The Third Fuel & Combustion Conference of IRAN

Tehran - IRAN Feb. 2010

Amirkabir Univ. of Technology
Aerospace Engineering Dept.

Iranian Combustion Institue

FCCI2010-1176

IMPROVING COMBUSTION BEHAVIOUR OF METHANE-AIR MIXTURES BY ADDITION HYDROGEN

A. R. Moghiman*,§, S. Baghdar Hosseini ** and M. Moghiman ***
* Islamic Azad University of Mashhad
** Islamic Azad University of Mashhad
*** Ferdowsi University of Mashhad
(§ amirmoghiman@yahoo.com)

ABSTRAC The methane–hydrogen–air freely propagated laminar premixed flames at normal temperature and pressure over a wide range of equivalence ratios and hydrogen fractions. The calculations are preformed by using PREMIX code of CHEMKIN II program with GRI-Mech 3.0 mechanism. The effect of hydrogen addition on temperature, pollutant species including, CO_2, CO, NO and NO_2 also CH_4 are investigated. The results show that the mole fractions of CH_4 and carbon-related species such as CO and CO_2 decrease as hydrogen is added. The reduction of carbon related species gives a potential to reduce the soot formation and aldehydes emissions from methane combustion. The results also show that the unstretched laminar burning velocity is increased hydrogen addition and the peak value of the unstretched laminar burning velocity shifts to the richer mixture side by increasing hydrogen fraction. The results reveal that flame temperature in the reaction zone is increased slightly with hydrogen addition and it has a little influence on NO_x formation in methane combustion. The calculated results compare well with the experimental measurements.

Keywords methane - hydrogen - premixed combustion - pollutants.

INTRODUCTION

Atmospheric pollutant emission and energy shortage are the main issues that industrial countries have to deal with them. About 85% of the total energy consumption of the world is obtained by fossil fuels (coal, petroleum, natural gas). The main combustion products such as CO, CO_2, NO_x, soot particles and their green house effect have to be considered [Chaumeix N 2007]. With reduction of crude oil reserves, the development of alternative fuel engines has been interested more and more in the combustion community. Natural gas is considered to be one of the approving fuels for engines and industrial furnaces. The combustion of natural gas produces fewer carbon related species emissions than that of gasoline and the gas oil fuels [Jinhua Wang 2007]. However natural gas which methane is its major spicies, has some disadvantages like slow burning velocity, low thermal efficiency, large cycle-by-cycle variation, and poor lean-burn capability. These characteristics of natural gas reduce the engine power output and rise the fuel consumption [S. Rousseau 1990, L. Ben 1999].

One of the beneficial methods to solve these problems is to blend the natural gas with a fuel that has high burning velocity. Hydrogen is considered as a good gaseous additive to enhance the combustion of natural gas. It will also increase gas reactivity, the flammability and stability ranges of the flame and the performance conditions can be moved towards lean combustion [Jackson GS 2003, Gauducheau JL 1998,] Ren J-Y 2001, Bell SR 1991]. Consequently, experimental and numerical researches have been conducted on the combustion characteristic of methane-hydrogen-air mixtures. A relatively early research (not first) was conducted by Varde [1981]. He studied the combustion characteristics of a single-cylinder spark ignition engine using hydrogen enriched gasoline, and concluded that small amount hydrogen addition could extend the lean limit and enhance the engine's thermal efficiency as well as combustion stability. Collier et al. [1996] investigated the untreated exhaust emissions of a hydrogen-enriched CNG production engine. They concluded that the addition of hydrogen would increase NO*x* and decrease total hydrocarbon emissions. Combustion stability was also improved as observed in their study. Larson and Wallace showed that spark ignition engines operated on a blend of natural gas and hydrogen produced lower exhaust emissions. Schefer RW [2003] further showed that hydrogen addition to natural gas extended the lean engine operating limit. Wang et al. [2007] examined the combustion behaviors of a direct-injection engine fuelled with various fractions of NG–hydrogen blends. The results showed that the brake effective thermal efficiency increased with the increase of hydrogen fraction at low and medium load. Yu et al. [1986] studied the laminar burning velocity of methane–hydrogen mixtures and showed that the laminar burning velocities of methane–hydrogen mixtures increased linearly with the increase of hydrogen fraction in the fuel blends. Halter et al. [2005] investigated the effect of initial pressure and hydrogen fraction on the laminar burning velocity of methane–hydrogen flame and they concluded that the laminar burning velocity increased with the increase of hydrogen fraction in fuel mixture and deceased with the increase of initial pressure.

