Effect of external conditions on the combustion characteristic of methane/hydrogen/air mixtures

Xu Mengtao[1*]

[1]College of Safety Science and Engineering, Henan Polytechnic University, 454003, Jiaozuo, Henan, China
*Email: xmtxxf123@gmail.com

Abstract To explore the effect of external conditions on combustion characteristics of methane/hydrogen/air, a kinetic calculator was used to analyze the combustion characteristics of methane/hydrogen/air mixtures. It was found that the hydrogen fraction, initial pressure and temperature, and the equivalence ratio had great effects on the adiabatic equilibrium pressure, laminar combustion rate and free radical molar fraction of methane/hydrogen/air mixture. The adiabatic equilibrium pressure decreased with the increase of hydrogen fraction and initial temperature, and increased with the increase of initial pressure, and showed a trend of first increasing and then decreasing with the increase of the equivalence ratio. Laminar burning velocity and free radical molar fraction show the same trend with the change of external conditions.

Keywords Hydrogen; Kinetic calculation; Adiabatic equilibrium pressure; Laminar burning velocity; Free radical mole fraction

1. Introduction

Hydrogen is an energy carrier that could play an important role in both industrial and domestic applications. In addition, hydrogen is also key to achieving carbon neutrality and reducing carbon emissions. In recent years, hydrogen has been widely used as a clean energy source in industry, production, and daily life. In particular, hydrogen-rich natural gas technology has been greatly developed. Methane is the main component of natural gas. Previous studies indicate adding hydrogen to methane can broaden the combustion limit range of methane and improve combustion efficiency [1,2]. However, as the explosion limit range increases, the explosion hazard of methane/hydrogen blends also increases [3-5]. To address the issue of safe use of methane/hydrogen blends, it is necessary to fully understand the combustion characteristic of the blends.

Several studies have already been conducted on the combustion characteristic of methane/hydrogen blends. Di et al. [6] calculated the laminar burning velocity of methane/hydrogen blends using CHEMKIN PREMIX code and found that the hydrogen fraction determines the dominant combustion state of the blends. Hu et al. [7] conducted experimental and numerical studies on the laminar burning velocity of methane-hydrogen-air premixed flames at room temperature and atmospheric pressure and found that as the hydrogen fraction increased, the unstretched laminar burning velocity of the premixed flame increased, and the burning velocity was strongly correlated with the maximum free radical concentrations of H and OH in the reaction zone of the premixed flame. Ma et al. [8] conducted experiments on the combustion characteristics of methane/hydrogen blends in a 20L spherical explosion vessel, and the experimental results showed that the hydrogen addition can increase the explosion pressure and temperature of the blends.

In summary, although many studies have shown that adding hydrogen to methane can effectively enhance its combustion characteristics, the effects of relevant external conditions on combustion characteristics have not been comprehensively analyzed. Under wider external conditions, such as higher hydrogen fraction, higher

initial pressure, and wider temperature range, there is still limited research on the impact of explosion pressure and laminar burning velocity on methane/hydrogen blends. Therefore, this study will discuss the effects of hydrogen fraction, initial pressure, temperature and equivalence ratio on adiabatic explosion pressure and laminar burning velocity of methane/hydrogen blends, and the effects of different external conditions on the concentration of free radicals in the reaction zone will be further analyzed.

2. Kinetic model calculation settings

The simulation of adiabatic explosion pressure and LBV is based on the gas-phase equilibrium calculator model and premixed LBV calculator model in the chemical kinetics calculation software respectively. To investigate the effect of external conditions on the combustion characteristics of methane/hydrogen blends (e.g., hydrogen fraction, initial pressure and temperature, equivalence ratio), Table 1 lists the initial setting values about each test parameter and the range of variation. Furthermore, to meet the calculation requirements, 300 K is set as the ambient temperature and the ending axial position is set to 10 cm. Hydrogen fraction (X_{H2}) is calculated by Equation (1).

$$X_{H2} = \frac{V_{H2}}{V_{H2} + V_{CH4}} \qquad (1)$$

Where X_{H2} is the hydrogen fraction, V_{H2} and V_{CH4} represent the volume of hydrogen and methane, respectively.

