Experimental and kinetic studies on NO emission during pulverized coal preheating-combustion process with high preheating temperature

Shuai Wang [a], Guangqing Zhu [a], Yanqing Niu [a,*], Yiyu Ding [b], Shi'en Hui [a]

[a] State Key Laboratory of Multiphase Flow in Power Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China

[b] Department of Energy and Process Engineering, Faculty of Engineering, NTNU — Norwegian University of Science and Technology, Trondheim, Norway

Abstract

In this study, two connected drop tube furnaces (DTFs) were used to clarify the NO emission characteristics during the high-temperature preheating-combustion process. The most important factors, including preheating temperatures, residence times, and excess air ratios (EAR), were studied systematically. Experimental results showed that both increasing the preheating temperature and prolonging the residence time in the preheating zone promoted the release of coal-N as volatile-N, the reduction of volatile-N, and the interaction between char-N and nitrogen-containing gases, and therefore enhanced NO reduction. With the EAR increased in the preheating zone, the NO emission first decreased and then increased. There was an optimal EAR for NO reduction, which was 0.4 in this work. Meanwhile, the lowest NO emission was 223 $mg \cdot m^{-3}$, corresponding conversion ratio of coal-N to NO was 12.6% and NO removal efficiency was 60.38%. Moreover, kinetic modeling confirmed the experimental results, and rate of production (ROP) analysis indicated that the main radicals for NO destruction were NH_2, hydrocarbon (C_iH_j), HCCO, NCO and HCO. In addition, the NO reduction by C_iH_j was stronger than other nitrogen-containing compounds, except NH_2, which contributed nearly 30% of overall NO destruction.

Keyword: Preheating-combustion; Temperature; Excess air ratio; Kinetic modeling; NO

1. Introduction

In China, the total energy consumption was 4.86 billion tons of standard coal in 2019, and coal consumption accounted for 57.7% (Society, 2020). Confined by the structure of energy resources, coal continues to contribute a significant part for China's energy strategy for a long term. However, the utilization of coal causes lots of environmental problems, among which nitrogen oxide (NO_x) is one of the major pollutants responsible for the smog and acid rain formation. Developing clean coal usage technologies with high efficiency and low NO_x emission is becoming more and more urgent under the stringent emission standards for air pollutants. In the last several decades, many NO_x reduction and removal technologies, such as low NO_x burner (Song et al., 2020), air staging (Wang, Y. et al., 2020), reburning (Chernetskiy et al., 2018), and moderate or intense low-oxygen dilution (MILD) combustion have been developed. However, ultra-low NO_x emission and high efficiency combustion technologies remain required, with increasingly stringent emission standards for coal combustion.

Based on the understanding of NO_x formation and destruction, a promising method, pulverized coal (PC) preheating-combustion technology, was proposed. PC was preheated before entered the combustion zone. During the preheating stage, volatile in coal would easily release and promote the conversion of most volatile-N into N_2 in an oxygen-deficient environment (Taniguchi et al., 2012; Wu et al., 2019). All-Russian Thermal Energy Institute (Rabovitser et al., 2003) first proposed and investigated the NO_x emission of PC preheating technology by means of natural gas combustion-supporting. The NO_x reduction efficiency of 80% and 60% were achieved when PC was preheated to 1083 K and 863 K respectively. Similarly, the Gas Technology Institute conducted above research on a 0.88 MW test furnace and reached similar conclusions (Bryan et al., 2005; Rabovitser et al., 2007). Recently, Liu et al. (Liu et al., 2015a; Liu et al., 2014; Liu et al., 2015b) also investigated the

effect of PC preheating on NO_x emission characteristics in a 35 kW furnace in detail and found that NO emission could be reduced by 74% and 67% for bituminous coals with volatile content of 34.4% and 38.0% (with preheating temperature at 1073 K). Liu et al. (Liu et al., 2015a) also pointed out that PC preheating could be incorporated with other de-NO_x technologies such as air staging and MILD combustion. Besides, series of self-preheating swirl burners with multi-air staging were designed and evaluated in the same drop tube furnace. About 70% of NO_x emission was reduced and the final NO emission could reach 217 $mg \cdot m^{-3}$ (Zhu et al., 2021).

Meanwhile, a method to achieve preheated PC through a circulating fluidized bed (CFB) has been proposed and adopted by the Academy of Chinese, which shows the ability to implement stable PC combustion, high burnout efficiency and low NO emission. Ouyang (Ouyang et al., 2020; Ouyang et al., 2018a; Ouyang et al., 2018c; Ouyang et al., 2013) found that the NO_x emission concentration could be reduced to 372, 295, 259 and 265 $mg \cdot m^{-3}$ with preheating temperature at 1073, 1123, 1173 and 1223 K, respectively. After further coupled with flameless combustion technology (Liu et al., 2018; Ouyang et al., 2018b; Zhu et al., 2018), the NO_x emission value could be further reduced to 108 $mg \cdot m^{-3}$ (6% O_2). Above studies demonstrated the potential advantages of preheating-combustion technology to reduce NO_x. Besides, Ouyang et al. (Ouyang et al., 2013) suggested that raising preheating temperature benefitted the corresponding NO reduction efficiency and combustion performance of low volatile PC.