The aim of this paper is to predict numerically the effect of hydrogen addition on flame temperature, pollutant species including, NO, NO_2, CO and CH_4 also CO_2 in methane-air combustion systems.

COMPUTATIONAL METHODS AND MECHANISM VALIDATION

The laminar burning velocities of hydrogen–methane/air mixtures at 300K and 1 atm were calculated by varying the equivalence ratio from lean to rich conditions and the fuel composition from pure methane to mixture of methane and hydrogen.

The volumetric percentage of hydrogen in the fuel blends (X_{H_2}) is defined as,

$$X_{H_2} = \frac{V_{H_2}}{V_{CH_4} + V_{H_2}} \tag{1}$$

where F/A is fuel–air ratio and $(F/A)_{st}$ refers to the stoichiometric value of F/A. For stoichiometric methane–air and hydrogen–air mixture combustion, the chemical formulas are as follows:

$$CH_4 + 2(O_2 + 3.76N_2) = CO_2 + 2H_2O + 2\times 3.76N_2 \tag{2}$$

$$H_2 + 0.5(O_2 + 3.76N_2) = H_2O + 0.5\times 3.76N_2 \tag{3}$$

mixture can be expressed as,

$$\left(1-X_{H_2}\right)CH_4 + X_{H_2}.H_2 + \left(\frac{2}{\phi}(1-X_{H_2}) + \frac{X_{H_2}}{2\phi}\right)\left(O_2 + 3.76N_2\right) \quad (4)$$

Table 1 shows that the reactant mole fraction of CH_4 is decreased with the increase of hydrogen fraction and this will affect the mole fraction of the carbon-related species in the flames.

Table 1
Reactant mole fractions of the calculated flames

Flame no.	H_2% (vol.%)	Methane	Hydrogen	Oxygen	Nitrogen
1	**0**	**0.095**	**0**	**0.19**	**0.715**
2	**10**	**0.0918**	**0.0102**	**0.1887**	**0.7093**
3	**20**	**0.088**	**0.022**	**0.187**	**0.703**
4	**30**	**0.0838**	**0.0358**	**0.185**	**0.6956**

A freely propagating adiabatic, premixed, planar flame was simulated using PREMIX [Kee RJ 1985], Sandia's steady state, laminar, one-dimensional flame code. PREMIX uses a hybrid time integrating/Newton iteration technique to solve the steady state mass, species and energy conservation equations and can simulate the propagating flame. Equations were solved by using the TWOPNT, a boundary value problem solver in the CHEMKIN package [Kee RJ 1989]. Also built in the CHEMKIN package area transport property processor and a gas-phase interpreter which provide the species transport properties and process the chemical reaction mechanism.
GRI-Mech is an optimized detailed chemical reaction mechanism for the calculation of natural gas chemical reaction process and the latest version is GRI 3.0. GRI 3.0 consists of 325 elementary chemical reactions with associated rate coefficient expressions and thermo chemical parameters for the 53 species. It includes the detailed combustion reaction mechanism for hydrogen. The ranges of GRI 3.0 are 1000–2500 K in temperature, 10 torr–10 atm in pressure and 0.1–5 in equivalence ratio.To simulate and interpret the effect of hydrogen addition on methane–air chemical reactions, the chemical kinetics mechanism used in the calculation must be capable of the calculation of the pure methane and methane–hydrogen fuel blends. Prior to the calculation, the GRI 3.0 mechanism needs to be validated by the experimental results. Figures 1,4 plot the unstretched laminar burning velocities of methane–hydrogen–air mixture both this study and the experimental data in literatures for the comparison. The results show that the data of the present study agree well with those of literatures in methane–hydrogen–air flames.
The results predict that the GRI 3.0 can well reproduce the laminar burning velocity of methane–hydrogen–air mixtures at stoichiometric mixture combustion and both rich and lean mixture combustion as well as wide range of hydrogen fractions.

