A Numerical Study on the Effect of Hydrogen mole Fraction on NO Formation in H$_2$/CO Syngas/Air Laminar Diffusion Flames

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1   Introduction

Hydrogen-rich fuel has become an important clean energy source because of its environmental friendliness. Syngas is a kind of hydrogen-rich fuel mainly composed of H$_2$ and CO. It also contains N$_2$, CO$_2$, H$_2$O, CH$_4$ and other hydrocarbons. Its composition depends on the composition of the fuel source and syngas production process. Different combustion characteristics and pollutant emission characteristics of syngas with different composition hinder the wide application of syngas, and bring difficulties to the design and operation of the combustion equipment. The variation of syngas composition caused by coal and biomass gasification process greatly affects the design and operation of integrated gasification combined cycle (IGCC) system. The composition of syngas also directly affects the combustion process, which is especially important for the formation of NO in the flue gas. Therefore, it is of great importance to investigate the effect of syngas composition on the formation of NO to reduce the emission of pollutants.

The counterflow diffusion flame model is widely used in the research of syngas diffusion combustion. The profound understanding of the combustion characteristics and pollutant emission characteristics in the counterflow diffusion flame under laminar flow conditions can lay the foundation for the investigation of complex working conditions. The existing studies of syngas mostly focused on the combustion characteristics and pollutant emission of syngas with fixed components and there is not enough attention has been paid to NO formation variable composition syngas with detailed chemical reaction mechanism and radiation model. [1,2,3,4] In this paper, the influence of H$_2$ mole fraction (0.1-1.0) in H$_2$/CO syngas on the NO emission and flame temperature were investigated. Detailed chemical reaction mechanism (GRI-

Mech 3.0) is applied to explore the formation routes of NO, which is important to reduce pollutant emission in the process of syngas combustion.

2   Numerical Model

The axisymmetric counterflow diffusion flame model was used in the numerical calculation, as shown in Figure 1. The distance between the two nozzles was maintained at 3.0 cm in all calculations, while the mass flow rate of air (V_{air}) was varied so that the stagnation plane was located close to the fuel nozzle. The pressure and temperature of the fresh mixture (both air and fuel stream) are 1 atm and 298 K, respectively, and the equivalence ratio is 1.2.
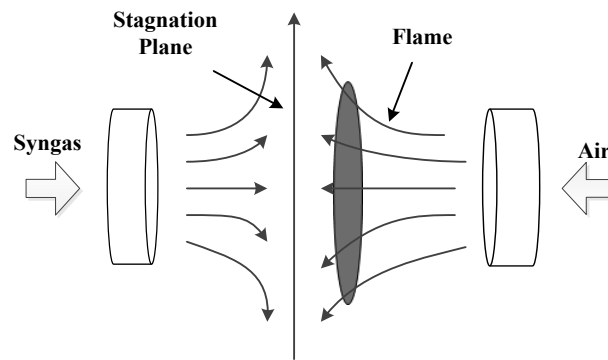
Figure 1. Flame structure

The governing equation of the axisymmetric problem can be simplified to one dimensional ordinary differential equations, containing the mass conservation equation, momentum conservation equation, energy conservation equation and composition equation, which were proposed by Kee et al. [7] The optical thin model was applied to calculate the radiation heat loss [6]. This model considers the radiative heat dissipation and neglects the radiation reabsorption of the gas molecules.

(10)

3   Results and discussion

3.1 Temperature

The influence of H_2 mole fraction on the adiabatic flame temperature and non-adiabatic flame temperature is shown in Figure 2. With the increase of hydrogen mole fraction in the syngas, the adiabatic flame temperature decreases slightly. It is due to the specific heat of H_2O produced by H_2 combustion is larger than that of CO_2 produced by CO combustion. Besides, the low heating value of H_2 is slightly lower than that of CO. As shown in Table 1, with the increase of hydrogen mole fraction, the heating value of the mixed gas decreases, resulting in the decrease of the adiabatic flame temperature.