Raising the temperature can induce more coal-N to release and convert under oxygen deficient atmosphere (LeBlanc et al., 2017). Thus, more NO precursor prefers to form N_2, which can significantly avoid the NO formation during following combustion process (Bai et al., 2014; Taniguchi et al., 2011; Wang, S. et al., 2020). However, aforementioned studies were limited by low

preheating temperature, which was usually lower than 1173 K, especially for that preheat PC with CFB. There has not been a detailed research on the NO_x reduction potential of preheating-combustion technology with higher preheating temperature. In this paper, two electric heating drop tube furnaces were connected in series to provide a high-temperature preheating and combustion environment respectively. Higher preheating temperature was chosen to extend the preheating-combustion to a higher temperature level and reveal the NO reduction potential under higher preheating temperature. The effects of preheating temperature, residence time and excess air ratio (EAR) in preheating zone on NO formation were evaluated to extend PC preheating technology to a higher preheating temperature. Moreover, the migration and transformation characteristics of coal-N were explored through kinetic modeling to reveal the mechanism of preheating-combustion technology to reduce NO with higher preheating temperatures.

2. Experiments

2.1 Fuel

Table.1 Fuel Analyses of Huangling (HL) Bituminous Coal

Parameter	Ultimate Analysis/%					Proximate Analysis/%			
	C_d	H_d	N_d	O_d	S_d	M_{ad}	A_d	V_{daf}	FC_{ad}
Value	70.65	4.39	0.86	12.15	0.49	3.80	11.46	37.69	53.08

$_d$: dry basis, $_{ad}$: air dried basis, $_{daf}$: dry and ash-free basis.

In this experiment, Huangling (HL) bituminous coal, characteristic by high volatile content up to 37.69%, was chosen. High volatile content favors the release of coal-N during devolatilization. Therefore, more nitrogen-containing compounds tend to migrate into gas phase and convert in oxygen-deficient condition during preheating, which would benefit NO reduction and give a better insight into the NO_x reduction potential of preheating-combustion technology. The coal sample was

sieved to 75~90 μm and dried at 378 K for 24 hours before the preheating-combustion experiments. The coal properties were summarized in Table 1.

2.2 Experimental apparatus

As shown in Fig.1, the PC preheating-combustion process was conducted in two connected electric heating DTF. The furnace can achieve the maximum temperature of 1873 K. A corundum tube, with an inner diameter of 51 mm and length of 1200 mm, was fixed in the center of the furnace to act as reactor. By controlling the interior temperature of the upper furnace for preheating the PC, the inner temperature of the bottom furnace was adjusted for burning the preheated product.

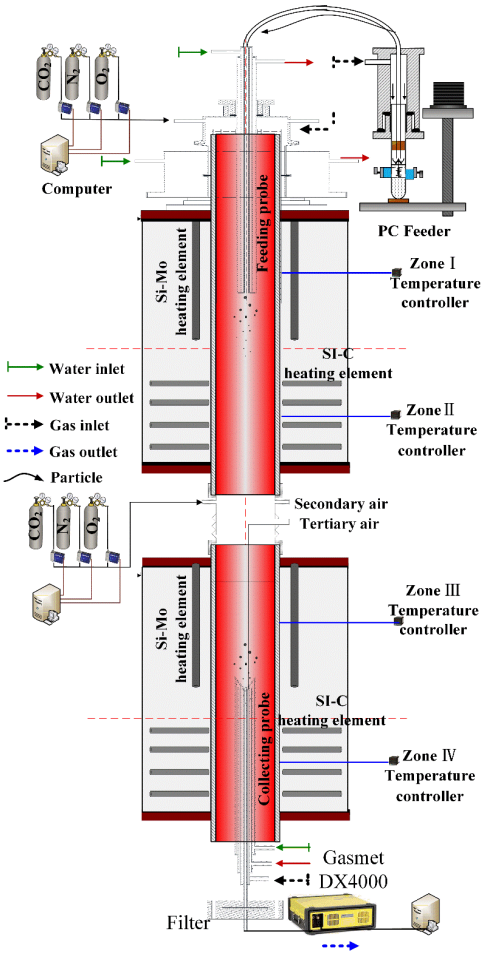


Fig.1 Schematic diagram of PC preheating-combustion system

In this work, two DTFs were used and each atmosphere could be controlled separately. Therefore, the preheating zone and combustion chamber have their own EAR and temperature,

101 using EAR_p, T_p and EAR_c, T_c to denote, respectively. EAR was defined as Eq.1.

