospheric pressure and initial gaseous mixture temperature equal to 298 K.

$$\varphi = \sum \frac{Fuel/Oxidant}{(Fuel/Oxidant)_{st}}$$

(1)

where fuel and oxidant are mole fractions and the subscript st stands for the stoichiometric composition for the complete combustion of the fuel mixtures.

$$R_i = m_i/(m_i + m_m)$$

(2)

where m represents the molar flowrate and subscript i and m the generic alkene (i.e. the subscript e and p will be adopted for ethylene and propylene, respectively) and methane flowrate, respectively. The investigated fuel mixtures were reported in Table 1 in terms of R_i.

Table 1: Composition of the investigated mixtures

	Mix 1	Mix 2	Mix 3	Mix 4
R_e [%]	20	40	0	0
R_p [%]	0	0	20	40

The limiting burning velocity theory (Hertzberg, 1984) was adopted to estimate the flammability limits of the investigated mixtures, since previous studies have indicated this procedure as suitable for the evaluation of the flammability limits of pure light alkenes (Pio and Salzano, 2018b) and methane (Pio and Salzano, 2019) at similar temperature and pressure conditions. This theory is based on the comparison of the S_u and a threshold value, referred as $S_{u,lim}$, i.e. the composition such that S_u equals the $S_{u,lim}$ are considered as flammability limits. The $S_{u,lim}$ is calculated by using the following equation:

$$S_{u,lim} = \sqrt[3]{2\alpha g \frac{\rho_b}{\rho_u}}$$

(3)

where the subscripts u and b stand for the unburned and burned conditions, respectively, ρ is the density, α the effective thermal diffusivity and g the gravitational acceleration.

2.1 Experimental apparatus

The experimental system applied in this work can be divided in the following sections: feeding section, consisting of three Bronkhorst mass flow controllers and a mixing path; the burned composed by a plenum chamber kept at homogeneous and constant temperature of 298 ± 2 K by cooling jacket and designed to guarantee the reactant mixing and homogeneous composition with respect to the radial position; the burner head composed by a porous plate surrounded by heating jacket kept at 358 ± 2 K to guarantee the flame

stability; finally the data acquisition system monitoring burner plate temperature distribution with respect to the radial position. Schematic representation of the heat flux burner and the ancillary systems are reported in Figure 1.
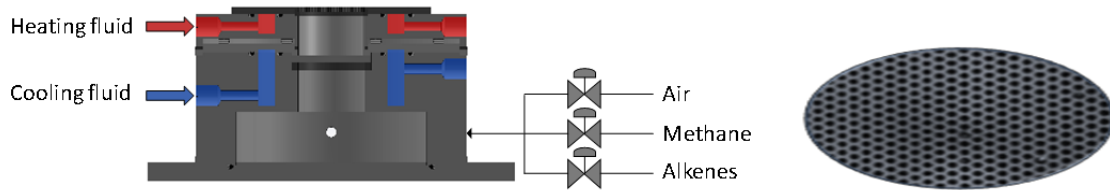

Figure 1: Left: Representation of the heat flux burner (HFB) in this work. Right: Top view of the burner plate.

The heat flux method is based on the evaluation of radial temperature distribution of the plate burner, assuming a parabolic trend with respect to the radial position (Eq. 4).

$$T\,(r) = T_c + \alpha \cdot r^2 \tag{4}$$

where T_c represents the temperature measured at the plate centre, r the radial position and α the polynomial coefficient depending on the net heat flux at the burner plate (Hermanns, 2017) Thus the adiabatic conditions and the laminar burning velocity are reached when the plate temperature is equal to T_c. However, the coexistence of null values of the net heat flux at the burner plate and stable flames are experimentally unfeasible, thus interpolation procedure of the inlet velocity, calculated by considering the flowrate and the effective burner plate area, with respect to the parameter α is required to collect experimental data of S_u. The uncertainties related to the S_u can be distinguished in terms of causes determining their presence and recombined to obtain the overall value, i.e. uncertainties related to the feeding flowrate, the temperature acquisition system, and interpolation process are commonly considered as ruling aspects for the evaluation of the experimental error for the measurement of the S_u by means of HFB (Konnov et al., 2018). Similarly, the uncertainty related to the mixture composition, thus to the equivalence ratio, can be attributed to the uncertainties of the corresponding mass flow controllers of fuel and oxidant. So that said, additional information regarding the procedure adopted for the estimation of the experimental uncertainties for each source and their recombination in the uncertainties of both S_u and φ can be found elsewhere (Salzano et al. 2018).