Table 1 calculation settings

Test parameter	Range
Hydrogen fraction	0.1-0.9
Initial pressure	1-9 atm
Initial temperature	300-700 K
Equivalence ratio	0.5-2.0

Table 2 Detailed mechanisms for CH_4/H_2 blends combustion included in the current evaluation

Mechanism name	Number of species	Number of reactions
GRI-MECH 3.0	53	325
San Diego	57	268
CRECK_2003_C1_C3_HT	114	1999

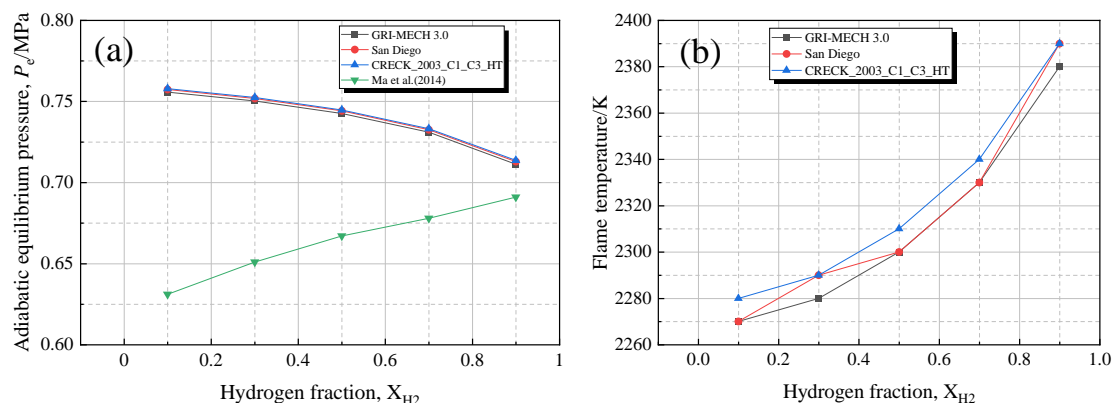## 3. Results and Discussion
3.1. Adiabatic equilibrium pressure

Figure 1: Adiabatic equilibrium pressure (P_e) and flame temperature for different mechanisms under various hydrogen fraction and compared with Ma et al. (2014) work.

Ideally, the combustion pressure in a closed vessel can be calculated through thermodynamic equilibrium by using the adiabatic assumption [9]. Fig. 1 shows the constant volume adiabatic equilibrium pressure calculated by different mechanisms and compared with the experimental results of Ma et al [8]. It is easy to see that both the experimentally derived peak overpressure and the mechanistically calculated adiabatic equilibrium pressure

are correlated with the hydrogen fraction. However, the experimental and theoretical results show a different trend: the peak overpressure decreases slightly with the addition of hydrogen in the theoretical results, while the exact opposite is observed in the experimental results. In addition, we observe that the difference between the experimental and theoretical values of the explosion pressure decreases as the hydrogen fraction increases. This phenomenon is due to the fact that the increasing hydrogen fraction increases the reaction rate, shortens the explosion time and reduces the heat loss during the reaction, resulting in a higher flame temperature (Fig. 1(b)).
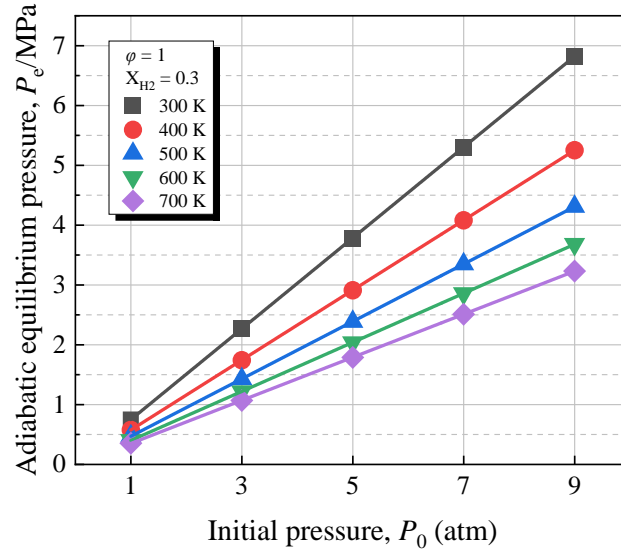

Figure 2: Adiabatic equilibrium pressure of stoichiometric methane/hydrogen/air at various initial pressures and temperatures.