Error! Not a valid link.
Figure 1. Comparison between the calculated and experimental laminar burning velocities of pure methane-air mixture

Error! Not a valid link.
Figure 2. Comparison between the calculated and experimental laminar burning velocities of methane-hydrogen-air mixture

Error! Not a valid link.
Figure 3. Comparison between the calculated and experimental laminar burning velocities of methane-hydrogen-air mixture
Error! Not a valid link.
Figure 4. Comparison between the calculated and experimental laminar burning velocities of methane-hydrogen-air mixture

RESULTS AND DISSCUTIONS

Figure 5, presents the effect of hydrogen fraction on maximum temperature inside the furnace. The figure shows that an increase in hydrogen mole fraction, slowly increases the maximum temperature inside the furnace.This occurs because the fuel composition from pure methane is changed to a mixture of methane and hydrogen (see eq.4). This is in accords with results of Jinhua Wang et al. [2009] It can be seen by addition 30% hydrogen fraction the equilibrium adiabatic flame temperature increases only 6 k from the pure methane flame to the methane-hydrogen flame.

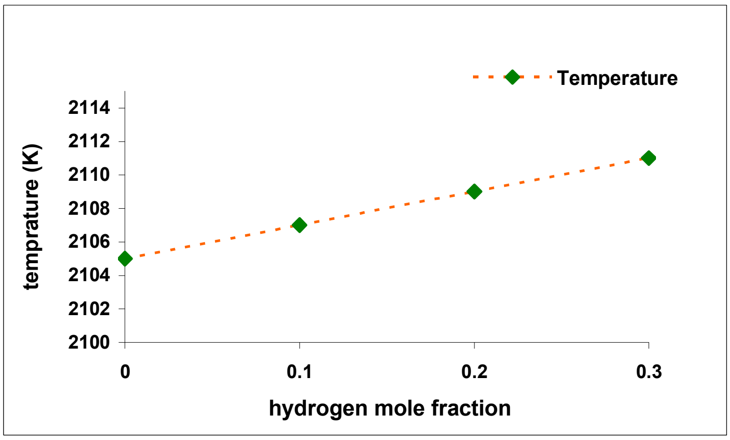

Figure 5. Effect of hydrogen fraction on maximum temperature

Figure 6, shows the Variations of CH_4 mole fraction along the furnace centerline for different hydrogen volumetric percentation. The figure shows that the combustion of ch4 is started from about x = 0.05cm and it is consumed completely at about x = 0.1 cm. CH_4 mole fraction is decreased with the increase of hydrogen addition. This is due to reduction of reactant CH4 mole fraction and the enhancement of chemical reaction as hydrogen is added. The dominant reactions contributing to CH_4 are as follows

$$OH + CH_4 \Leftrightarrow CH_3 + H_2O \qquad \text{(R98)}$$

$$H + CH_4 \Leftrightarrow CH_3 + H_2 \qquad \text{(R53)}$$

$$O + CH_4 \Leftrightarrow OH + CH_3 \qquad \text{(R11)}$$

$$H + CH_3(+M) \Leftrightarrow CH_4(+M) \qquad \text{(R52)}$$

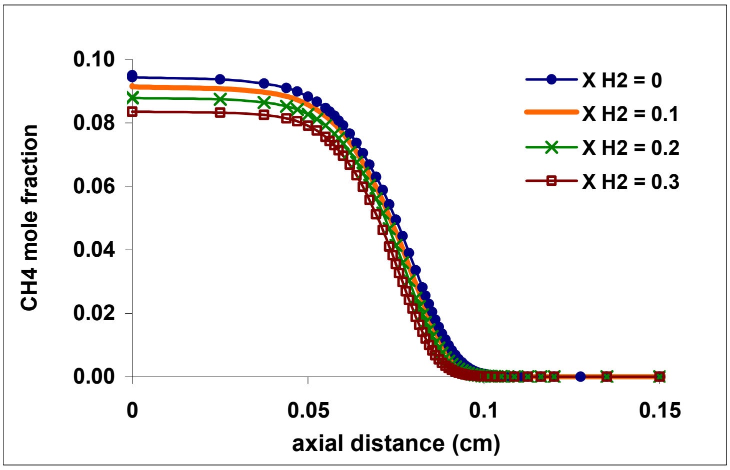

Figure 6. Variations of CH_4 mole fraction along the furnace centerline for different hydrogen volumetric percentation

