

# STUDY OF HYDROGEN ENRICHED PREMIXED FLAMES

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## ABSTRACT

In the present paper the theoretical study of the un-stretched laminar premixed flames of hydrogen-methane mixtures is carried out by using the detailed reaction mechanism GRI-Mech 3.0 implemented in the CHEMKIN software to find out the effect of hydrogen addition on the hybrid fuel burning velocity.

The model results show that the laminar burning velocity of the hydrogen-methane mixtures is not the linear regression of those of the pure fuels since it results substantially less than the proportional averaging of the values for the fuel constituents. Moreover, the effect of hydrogen addition in terms of enhancement of the mixture laminar burning velocity with respect to the methane is relevant only at very high values of the hydrogen content in the hybrid mixtures (> 70 % mol.).

The performed sensitivity analysis shows that these results can be attributed to kinetics and in particular to the concentration of H radicals: depending on the hydrogen content in the fuels mixture, the production of the H radicals can affect the limiting reaction step for methane combustion. Two regimes are identified in the hydrogen-methane combustion. The first regime is controlled by the methane reactivity, the hydrogen being not able to significantly affect the laminar burning velocity (< 70 % mol.). In the second regime the hydrogen combustion has a relevant role as its high content in the hybrid fuel leads to a significant H radicals pool, thus enhancing the reaction rate of the more slowly combusting methane.

## NOMENCLATURE

$D_d$  diffusion coefficient of the deficient reactant,  $m^2/s$

$D_e$  diffusion coefficient of the excess reactant,  $m^2/s$

Le Lewis number ( $= \kappa/D_d$ )

$k_i$  pre-exponential factor in the Arrhenius kinetics of step i

$SF_i$  sensitivity factor of the methane mole fraction to the reaction step i

$S_1$  laminar burning velocity of the hybrid ( $CH_4+H_2$ ) mixture, cm/s

$S_{1,CH_4}$  laminar burning velocity of methane, cm/s

$S_{1,H_2}$  laminar burning velocity of hydrogen, cm/s

$S_{1,Le=1,\alpha=1}$  laminar burning velocity of the hybrid ( $CH_4+H_2$ ) mixture at  $Le = 1$  and  $\alpha=1$ , cm/s

$X_{H_2}$  hydrogen mole fraction in the hybrid ( $CH_4+H_2$ ) mixture

$x_{CH_4}$  methane mole fraction

$x_{H_2}$  hydrogen mole fraction

## Greek symbols

$\alpha$  ratio between the diffusion coefficients of the deficient reactant and of the excess reactant ( $= D_d/D_e$ )

$\alpha_H$  ratio between the maximum value of the H radical mole fraction in the reaction zone and the corresponding value at  $X_{H_2}=0$

$\phi_{CH_4+H_2}$  global fuel ( $CH_4+H_2$ ) equivalence ratio

$\kappa$  thermal diffusivity,  $s/m^2$

## 1.0 INTRODUCTION

In recent years hydrogen-hydrocarbon blends have received increased attention as alternative fuels for power generation applications for two main reasons. The first reason is related to the global warming concern which pushes the interest in the use of hydrogen as energy source in either combustion devices or fuel cells. Indeed, stringent problems of safety and storage make difficult the use of pure hydrogen in most practical combustion applications. In this context, a hydrogen-hydrocarbon hybrid fuel is an attractive solution. The second reason is related to the opportunity of co-feeding hydrogen together with hydrocarbons in order to stabilise lean premixed combustion in stationary applications.

The effective and safe use of hydrogen-hydrocarbon mixtures in practical combustion systems requires that the physiochemical properties of such hybrid fuels have to be determined. To this end, the study of laminar flame propagation is the first step. Indeed, the achievement of a deep knowledge about the laminar flames is relevant not only for laminar propagation but also for understanding the propagation of turbulent flames: in most explosion conditions the premixed turbulent flames may be considered as a set of stretched laminar-like flamelets whose characteristics are the fundamental input parameters for modelling turbulent combustion [3].