On the contrary, the flame temperature increases monotonically with the increase of hydrogen mole fraction in the syngas under non-adiabatic condition. This is because the thermodynamic effect in syngas combustion process caused by the H_2 mole fraction variation is mainly reflected in three aspects: the variation of syngas adiabatic flame temperature, the Lewis number and the variation of radiant heat loss.

The Lewis number of H_2 is significantly lower than unity. As a result, the fuel Lewis number is reduced to a value lower than unity, which tends to increase flame temperature and causes super-adiabatic temperature as H_2 is added[1]. The wide range of H_2/CO volume ratio of syngas will lead to a large range of H_2O/CO_2 volume ratio in flue gas. The emissivity of CO_2 is much higher than that of H_2O at high temperature, so the heat loss of syngas flame with different H_2/CO volume ratio will be significantly different. When the ratio of H_2 is lower in the H_2/CO syngas, the concentration of CO_2 in the product is higher, resulting in larger radiation heat loss. The peak flame temperature of syngas with low H_2 mole fraction (0.1) is about 200 K lower than the adiabatic flame temperature of the same syngas. But with the increase of H_2 fraction, the concentration of CO_2 in flue gas decreases, so the heat loss decreases and the flame temperature increases gradually, approaching the adiabatic flame temperature.
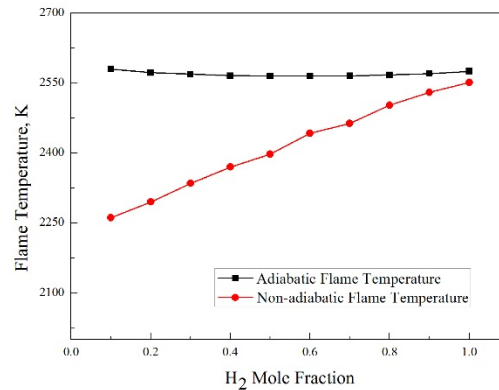

Figure 2. Effect of H_2 fraction on adiabatic flame temperature and non-adiabatic flame temperature

Table 1: Syngas heat value of different H_2 fraction

H_2 Mole Fraction	Heat Value(MJ/m^3)
0	12.562
0.2	12.0272
0.4	11.8524
0.6	11.4976
0.8	11.1428
1	10.788

3.2 NO Emission

The influence of H_2 mole fraction on NO emission at different strain rate is shown in Figure 3. With the increase of H_2 mole fraction in the syngas, the NO emission increases monotonically. However, with the increase of strain rate, the NO emission decreases. It is due to that the effect of Lewis number becomes weaker with strain rate increasing, which tends to decrease flame temperature.
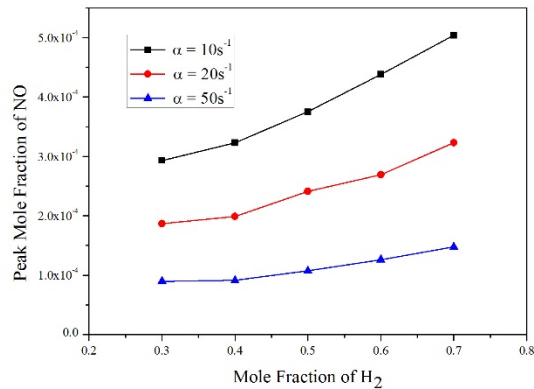
Figure 3. Effect of H_2 mole fraction on NO peak mole fraction at different strain rate