Figure 7, illustrates the variations of CO mole fraction along the furnace center line for different hydrogen volumetric percentation. The mole fraction of CO is decreased with increase of hydrogen fraction and this is due to the decrease of reactant CH_4 mole fraction with the increase of hydrogen fraction. The main CO formation reaction pathways are,

$$HCO + O_2 \Leftrightarrow HO_2 + CO \qquad \text{(R168)}$$

$$HCO + H_2O \Leftrightarrow H + CO + H_2O \qquad \text{(R166)}$$

and the main CO consumption reaction is,

$$OH + CO \Leftrightarrow H + CO_2 \qquad \text{(R99)}$$

Figure 8, depict the mole fraction of CO_2 along the furnace centerline for different hydrogen volumetric percentation. The CO_2 mole fraction is decreased as hydrogen is added since the reactant CH_4 mole fraction is decreased with hydrogen addition.

Figure 9, shows the NO mole fraction along the furnace line for different hydrogen volumetric percentation Preceding studies in flame and engines demonstrated that the NOx emission concentration of methane-air combustion was increased as hydrogen is added especially at larger hydrogen fraction [Jinhua Wang 2007, Fanhua Ma 2009, Hongsheng Guo 2005] due to the increase of combustion temperature as hydrogen is added. NO mole fraction is decreased slightly with hydrogen addition.

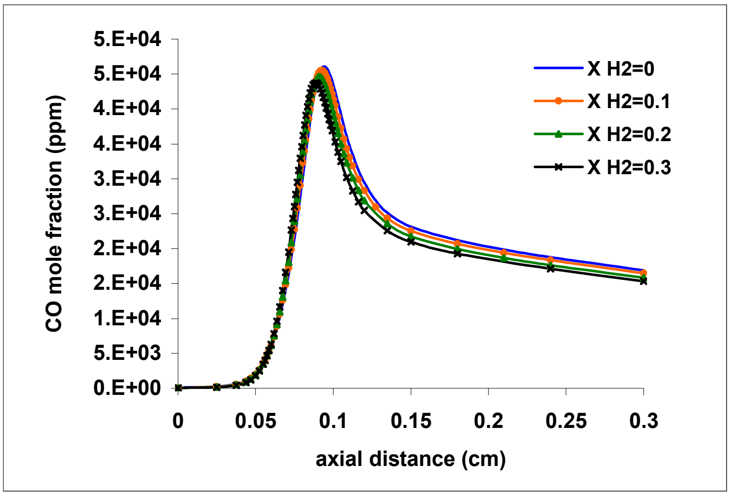

Figure 7. Variation of CO mole fraction along the furnace centerline for different hydrogen volumetric percentation

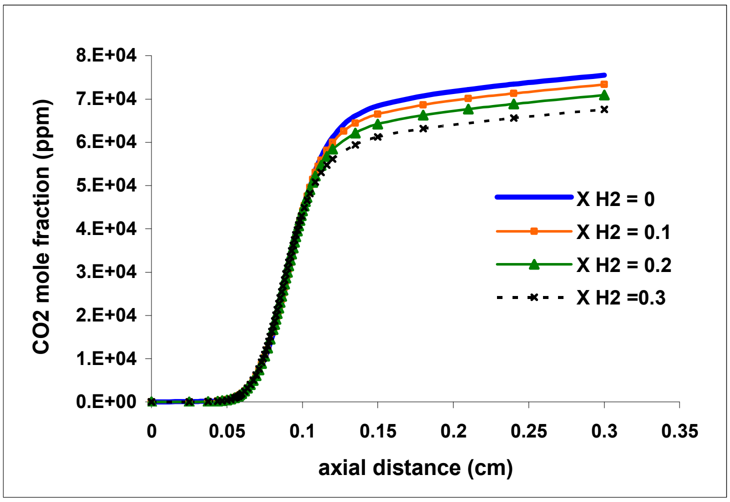

Figure 8. Variation of CO_2 mole fraction along the furnace centerline for different hydrogen volumetric percentation