The laminar burning velocity of hydrogen-hydrocarbon premixed flames has been evaluated both experimentally [4-8] and theoretically [7-11] for different ranges of the global equivalence ratio and of the hydrogen content in the fuels mixture. The obtained results show that the presence of hydrogen increases the flame speed of the hybrid fuel with respect to that of the pure hydrocarbon, as it can be expected from the higher hydrogen reactivity. Indeed, because of the importance of the H radical in the overall hydrocarbon/air reaction scheme, the addition of hydrogen in the freestream enhances the hydrocarbon burning intensity through the increase of the concentration of the radicals, which otherwise would have to be supplied through back diffusion from the active region where they are generated [5, 10].

Moreover, from all the literature results it can be observed that the laminar burning velocity of hydrogen-hydrocarbon mixtures is substantially less than the proportional averaging of the values for the pure constituents. Among the authors who have realized this trend [4, 7, 9, 11], an attempt of explanation has been furnished only in the numerical study of lean hydrogen-methane premixed flames by Gauducheau et al. [9]. They have related the little increase of the laminar burning velocity at low values of hydrogen addition to the fact that at lean conditions the radical concentrations relevant for the hydrogen/oxygen chemistry, such as H, OH and O, are only slightly increased by the presence of hydrogen compared to the pure methane. However, any demonstration for this has been given. The understanding of the mechanism underlying such behavior is relevant when modeling flame propagation as in this case it is necessary to properly include at least its effect on the combustion rate.

In the present paper we calculated the laminar burning velocity of hydrogen-methane flames to find out the role of the hydrogen on the enhancement of the hybrid fuel burning velocity. We simulated the adiabatic, steady, un-stretched, planar flame propagation by means of the CHEMKIN premixed flame module [1] in which the detailed chemical reaction mechanism GRI-Mech 3.0 [2] was implemented. The laminar flame propagation was simulated in a wide range of equivalence ratio and hydrogen content in the fuels mixture. The computed laminar burning velocities were compared to the linear trend resulting from the combination of the corresponding values of the pure fuels. It is found that the obtained values are lower than the corresponding linear trend. Moreover, the presence of hydrogen is not able to significantly enhance the laminar burning velocity with respect to the methane for hydrogen content lower than a threshold value ( $\approx 70\%$  mol.). We run the sensitivity analysis in order to understand how the interaction between methane and hydrogen reactivities affects the laminar burning velocity. We found that the model results can be explained through the effect of the H radicals on the methane combustion: only at high values of the

hydrogen content the H radicals are sufficient to increase the mixture reactivity by accelerating the methane combustion rate determining step which involves H concentration.

## 2.0 MODEL

### 2.1 Description of the model

The laminar burning velocity of hydrogen-methane mixtures was calculated by implementing the GRI-Mech 3.0 detailed chemical reaction mechanism [2] in the flame propagation module of the CHEMKIN software [1]. A wide range of global fuel equivalence ratios ( $\phi_{\text{CH}_4+\text{H}_2} = [(x_{\text{CH}_4} + x_{\text{H}_2}) / x_{\text{O}_2}] / [(x_{\text{CH}_4} + x_{\text{H}_2}) / x_{\text{O}_2}]_{\text{stoich}}$ ) and of hydrogen contents in the hybrid mixture ( $X_{\text{H}_2} = x_{\text{H}_2} / (x_{\text{CH}_4} + x_{\text{H}_2})$ ) was explored.

The GRI-Mech reaction mechanism has been already used in the study of hydrogen-methane flames [7, 9, 11]. Among these works, Ren et al. [7] have validated this mechanism by comparing the computed results with experiments at low values of the fuel equivalence ratios ( $0.63 \leq \phi_{\text{CH}_4+\text{H}_2} \leq 0.73$ ) and of hydrogen substitution in the fuels mixture ( $0 \leq X_{\text{H}_2} \leq 0.08$ ). In the present paper we extended the validation of the model also to stoichiometric and rich conditions and to higher contents of hydrogen in the hybrid mixtures ( $X_{\text{H}_2} > 0.08$ ).