According to the simulation results in Fig. 1, it can be seen that the three different mechanisms have a good consistency in the calculation of the adiabatic equilibrium pressure of stoichiometric methane/hydrogen/air. Therefore, GRI-MECH 3.0 is used in Fig. 2 to analyze the influence of initial pressures and temperatures on the adiabatic equilibrium pressure of stoichiometric methane/hydrogen/air. At a given initial temperature, the adiabatic equilibrium pressure of the mixture is linearly related to the initial pressure. The lower the initial temperature, the more obvious the change of the adiabatic equilibrium pressure of the mixture with the initial pressure. This is due to when the initial pressure is constant, the increasing initial temperature leads to the decrease of the premixed gas density, which makes the premixed gas release less heat during the explosion process [10]. Based on the above analysis, we should pay more attention to the influence of temperature and pressure on the explosion characteristics of premixed gas.
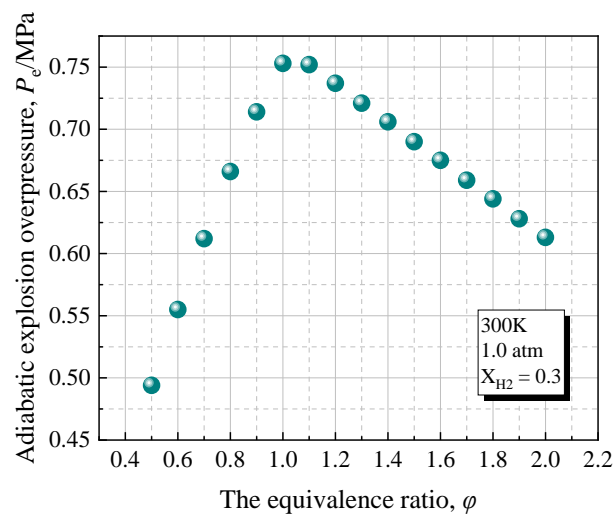

Figure 3: Adiabatic equilibrium pressure of stoichiometric methane/hydrogen/air at various equivalence ratio.

Fig. 3 analyzes the influence of the equivalence ratio on the adiabatic equilibrium pressure of methane/hydrogen/air premixed gases with a hydrogen fraction of 0.3 at ambient pressure. It can be seen from Fig. 3 that the equivalent ratio has a great influence on the adiabatic equilibrium pressure of premixed gas. The adiabatic equilibrium pressure increases first, then decreases with the increasing equivalence ratio, and the adiabatic equilibrium pressure reaches the maximum value near the stoichiometric ratio.

3.2. Laminar burning velocity

Laminar burning velocity (S_L) is one of the key parameters to determine the combustion characteristics of the combustible mixture, which is closely related to many complex phenomena in the flame propagation process such as flame stability and flame height. In addition, laminar burning velocity is also an important basis for the development and verification of chemical kinetic mechanisms and combustion models. Several experimental methods have been developed for S_L measurement, such as an out an outwardly spherical propagating flame method, a stagnation/counter flow flame method, a heat flux method, an annular stepwise diverging tube, an externally heated diverging channel method and a conical flame method [11].

In this section, the premixed LBV calculation model is selected and the GRI-MECH 3.0 mechanism is introduced to analyze the effects of hydrogen fraction, initial pressure and temperature, and equivalent ratio on the S_L of premixed methane/hydrogen/air.

Fig. 4a shows the variation of the S_L of stoichiometric methane/hydrogen/air premixed gas as a function of the hydrogen fraction at ambient temperature and pressure. It is easy to see that methane dominated combustion occurs at low hydrogen fraction ($0 \leq X_{H2} \leq 0.5$), which is characterized by a linear slight increase in methane laminar burning velocity with the addition of hydrogen. At high hydrogen fraction ($0.5 \leq X_{H2} \leq 0.9$), the combustion state of methane/hydrogen/air premixed gas is dominated by hydrogen, and the SL of premixed gas increases sharply with the increasing hydrogen fraction.

The variation of the S_L with different initial temperatures and initial pressures for GRI-MECH 3.0 is plotted in Fig. 4b. As is evident from the diagram that elevated pressure has an adverse impact on S_L due to the elevated pressure decreases the mole fractions of H, O and OH radicals in the flame zone, while the effect of promotion of S_L is enhanced by higher initial temperatures, mainly because the increasing initial temperature increases the adiabatic flame temperature correspondingly.

