

Experimental and Numerical Study of rich methane/hydrogen/air Laminar Premixed Flames at Atmospheric Pressure: Influence of Hydrogen Addition on Soot Precursors

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Abstract

A kinetic scheme based on previous studies from this laboratory has been proposed to predict the formation of soot gaseous precursors in sooting methane premixed flames enriched by hydrogen at atmospheric pressure. This study examines the influence of hydrogen in the formation of soot precursors in laminar fuel-rich methane flames. Experiments were performed previously in two flames stabilized by using a McKenna type burner with and without 40% of hydrogen on the fuel. Chemical analyses by FTIR and GC were used for the measurement of the mole fractions of species. The chemical reaction mechanism was validated by comparison with experimental results. Overall, the kinetic modeling presents good agreement with the experimental data. Reactions path analyses have been also carried out.

Introduction

To reduce pollutant emissions from fossil fuels and to cope with the exhaustion of these fuels, great interest has been focused on the use of hydrogen as a potential alternative to fossil fuels. Enrichment by hydrogen is an attractive concept in order to reducing pollutant emissions and also fuel consumption. Previous studies [1-3] showed a decrease of unburned hydrocarbons, carbon monoxide, carbon dioxide and nitrogen oxide, with the addition of hydrogen in hydrocarbon fuels. Indeed the use of H₂ leads a more complete combustion of fuels. Hydrogen can also enhance some fuel performances such as ignition delay times and burning velocities [4-12]. The objective of this present work is the understanding of the chemical details of hydrogen-enriched methane flames in sooting conditions. This work completes our previous studies conducted on the effect of hydrogen on the chemical structure in laminar premixed alkanes flames operating at low and atmospheric pressure [3, 13, 14]. Sepman et al. [2] studied the effect of hydrogen on laminar fuel-rich premixed alkanes (methane, ethane and propane) flames at atmospheric pressure. The authors measured and calculated temperature and NO profiles in methane flames with and without hydrogen addition (0 and 0.2 mole fraction of H₂). They observed a reduction of temperature (~40 K) and NO mole fraction (~20%) in CH₄/20%H₂/Air flames. Konnov et al. [6] studied the effect of hydrogen (10-20%) on the atmospheric methane laminar flame speeds in the large equivalence ratio range ($\phi = 0.8-1.4$). The authors noted a positive effect of hydrogen addition on the laminar burning velocities. Similar observations have been reported by Hu et al. [1] in the case of fuel-lean mixtures. Okafor et al. [7] studied the influence of hydrogen on laminar burning velocities of methane flames in a combustion

chamber at atmospheric pressure, for different equivalence ratios ($\phi = 0.8, 1.0, 1.2$) and initial temperature of 350 K. The fraction of H₂ in fuel varies from 0 to 100%. Authors observed an increase of laminar burning velocities with the fraction of hydrogen in the blend for the three equivalence ratios.

The oxidation of natural gas and methane enriched by hydrogen was also studied in Jet-Stirred Reactor (JSR) conditions [15, 16]. Various concentration profiles of reactants, stable intermediates and final products have been measured. Ignition delays of natural gas/hydrogen/air and methane/hydrogen/air mixtures were also studied in shock tube [9-12] and Rapid Compression Machine (RCM) [17, 18]. They observed a decrease of the ignition delays with the presence of H₂. The accelerating effect of hydrogen is due relative evolution of H, O and OH active species. Zhang et al. [11] studied the ignition of methane/hydrogen blends with various hydrogen volumetric contents (0%, 20%, 40%, 60%, 80% and 100%) in a shock tube at high pressure ($P = 18$ atm), over the temperature range from 900 to 2000 K and equivalence ratios from 0.5 to 2.0. They studied the effects of equivalence ratio on ignition of different fuels. They observed an increase of the ignition delays with the increase of equivalence ratio at high temperature region for H₂ ≤ 80%. At middle-low temperature range the ignition still increases with the increase of equivalence ratios for H₂ ≤ 40%. For 40%CH₄/60%H₂ and 20%CH₄80%H₂ the ignition delay times are insensitive to the variation of equivalence ratio at middle-low temperature region.

The influence of hydrogen addition on soot formation in a coflow laminar methane-air diffusion flame was studied numerically by Liu et al. [19]. Authors observed a reduction of the soot formation (soot volume fraction decreases with H₂ addition) when hydrogen was added to the fuel.