### 2.2 Literature experimental results

Three sets of experiments were taken into account in order to validate the model. The first set has been obtained by Yu et al. [5] at global equivalence ratio varying in the range  $0.51 \leq \phi_{\text{CH}_4+\text{H}_2} \leq 1.25$  and at low values of hydrogen molar content ( $0 \leq X_{\text{H}_2} \leq 0.75$ ). The second set has been obtained by Liu et al. [6] which have investigated a wide range of experimental conditions. In particular, they have measured the values of the laminar burning velocity in the range 0.7 - 2.2 of equivalence ratio by exploring the entire range of the hydrogen molar fraction in the fuels mixture ( $0 \leq X_{\text{H}_2} \leq 1$ ). The third set by Law & Kwon [8] has been obtained at equivalence ratio values equal to 0.6, 1 and 1.67 and at high values of hydrogen presence ( $0.85 \leq X_{\text{H}_2} \leq 1$ ). The data by Yu et al. and Law & Kwon are corrected to take into account the stretch, while the data by Liu et al. are not stretch-free.

### 2.3 Laminar burning velocity results

We run simulations to calculate the laminar burning velocity of the hydrogen-methane mixture at different values of the global equivalence ratio,  $\phi_{\text{CH}_4+\text{H}_2}$ , by varying the hydrogen content in the fuels mixture,  $X_{\text{H}_2}$ . In order to first validate the model results we run simulations in the same conditions as in the experiments. In Fig. 1 the comparison between the experimental and the model data is shown. It is found a good agreement with the experimental results of Yu et al. [5] and Law & Kwon [8], while a worst agreement is found with the results of Liu et al. [6]. This is related to the fact that the latter experimental values are not corrected for the stretch. This result shows the strong effect of the strain rate on the laminar burning velocity for highly diffusive fuel such as hydrogen. This validation allows us to conclude that the GRI-Mech 3.0 is a good mechanism for the simulations of the laminar burning velocity of hydrogen-methane mixtures in a wide range of global fuel equivalence ratios and of hydrogen contents in the hybrid mixture, thus providing confidence on the results of additional flame simulations that are presented next.

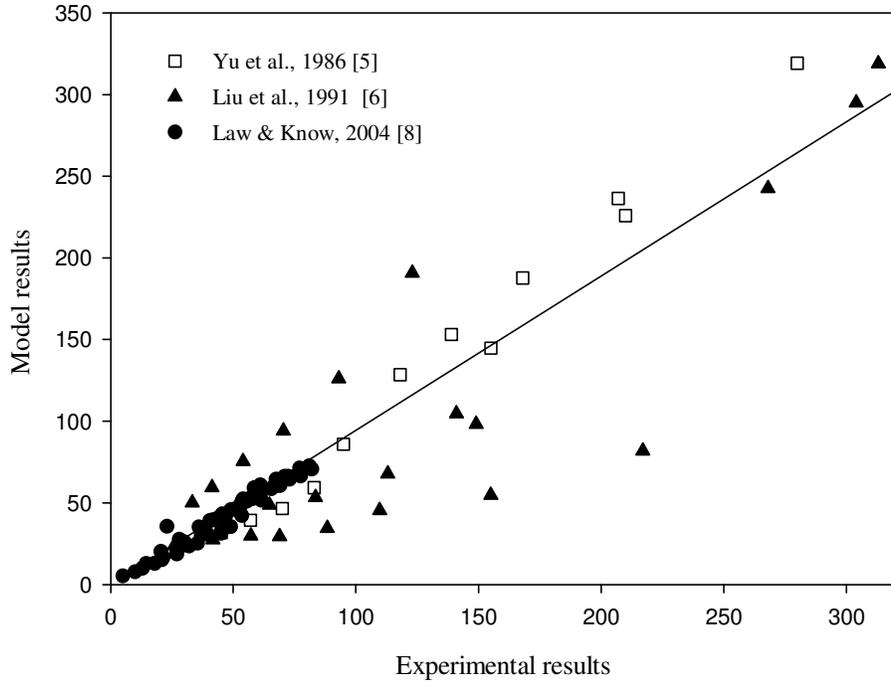


Figure 1. Model versus experimental results of the laminar burning velocity of hydrogen-methane mixtures.

