

Experimental and numerical study on fuel-NO_x formation in oxy-fuel processes in a jet stirred reactor

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1 Abstracts

New experimental results on fuel-NO_x formation in oxy-fuel processes are obtained in a jet stirred reactor. In the present work, effects of CO₂ (0~97.4%), temperature (873~1323 K) and equivalence ratio (0.56~1.61) on fuel-NO_x in oxy-fuel processes are experimentally and numerically researched. NH₃ is selected as the N element source. The predicted results by the PG2018 mechanism (Progress in Energy and Combustion Science, 67, 31-68, 2018) are consistent with the experimental results. Compared with N₂ diluted conditions, CO₂ increases in diluents can reduce NO formation in fuel-lean conditions and HCN formation in fuel-rich conditions. Under fuel-lean conditions, the NO formation path: NH₃→NH₂→HNO→NO weakens with the increase of CO₂ concentrations. Under the fuel-rich conditions, HCN is abundantly produced and reduced with the increase of CO₂. Moreover, the N₂O formation is basically insensitive to the CO₂ concentration.

Key words: oxy-fuel, fuel-NO_x, NH₃, Jet stirred reactor

2 Introduction

CO₂ is formed from combustion processes and is the main source of greenhouse gas. The greenhouse effect has caused significant effects on global climate change. To meet this challenge and as an important step of carbon capture and storage, oxy-fuel combustion adopts O₂/CO₂, not air, as a diluent. Thus, the CO₂ concentration in flue gas can be increased such that the efficiency of CO₂ capture is increased and the cost of CO₂ capture is decreased. Oxy-fuel combustion can reduce NO_x formation from N₂ because N₂ is separated. However, elemental N exists in solid fuel, such as coal and biomass. Elemental N in solid fuel is the main source for the combustion process. CH₄ and most elemental N are gasified in the devolatilization process. HCN and NH₃ in volatiles are the main source of fuel-NO_x. NH₃ is the primary fuel NO precursor in low rank coal volatiles¹. In the present study, a mixture of CH₄ and NH₃ simulates fuel containing elemental N.

To the best of our knowledge, numerous studies on fuel-NO_x in air atmosphere have been performed. Mendiara et al.² experimentally researched NO formation characteristics in a flow reactor at high CO₂ concentrations when NH₃ is selected as the N source. High CO₂ can reduce NO formation under fuel-lean conditions and promote NO formation under fuel-rich conditions. Tian et al.³ experimentally studied NH₃ transformation characteristics in a CH₄/NH₃/Ar/O₂ premixed flame in a McKenna burner. They found that NH₂ + O ↔ HNO + H, NH₂ + NO ↔ N₂ + H₂O and NH + NO ↔ N₂O + H exhibit important effects on NO formation. No studies have assessed NO and HCN formation characteristic in a 0D reactor when NH₃ is selected as an N source. JSR (jet stirred reactor) is a type of 0D reactor. When a reactant and oxidizer enter this reactor, intensive mixing is noted, approximately reaching a completely premixed and stirred state.

Therefore, in the present study, the formation characteristics of fuel-NO_x in conventional and oxy-fuel conditions are studied in a JSR reactor. NH₃ is selected as the N element source. The effect of CO₂ concentration (0~97.4%), temperature (873~1323 K), and equivalence ratio (0.56~1.61) on fuel-NO_x formation in oxy-fuel processes are researched based on JSR experiments.

3 Experimental and numerical section

3.1 Jet stirred reactor

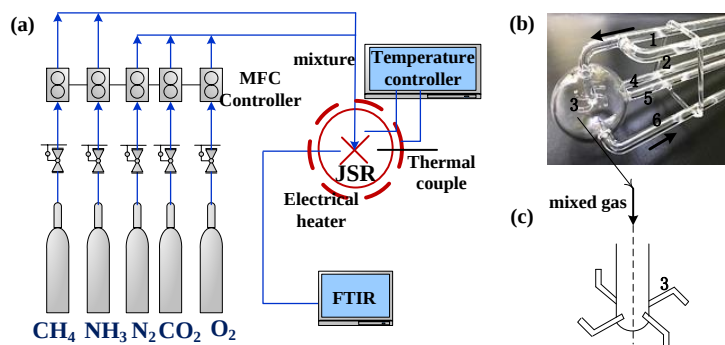


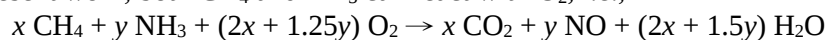
Figure 1. Schematic diagram of experimental facility: (a) system diagram, (b) picture of jet stirred reactor, (c) diagram of injects of jet stirred reactor

