NO Reburning by CH$_4$-H$_2$ Mixture under High CO$_2$ Concentration in a Jet-Stirred Reactor

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Abstract. New experimental and numerical results for NO reduction of CH$_4$-H$_2$ mixture were obtained in a 0-dimensional jet stirred reactor (JSR), the effects of the following four factors are considered: temperature($T$): 800-1300 K; equivalence ratio($\phi$): 0.5-2.5; proportions of H$_2$:CH$_4$ in fuel: 0:6, 1:5, 3:3 and 5:1 (expressed in terms of FUEL-CH$_4$, FUEL-1:5, FUEL-3:3 and FUEL-5:1, respectively); CO$_2$ concentration in dilution gas: 0, 30% and 60% (expressed by terms D-N$_2$, D-30%CO$_2$ and D-60%CO$_2$, respectively). Compared with pure CH$_4$, mixing with H$_2$ weaken the NO reduction in high temperature region, The NO reburning reduction rate of FUEL-3:3 increases first and then decreases with the increase of $\phi$. The strongest reduction effect is obtained at $T=1300$ K and $\phi=1.2$, and the reduction efficiency is about 70%. The NO reburning reaction was obviously inhibited by increasing CO$_2$ concentration, but the effect was limited when the CO$_2$ concentration reached a certain level. The reburning effect of FUEL-CH$_4$, FUEL-1:5, FUEL-3:3 is approximative, but the reburning effect of FUEL-5:1 is significantly inhibited by high proportions of H$_2$:CH$_4$.

1. Introduction

Hydrogen-blended natural gas combustion is one of the feasible schemes for transition from fossil energy to hydrogen energy and accelerate the development of hydrogen energy industry. Combined with oxy-fuel combustion technology, it is at high CO$_2$ concentration atmosphere and conducive to carbon capture, so as to realize low-carbon utilization of hydrogen-blended natural gas. When methane is mixed with hydrogen, the combustion characteristics of fuel will change obviously: the high reactivity and high diffusivity of hydrogen can accelerate the ignition, enhance the combustion intensity, expand the flammability limit, etc.; it may also cause ignition oscillation, increase the combustion temperature and produce more NO$_x$ emissions. It is necessary to pay attention to the NO reburning reduction characteristics of methane mixed with hydrogen combustion at high CO$_2$ concentration atmosphere to promote NO reduction.

Fortunato et al. [8] studied the NO reduction mechanism in a flameless combustion furnace rich in H$_2$ and low calorific value fuel, and proposed a simplified NO reduction mechanism suitable for the combustion atmosphere. Galletti et al. [10] pointed out that the intermediate pathway of NNH and N$_2$O is the main formation path of NO$_x$ in CH$_4$-H$_2$ mixture flameless combustion. Mardani et al. [9] found that the importance of N$_2$O-intermediate route decreased with the decrease of hydrogen content. Most of the researches on the combustion of methane hydrogen blended fuel are focused on the laboratory scale burners and the oxidant is air, and little attention is paid to the NO reburning and reduction
characteristics of methane hydrogen blended fuel in high CO$_2$ atmosphere. In this paper, JSR was used to precisely control the reaction conditions to explore the effects of temperature, equivalence ratio, dilution atmosphere and H$_2$:CH$_4$ ratio on NO reburning reduction of CH$_4$-H$_2$ mixture under air and high CO$_2$ concentration atmosphere.

2. Research methods
The experimental equipment used is the same as that of Li. [1] and Li. [4]. The experiments of the effect of temperature (800~1300 K), the effect of equivalence ratio (0.5~2.5), the effect of CO$_2$ concentration in dilution atmosphere (0, 30% and 60%) and the effect of H$_2$:CH$_4$ ratio (0:6, 1:5, 3:3 and 5:1) had been carried out. CH$_4$-H$_2$ mixture are used as fuel, and their total amount remains unchanged at 6000 ppm, NO is used as the initial NO source at 1000 ppm for reburning reduction, and O$_2$ is used as oxidant. The dilution gas is a mixture of N$_2$ and CO$_2$. When the CO$_2$ concentration is 0, it means pure N$_2$.

The Perfectly-Stirred Reactor model of CHEMKIN-PRO was used to simulate the experimental conditions. It can calculate a series of steady-state conditions by changing one or more parameters. (such as temperature, pressure, etc.). The fixed temperature method is used to solve the Perfectly-Stirred Reactor model. The detailed chemical reaction mechanism (called PG2018) developed by Peter Glarborg et al. [6] in 2018 was used, which includes the oxidation of CO, H$_2$, C1-C4 hydrocarbons, HCN and NH$_3$, and the coupling reaction between hydrocarbons and nitrogen components.