In Fig. 2 the computed values of the laminar burning velocity of hydrogen-methane mixtures,  $S_l$ , are plotted versus the hydrogen molar content in the fuels mixture,  $X_{H_2}$ , at different values of the global equivalence ratio ( $\phi_{CH_4+H_2} = 0.6; 1; 1.5$ ). In the same plot the linear combination of the pure fuels laminar burning velocity is also shown, calculated as follows:

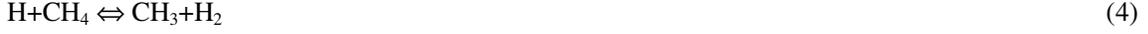
$$S_l(\phi, X_{H_2}) = S_{l,H_2}(\phi) \cdot X_{H_2} + S_{l,CH_4}(\phi) \cdot (1 - X_{H_2}) \quad (1)$$

where  $S_{l,H_2}$  and  $S_{l,CH_4}$  are the laminar burning velocity of the pure constituents (evaluated at the same equivalence ratio, i.e.  $\phi = \phi_{H_2} = \phi_{CH_4} = \phi_{CH_4+H_2}$ ) and  $X_{H_2}$  is the hydrogen molar fraction in the fuels mixture. It is found that the laminar burning velocity of the hybrid fuel is well below the linear trend.

In order to verify if non-equidiffusion effects play a role in determining the difference between the calculated values and the linear trend of the laminar burning velocity, we carried out simulations by assuming the same transport properties for all the species present in the mixture. In particular, we modified the GRI transport file by fixing for hydrogen, methane and oxygen the transport properties of nitrogen. This allowed us to eliminate the disparity between the thermal diffusivity of the mixture and the mass diffusivity of the deficient reactants thus having a mixture Lewis number ( $Le = \kappa/D_d$ ) equal to 1. Moreover, since all the diffusivities are equal the preferential diffusion effects are not present anymore ( $\alpha = D_d/D_e = 1$ ). In these conditions, the computed values of the laminar burning velocity ( $S_{l,Le=1,\alpha=1}$ ), reported in Fig. 2, appear only slightly different from the obtained results for  $S_l$ .

As a conclusion, the non-equidiffusivity is not responsible for the slight enhancement of the laminar burning velocity by hydrogen addition with respect to the linear trend. In order to get insights about the reason why this happens we then run a sensitivity analysis for the simulations of Fig. 2. We found that the methane conversion is controlled by the following reaction steps:





In Fig. 3 the sensitivity factors of the methane mole fraction higher than 1, as defined in Eq.7, are plotted at different hydrogen contents for the three values of the equivalence ratio.

$$SF_i = \frac{k_i}{\chi_{\text{CH}_4}} \frac{\partial \chi_{\text{CH}_4}}{\partial k_i} \quad (7)$$

From Fig. 3 it appears that the fuel equivalence ratio value, i.e. the extent of oxygen excess with respect to the stoichiometric conditions, affects the steps controlling the methane conversion with the exception of step 3. Indeed, at all the equivalence ratio values the step with the higher sensitivity factor for methane molar fraction is step 3 which involves reaction between oxygen and H radicals and produces O and OH radicals necessary for methane oxidation. The relevance of step 3 for methane combustion is well known in the literature [12]. Moreover, it has been recently shown that step 3 is the step through which H<sub>2</sub> addition enhances the methane laminar burning velocity [10].

On increasing the hydrogen content in the hybrid mixture, at all the values of the equivalence ratio, the sensitivity factor of step 3 does not change significantly up to a value of X<sub>H2</sub> higher than about 0.7. On the other side, the hydrogen-methane mixture burning velocity significantly increases only at X<sub>H2</sub> > 0.7, thus suggesting its strong dependence on the fate of H radicals through step 3.