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Proceedings of the European Combustion Meeting 2015

Experimental section

The methane/O₂/N₂ and 60%methane/40%H₂/O₂/N₂ flames were stabilized on a 6-cm diameter McKenna flat flame burner water-cooled. Experiments were performed in sooting conditions with equivalence ratio relative to methane defined as $\phi_c=2(X_{CH_4}/X_{O_2})$ keeping constant at $\phi_c=2.2$ and operating at atmospheric pressure. Table 1 gives the experimental conditions used. The gas mixture is introduced into the burner through internal porous plug. The cold gas flow velocity (V_{gas}^o) were kept quite constant for the two flames studied. A nitrogen flow introduced in a bronze porous ring was used to protect the flame from atmospheric oxygen. In order to stabilize the fuel-rich flame in its upper part, a stainless steel disk was used.

A water cooling circuit water allows to keep the temperature of the burner plate constant during experiments. The sampling system assembly includes a low pressure quartz micro-probe (tip diameter equal to 126 μ m) coupled with Fourier Transform Infrared (FTIR) spectrometry and Gas Chromatography (GC, CP-3800) which allowed to quantify reactants, stable intermediates and final products by moving vertically the micro-probe in the flame in respect to the burner surface.

Table 1. Experimental conditions for the studied flames (Mass flow, Flame 1: 6.75E-03 g/(cm².s), Flame 2: 6.37E-03 g/(cm².s), P=1 atm).

	CH ₄ % vol.	H ₂ % vol.	O ₂ % vol.	N ₂ % vol.	ϕ_c	ϕ_{C+H}	C/O
Flame 1	27.16	-	24.71	48.1	2.2	-	0.55
Flame 2	25.88	10.36	23.54	48.1	2.2	2.42	0.55

The species analyzed by FTIR were water, carbon monoxide and carbon dioxide. Oxygen, hydrogen, carbon monoxide, C₁-C₄ light hydrocarbons (from methane to 1-butene) and small aromatic compounds such as benzene and toluene were analyzed on-line by GC equipped with capillary columns (HP-Plot Al₂O₃ capillary column, \varnothing 0.32 mm and molecular sieve 5A column (\varnothing 0.53 mm) coupled with flame ionization detector (FID), thermal conductivity detector (TCD) and mass spectrometry (MS). In order to reduce water and minimize adsorption of heavy compounds, the sampling system is heated (T=120°C).

Mole fraction obtained in premixed laminar flames configurations were measured versus the height above the burner (HBA). Temperature measurements were performed thanks to a coated Pt/Rh 6%-Pt/ Rh 30% thermocouple in the two flames studied. Note that temperature profiles obtained for the flames with and

without hydrogen have not been corrected for heat losses.

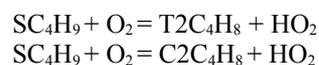
Modeling

Numerical study was performed by using the PREMIX code [20] from the Chemkin II package [21] to compute experimental results obtained in two flames at atmospheric pressure and fuel-rich conditions ($\phi_c = 2.2$). The kinetic parameters were provided in the form of three coefficients A (cm³, mol, and s⁻¹ units), n, and E (cal.mol⁻¹) appearing in the modified Arrhenius equation: $k = AT^n \exp(-E/RT)$

Thermochemical and transport properties of chemical species included in the detailed kinetic mechanism were provided from the literature database [20, 22-25]. The detailed chemical kinetic scheme used in this study is based on the work performed previously by El Bakali et al. [26].

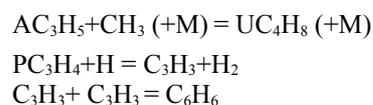
Concentration profiles of main species obtained in Jet-Stirred Reactor were also computed with PSR code [27]. The presented mechanism was also tested against ignition delay times of CH₄ and CH₄/H₂ mixtures obtained in shock tube by using SENKIN computer code [28].

To improve the species predictions which play a key-role in the formation of PAHs and soot such as acetylene (C₂H₂), propyne (PC₃H₄), allene (AC₃H₄) and benzene (C₆H₆), some reactions have been adjusted and added in the present mechanism. The following reactions yielding the isomeric butenes (trans-2-butene and cis-2-butene) by oxidation of 2-butyl radical have been added to the kinetic mechanism:



The kinetic parameters of the previous reactions derived from the recommendations of Pitz [29].