3. Results and discussion

3.1. Effect of temperature

![Figure 1. Experimental and numerical results of O$_2$, CO, NO, HCN and Reduction Efficiency versus temperature](image)

Figure 1 displays the reburning results of FUEL-CH$_4$ and FUEL-3:3 in N$_2$ atmosphere (D-N$_2$) and CO$_2$ rich atmosphere (D-30%CO$_2$), respectively. The scatter points represent the experimental results and the curves represent the simulation results. The simulation results obtained using the PG2018 mechanism are basically consistent with the experimental results. The results of FUEL-CH$_4$ are used as reference to analyse the results of FUEL-3:3, that is, to analyse the impact of methane mixed with hydrogen on NO reburning. The less NO and HCN in the reaction products, the better the NO reburning effect is, and the more helpful to reduce pollutant emissions. The NO reburning reduction process also produces other nitrogen-containing components, rather than complete reduction to N$_2$. In
this experiment, other nitrogen components (NO₂, N₂O, NH₃ and HCN) in the jet stirred reactor were detected quantitatively. The results showed that the concentrations of other nitrogen components (NO₂, N₂O and NH₃) were always lower than 10 ppm except HCN. Therefore, TFN (Total Fraction of N), the sum of NO and HCN concentration, was used as the standard to evaluate the NO reduction rate. The NO reduction efficiency is expressed as follows:

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\text{NO Reduction Efficiency (\%) = 100\% \times \frac{\text{IFN} - \text{TFN}}{\text{IFN}}}
\]

Where: TFN (Total Fraction of N) is the sum of NO and HCN concentrations, and IFN (Initial Fraction of N) is the initial concentration of NO added.

According to the results of FUEL-CH₄, the effect of temperature on NO reburning reaction of CH₄ can be analysed. For fuel oxidation, under N₂ atmosphere, at a fixed reaction equivalence ratio, the temperature increases the CO first and then declines, and there is a peak value. The peak value of CO in fuel-rich atmosphere (φ=1.5) is higher than that in fuel-lean atmosphere (φ=0.5). In the D-30%CO₂, at the temperature of 1100-1300 K, the CO₂ in the dilution gas makes the CO increase significantly. For NO reduction: in N₂ atmosphere, the reburning effect increases with the increase of temperature. The corresponding temperature of reburning reaction occurs in stoichiometric atmosphere (φ=1) is 910 K, and that of fuel-rich atmosphere (φ=1.5) is 1000 K, which is 90 K higher than that of φ=1. At 1300 K, the reduction efficiency of D-30%CO₂ is 35.7%, 22% lower than that of D-N₂ at φ=1, φ=1.5 respectively.

Compared with pure CH₄, after mixing with H₂, the oxidation reaction of FUEL-3:3 can reach stable state at lower temperature, stable after 1150 K at φ=0.5, and stable after 1200 K at φ=1, indicating that the reactivity of the fuel is enhanced. Comparing the results of CO under the condition of φ=1.5, D-30% CO₂, the chemical properties of CO₂ play a role in the reaction of FUEL-3:3 in the temperature range of 1000-1300 K, which makes the CO increase significantly, and the corresponding temperature range is wider than that of FUEL-CH₄ (1100-1300 K), indicating that H₂ tends to reduce CO₂ to CO more than CH₄, and H₂ has better reducibility. Comparing the NO reburning effect, it is found that the reduction efficiency of FUEL-3:3 is significantly higher than that of FUEL-CH₄ at φ=1, 1.5 and T=1000-1250 K in D-N₂. The NO reduction efficiency can reach 55% at φ=1.5, 1300 K. In D-30%CO₂ atmosphere, FUEL-3:3 has better NO reduction efficiency than FUEL-CH₄ at φ=1.5, T=1150-1300 K. The addition of CO₂ has a great adverse effect on the NO reduction of FUEL-3:3. The results show that the reburning effect of FUEL-3:3 increases with the increase of temperature, but there is a peak value at 1200-1250 K when φ=1. The NO reduction efficiency is only 38% at φ=1.5, 1300 K.

