Numerical study of the Effect of CO₂ on the NH₃/CH₄ Counterflow Diffusion Flame in O₂/CO₂/N₂ Atmosphere

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Abstract. Ammonia, as a carbon-neutral fuel, draws people attentions recently. NH₃/CH₄ blends is considered as a kind of fuel. A numerical simulation of the effects of CO₂ dilution on the combustion characteristics and NO emission of NH₃/CH₄ counterflow diffusion flame was conducted in this study. Diffusion flame structure, the influence of CO₂ radiation characteristics on temperature and NO emission characteristics were studies at normal temperature and pressure. The dilution and radiation of CO₂ reduce the flame temperature significantly. NO concentration decreased with the CO₂ mole fraction increase effectively. The study extends the basic combustion characteristics of NH₃ containing fuel.

Keywords: Ammonia; Methane; CO₂ dilution; Counterflow flame; NO emission.

1. Introduction
Ammonia (NH₃), as an energy vector hydrogen, has a high hydrogen density [1]. It has a relatively high energy density, about 22.5MJ/kg. Only water and nitrogen are produced after ammonia is completely burned, which has great potential in reducing carbon emission. However, Ammonia has a low laminar burning velocity compared to methane, a narrow flammable limit as well as auto-ignition temperature [2]. Ammonia requires a longer residence time during combustion process, which not only inhibits turbulent mixing and flame stability, but also promotes NOₓ emission and forms pollutants with unburned ammonia[3].

For the purpose of improve the characteristics of ammonia, ammonia and other fuels, such as methane, are used for combustion and power supply to solve the low flame propagation speed problem [4]. Tian et al [5] confirmed the detailed flame structure characteristics by measuring 11 kinds of premixed flames with different NH₃/CH₄ molar ratios, developed Tian mechanism, and obtained the conclusion that NO production increased with the increase of NH₃ mole fraction, while the NH₃ ratio in mixed fuel is up to 50%. The flame combustion characteristics and NO emission of high ammonia concentration need to be further investigated.

Exhaust gas recirculation (EGR) is a special CO₂ dilution technology. CO₂, N₂ and H₂O, as the main combustion production of NH₃/CH₄ blends, are condensed and re-entered into the combustion chamber, which provides convenient conditions for carbon capture and storage (CCS). The flame characteristics and NO emission of NH₃/CH₄ mixture fuel will change with the CO₂ dilution, which provide a theoretical basis for mixture fuel of using EGR.
2. Numerical Modelling
OPPDIF model in CHEMKIN-Pro software was performed in numerical simulation of the counterflow flame [6]. As shown in Fig 1, the nozzles separation distance L=2cm, the stretch rate \( \alpha = 20 \text{s}^{-1} \). Considering the optical thin model (OPM) as radiation model. Besides, the gas jet velocities of two nozzles should satisfy the momentum theorem [7]:

\[
\rho_F v_F^2 = \rho_O v_O^2
\]

(1)

Where \( v_F \) and \( v_O \) indicates the velocity of fuel and oxidizer, respectively. \( \rho_F \) and \( \rho_O \) represent the density of two nozzles blends.

Figure 1. The structure of the counterflow flame.

The Tian mechanism contains 84 species and 703 reactions, which is suitable for NH3/CH4 blends with higher NH3 concentration. It has been validated on high concentration of ammonia for example of NOx emission and free propagation flame. This mechanism is widely used in combustion kinetics of ammonia-based fuels and shows good performance.

3. Result and Discussion

3.1. Boundary Condition
The dilution ratio of CO2 as a diluent added to the oxidizer side is defined as:

\[
\beta = \frac{\lambda_{CO_2}}{\lambda_{CO_2} + \lambda_{O_2} + \lambda_{N_2}}
\]

(2)

where \( \lambda \) represents mole fraction in oxidizer, the subscript indicates the three different gas. The mole fraction of N2 is fixed at 10%. CO2 dilution ratio varies from 0-50%. The composition of fuel is 50%NH3/50%CH4. The pressure is 1atm and the inlet temperature is specified as 298K.

3.2. The Effect of CO2 Dilution on the Combustion Performance

3.2.1. Flame structure. To understand the effect of CO2 dilution in NH3/CH4 mixtures combustion, flame structures were displayed in Fig 2. As shown in Figure 2, the reactants and main products of the NH3/CH4 fuel mixtures were displays when the CO2 dilution ratio is 0 and 0.4. It is found that the curve without the CO2 dilution has a wider reaction area. Whether CO2 dilution or not, both fuel and oxidant decrease to 0 simultaneous. It is shown in Fig 2(b) that with the CO2 dilution ratio increase, the NO concentration decreases significantly. This is mainly due to the addition of CO2 will reduce the temperature, thereby reducing the generation of thermal NO and change the elementary reaction path as well as reaction rate for NO generation. Parts of N radicals converted into N2O intermediates with the effect of CO2. In the post-combustion zone, the ratio of NO to NO2 is also elevated.
3.2.2. The effect of CO2 radiation on the flame temperature. Fig 3 shows the influence of CO2 radiation characteristics on flame temperature of counterflow flame. The radiation effect of CO2 can reduce the temperature at any position in flame zone. CO2 dilution remarkably narrowed the reaction zone and decrease the peak flame temperature. Furthermore, the degree of decrease gradually increases with the increase of CO2 dilution ratio. CO2 molecules have strong radiation and strong absorption characteristics, which will inevitably affect the temperature distribution and flame peak temperature. As shown is Fig 3, under both adiabatic and non-adiabatic conditions, the peak flame temperature reduced substantially. However, considering the CO2 radiation characteristics, the peak flame temperature further decreased. The descending gradient of flame peak temperature is larger under non-adiabatic conditions.