Figure 1 shows the experimental facility in the present work. Figure 1a is experimental system, including the gas supply system, electrically heated JSR reactor and measure system. As shown in Figure 1b, JSR consists of a 5-cm i.d. spherical fused silica sphere. Four injectors with nozzles of 1-mm i.d. are equipped for the admission of the gases to achieve stirring, as detailedly shown in Figure 1c. The JSR is placed inside the electrically heated system at 1.5 kW surrounded by insulation material. In Figure 1b, Inlet 1 means the mixture of CH₄ and NH₃. The ratio of CH₄ to NH₃ is 5:1. Inlet 2 means the mixture of O₂, N₂ and CO₂. Gases in Inlet 1 and 2 are premixed and stirred in advance before entering the spherical reactor. The length of this regime from the Inlet of jet stirred reactor to the inside of the spherical reactor is 10 cm. The residence time in the regime is only 1/200 of that in spherical reactor, efficiently preventing reaction occurrence before entering the reactor. The thermocouple (Pt–Pt10%Rh, 0.25% T) is inserted in Inlet 4 to assess temperature inside reactor. The stability of the electrical heater and temperature uniformity inside reactor have been tested.

In the present work, gas purity is greater than 99.99%. The gas flow is precisely controlled by mass flowmeter. The gas component after reaction is tested on-line by FTIR (DX4000, Gasmeter) with a resolution of 8 cm⁻¹ and scanning speed of 10 scans/s. Before entering the FTIR analyzer, the flue gas temperature is maintained at 180 °C. The concentrations of O₂, CO₂, NO, CO, HCN, N₂O can be tested by FTIR with ±1% error. In addition, O₂, CO₂, CO and NO concentrations are tested by an on-line gas analyzer (HORIBA PG350). Very good agreement between FTIR and PG350 analyses is noted for the compounds measured by both technologies (CO, NO and O₂).

2.2 Conditions setting

All conditions in the present work maintain total flow at 1 dm³/min (STP). CH₄ is 5000 ppm, and NH₃ is 1000 ppm. For the present work, both CH₄ and NH₃ can react with O₂, i.e.,



Therefore, the equivalence ratio is defined as

$$\phi = \frac{(\text{CH}_4 + \text{NH}_3)/\text{O}_2}{[(\text{CH}_4 + \text{NH}_3)/\text{O}_2]_{\text{stoic}}}$$

Cases 1~2 are used to study the effect of temperature under an oxy-fuel atmosphere. The temperature is 873~1323 K. Cases 3~5 are used to study the effect of the equivalence ratio under oxy-fuel atmosphere with an equivalence ratio of 0.56~1.61. CO₂ concentrations in diluent are 0, 0.3 and 0.6, respectively at Case 3, 4, 5. The detailed settings are listed in Table 1.

Table 1 Experimental conditions setting

Case	O ₂ -%	CO ₂ -%	T-K	Φ
1	2.0,1.13,0.7	0	873~1323	0.56,1.0,1.61
2	2.0,1.13,0.7	30	873~1323	0.56,1.0,1.61
3	2.0~0.7	0	1273	0.56~1.61
4	2.0~0.7	30	1273	0.56~1.61
5	2.0~0.7	60	1273	0.56~1.61

2.3 Numerical model

Numerical results are calculated through the PSR module in CHEMKIN PRO. AURORA code is adopted to perform chemical kinetics analysis. The reaction conditions in simulation process are consistent with that in experiments. The chemical mechanism (151 species, 1397 reactions) used in the work is put forward in the review about N components by Glarborg et al.⁴. This mechanism combines studies published over the last 40 years regarding N-containing chemical mechanisms based on the work of Miller et al.⁵. Predicted results based on this new mechanism are consistent with the experimental results with the exception of NO in high CO₂ atmospheres in fuel-rich cases.

