Experimental and Numerical Analysis of Laminar Burning Velocity of Binary and Ternary Hydrocarbon/H$_2$ Mixtures

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The evaluation of safety parameters for binary and ternary mixtures of hydrogen and light hydro-carbons is essential for the definition of the combustion characteristics of bio-derived fuel-gas mixtures. Furthermore, with specific reference to laminar burning velocity, there is a strong need to define simple correlations, which would allow a fast prediction of global burning velocity of the mixtures starting from molar compositions and laminar burning velocity of the pure components, in analogy with Le Chatelier's rule for flammability limits. In this paper, a preliminary experimental and numerical study is performed for the assessment of safety parameters for mixtures of methane, propane and hydrogen with air at initial ambient pressure. Explosion tests have been conducted in a reinforced 5 liters steel vessel. The PREMIX module of the CHEMKIN package, coupled to the Marinov detailed reaction scheme, has been used to compute the un-stretched laminar burning velocity. For model validation, results have been compared to experimental data.

1. Introduction

Most of experimental and numerical studies on laminar flame propagation have been carried out on single or binary hydrocarbon fuel mixtures (Hu et al., 2009, Huzayyin et al., 2008,Tang et al., 2008).Industrial gases are often composed by several fuel gases (i.e. hydrogen, methane, propane) hence it could be useful to be able of predicting the global burning velocity of more complex mixtures starting from measurements on single components. Scientific literature provides several mixing rules starting from the pioneering work of Spalding (1956), who proposed a procedure for calculating flame speeds of fuel mixtures based on the flame temperature of the mixture and on the assumption that the reaction rate is additive on a mass basis of mixture components. The laminar burning velocity of fuel mixtures $S_{u,m}$ is then given through the following equation:

$$\left.\frac{\left(\rho_u c_p \Delta T S_u\right)^2}{k}\right|_m = \sum_i \alpha_i \frac{\left(\rho_{u,i} c_{p,i} \Delta T_i S_{u,i}\right)^2}{k_i} \tag{1}$$

where k, ρ_u, c_p are the conductivities, density and the specific heat at constant pressure of the mixture (m) and pure fuels (i), ΔT is the difference between the adiabatic flame temperature and the initial temperature and $S_{u,i}$ is the laminar flame speed of the i-unburned pure fuel/oxidant. In Eq.(1) α_i is the mass ratio of fuel i plus the corresponding amount of oxidant and total mass of (fuel + oxidant).

Yumlu (1967) simplified the Spalding mixing rule on the assumption that the heat release rate, which is proportional to S_u^2, is additive for all the components of the mixture:

$$S_{u,m}^2 = \sum \alpha_i S_{u,i}^2 \tag{2}$$

Harris & Lovelace (1968), as cited in Skrbić et al. (1984), proposed a predictive method considering also the effect of inerts, and adopting the volume fraction x_i of any component of the gas mixture, however excluding H_2, O_2, N_2 or CO_2:

$$S_{u,m} = \frac{\sum x_i S_{u,i}(A_i+1) + x_{H_2} S_{u,H2}(A_{H2}+1)}{\sum x_i(A_i+1) + x_{H_2}(A_{H2}+1)} \cdot$$

$$\left(1 - \frac{4.4 x \sum x_i(A_i+1)}{\left[\sum x_i(A_i+1) + x_{H_2}(A_{H2}+1)\right] \cdot \left[\sum x_i(A_i+1) + x_{H_2}(A_{H2}+1) + x\right]}\right) \tag{3}$$

where A_i is the air volumes required to burn the single pure fuel. In Eq.(3) the term x is the total volume fraction of O_2, N_2 and CO_2 in mixture as given by:

$$x = x_{N2} + 1.8 x_{CO2} - 3.76 x_{O2} \tag{4}$$

and S_{uH2} is the burning velocity of hydrogen given by the equation:

$$S_{H2} = 2.80 - 1.00 \cdot \left(\frac{\sum x_i(A_i+1)}{\sum x_i(A_i+1) + x_{H_2}(A_{H2}+1)}\right)^2 \tag{5}$$

More recently, Di Sarli et al. (2007) proposed a Le Chatelier's Rule-like correlation to evaluate the laminar burning velocity of hydrogen–methane/air mixtures according to the following equation:

$$S_{u,m} = \frac{1}{\sum \dfrac{y_i}{S_{u,i}}} \tag{7}$$

where yi is the molar fraction based on fuel mixture only. This correlation was further validated for similar mixtures by Salzano et al. (2011).