The following reactions have been also updated in the model:



Their kinetic parameters have been taken from the Tsang [30], Saffaripour et al. [31] and Miller et al. [32] investigations.

The final version of the kinetic model used in this work includes 280 species and 1383 reversible reactions. Because of unknown radiative losses of the thermocouple, the uncertainty on the temperature measurements has been estimated at about 80 K at the peak of the profile.

Results and discussion

Concentration profiles results

In this present work, numerical study was conducted for two laminar methane premixed flames with and without hydrogen in fuel-rich mixtures ($\phi_c = 2.2$) and at atmospheric pressure. The oxidation of $\text{CH}_4/\text{O}_2/\text{N}_2$ (Flame 1) and $60\%\text{CH}_4/40\%\text{H}_2/\text{O}_2/\text{N}_2$ (Flame 2) have been performed earlier on a McKenna flat flame burner. The effect of hydrogen on soot gaseous precursors was studied on methane flames. Mole fraction profiles of reactants, stable intermediates and final products are calculated versus the height above the burner. Presented in this section are the comparison between the predictions of the current model and the experimental data of main species which play a key-role in the formation of PAHs (acetylene, propyne, allene, benzene and toluene). They are showed in Figures 1-6 for HAB up to 10 mm.

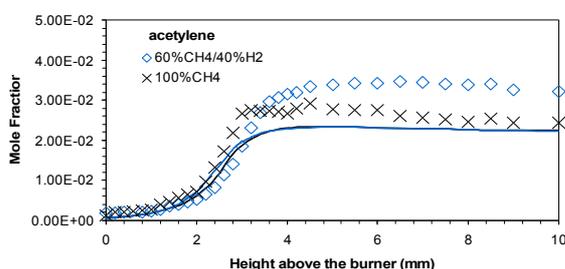


Fig. 1. Experimental mole fraction profiles (symbols) of C_2H_2 obtained in CH_4 and $60\%\text{CH}_4/40\%\text{H}_2$ flames [13] are compared to the computations (100% CH_4 : black line, 60% $\text{CH}_4/0\%\text{H}_2$: blue line).

The present model represents fairly well mole fraction profiles of acetylene (see Fig. 1) for methane flame. However, the effect of hydrogen is not visible for the acetylene specie compared to the experimental data. Similar agreement was observed between the model and experiment for C_3 hydrocarbons species (propyne and allene) in the methane and methane/hydrogen flames, see Figs. 2 and 3.

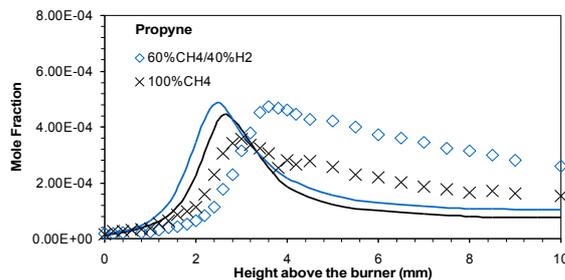


Fig. 2. Experimental mole fraction profiles (symbols) of PC_3H_4 obtained in CH_4 and $60\%\text{CH}_4/40\%\text{H}_2$ flames [13] are compared to the computations (100% CH_4 : black line, 60% $\text{CH}_4/40\%\text{H}_2$: blue line).

The computations show that mole fraction profiles of unsaturated species such as propyne and allene are higher in the methane flame enriched with hydrogen in

the sooting zone.

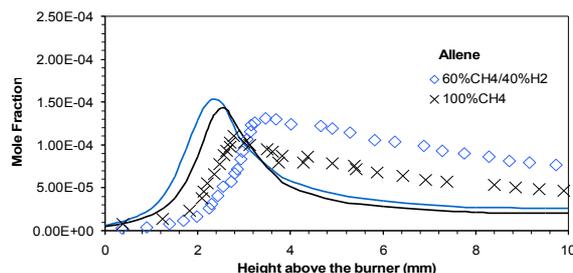


Fig. 3. Experimental mole fraction profiles (symbols) of AC_3H_4 obtained in CH_4 and $60\%\text{CH}_4/40\%\text{H}_2$ flames [13] are compared to the computations (100% CH_4 : black line, 60% $\text{CH}_4/40\%\text{H}_2$: blue line).