3 Results and discussions

3.1 Effect of CO₂ concentration

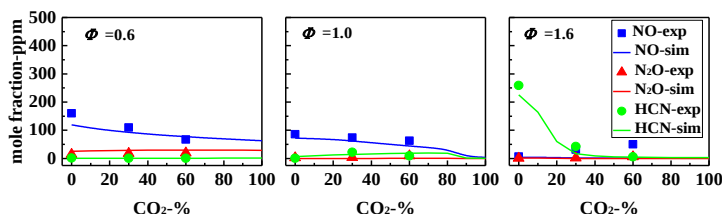


Figure 2. Profiles of NO, HCN, N₂O in oxidation process of CH₄ and NH₃ under 1273 K at different CO₂ (0~100%) and different equivalence ratio (a) 0.6; (b) 1.0; (c) 1.6

Figure 2 shows the profiles of NO, HCN and N₂O in different CO₂ concentrations in dilutions and different equivalence ratios at 1273 K. Under fuel-lean conditions ($\Phi=0.6$), when CO₂ is 0 in diluent, the NO formation is 160 ppm. In fuel-lean conditions, as the CO₂ concentration increases, NO formation gradually decreases. In this case, HCN formation is approximately zero. The formation of N₂O gradually increases as CO₂ increases but is still maintained at approximately 15 ppm. Under stoichiometric conditions ($\Phi=1$), NO formation decreases at all CO₂ concentrations compared with that in $\Phi=0.6$. The formation of N₂O decreases to less than 10 ppm. HCN formation is greater than 5 ppm. Under fuel-rich conditions ($\Phi=1.6$), N₂O formation is approximately zero. For NO formation in this case, NO formation increases as CO₂ concentration increases. When the CO₂ concentration in the diluent is 60%, NO formation reaches 50 ppm. However, the mechanism adopted in the work poorly predicts NO formation in fuel-rich conditions. Under $\Phi=1.6$, when the diluent is N₂, HCN formation is greater than 260 ppm. When the CO₂ concentration in diluent is 30%, HCN formation is sharply decreased to 46 ppm. As CO₂ increases further, less HCN is formed. Through simulation, when the CO₂ concentration in the diluent increases to 100%, HCN formation plateaus at zero.

Based on rate-of-production analysis under $\Phi=0.6$ and 1273 K, the conversion rate of NH₃ to NO or N₂ through different path are analyzed and shown in Figure 3. NH₃→NH₂→HNO→NO is the first important path of NO formation under $\Phi=0.6$ and 1273 K. When the diluent is N₂, the conversion rate of this path is greater than 25%. As the CO₂ concentration in diluent increases from 0 to 100%, the conversion rate of this path decreased to 17%, mainly because the increased CO₂ concentration weakens NH₂+O ↔ HNO+H, according to the sensitivity analysis. Among the six NO formation paths, NH₃→NH₂→H₂NO→HNO→NO strengthens as CO₂ increases mainly because the increased CO₂ concentration enhances NH₂+HO₂ ↔ H₂NO+OH. However, this path is not the main path for conversion of NH₃ to NO. When CO₂ in the diluent increases to 100%, the conversion rate of this path increases to only 6%. For NO formation, increased CO₂ inhibits NO formation. As shown in Figure 4, NH₃→NH₂→N₂, is the first important path of NH₃ transformation to N₂. As the CO₂ concentration increases from 0 to 100%, the conversion rate of this path increases from 18% to 22%, mainly because the increased CO₂ concentration enhances NH₂+NO ↔ N₂+H₂O, according to the sensitivity analysis. As the second important pathway for transformation of NH₃ to N₂, NH₃→NH₂→NNH→N₂ also increases from 10% to 13% as the CO₂ concentration increases from 0 to 100%. Because the increased CO₂ concentration enhances NH₂+NO ↔ NNH+OH and NNH ↔ N₂+H. Comprehensively, under fuel lean conditions, NO decreases as CO₂ increases in the diluent for two main reasons: (1) the transformation of NH₃ to NO is weakened; (2) the transformation of NH₃ to N₂ is strengthened.

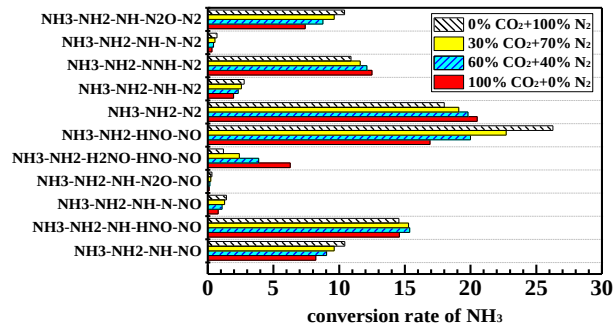


Figure 3. conversion rate analysis of NH₃ to NO or N₂ through different path under different CO₂ concentration (0,30%,60%,100%) based on rate of production analysis at fuel-lean ($\Phi=0.6$) condition and 1273 K