In Fig. 4 the laminar burning velocity and the maximum value of the H radical mole fraction in the reaction zone, α<sub>H</sub>, both normalized by means of the respective values at X<sub>H2</sub>=0, are reported as function of the hydrogen content. It appears that S<sub>l</sub> follows the α<sub>H</sub> trend. This clearly shows that the enhancement of S<sub>l</sub> takes place only at X<sub>H2</sub> > 0.7 since, starting from this value of fuel composition, the methane request of H radicals can be compensated by the hydrogen presence in the fuels mixture.

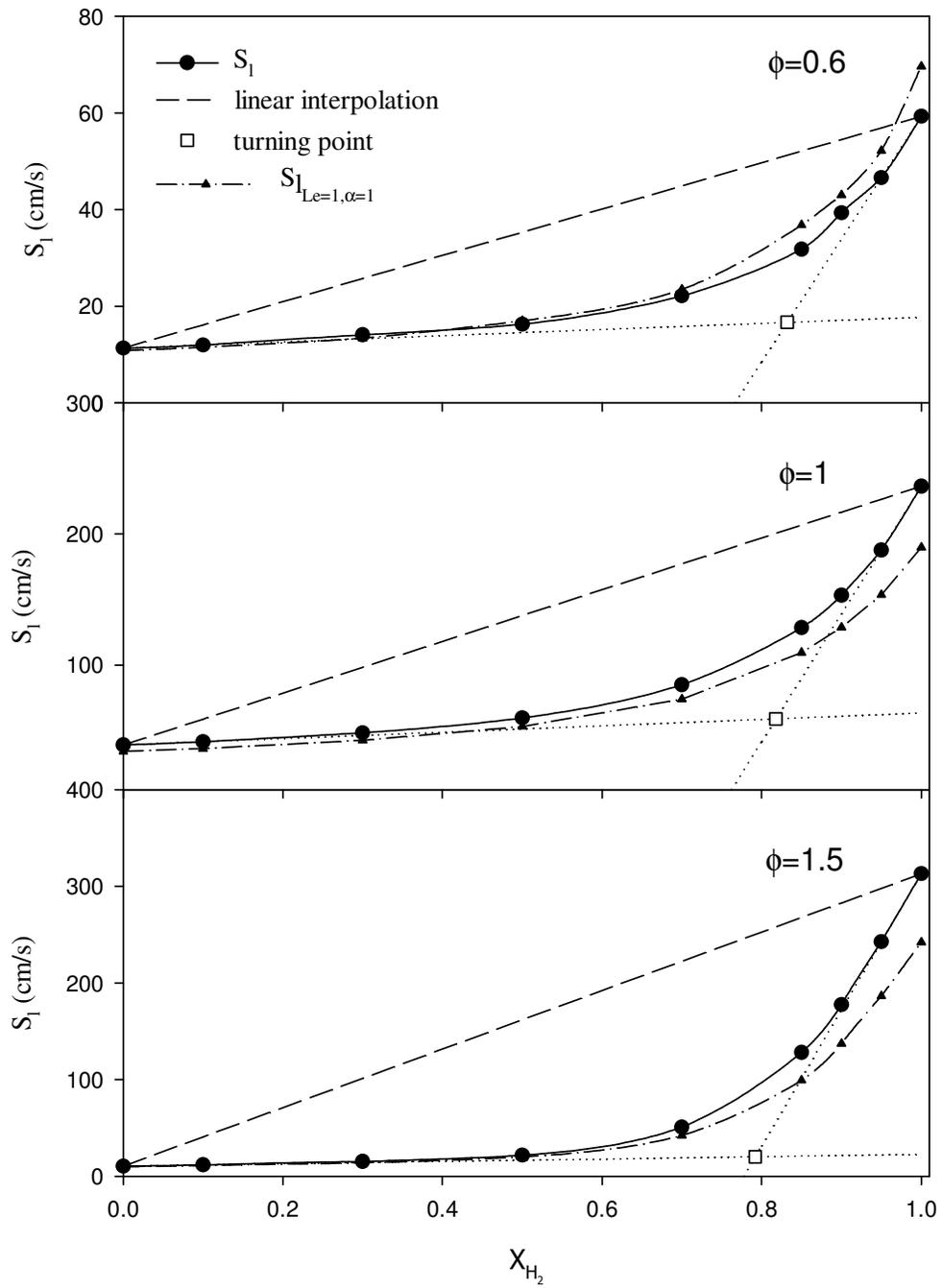


Figure 2. Laminar burning velocity of hydrogen-methane mixtures as function of the hydrogen content at three values of the equivalence ratio.