Fig. 4c shows the relationship between laminar burning velocity S_L, and equivalence ratio φ at ambient pressure and temperature. The numerical results with GRI-MECH 3.0 show that the calculated S_L increases with φ and reaches its maximum value at φ of 1.1, and then the S_L decreases with the further increasing φ. This tendency is the same to the hydrocarbon fuels, and these values are close to those for methane/hydrogen/air under the same conditions.
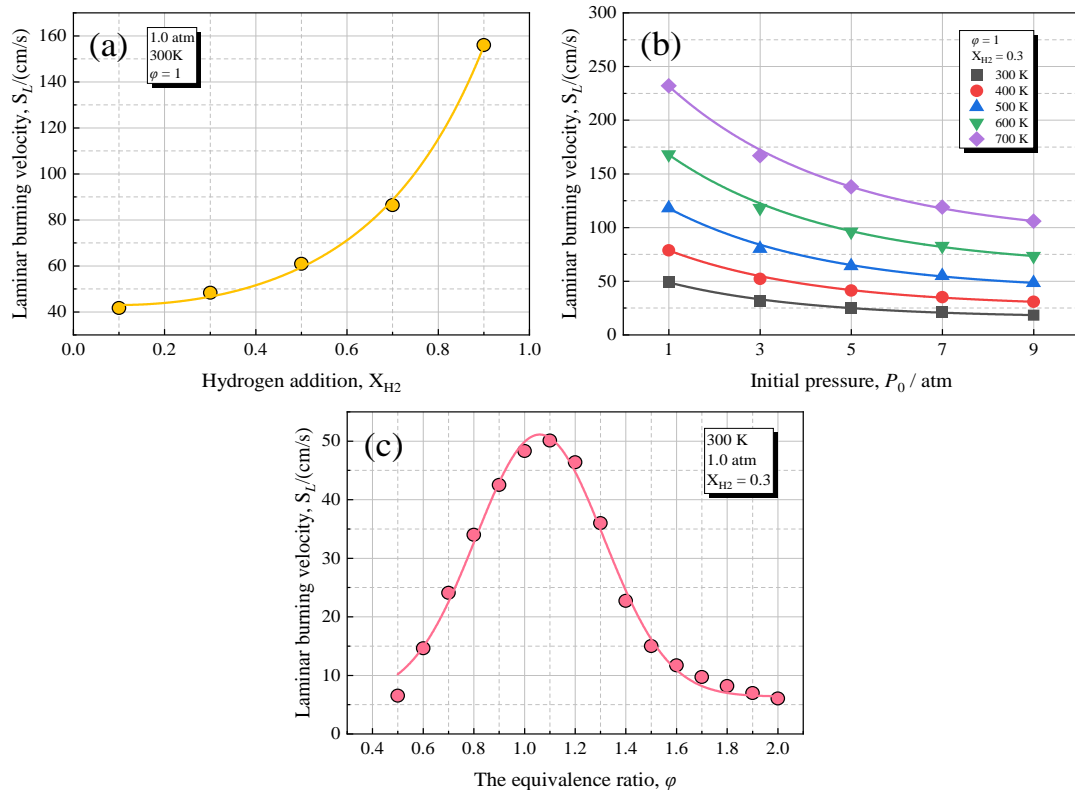
Figure 4: Variation in S_L with (a) hydrogen fraction, X_{H2}; (b) initial pressures and temperatures; (c) equivalence ratio, φ.
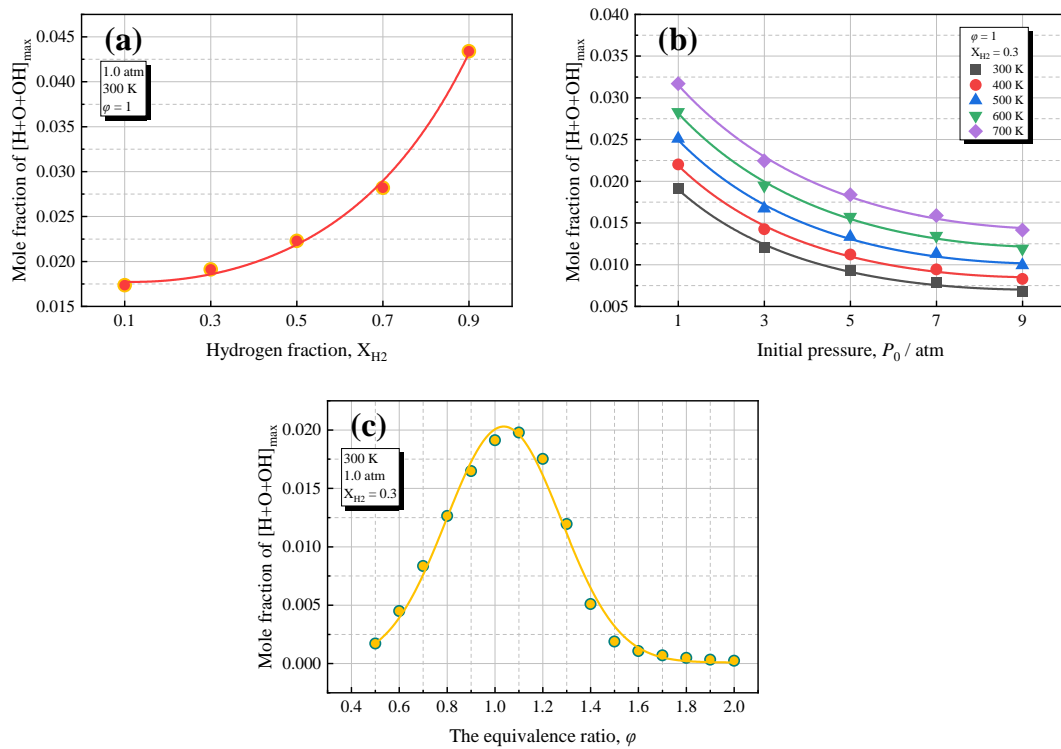
3.3. Free radical mole fraction