3.2 Effect of equivalence ratio

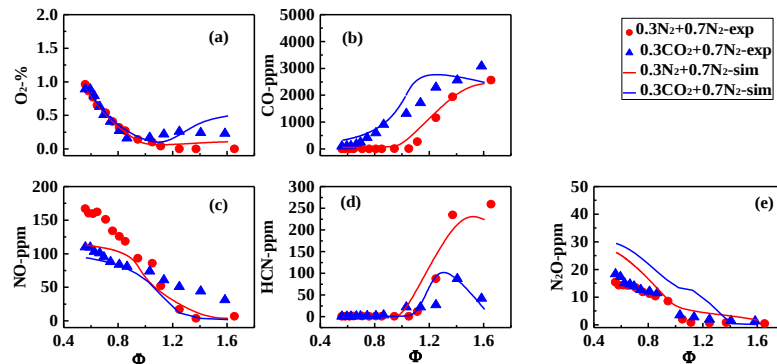


Figure 4. Experimental (symbols) and simulation (lines) results of NO, HCN and N₂O as a function of equivalence ratio (0.56~1.61) diluted by different CO₂ in diluent (0,30%). The inlet conditions correspond to case 3 and 4

Figure 4 presents profiles of NO, HCN and N₂O concentrations as a function of equivalence ratio (0.56~1.61) under 1273 K and different CO₂ concentrations in diluent (0 and 30%). Generally, under N₂ and 30% CO₂+70% N₂ atmosphere as the equivalence ratio increases, NO and N₂O concentrations gradually decrease. The HCN concentration initially increases and then decreases. Under N₂ atmosphere, the HCN peak occurs at $\Phi=1.45$. However, under 30% CO₂+70% N₂, the HCN peak occurs at $\Phi=1.4$. When $\Phi \geq 1$ and <1.4 , significant NH₂ is formed and promotes HCN formation. When $\Phi \geq 1.4$, NH₂ is transformed to NH₃. Less NH₂ is transformed to HCN.

3.3 Effect of temperature

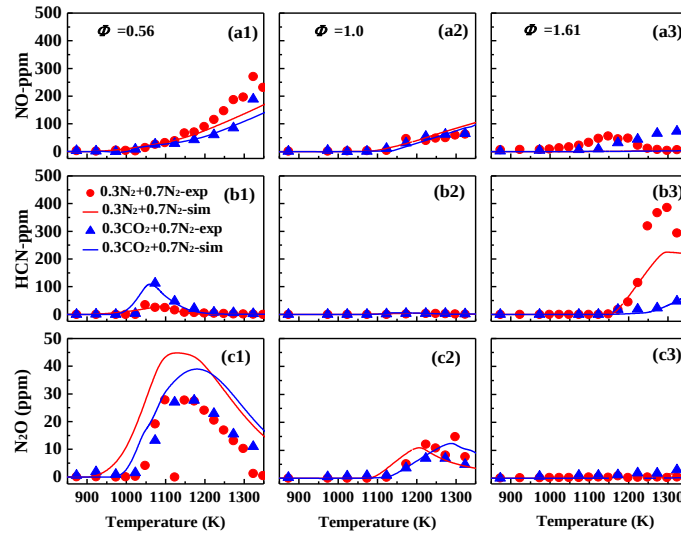


Figure 5. Experimental (symbols) and simulation (lines) results of NO, HCN, N₂O as a function of temperature (800~1400 K) at different equivalence ratio (0.56, 1.0, 1.61) and different CO₂ concentration in diluent (0, 30%). The inlet conditions correspond to case 1 and 2

Figure 5 presents the profiles of NO, HCN and N₂O as a function of temperature (800~1400 K) under different equivalence ratios (0.56 (a1,b1,c1), 1.0 (a2,b2,c2), 1.61 (a3,b2,c2)) and different CO₂ concentrations in diluent (0 (red), 30% (blue)) in a JSR reactor. For NO formation under fuel-lean conditions whether in conventional processor or oxy-fuel processes, NO formation gradually increases as the temperature increases. Under $\Phi=0.56$, NO formation begins at 1000 K. When 30% CO₂ is added to diluent, NO formation decreases by approximately 50 ppm. Under $\Phi=1$, NO formation begins at 1100 K. The addition of 30% CO₂ decreases NO formation to less than 10 ppm. In $\Phi=0.56$ and 1, increased temperature increases NO formation. According to sensitivity analysis and production rate analysis, $\text{NH}_2 + \text{NO} \leftrightarrow \text{N}_2 + \text{H}_2\text{O}$ is weakened and $\text{HNO} + \text{M} \leftrightarrow \text{H} + \text{NO} + \text{M}$ is strengthened under oxy-fuel processes as temperature increases.