In this work laminar burning velocity for combustion in air at stoichiometric conditions of binary and ternary mixtures of $H_2/CH_4/C_3H_8$ has been evaluated, experimentally and numerically by means of the PREMIX module (Kee et al. 1985) of the CHEMKIN package, coupled to the detailed reaction mechanism elaborated by Marinov et al. (1998). The results have been compared with those obtained by means of analytical correlations found in literature. A modified Le Chatelier's rule is proposed.

2. Experimental apparatus

Experimental tests have been conducted in a AISI 316 SS steel, cylindrical vessel (5 lt), wall thickness of 5 cm. Maximum allowable working pressure is 400 bar. A transformer KSEP 320, 220-230 V and 50 Hz with 25 kV discharge current has been used for spark ignition. Spark gap is 1 mm. Mixture compositions have been obtained by partial pressure method, starting from vacuum conditions. The mixture was stirred few seconds before ignition in order to produce homogeneous mixtures. Each run was performed two times and the average value was taken. Pressure histories were recorded by KULITE ETS-IA-375 (M) series transducers, and recorded by means of National Instrument USB-6251 data acquisition system (1.25 Msamples/s). For all tests, the initial pressure was set to 1 bar and the initial temperature to 298 K. The fuel compositions investigated are given in Table 1. In the table, the corresponding values of adiabatic temperature (T_{ad}) and pressure (P_{ad}) at constant volume, as computed by using the GASEQ Chemical Equilibrium Program (GASEQ, 2011) are also given. All mixtures are at stoichiometric condition in air. The term λ is defined as the molar fraction of propane in the total fuel mixture.
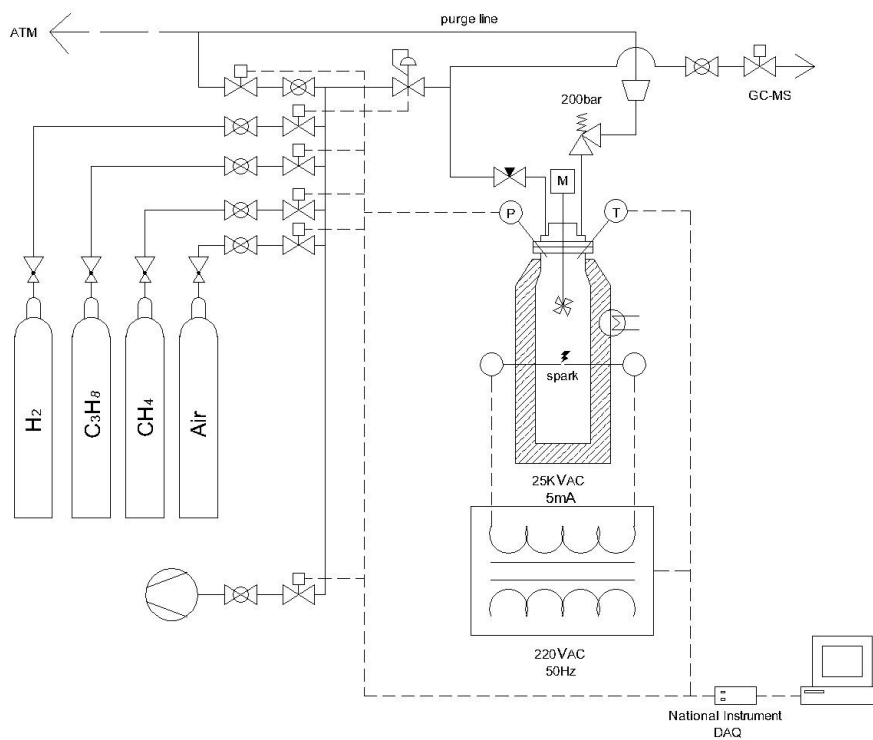
Figure 1: Equipment adopted for the experimental tests