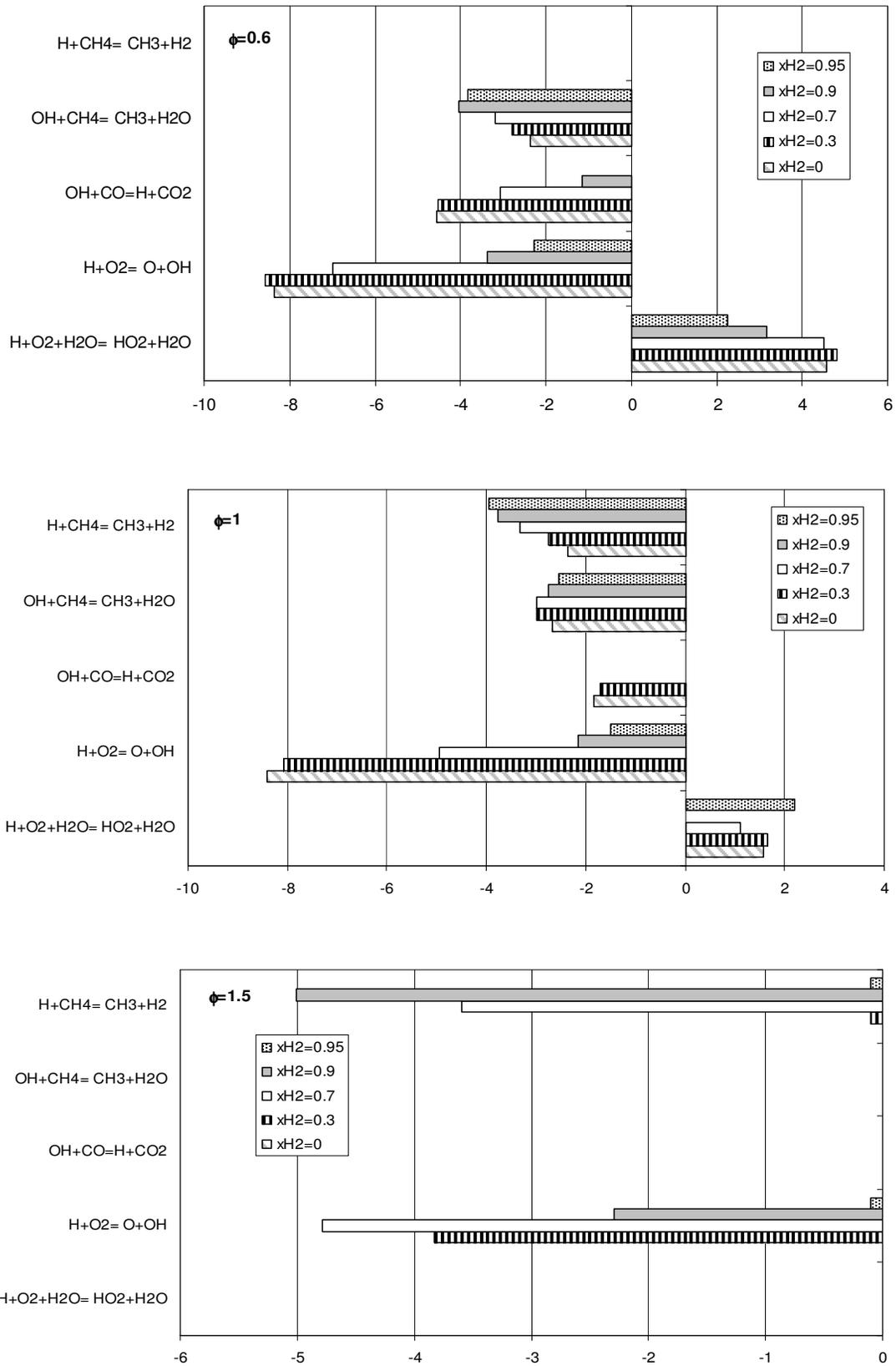


Figure 3. Sensitivity factors of the methane molar fraction as function of the hydrogen content at different values of the equivalence ratio.