2.2 Numerical analysis

The detailed kinetic model developed at the University of Bologna (KIBO) was adopted, since previous studies have indicated KIBO as suitable mechanism for light hydrocarbons at the investigated conditions (Pio et al., 2018). To this aim, a tailor-made code was developed by using the open-source code Cantera, based on an optimized Newton method to obtain complete convergence. The main parameters required were: ratio, slope, curve, the relative error criteria (RTol) and absolute error criteria (ATol). The refiner function ratio, slope and curve represent the maximum acceptable value between grid spacing at adjacent intervals, fractional change in the solution of adjacent grid point for each component and fractional change in the derivative of each solution of adjacent grid point for each component, respectively. RTol represents the threshold value for negligible relative error to the size of each solution component, whereas ATol is a threshold below which the value of the ith solution component can be neglected. Since different order of magnitude can be involved in steady-state and time stepping problems, two different sets of RTol and ATol values were adopted.
The corresponding values adopted in this work for ratio, slope and curve were 3, 0.07, 0.14; for RTol and ATol $1.0 \cdot 10^{-9}$ and $1.0 \cdot 10^{-14}$ for the steady-state problem and $1.0 \cdot 10^{-5}$ and $1.0 \cdot 10^{-14}$ for time stepping problem, respectively. These values were indicated as optimal in terms of results accuracy and computational costs required to perform the simulation by grid sensitivity reported elsewhere (Pio and Salzano, 2018b).

3. Results and discussions

The experimental data for the S_u of ethylene/air and propylene/air (Figure 2) mixtures at ambient conditions were first compared with numerical results data either retrieved from the current literature or obtained by the KIBO model.
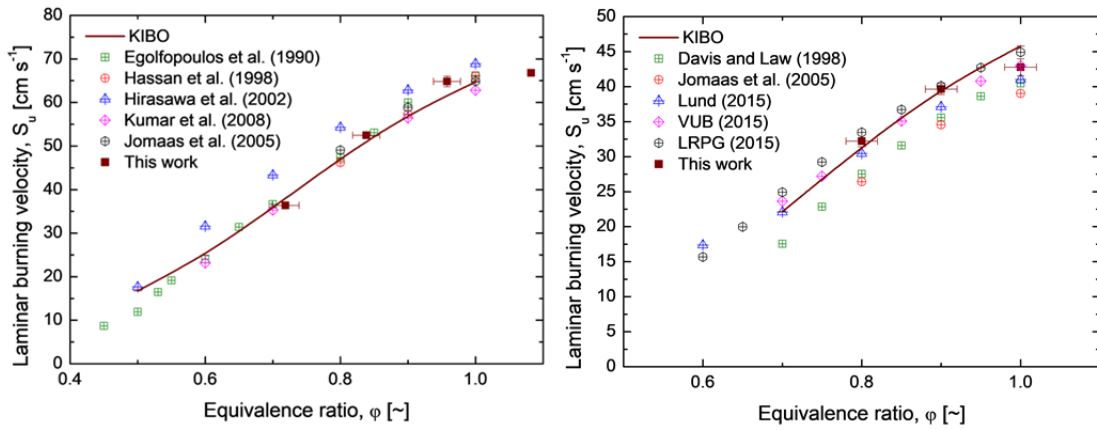
Figure 2: Experimental and numerical data for the Su of ethylene (left) and propylene (right) with respect to the equivalence ratio in air at 298 ± 1 K and 1 bar. Note that the data for the propylene reported by Burke et al. (2015) were distinguished in VUB (Vrije Universiteit of Brussel), Lund (Lund University) and LRPG (University of Lorraine).

In Figure 2, it is worth noting the good accordance between the experimental obtained by the HFB and numerical results obtained by KIBO, which have been obtained without constant setting. Although the tendency to slightly underestimate the ethylene experimental data should be considered for further evaluation and improvements. As well-known the ethylene is more reactive with respect to propylene for given conditions, as confirmed by higher values of S_u at a given equivalence ratio, although further increase in the number of carbon atoms of alkenes does not follow this trend, i.e. the butylene S_u is close to propylene S_u (Ranzi et al. 2012). The experimental data were also considered for the evaluation of the predictive quality of the mixing rules commonly adopted for the S_u. More specifically, three different mixing rules were selected : the Le Chatelier's rule (Eq. 5) was considered as representative of the heat balance based rules, the mole fraction averaged rule (Eq. 6) for the molar-based and the Hirasawa rule (Hirasawa et al., 2002) (Eq. 7) for the mixing rules based on flame temperature.

$$S_{u,mix} = \frac{1}{\sum_i^N z_i/S_{u,i}} \tag{5}$$

$$S_{u,mix} = \sum_i^N x_i S_{u,i} \tag{6}$$

$$S_{u,mix} = \exp\left[\sum_i^N \frac{z_i n T_{f,i}}{n_{mix} T_{f,mix}} \ln(S_u)\right] \tag{7}$$

where z represents the fuel composition in terms of mole fraction, x the mixture composition including the oxidant agent and inert, T_f the flame temperature, N the number of chemicals present in the mixture and n the mole number, whereas the subscript i stands for the i-th component and mix for the global mixture properties. The estimation quality was expressed in terms of percentage variation from the experimental data for each fuel composition. Then, to give a single value representative for all the investigated mixtures, taking into account of both the over and under estimation tendencies, the average of the absolute values was calculated for each predictive approach and referred as overall (Table 2).