Figure 10, shows the NO_2 mole fraction along the furnace line for different hydrogen volumetric percentation. The mole fraction of NO_2 is decreased a little with hydrogen addition. The flame temperature in the reaction zone is increased slightly with hydrogen addition as illustrated in Figure 5. It is well-known that the NO can be formed through the thermal, the N_2O intermediate and the prompt routes [Hongsheng Guo 2005]. the thermal mechanism which is also called the Zeldovich mechanism is the main route in the methane–hydrogen–air premixed flame. The dominant reactions contributing to NO are,

$$N + OH \Leftrightarrow NO + H \tag{R180}$$

$$N + O_2 \Leftrightarrow NO + O \tag{R179}$$

$$HNO + H \Leftrightarrow H_2 + NO \tag{R214}$$

$$NO_2 + H \Leftrightarrow NO + OH \tag{R189}$$

$$CH_2 + NO \Leftrightarrow H + HCNO \tag{R249}$$

$$HO_2 + NO \Leftrightarrow NO_2 + OH \tag{R186}$$

One of the reactions contributing in producing N is R240: CH+N_2↔HCN+N. It can be seen from table 1, that the mole fraction of reactant N_2 is decreased slightly with hydrogen addition. The CH mole fraction will decrease as hydrogen is added [Hongsheng Guo 2005].Moreover, the flame temperature is kept almost invariable with hydrogen addition. These will shift the reaction R240 to the left direction and decreases N which would affect the NO_x production.

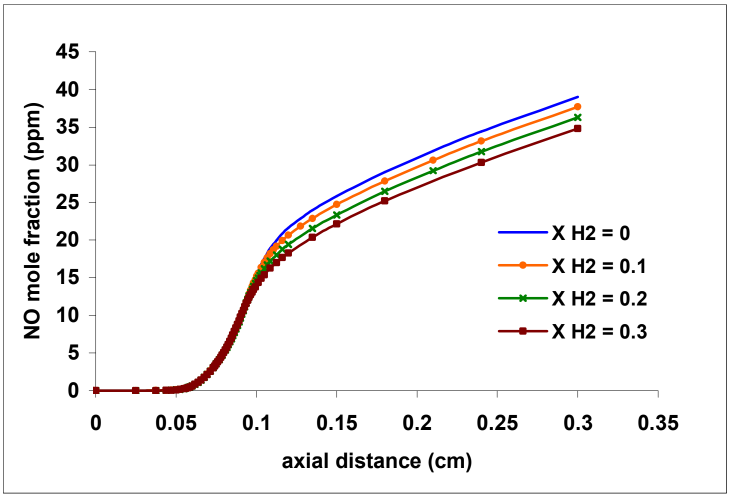

Figure 9. Variation of NO mole fraction along the furnace centerline for different hydrogen volumetric percentation

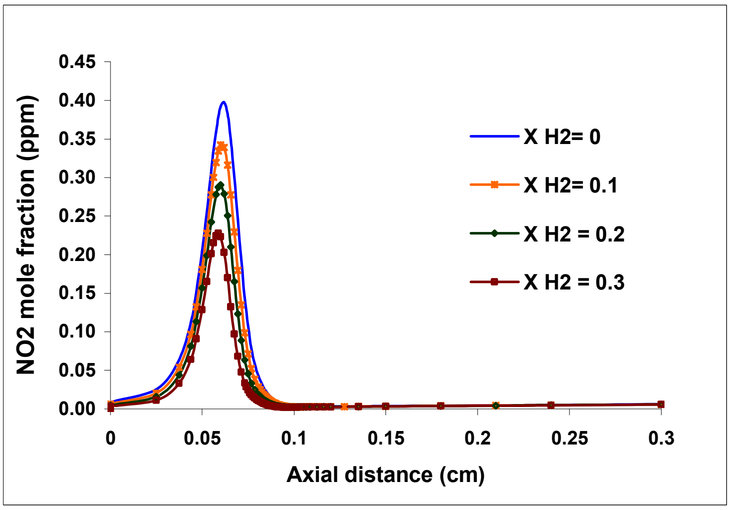

Figure 10. Variation of NO_2 mole fraction along the furnace centerline for different hydrogen volumetric percentation

CONCLUSIONS

In this study, stoichiometric methane–hydrogen–air freely propagated laminar premixed flames were calculated by using PREMIX code of CHEMKIN II program with GRI-Mech 3.0 mechanism. The effect of hydrogen addition and equivalence ratio on the pollutants of methane–air combustion was surveyed. Based on the presented results, the following conclusions may be drawn:

- The mole fraction of CH_4 and carbon-related species are decreased with hydrogen addition to methane-air mixture.
- The addition of hydrogen to methane-air mixture decreases pollutant emissions from methane-air combustion system.
- The addition of hydrogen to methane-air mixture has a little influence on both furnace temperature and NO formation.
- Comparison of experimental measurements with computed results shows good agreement.