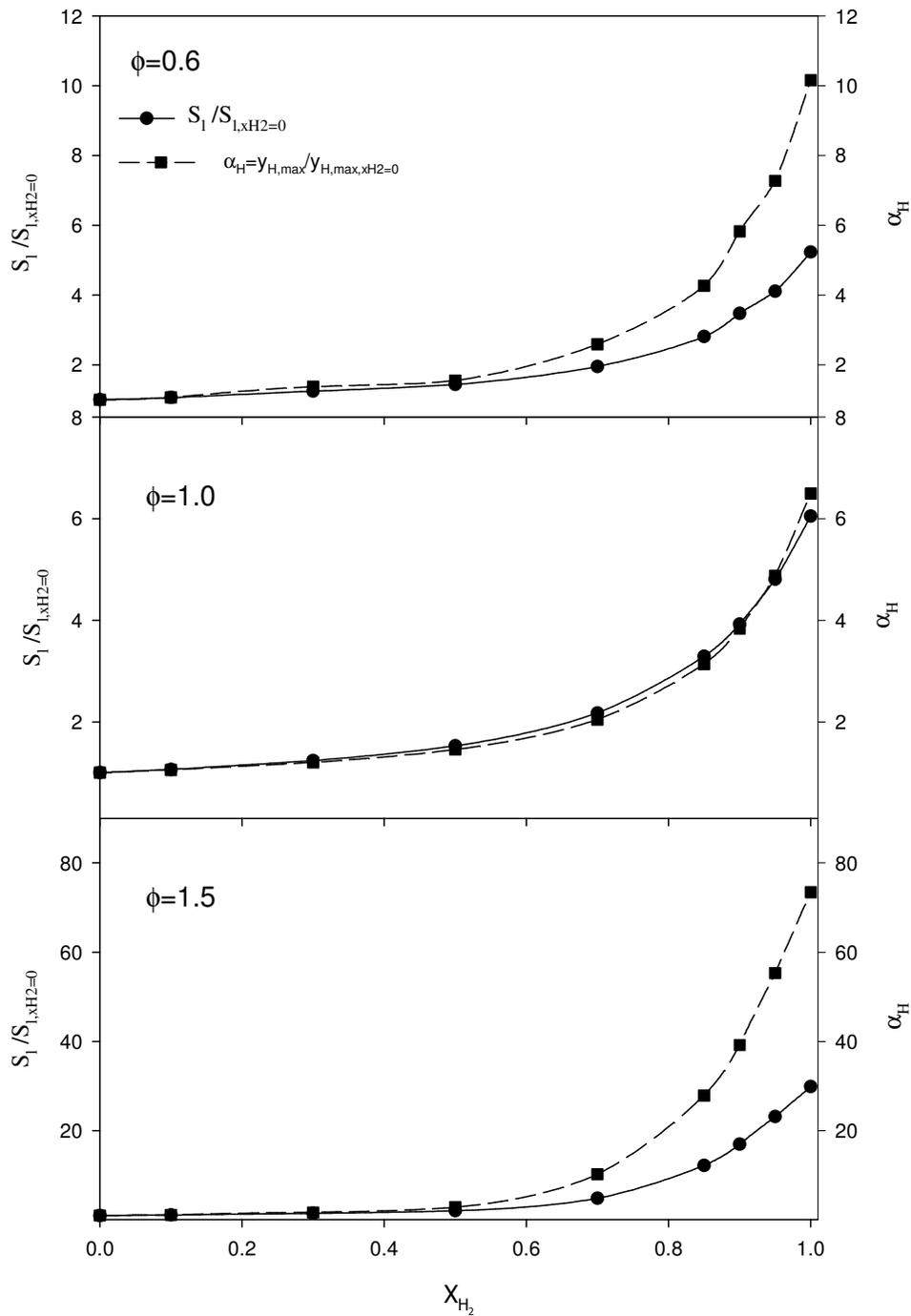


Figure 4. Normalized laminar burning velocity and H concentration as function of the hydrogen content, at different values of the equivalence ratio.

