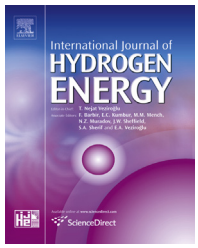
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 40 (2015) 3777–3788

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Detailed influences of chemical effects of hydrogen as fuel additive on methane flame

Yaoyao Ying, Dong Liu *

School of Energy and Power Engineering, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China

ARTICLE INFO

Article history:
Received 8 December 2014
Received in revised form
12 January 2015
Accepted 14 January 2015
Available online 7 February 2015

Keywords:
Methane flame
Hydrogen addition
Chemical effects
Kinetic analysis
Blended fuel

ABSTRACT

A detailed kinetic analysis of chemical effects of hydrogen addition on laminar premixed stoichiometric methane-air flames was conducted at atmospheric pressure. Flame structures and mole fraction profiles affected by chemical effects of hydrogen addition for major species, free radicals and intermediate species are analyzed with particular emphasis on the formations of soot precursor and oxygenated air pollutants. The results illustrate that chemical effects of hydrogen additive lead the methane profile to move towards the upstream side and suppress the formation of acetylene and ketene. The concentrations of free radical H, O and OH increase as methane is replaced by hydrogen mainly due to its chemical effects. In contrast, although the chemical effects of hydrogen addition facilitate the productions of formaldehyde and acetaldehyde, the hydrogen dilution and thermal effects on reducing mole fractions of both species are more significant. As a consequence, the total effects of hydrogen addition lead to a decrease in formaldehyde and acetaldehyde concentrations. Compared to formaldehyde and acetaldehyde, NO mole fraction diminishes in a similar fashion with increased hydrogen additive that the decrease of NO concentration caused by hydrogen dilution and thermal effects is larger than the increase due to its chemical effects.

Introduction

With the increasing concern of energy saving and emission reduction, many small hydrocarbons have been used widely as potentially important replacements for conventional fossil fuel. Methane, as the main composition of natural gas, has received lots of research interest, since it is regarded as one of the most promising alternative and cleanest fuels in combustion [1]. Due to its unique tetrahedral molecular structure with large C–H bond energies, methane has a high ignition temperature, low flame propagation velocity and low reactivity, which lead to narrow flammability limits [2]. Several basic combustion chemistry researches of methane have been carried out [3–6]. Dounit et al. [3] validated the natural gas combustion in a fluidized-bed reactor via modeling and experiment, and they found that initial conditions, e.g. the dense bed temperature, the fluidizing velocity and the mean particle diameter had a remarkable effect on combustion. Matynia et al. [4] used laser-induced fluorescence to measure OH mole fraction profiles in high-pressure premixed counterflow CH_4/air and CH_4/CO_2/air laminar flames and compared the measurements with simulations using three different kinetic mechanisms. Xie et al. [5]

* *Corresponding author*. Tel.: +86 18362962967; fax: +86 25 84314960.
E-mail address: dongliu@njust.edu.cn (D. Liu).
http://dx.doi.org/10.1016/j.ijhydene.2015.01.076

experimentally and numerically investigated the effects of high CO_2 dilution on characteristics including combustion chemical reaction, flame instability and flame radiation of laminar $CH_4/CO_2/O_2$ flames. Sadeghi et al. [6] conducted a study on the effects of equivalence ratios, inlet mixture velocity and dilution on premixed methane-oxygen flame dynamics in a meso scale reactor.

Hydrogen is also extensively investigated as a clean fuel or fuel additive, because hydrogen combustion ideally does not generate any pollutant emissions other than oxides of nitrogen. Moreover, hydrogen exhibits some unique combustion characteristics such as low ignition energy (only 6 percent of methane), high flame speed, wide flammability limits which is 2 times to that of methane [2], and high reactivity etc. Therefore, one of effective ways to improve the combustion characteristics of methane is to add hydrogen to methane, which can efficiently promote methane combustion [7–12]. Fotache et al. [10] conducted an investigation on the effects of hydrogen addition on ignition of nonpremixed, counterflowing jets of methane vs heated air experimentally and computationally. They found hydrogen addition could improve methane ignition significantly and identified three ignition regimes of methane-hydrogen blended fuel. Dai et al. [11] carried out a numerical study on premixed and non-premixed ignition of CH_4/H_2 and CH_4/DME binary fuel blends and respectively discussed the kinetic and transport effects on CH_4 ignition enhancement caused by H_2 and DME addition with special attention. Chen et al. [12] developed a model for the premixed laminar flame speed of binary fuel blends and applied it to CH_4/H_2 mixtures at different initial conditions. Some numerical studies of atmospheric pressure methane-hydrogen-air flames have been conducted in recent years [13–16]. Wang et al. [13] numerically studied the effects of hydrogen addition on methane-air flames. They carried out the rate of production analysis and analyzed the effects of hydrogen additive on the dominant reactions of specific species. Hu et al. [14] experimentally detect the burning velocity of laminar premixed CH_4/H_2/Air flame and compared with numerical model at room temperature and atmospheric pressure. Yan et al. [15] used a two-dimensional model to simulate hydrogen assisted catalytic micro-combustion of CH_4/H_2/Air, and found that hydrogen could lower the methane ignition temperature and shorten ignition time. Li et al. [16] investigated the kinetic effects of hydrogen additive on the thermal characteristics of hydrogen-rich methane-air premixed flames via analysis of the heat release rate and governing reactions.