Table 1: Mixture compositions analyzed in this work: Y is the molar fraction of fuel gas mixture; Tad and Pad are, respectively, the adiabatic flame temperature and pressure as calculated using GASEQ

test	λ	Y_{H2}	Y_{CH4}	Y_{C3H8}	T_{ad}, K	P_{ad}, atm
1	1.00	0.00	0.00	1.00	2630.90	9.34
2	0.75	0.25	0.00	0.75	2635.00	9.28
3	0.50	0.50	0.00	0.50	2648.30	9.20
4	0.25	0.75	0.00	0.25	2655.90	8.95
5	0.00	1.00	0.00	0.00	2744.40	8.06
6	1.00	0.00	0.00	1.00	2630.90	9.34
7	0.75	0.00	0.25	0.75	2627.70	9.28
8	0.50	0.00	0.50	0.50	2616.50	9.17
9	0.25	0.00	0.75	0.25	2614.00	9.06
10	0.00	0.00	1.00	0.00	2589.50	8.81
11	0.67	0.00	0.33	0.67	2622.00	9.17
12	0.50	0.25	0.25	0.50	2623.80	9.13
13	0.33	0.50	0.17	0.33	2638.60	9.00
14	0.17	0.75	0.08	0.17	2657.00	8.76
15	0.38	0.25	0.38	0.38	2631.30	9.17
16	0.25	0.50	0.25	0.25	2637.40	9.06
17	0.13	0.75	0.13	0.13	2664.00	8.82

Starting from the pressure history of the explosion. we adopted the equations of Dahoe et al. (2003, 2005) for the flame radius, r_f, and the laminar burning velocity, S_u:

$$r_f = \left(\frac{3V}{4\pi} \right)^{\frac{1}{3}} \left[1 - \left(\frac{P^\circ}{P} \right)^{\frac{1}{\gamma}} \left(\frac{P_{max} - P}{P_{max} - P^\circ} \right) \right]^{\frac{1}{3}}$$ (8)

where γ is the heat capacity ratio, P_{max} is the maximum measured explosion pressure, P° is the initial pressure, and V is the vessel volume. The (un-stretched) laminar burning velocity, Sl, was then calculated according to:

$$S_l = \lim_{r_f \to r_{f0}} \left[\frac{d}{dt} r(t) \right]_{\Delta r_f}$$ (9)

where r(t) is the best fit function in the range $\Delta r_f = (r_f - r_{fo})$ that refers to the range of the flame radius for which either ignition or wall and vessel shape effects on the flame propagation can be neglected. The boundaries of this range were evaluated by considering the places where the time derivative of radius is always positive with radius:

$$\frac{d}{dr} \left(\frac{dr}{dt} \right)_{\Delta r_f} \geq 0$$ (10)

3. Model Description

In this work, the calculation of the laminar burning velocities for binary and ternary H_2/CH_4/C_3H_8/air mixtures has been carried out by means of simulation of the one-dimensional, planar, adiabatic, steady, un-stretched, laminar flame propagation. To this aim, the Sandia PREMIX module (Kee et al. 1985) of the CHEMKIN package was used, coupled to the detailed reaction mechanism elaborated by Marinov et al. (1998), which consists of 56 species and 351 reversible reactions. The code, which adopts a hybrid time-integration/Newton-iteration technique to solve the steady-state mass, species, and energy conservation equations, was set up to simulate a freely propagating flame with mixture-averaged formulas. The initial flow rate of the unburned mixture was set to 0.04 g/cm^2s^{-1}. At the inlet boundary, pressure (100 kPa), temperature (300 K), and composition of the fresh mixture were assigned. At the exit boundary, all gradients were imposed to vanish.

The adopted type of formulation requires an additional boundary condition for the mass flow rate that was assigned by fixing the flame location and, in particular, the point at which the flame temperature reaches a value of 400 K. To start the iteration, the temperature profile estimation obtained by Van Maaren et al. (1994) for stoichiometric methane/air flame was adopted, as suggested by Uykur et al (2001). The temperature profile resulting from the first simulation step was used for the next step.

The model uses a non-uniform grid that is successively and automatically adapted based on solution gradients determined on an initially coarse grid. Relative gradient and curvature parameters, which determine the extent to which the solution is refined for each case, have to be provided. In our study solutions were obtained with gradient and curvature values of 0.2. The total length of the calculation domain was chosen equal to 12 cm.

4. Results

Figure 2 (left) shows experimental pressure time histories for the four ternary mixtures analysed in this work. Typical s-shape in cylindrical vessel can be observed. The maximum pressure reached during the experiments is always lower than the corresponding adiabatic value reported in Table 1, due to the heat losses towards the external environment.