3.3. The Effect of CO2 Dilution on the NO Emission

Fig.4 displays the NO concentration and peak NO along with the distance between the two nozzles at different CO2 dilution. What can be clearly seen is that in the case of $\beta=0$ and $\beta=0.1$, there are two formation peak of NO, which are the unique properties of the counterflow flame under high oxygen concentration conditions [8]. In addition, the NO peak is also affected by the CO2 dilution. The negative
influence of CO₂ dilution on NO peak is more obvious in small number of dilution ratio (β=0~0.2) than in large number (β=0.2~0.5). When the dilution degree is little, NO peak value decreases non-linearly and to a large extent; As the CO₂ dilution ratio increases in an arithmetic progression (10% as common different), the decline of NO peak was negatively correlated with dilution ration, and could be attributed to linear. The reason for this situation is CO₂ molecule has the characteristics of strong radiation and strong absorption, which is bound to affect the flame temperature distribution and flame peak temperature.

Figure 4. Effect of CO₂ dilution ratio on NO distribution and NO maximum of α=20s⁻¹ at NTP.

Figure 5. Effect of CO₂ dilution ratio on NO production rate and NO concentration at NTP, β=0, 0.3. Fig.5 reflects the effect on the NO production rate under two different conditions, β=0 and β=0.3. When the NO production rate is positive, its absolute value is defined as the NO generation rate. Otherwise, its absolute value is defined as the NO consumption rate. CO₂ has an inhibitory effect on the generation and consumption of NO, and the inhibitory effect on NO consumption is reflected in the reduction of NO peak, while the inhibitory effect on NO generation is reflected in the weakening of the secondary peak until zero. At the same time, the NO production rate curve can also correspond well to the NO mole fraction. In general, the negative effect of CO₂ on the NO generation rate is greater than the negative effect on the NO consumption rate, resulting in a decline in the NO mole fraction. The elementary reaction on the NO generation rate and NO consumption rate are displayed in Fig.6
separately. In Fig.6(a), R388 N+OH<=>NO+H, R304 HNO+H<=>NO+H_2 and R310 NO+H(+M)<=>HNO(+M) have great contribute to NO generation rate, which means NO is mainly formed by N radicals and HNO is the important intermediate in NO production. With the increase of CO_2 mole fraction, the generation rate of NO decreases. Among them, the contribution of the elementary reaction R388 to the NO production rate is most obviously suppressed, which is reduced by 28.9%. In Fig.6(b) R390 N+NO<=>N_2+O, R383 NH+NO<=>N_2O+H, R385 NH+NO<=>N_2+OH has majority influence to NO consumption. These three reactions can be summarized as the NH_i (i=0,1) group reduces NO to produce N_2 and N_2O intermediates, which also decline by the CO_2 dilution ratio.

Figure 6. Effect of CO_2 dilution ratio of the rate constants of the elementary reactions on NO generation rate (a) and NO consumption rate (b) at NTP, β=0, 0.3.

Figure 7. Normalized sensitivity of the NO mole fraction of basic reaction rate constant at highest temperature point in flame.

The normalized first order sensitivity coefficients pertaining to NO concentration of different CO_2 dilution ratio as shown in Fig.7. The reaction R390 N+NO<=>N_2+O, which has a significant positive effect on NO concentration, was reverse due to the increased of substituted CO_2. Since there is no CO_2 added into oxidant side, a large amount of N radicals are formed after ammonia is burned in high concentration of oxygen. However, with the rise of the dilution ratio, R390 shows that CO_2 can deduct NO concentration by affecting the N radicals in the combustion zone. At the same time, the elementary reaction containing NH_2 radicals inhibits NO formation increases significantly with the CO_2 dilution ratio increment. These reactions directly or indirectly generate hydroxyl and O radicals, maintaining the thermal denitrification mechanism in ammonia chemistry [9].
4. Conclusions

NH₃/CH₄ mixtures fuel has a good prospect in energy substitution. Doping CO₂ to the oxidizer side can reduce NO emissions as well as play a very significant role in CO₂ recycle. The conclusions are as follows:

1. Flame peak temperature decreased significantly with the increase of CO₂ dilution ratio, while the reaction zone narrows and moves to the oxidant side. Strong radiation and strong absorption of CO₂ molecules result in a greater decline in peak flame temperature.

2. Adding CO₂ to the oxidant side can remarkably deduct the peak NO, and the secondary peak of NO gradually vanished. When extent of CO₂ dilution is small, the inhibition effect of CO₂ dilution ratio on NO production is obviously.

3. The effect of CO₂ mainly reduces the NO production rate by diminished the secondary generation rate of NO. Sensitivity analysis of NO emission characteristics under different CO₂ mole fractions reveals that the elementary reaction R390 N+NO<=>N₂+O, which originally promoted to NO production, turned to an inhibitory effect, reflecting that CO₂ could reduce NO concentration by affecting N radicals in the reaction zone.

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