The reaction mechanism of NO at $a = 10s^{-1}$ is analyzed to investigate the route of NO production. Based on the results of the relevant literature [15], the key to identify the mechanism of NO formation in a flame should not lies in how NO is finally formed, but lies in how molecular nitrogen is initially converted to atomic nitrogen or nitrogen-containing species. In this study, NO produced through prompt mechanism is much smaller than that through other mechanism, which is due to the prompt NO usually generates under lean-burn condition of hydrocarbon fuel combustion. In this study, H_2/CO syngas with the equivalence ratio of 1.2 is used, therefore prompt NO production is very small and negligible. As shown in Figure 4, N_2 is mainly consumed through thermal route. In the discussion on the temperature variation (section 3.1), the flame temperature increases monotonically with the increase of H_2 mole fraction. This conclusion is consistent with the result in figure 4. With the increase of the volume fraction of H_2, the flame temperature increases, which further increases the generation of thermal NO. It is also shown in Figure 4 that with the increase of H_2 mole fraction, NO production through N_2O route decreases, while NO production through NNH route increases. However, the trend is not significant compared with the thermal route. The sensitivity coefficient variation of NO formation reaction with the variation of H_2 mole fraction from 0.1 to 0.9 is shown in Figure5. The most sensitive reaction is R178, followed by R179 and R180, which are the main reactions of thermal NO route. It also can be observed that the sensitivity of the reactions decrease with the increase of H_2 mole fraction. This is due to the decreasing formation rate of the thermal NO with increasing H_2 mole fraction (figure 4).
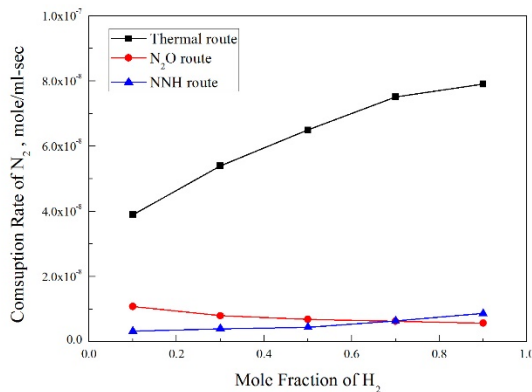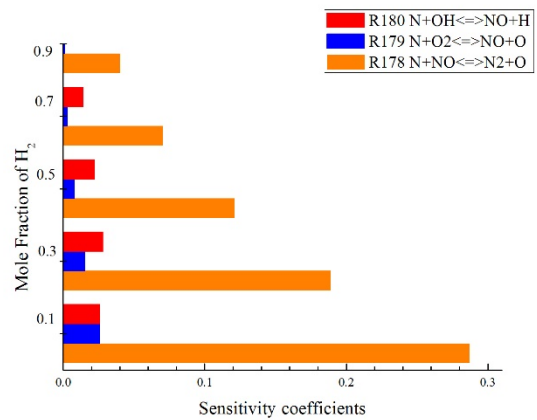