The maximum pressure does not change significantly by enhancing hydrogen content and decreasing propane content in the fuel mixture whereas the rate of pressure rise increases consistently as the mixture becomes more reactive when enriched by hydrogen (Figure 2, right).
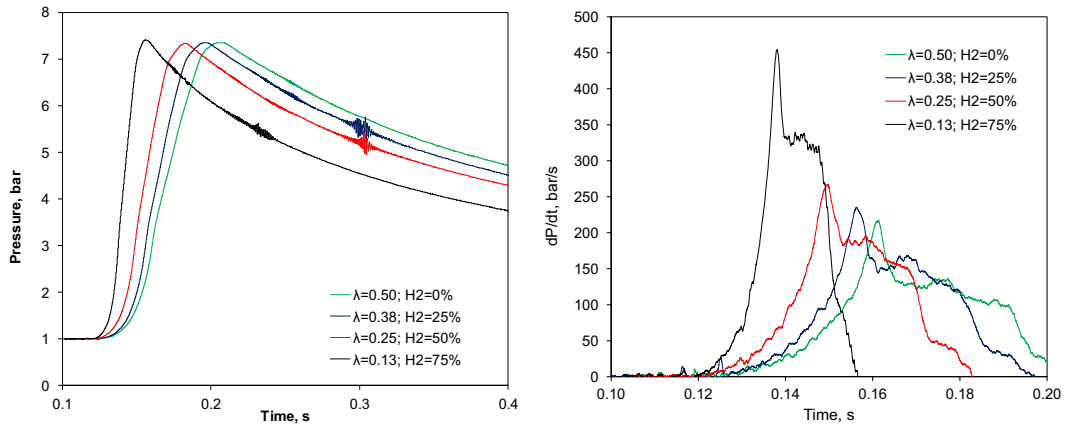
Figure 2. Pressure histories (left) and rate of pressure rise (right) for four ternary mixtures: effect of hydrogen content

The laminar burning velocity resulting from experiments and Chemkin simulations, together with values obtained by the use of empirical correlations cited above are showed in the following Figures 3 and 4.
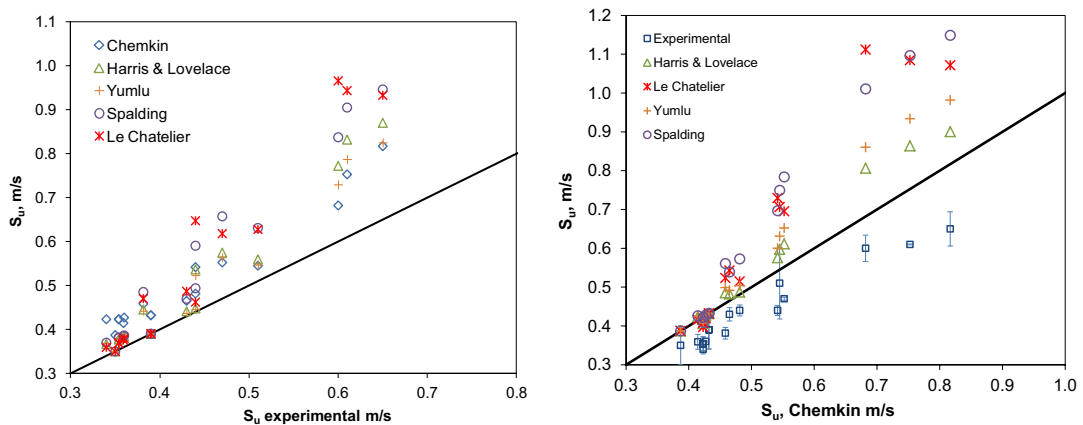

Figure 3. Experimental and calculated laminar burning velocities as function of experimental results (left) and Chemkin results (right).

In Figure 3, all numerical and experimental results presented previously, together with correlations results, are plotted as function of either experimental or Chemkin simulations results. First, it can be noted that Chemkin simulations slightly over- predict the experimental results in all the range of composition investigated. Among the correlations used, that of Harris & Lovelace seems the best for predicting the additivity of fuel, either by considering experimental or Chemkin results. The correlation by Yumlu fits the data for lower values of S_u. That similarly to the Le Chatelier's rule-like correlation, which reproduces correctly the data only for lower value of S_u. In general, however, it should be noted that all analytical correlations become inaccurate when the S_u values become higher, which in our case corresponds to hydrogen contents higher than 50 % of fuel, thus confirming the results of Salzano et al. (2011) for methane/hydrogen/air mixtures.

5. Conclusions

For the fuels analysed in this work, the best correlation for binary and ternary fuel mixtures is that of Harris and Lovelace (1968) or alternatively the simple correlation by Yumlu (1967). The addition of hydrogen in large amount reduces the ability of any tool to reproduce the behaviour of fuel explosions. Some improvement are foreseen in the next future for improving the correlations. In any case, Chemkin simulations are the most efficient and should be always adopted for the prediction of fuel/oxidant explosion.

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