As in the experiments, the add of H_2 in the methane flame promotes benzene and toluene formation in the post flame region of methane/ H_2 flame, see Figs. 4 and 5. The computed profiles of single-ring aromatic compounds particularly toluene were in good agreement with the experimental data.

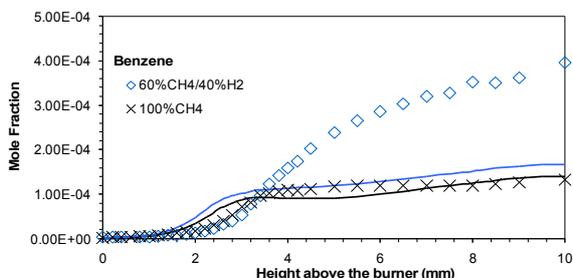


Fig. 4. Experimental mole fraction profiles (symbols) of C_6H_6 obtained in CH_4 and $60\%\text{CH}_4/40\%\text{H}_2$ flames [13] are compared to the computations (100% CH_4 : black line, 60% $\text{CH}_4/40\%\text{H}_2$: blue line).

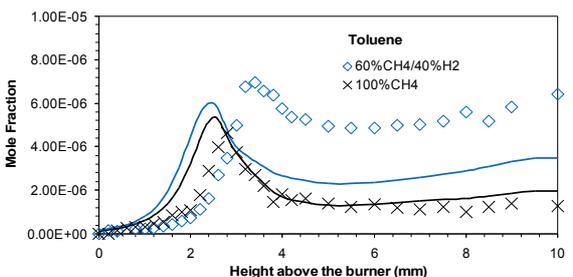


Fig. 5. Experimental mole fraction profiles (symbols) of C_7H_8 obtained in CH_4 and $60\%\text{CH}_4/40\%\text{H}_2$ flames [13] are compared to the computations (100% CH_4 : black line, 60% $\text{CH}_4/40\%\text{H}_2$: blue line).

In order to know the different reactions paths of methane consumption, kinetic analysis on the rate of production and consumption of methane in the two flames was carried out in this work. Methane is mainly consumed via metathesis reactions with H , OH and O atoms. The reaction $\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2$ (1) is the main reaction which dominates the H -abstraction processes in

fuel-rich conditions in the methane flames ($v=4.31E-04$ mol.cm³.s⁻¹). In the methane/hydrogen flames the reaction (1) is still responsible of methane consumption however, the presence of H₂ in the blend reduces the rate of consumption of methane ($v=3.17E-04$ mol.cm³.s⁻¹). These results are in agreement with previous study performed on a sooting CH₄/H₂/Air laminar premixed flame at atmospheric pressure [33]. The formation of benzene in the post flame region is mainly governed by self propargyl radicals recombination $2C_3H_3 = C_6H_6$. However for lower HABs ($x < 2.75$ cm) the reaction between acetylene and 1,3-butadiene-1-yl radical $C_2H_2 + nC_4H_5 = C_6H_6 + H$ was the main reaction path of benzene formation. Sensitivity analyses ($x=0.275$ cm) were also performed but not presented here, for the methane and methane/hydrogen flames under the fuel-rich conditions and atmospheric pressure for some species (propyne and benzene) that promote the formation of PAHs and soot formation.

JSR results

The oxidation of methane enriched with hydrogen has been studied in a Jet-Stirred reactor by Le Cong and Dagaut [34] in various conditions. To validate the current model, results obtained in the literature are compared with simulated results from our kinetic model under a wide range of conditions with variable equivalence ratios ($\phi=0.6$ and 1.5), pressures ($P=1$ and 10 atm), residence times ($\tau=0.12$ and 0.25 s) and temperatures from 925 and 1400 K. In this section only predictions in fuel-rich condition are presented. Results are shown in Fig. 6.