3.2. Effect of equivalence ratio

Figure 2 shows the variation of O₂, CO, NO, HCN and NO reduction efficiency with equivalence ratio. Compared with O₂ results, in the same equivalence ratio range, it is found that FUEL-CH₄ still fluctuates, while FUEL-3:3 almost achieves complete reaction, indicating that the oxidation rate of H₂ is faster than that of CH₄ and the reactivity of H₂ is better than that of CH₄. Compared with the results of CO, it is found that the critical equivalence ratio to the peak value of CO basically at φ=1~1.5, and the peak value is related to the temperature. The temperature increases the critical equivalence ratio corresponding to the peak value. The reburning effect of FUEL-3:3 is similar to that of FUEL-CH₄, which increases first and then decreases. There is an optimal condition for NO reduction, In D-N₂, the optimal equivalence ratio of FUEL-3:3 is consistent with that of FUEL-CH₄, and its optimal equivalence ratio hardly changes with temperature. Under D-30%CO₂, the optimal equivalence ratio of FUEL-3:3 is larger and increases slowly with the increase of temperature. At 1300 K, D-N₂, the reburning law and optimal operating conditions of FUEL-3:3 with equivalence ratio are very similar and close to those of FUEL-CH₄ in quantity. The optimal working condition is about φ=1.2, and the corresponding reduction efficiency is about 75%. The reburning efficiency of D-30%CO₂ is relatively poor, and the maximum reduction efficiency is about 35%.
3.3. Effect of dilution atmosphere

Figure 3 shows the variation of O$_2$, CO and NO with equivalence ratio under different dilution atmospheres. The increase of CO$_2$ concentration in dilution gas has obvious inhibition effect on oxidation process and reburning process. At the same time, it promotes the formation of high concentration CO. However, the trend of O$_2$, CO, NO versus equivalence ratio in the three different CO$_2$ concentration is still consistent. Comparing the difference between effects of D-30%CO$_2$ and D-60%CO$_2$ to the difference between effects of D-N$_2$ and D-30%CO$_2$, it can be found that when the
increase of CO$_2$ in dilution gas is 30%, the results of D-N$_2$ and D-30%CO$_2$ are obviously different, while the results of D-30%CO$_3$ and D-60%CO$_2$ are very close, which indicates that the influence of CO$_2$ concentration to a certain extent is limited.

3.4. Effect of H$_2$:CH$_4$ ratios

Figure 4. (a) D-N$_2$ (b) D-30%CO$_2$, the results of CO$_2$, CO and NO versus $\phi$ in different H$_2$:CH$_4$ ratios

Figure 4 shows the experimental and numerical results of CO$_2$, CO and NO with equivalence ratio at different H$_2$:CH$_4$ ratios. From FUEL-CH$_4$ to FUEL-5:1, according to the carbon-neutrality of H$_2$, the carbon emission will decrease with the increase of the mixing ratio of H$_2$, which is also verified by the results of CO and CO$_2$ in Figure 4a. With the H$_2$:CH$_4$ ratio from FUEL-CH$_4$ to FUEL-3:3, the peak values of the optimal operating conditions at 1100 K and 1200 K are reduced, but the reburning is optimized in the range of $\phi$=1-2.5, which makes the equivalence ratio range of good reburning conditions increase. At 1300 K, the reburning effects of the three ratios are very close. The simulation results show that the NO reduction effect of FUEL-5:1 is destroyed by the reaction environment produced by high H$_2$:CH$_4$. For NO reduction, H$_2$:CH$_4$=5:1 is not the appropriate fuel ratio.

From Figure 4b, it is found that the situation of NO reduction effect versus H$_2$:CH$_4$ at D-30%CO$_2$ is similar to that of D-N$_2$, which indicates that the clean combustion of carbon emission reduction and NO$_x$ emission reduction can be achieved simultaneously by mixing appropriate proportion of H$_2$ in CH$_4$, which has been verified under conventional combustion conditions (D-N$_2$) and high CO$_2$ combustion conditions (D-30%CO$_2$). Considering the carbon content of the fuel and the reburning effect obtained in this paper, H$_2$:CH$_4$=3:3 is a better ratio.

4. Conclusions

The effects of temperature, equivalence ratio, dilution atmosphere and H$_2$:CH$_4$ ratios on CH$_4$-H$_2$ mixture NO reburning were systematically studied. The conclusions are as follows:

The results of oxidation reaction in the variable temperature experiment and the variable equivalence ratio experiment show that the reactivity of the fuel after mixing with H$_2$ is enhanced. The NO reduction efficiency is higher in the range of 1000-1250 K after mixing with H$_2$. the maximum NO reduction can reach 55% under N$_2$ atmosphere and 38% under high CO$_2$ atmosphere.

The maximum NO reduction of FUEL-3:3 occurs at the temperature of 1300 K and the optimal equivalence ratio is 1.2, corresponding to the NO reduction efficiency is 75%. The NO reburning
The reburning effect of the fuel with the H₂:CH₄ ratio of 0:6, 1:5 and 3:3 is close, and more higher than that of the H₂:CH₄ ratio of 5:1, so the hydrogen blending ratio should not exceed 3:3. Considering the carbon content and NO reburning effect of the fuel, the H₂:CH₄ ratio of 3:3 is a better ratio.

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