REFERENCES

Bell SR, Gupta M. Extension of the lean operating limit for natural gas fueling of a spark ignited engine using hydrogen blending. Combust Sci Tech 1997; 123:23–48.

Chaumeix N, Pichon S, Lafosse F, Paillard CE [2007], Role of chemical kinetics on the detonation properties of hydrogen/ natural gas/air mixtures. International Journal of Hydrogen Energy;32(13):2216–26.

Collier K, Hoekstra RL, Mulligan N, et al [1996],Untreated exhaust emissions of a hydrogen-enriched CNG production engine conversion. SAE paper no. 960858.

Fanhua Ma, Yu Wang, Haiquan Liu, Yong Li, Junjun Wang, Shuli Zhao[2007], Experimental study on thermal efficiency and emission characteristics of a lean burn hydrogen enriched natural gas engine. International Journal of Hydrogen Energy; 32(18):5067–75.

Gauducheau JL, Denet B, Searby G. A numerical study of lean CH4/H2/air premixed flames at high pressure. Combust Sci Tech 1998;137:81–99.

Halter F, Chauveau C, Djebaili-Chaumeix N, Gokalp I. Characterization of the effects of pressure and hydrogen concentration on laminar burning velocities of methane– hydrogen–air mixtures. Proceedings of the Combustion Institute 2005;30(1):201–8.

Hongsheng Guo, Smallwood Gregory J, Fengshan Liu, Yiguang Ju, Gulder Omer L. The effect of hydrogen addition on flammability limit and NOx emission in ultra-lean counterflow CH4/air premixed flames. Proceedings of the Combustion Institute 2005;30(1):303–11.

Jackson GS, Sai R, Plaia JM, Boggs CM, Kiger KT [2003], Influence of H2 on the response of lean premixed CH4 flames to high strained flows. Combust Flame;132:503–11.

Jinhua Wang, Zuohua Huang, Yu Fang, Bing Liu, Ke Zeng, Haiyan Miao, et al [2007], Combustion behaviors of a directinjection engine operating on various fractions of natural gas–hydrogen blends. International Journal of Hydrogen Energy;32(15):3555–64.

Jinhua Wang, Zuohua Huang, Chenglong Tang, Haiyan Miao, Xibin Wang [2009], Numerical study of the effect of hydrogen addition on methane–air mixtures combustion. International Journal of Hydrogen Energy; 34: 1084-1096

Kee RJ, Grcar JF, Smooke MD, Miller JA. PRMIX: a FORTRAN program for modeling steady laminar one-dimensional premixed flames. Report. Sandia National Laboratories; 1985.SAND 85–8240.

Kee RJ, Rupley FM, Miller JA. CHEMKIN-II: a fortran chemical kinetics package for the analysis of gas-phase chemical kinetics. Technical report SAND89-8009. Sandia National Laboratories; 1989.

L. Ben, N.R. Dacros, R. Truquet, G. Charnay [1999] , Influence of Air/Fuel Ratio on Cyclic Variation and Exhaust Emission in Natural Gas SI Engine, SAE Paper 992901.

Ren J-Y, Qin W, Egolfopoulos FN, Tsotsis TT [2001], Strain-rate effects on hydrogen-enhanced lean premixed combustion. Combust Flame;124:717–20.

Schefer RW [2003] Hydrogen enrichment for improved lean flame stability. International Journal of Hydrogen Energy; 28(10):1131–41.

S. Rousseau, B. Lemoult, M. Tazerout, Proc. Inst. Mech. Eng. D J. Automobile Eng. 213 (D5) (1999) 481–489.

Varde KS [1981], Combustion characteristics of small spark ignition engines using hydrogen supplemented fuel mixtures. SAE paper no. 810921.

Wang J, et al [2007], Combustion behaviors of a direct-injection engine operating on various fractions of natural gas-hydrogen blends. IntJ Hydrogen Energy, [doi:10.1016/j.ijhydene.2007.03.011.]

Yu G, Law CK, Wu CK [1986], Laminar flame speeds of hydrocarbon þ air mixtures with hydrogen addition. Combustion and Flame;63(3):339–47.