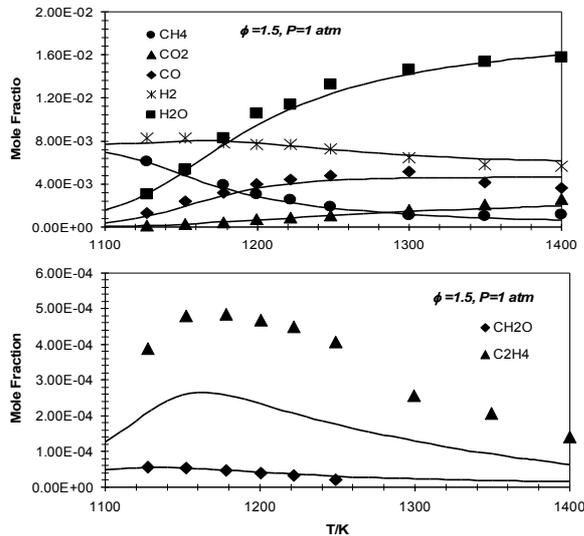


Fig.6. Concentration profiles measured from the oxidation of CH₄/H₂/O₂/N₂ mixtures in a JSR at 1 atm ($\phi=1.5$; $\tau=0.12$ s) by Le Cong and Dagaut [34]. Experimental data (closed symbols) are compared to the computations (lines) from the present model.

As can be seen from the Figure 6, the predictions from the proposed mechanism represent reasonably well the mole fraction profiles of the main species (CH₄, H₂, CO, CO₂, H₂O, CH₂O) obtained in JSR by Le Cong and Dagaut [34]. However, the mole fraction of ethylene was underestimated.

Ignition delay times results

This section presents a comparison between the experimental data from literature [11] and simulation results from the current model on the ignition delays for methane flames with and without hydrogen. In order to test the validity of our model under shock tube conditions, experimental data obtained in shock tubes were compared to our computed results.

Zhang et al. [11] studied the ignition of methane/ (0%, 20%, 40%) hydrogen blends in a shock tube at high pressure ($P = 18$ atm), at temperatures ranging from 1220 to 1968 K and under fuel-rich condition ($\phi=2.0$).

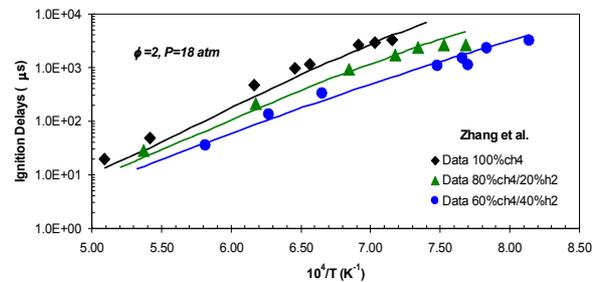
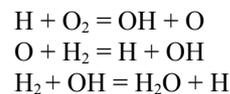


Fig. 7. Ignition delays for 100%CH₄, 80%CH₄/20%H₂ and 60%CH₄/40%H₂ at $P=18$ atm, $\phi=2$. Comparison between experimental data measurements by Zhang et al. [11] (closed symbols) and present modeling results (solid line).

The effects of hydrogen addition on the auto-ignition of CH₄/H₂ blends are shown in Figure 7. As can be seen from this figure, the computed ignition delays are in good agreement with the experimental data of Zhang et al. [11]. However, the ignition delays are slightly shorter than measured for 100% CH₄. The ignition delay times decrease as the amount of hydrogen in the mixture is increased (Fig.7). This is explained by the rise of the production of H, OH and O radicals via the following reactions when H₂ is added in the fuel:



Conclusions

The objective of the present work is to identify the impact of hydrogen on the chemical structure of atmospheric methane flames, especially on the some instaurated aliphatic species considered as benzene and/or PAHs precursors. A detailed chemical kinetic mechanism has been validated against experimental results

obtained in the case of atmospheric rich premixed methane flames with and without hydrogen ($X_{H_2} = 0$ and 40% in fuel). A good agreement between the proposed model and experiments was found for the most stable species analysed. Species mole fraction obtained in JSR conditions are also well predicted by the model.

Reactions path analyses showed that self propargyl recombination radicals is the most source of benzene formation in the post flame region whereas the addition of acetylene on the nC_4H_5 radicals governs its formation in the reaction zone.

Acknowledgments

The research leading to these results was supported by the labex Chemical and Physical Properties of the Atmosphere (CaPPA) through the Programme d'Investissement d'Avenir (ANR-11-LABX-005-01).

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