As expected the Le Chatelier rule gives large errors for all the investigated mixtures, thus confirming the inaccuracy for fuel mixtures involving non-alkanes species only, as also reported for the hydrogen case (Salzano et al. 2012). It is worth noting that both the mole fraction correlation and the Hirasawa rules underestimate the S_u at low ethylene content (i.e. Mix 1) and overestimate the S_u of mixture containing elevated quantity of alkenes (Mix 2 and Mix 4). The overall values clearly indicate KIBO as the most accurate approach, although Hirasawa rule is more accurate for the estimation of the S_u of Mix 3. Eventually, considering only the simplified mixing rules, the Hirasawa rule shows higher estimation quality, thus

suggesting the flame temperature as ruling parameter for the $S_{u,mix}$ determination of alkene mixtures analysed int his work.

Table 2: Evaluation of the estimation quality of mixing rules, in terms of variation with respect to experimental data collected in this work.

	Mix 1	Mix 2	Mix 3	Mix 4	Overall
Le Chatelier	9.44	24.53	10.54	24.19	17.18
Mole fraction	-2.09	9.17	8.52	22.13	10.48
Hirasawa	-4.55	5.85	1.47	15.76	6.91
KIBO	2.72	4.23	3.26	6.65	4.21

The kinetic mechanism and the obtained S_u were utilized to estimate the $S_{u,lim}$ and the LFL of methane/alkene/air mixtures at 298 K, by using the limiting burning velocity theory (Hertzberg, 1984). For the sake of discussions, pure methane, ethylene and propylene numerical data were also obtained and compared with experimental data retrieved from the current literature (Coward and Jones, 1952) and reported in brackets (Table 3).

Table 3: The limiting burning velocity $S_{u,lim}$ and the LFL for pure substances and mixtures at 298 K and 1 bar. Literature data (Coward and Jones, 1952) are reported in brackets, when available.

Mixture	Methane	Ethylene	Propylene	Mix 1	Mix 2	Mix 3	Mix 4
$S_{u,lim}$ [cm s^{-1}]	4.22	4.38	4.16	4.25	4.28	4.21	4.19
LFL [%v/v]	4.99 (5.00)	2.72 (2.75)	2.03 (2.20)	3.85	3.38	3.72	3.25

The agreement with the experimental data retrieved in the literature validates the adopted procedure for the investigated conditions. It is worth noting that the addition of ethylene and propylene decreases the methane LFL up to 33% and 35%, respectively. Nevertheless, the variation in terms of $S_{u,lim}$ is much more limited, because all the mixtures are mainly composed by air, thus similar properties were found. This observation demonstrates that the reported LFL variation can be mainly attributed exclusively to the increase of S_u related to the presence of alkenes with respect to pure methane. Quite obviously the propylene enriched mixtures show lower LFL than the corresponding mixtures with the same content of ethylene, because pure propylene is more reactive than ethylene in lean conditions.

4. Conclusions

In this work the effect of ethylene and propylene enrichment on methane flame was investigated both experimentally and numerically. More specifically, the laminar burning velocity (S_u) data were collected by using the heat flux burner and estimated by means of the detailed kinetic model KIBO. The validation was performed by comparing the obtained results for pure fuel with experimental data retrieved in the current literature. The methane/alkene mixtures containing up to 40 %v/v of alkene were investigated. The experimental data of S_u in air were utilized to evaluate the quality of the estimation of the detailed kinetic mechanism and different mixing rules, selected as representative of different assumptions. Among the simplified correlations, the Hirasawa rule was found the most accurate. The agreement with the experimental data could be due to the hypothesis of flame temperature as ruling parameter for the determination of the $S_{u,mix}$ and the utilization of Arrhenius-like equation. The addition of alkenes leads to significant reduction of the methane LFL, up to 35%. This variation can be mainly attributed to the increase of S_u at given concentration in the case of alkenes addition, as small variations in terms of $S_{u,lim}$ were reported. The numerical estimations were fairly in agreement with both the experimental data retrieved from the current literature and the experimental data observed in this work. The ability to accurately predict the LFL with respect to operative conditions could represent a crucial aspect for the process safety.

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