Under fuel-rich conditions, compared with $\Phi=0.5$ and 1, less NO is formed. Under conventional conditions, as temperature increases, NO formation increases at first and later decreases, reaching the peak at 1150 K. However, under oxy-fuel processes (30% CO₂+70% N₂), more NO is formed as the temperature increases. The simulated results under fuel-rich conditions are not consistent with experimental results.

Regarding N₂O formation in reaction processes, as the temperature increases, N₂O formation increases at first and then decreases. At $\Phi=0.56$, the N₂O peak occurs at 1100 K and is approximately 30 ppm. At $\Phi=1$, the N₂O peak occurs at 1250 K and is approximately 15 ppm. At $\Phi=1.61$, minimal N₂O is formed. Compared with N₂ atmosphere, N₂O formation exhibits no obvious difference in oxy-fuel processes. According to sensitivity analyses and rate-of-production analyses, $\text{NH} + \text{NO} \leftrightarrow \text{N}_2\text{O} + \text{H}$ and $\text{N}_2\text{O} + \text{M} \leftrightarrow \text{N}_2 + \text{O} + \text{M}$

control N₂O formation. At temperatures greater than the critical temperature, N₂O(+M) ↔ N₂+O(+M) sharply increases. At higher temperatures, N₂O is decomposed.

For HCN formation, under fuel-lean conditions ($\Phi=0.56$), HCN occurs at a regime of 1000~1200 K because CH_x forms from underoxidized CH₄. CH_x reacts with NH₂ to form HCN through NH₂ → CH_xNH_y → (H₂CN, HCNH) → HCN. Under fuel-rich conditions ($\Phi=1.61$), HCN formation begins at 1150 K. Under N₂ atmosphere and as the temperature increases, HCN increases at first and then decreases, reaching the peak at 1250 K. However, under oxy-fuel conditions (30% CO₂+70% N₂), more HCN is formed as the temperature increases. In general, HCN in oxy-fuel conditions (30% CO₂+70% N₂) is reduced compared with conventional conditions. Under fuel-rich conditions, CH₄ oxidation is insufficient, and CH_x is formed. Under oxy-fuel processes (30% CO₂+70% N₂), more CH_x is formed as the temperature increases; therefore, HCN is formed.

4 Conclusions

In the present work, the effect of CO₂ concentration (0~97.4%), temperature (873~1323 K), and equivalence ratio (0.56~1.61) on NO, N₂O and HCN formation in oxy-fuel processes are experimentally researched in a JSR reactor. NH₃ is selected as the source of N element. The results predicted by PG2018 are consistent with the experimental results. Based on experimental and numerical results, the following conclusions can be made:

- (1) The main fuel-NO formation path is NH₃ → NH₂ → HNO → NO, regardless of N₂ or CO₂ as diluent. The NO-reburning chemistry cannot be ignored and it can even reduce the majority of NO at fuel-rich conditions. With the increase of CO₂ concentration, the fuel-NO formation path strengthens and the NO-reburning chemistry weakens, leading to the decrease of NO;
- (2) For the formation of NO, under fuel-lean conditions, it increases with the increase of temperature from 1100 K to 1400 K. Under the stoichiometric condition, the NO productions from N₂ and CO₂ atmospheres are nearly the same. Under fuel-rich conditions and temperatures above 1200 K, the high CO₂ concentration enhances the NO production due to the reduced NO-reburning chemistry;
- (3) For the formation of HCN, it is formed mainly through the pathway of NH₃ → NH₂ → CH_xNH_y → (H₂CN, HCNH) → HCN and the CH_x radical is significant for the HCN production;
- (4) Although the reaction is slightly delayed under high CO₂ concentration, the N₂O formation is basically insensitive to the CO₂ concentration, because the main N₂O formation reactions of NH+NO ↔ N₂O+H, N₂+O(+M) ↔ N₂O(+M) and N₂O(+M) ↔ N₂+O(+M) are insensitive to the variation of the CO₂ concentration, regardless of temperature, equivalence ratio;
- (5) For the present study, the prediction by PG2018 is found to be consistent well with the overwhelming majority of the present experimental data under both N₂ and CO₂ atmospheres. Important reactions such as NH₂+O ↔ HNO+H, HNO+OH ↔ NO+H₂O and NH₂+NO ↔ N₂+H₂O are identified for future development of the fuel-NO_x mechanism, especially for fuel-rich conditions under high CO₂ concentrations.

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