102 $$EAR = \frac{\text{amount of oxygen supplied}}{\text{amount of oxygen required for stoichiometry}} \quad \text{(Eq.1)}$$

103 During experiment process, the preheating oxidizer was injected from the upper furnace,
104 whereas the oxidizer for combustion of preheated fuel was injected from the connector between
105 those two DTFs. Each flow rate was controlled according to the PC feeding rate and EAR. The
106 overall EAR was kept constant at 1.2, i.e., $EAR_p + EAR_c = 1.2$, which was the same as that in actual
107 boiler. The experimental system consisted of some auxiliaries, including PC feeder, gas distributer,
108 particle filter and flue gas analyzer. Detailed information on each auxiliary and calculation method
109 of coal-N conversion can be found in our previous paper (Wang, S. et al., 2020).

110 Table.2 Experimental conditions

Parameters	Values
T_p/K	1373,1473,1573
T_c/K	1273,1473
EAR_p	0,0.1,0.2,0.4,0.6,0.8,1.2
Residence time/s	0.1,0.15,0.185,0.225,0.3,0.45
EAR_p+EAR_c	1.2
Overall residence time/s	~1.0

111 ## 2.3 Kinetic modeling

112 In order to quantitatively investigate the migration and conversion of coal-N, preheating
113 combustion process is modeled using two connected plug flow reactors (PFR) with Chemkin-Pro.
114 Two gas inlets were required, namely Inlet I (representing the devolatilization products, char, and
115 oxidizer for preheating stage) and Inlet II (oxidizer for preheated products). The detailed kinetic
116 mechanism used herein was a combination of the heterogeneous mechanisms developed by

Hashemi et al. (Hashemi et al., 2011) and the homogeneous mechanisms developed by Glarborg et al. (Glarborg et al., 2018). The heterogeneous mechanisms were used to simulate the combustion of char and conversion of char-N, and the homogeneous mechanisms was used to simulate the conversion of gaseous species. Actually, Hashemi also propose a single step reaction, as shown in R1, to handle the devolatilization of PC (Hashemi et al., 2011).

$$C_{290}O_{51}N_5H_{525} \rightarrow 18H_2O+5HCN+C_{166}+32CH_4+25CO+4CO_2+29C_2H_4+120H_2 \quad \text{(R1)}$$

However, this single reaction can't fully capture the effect of devolatilization temperature on the proportion of volatile and char, especially the release of coal-N into gas phase. A modification must consider the influence of preheating temperature. Therefore, the chemical percolation devolatilization (CPD) model (Tian et al., 2001) was used here to predict the composition of volatile and the release of coal-N. The results of CPD prediction were taken as input condition for above-mentioned kinetic modeling. The assumed chemical formula of char, $C_{412}N_5$, proposed by Hashemi (Hashemi et al., 2011), is adopted. We keep using the same formula even though there are some slightly difference regarding to the ratio of N/C between the coal used here and the coal used by Hashemi (Hashemi et al., 2011). Since what we focus is the conversion ratio of coal-N to NO rather than the burnout of char. Therefore, the amount of char for simulation input is decide according to the coal-N balance. Input of char is calculated according to Eq.2. The detailed input parameters for Chemkin-Pro can be found in Supplementary file.

$$n_{\text{char}} = \frac{m_{\text{coal}} \times N_{\text{d}} \times N_{\text{char}}}{M \cdot 5} \quad \text{(Eq.2)}$$

where n_{char} denotes the mole of char for calculation input; m_{coal} is the feeding mass of PC; N_{d} is the nitrogen content in coal as shown in table 1; N_{char} is the fraction of coal-N remain in char after devolatilization during modeling process; M is the molar mass of nitrogen, which is 14 here.

3. Results and discussion

3.1 Effect of preheating temperatures on NO emission

Fig.2 shows the effects of preheating temperatures on NO emission under different EAR_p. Compared with conventional PC combustion (EAR_p=1.2), preheating was observed to pose an extraordinary impact on NO emissions (EAR_p=0.2, 0.4). NO emission was reduced significantly after preheating, confirming the excellent NO reduction potential of PC preheating-combustion technology. Furthermore, as the preheating temperature increased, the NO emission decreased. For instance, the NO emission decreased from 288 to 223 $mg \cdot m^{-3}$ with an increase in the preheating temperature from 1373 to 1573 K (EAR_p = 0.4). Besides, NO was reduced by 252, 297, and 350 $mg \cdot m^{-3}$ when PC was preheated to 1373, 1473, and 1573 K, respectively. The difference in NO emission under conditions with and without preheating became more pronounced with elevated preheating temperatures. The corresponding performance of the NO reduction was improved from 46.67% to 60.38%, and the post-combustion processing of flue gas would benefit greatly in meeting the NO_x emission requirements.