Figure 4. Consumption rate analysis of N_2

Figure 5. Sensitivity analysis of NO formation

The influence of H_2 mole fraction on the concentrations of important intermediate products (N, HCN, NNH and N_2O) are shown in Figure 6,7,8,9. With the increase of H_2 mole fraction, N concentration increases monotonically, and the trend is more obvious when H_2 mole fraction is above 0.6. It is due to the increase the temperature caused by the increase of H_2 mole fraction leading to the rapid reaction of $N_2 + O \leftrightarrow N + NO$. This reaction is the rate limiting reaction of thermal NO formation [9], so the variation trend of N concentration can indirectly indicate the variation trend of thermal NO. With the increase of H_2 mole fraction, HCN concentration shows a trend of first increase and then decrease. This is due to the fact that the formation of HCN depends mainly on CH. With the increase of H_2 mole fraction, CH concentration also increases. But when H_2 increases to a certain extent, the CH concentration will decrease, so the HCN concentration decreases. As the important intermediate product of prompt NO, the variation of HCN concentration represents the variation of prompt NO formation [10]. Therefore, with the increase of H_2 mole fraction, prompt NO formation first increase and the decrease. With the increase of H_2 mole fraction, NNH concentration increases and N_2O concentration decreases respectively. It is due to the increase of H concentration resulting from the increase of H_2 mole fraction will lead to rapid reaction of $N_2 + H \leftrightarrow NNH$, causing the increase of NNH concentration [12]. However, with the increase of H concentration, the positive reaction rate of $N_2O + H \leftrightarrow N_2 + OH$ increases, leading to the decrease of N_2O concentration [11]. Therefore with the increase of H_2 mole fraction, NO formation through NNH route increases and NO formation through N_2O route decreases respectively. This is consistent with the results of sensitivity analysis in Figure 5.
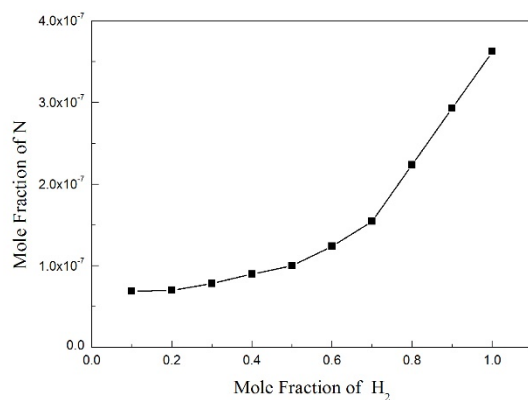
Figure 6. Effect of H_2 fraction on N mole fraction
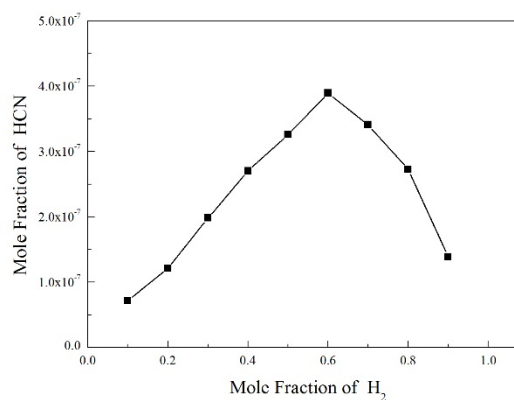
Figure 7. Effect of H_2 fraction on HCN mole fraction
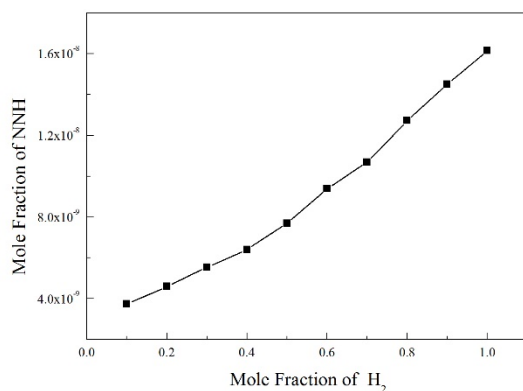
Figure 8. Effect of H_2 fraction on NNH mole fraction
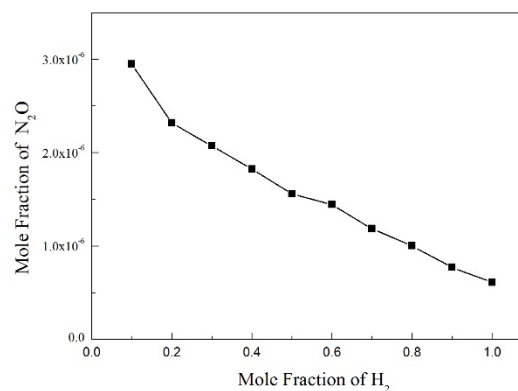
Figure 9. Effect of H_2 fraction on N_2O mole fraction

4   Conclusion

This paper reports a numerical investigation of NO formation in a H_2/CO/air counterflow diffusion flame. An analysis of how hydrogen mole fraction influence the NO emission is provided. The results show that:

a. With the increase of hydrogen mole fraction in the syngas, the adiabatic flame temperature decreases slightly. It is due to the specific heat of H_2O is larger than CO_2 and the heating value of mixed gas decreased. While flame temperature increases monotonically with the increase of hydrogen mole fraction in the syngas under non-adiabatic condition. This is because the emissivity of CO_2 is much higher than that of H_2O at high temperature, so the heat loss will be significantly different with the variation of H_2 mole fraction, leading to the variation of flame temperature. On the other hand, the fuel Lewis number is reduced to a value lower than unity, which tends to increase flame temperature and causes super-adiabatic temperature as H_2 is added.

b. With the increase of H_2 mole fraction, the NO emission of syngas flame increases obviously, and thermal route contributes the largest part of NO emission increasing, leading the variation of NO emission. The prompt NO formation shows a trend of first increase and then decrease, but the formation of prompt NO is much smaller than other route. With the increase of H_2 mole fraction, NO formation through NNH route increases and NO formation through N_2O route decreases respectively due to the variation of H_2 fraction.

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