Figure 5: Variation in mole fraction of $[H+O+OH]_{max}$ with (a) hydrogen fraction, X_{H2}; (b) initial pressures and temperatures; (c) equivalence ratio, φ.

Studying the molar fraction of free radicals in flames helps to understand the chemical reaction mechanisms during combustion. Free radicals are molecules or atoms with unpaired electrons that play a crucial role in flames, affecting the rate of combustion and the formation of products. By understanding the concentration of free radicals, scientists can optimize the combustion process, improve energy efficiency, and reduce the generation of pollutants. In addition, this also helps to design more effective flame control systems, such as in industry and engines, to improve energy conversion and reduce environmental impacts. Fig. 5 illustrates the effect of external external conditions on the molar fractions of H, O and OH radicals in the methane/hydrogen/air flame. We can clearly see that there is a good similarity in the influence of external conditions on the mole fraction of free radicals and laminar burning velocity. This is due to the fact that flame combustion is a complex chain of chemical reactions that includes ignition, propagation and termination stages. The process involves several intermediate products, of which free radicals are a key component. In flames, the most common free radicals include hydrogen radicals (H), oxygen radicals (O), and hydroxide radicals (OH). These free radicals play important roles in the combustion reaction chain. From the microscopic point of view, the external conditions have a great influence on the molar fraction of free radicals, and from the macroscopic point of view, the laminar burning velocity changes with the external conditions.

4. Conclusions

In this research, the adiabatic equilibrium pressure, laminar burning velocity and free radical mole fraction of methane/hydrogen/air mixtures are investigated under different external conditions by chemical kinetic calculations. The main conclusions are as follows:

(1) The adiabatic equilibrium pressure of methane/hydrogen/air mixture varies with the external parameters, increasing with initial pressure rising, decreasing with hydrogen fraction and initial temperature going up. When the equivalence ratio goes up, the adiabatic equilibrium pressure shows an increasing trend followed by a decreasing trend.

(2) Laminar burning velocity and free radical molar fraction are positively correlated with external parameters. Both the initial temperature and the hydrogen fraction in the mixture can increase the laminar burning velocity and the free radical mole fraction. However, with the increasing initial pressure, laminar burning velocity and free radical molar fraction decrease. The variation trend of laminar burning velocity and free radical molar fraction with the equivalence ratio is consistent with that of adiabatic equilibrium pressure.

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