When methane is substituted by hydrogen, the methane mole fraction decreases, meanwhile, the features of combustion could be consequently changed including mole fractions of major species and specific intermediate species etc. However, we don't know what really influences these changes, either because of the dilution and thermal effects of H_2, or due to the chemical reactions of H_2. Moreover, it is not clear how different effects (dilution, thermal and chemical effects) of hydrogen addition influence the formations and consumptions of important species including some soot precursors and oxygenated air pollutants in methane flames.

To our best knowledge, there is little work on distinguishing the detailed effects of reactive additive H_2 and then analyzing different effects of H_2 addition on the formations and consumptions of important species including some soot precursors and oxygenated air pollutants in the CH_4/H_2 blended fuels flames. Therefore, in the present study, detailed chemical effects of H_2 addition on methane flames are comprehensively discussed via kinetic analysis to complement the inadequate available work for CH_4/H_2/Air blended fuels flames.

Kinetic modeling and analysis method

The detailed chemical reaction mechanism for CH_4 oxidation and combustion used here is GRI-Mech 3.0, an optimized mechanism designed to model natural gas combustion, including NO formation and reburn chemistry [17]. The mechanism consists of 53 species and 325 reactions. The accuracy of the mechanism has been proved by numerous works and studies [4,13,14,16,18–21]. What's more, the detailed H_2 combustion mechanism was included in this mechanism. Model predictions for laminar premixed stoichiometric CH_4/H_2/Air flames are calculated by using a modified ChemkinII/Premix code [22]. The calculation domain is from −2.0 cm at the upstream to 5.0 cm at the downstream, and we have already checked this computational domain is long enough to achieve the adiabatic equilibrium. The initial temperature and pressure at the upstream are set to 298 K and 1.0 atm. The equivalence ratios for all the flames stay the same. The detailed flame conditions are given in Table 1, which were taken or calculated from Ref. [13]. The added hydrogen fraction (R_{H2}) in the CH_4/H_2 fuel mixtures is defined as mole fraction.

In order to distinguish and analyze the chemical effects of hydrogen addition on CH_4/H_2/Air blended fuels flames, the following method is adopted [23]. The added H_2 is assumed as normal reactive H_2 and fictitious inert H_2 which is written as F−H_2. Normal reactive H_2 participates in chemical reactions in flames as usual. However, the thermochemical, transport data and the third-body collision efficiency of fictitious inert H_2 are completely same as normal reactive H_2, but F−H_2 does not participate in any related chemical reactions. Moreover, in order to keep equivalence ratios of all flame conditions staying the same, including those conditions with F−H_2 replacement, a part of oxygen should be separated as fictitious inert O_2 (written as F−O_2) from total O_2. The properties of F−O_2 are similar with F−H_2 that F−O_2 has exactly the same thermochemical, transport data and third-body collision efficiency as normal O_2, but is inert in all related reactions. In the present analysis, the above analysis approach is adopted to trace the real chemical effects of H_2 additive on the CH_4/H_2/Air blended fuels flames. The flame temperature profiles and mole fraction profiles of 15 representative species for five CH_4/H_2/Air and five matching CH_4/F−H_2/Air fuel mixtures containing 0%, 10%, 20%, 30%, and 40% H_2 or F−H_2 are calculated and analyzed. So we obtain 9 different blended fuels flames totally.

Results and discussion

The mole fraction profiles and rate of production of flame components are calculated for the series of 9 flames. Only the