According to the laminar burning velocity and the sensitivity analysis results it is possible to conclude that two regimes may be identified in the hybrid mixtures combustion. The first regime is dominated by the methane combustion and hydrogen is able to only slightly affect the laminar burning velocity as the H radicals pool is not sufficient to accelerate the methane combustion controlled by step 3. It is saying that a similar behavior has been already experimentally found by Yu et al. [5]. In particular, for the same values of the hydrogen blending ( $0 \leq X_{H_2} \leq 0.75$ ), these authors have been able to linearly correlate the laminar burning velocity of the hydrogen-methane flame with the burning velocity without hydrogen addition and a

single parameter indicating the extent of the hydrogen presence. In the second regime the hydrogen combustion has a significant role in enhancing the laminar burning velocity through a relevant production of H radicals. The separation of these regimes may be visualized in Fig. 2 by the two lines crossing at a point which can be viewed as the point of passage from one regime to the other (turning point, □). This point shifts at higher values of the hydrogen content when the equivalence ratio is decreased. At lean conditions a higher amount of hydrogen is required to produce the threshold H radicals pool, as also confirmed by the sensitivity analysis. It is interesting to note that the limiting value of the hydrogen content corresponding to the turning point decreases when the equivalence ratio increases as at rich conditions a higher value of H radicals is present.

The obtained results suggest that in hydrogen-methane turbulent combustion modeling, the equivalence ratio and the hydrogen to methane content fields have to be accurately predicted as their spatial variations may strongly affect the flame propagation. Moreover, due to the high diffusivity of hydrogen with respect to methane and oxygen, it can be expected that in a high strained turbulent flow the local value of hydrogen content may be significantly different from the feed nominal value.

### 3.0 CONCLUSIONS

We studied the laminar flame propagation of hydrogen-methane mixtures by means of the detailed reaction mechanism GRI-Mech 3.0 implemented in the flame propagation module of the CHEMKIN software. Simulations were carried out to evaluate the laminar burning velocity in a wide range of fuel equivalence ratios and of hydrogen contents in the hybrid mixture. The calculated laminar burning velocities were compared to the linear trend resulting from the combination of the corresponding values of the pure fuels. It was found that the computed values are well below the linear trend. Moreover, the effect of hydrogen addition in terms of enhancement of the mixture laminar burning velocity with respect to the methane is efficient only at very high values of the hydrogen content in the hybrid mixtures (> 70 % mol.).

The performed sensitivity analysis showed that these results can be attributed to the strong effect of the radicals interactions on the combustion reaction. In particular, the methane consumption is controlled by the following branching step:



which involves H radicals reacting with oxygen to give O and OH radicals necessary for methane oxidation.

Depending on the hydrogen content in the fuels mixture, the production of the H radicals can affect the limiting reaction step for methane conversion giving rise to two possible regimes in the hydrogen-methane mixtures combustion. The first regime is controlled by the methane reactivity, hydrogen being not able to compensate the methane request of H radicals (< 70 % mol.). In the second regime the hydrogen combustion has a relevant role as its high content in the hybrid fuel leads to a significant H radicals pool, thus enhancing the methane reaction rate. This result is relevant in practical applications where even if the nominal hydrogen content is lower than the found threshold value, the local hydrogen concentration may be higher as the result of the high diffusivity of hydrogen with respect to methane. As a consequence, depending on the spatial-temporal profiles, both the reactivity regimes here identified may establish and have to be properly taken into account in the combustion model and then in the evaluation of the peak pressure in explosions.

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