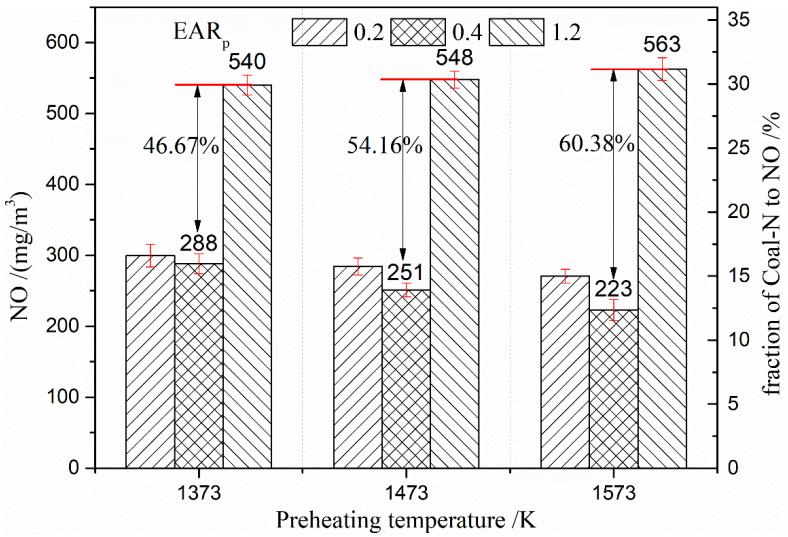


Fig.2 Effects of preheating temperatures on NO emission under different EAR_p.

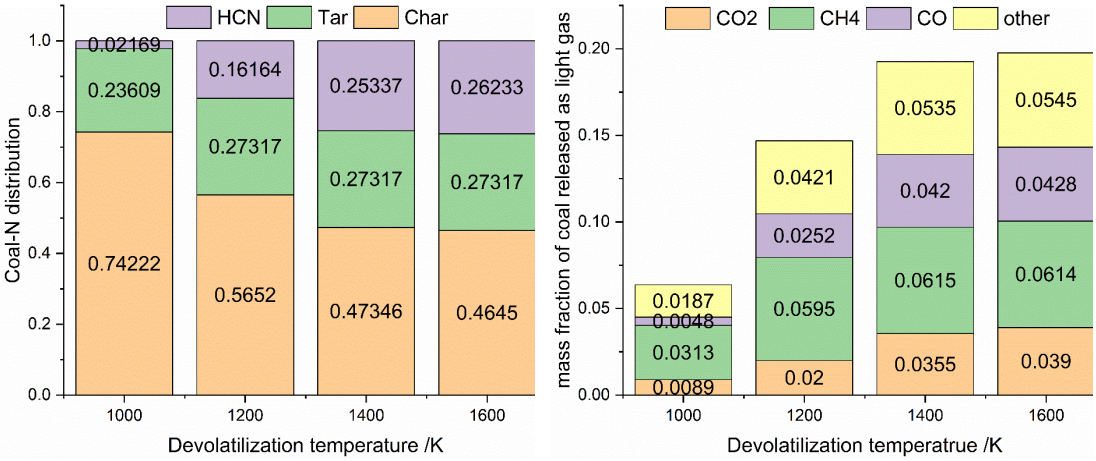
In this study, all experimental temperatures for both preheating and combustion were less than

1773 K. Consequently, the contribution of thermal NO to the final NO emissions would be significantly low (Glarborg et al., 2003). The measured NO was mainly derived from the oxidation of coal-N. Thus, subsequent analysis on the effects of preheating temperature mainly focused on the conversion of coal-N. Based on information in the literature, temperature is thought to have a significant influence on the splitting of coal-N into volatiles and char (Niksa, 2019a, b). The effect of the preheating temperature on coal-N distribution can be predicted using CPD model. The results are shown in Fig.3a. Around a quarter of coal-N at the preheating temperature of 1000 K was released as volatile-N, while it reached more than a half at the preheating temperature of 1600 K. Similar results that the nitrogen fraction released as volatile increased dramatically with increased temperature were reported in the literature (Niksa, 2019a, b). Under high preheating temperatures and fuel-rich atmospheres, more coal-N tends to be released and converted to N_2 rather than to NO in preheating stage (Liu et al., 2014), thus enhancing the potential for NO reduction with PC combustion (Niu et al., 2017). This conclusion is consistent with the results of He et al. (He et al., 2004), who indicated that the greater the proportion of volatile-N to coal-N, the more fuel nitrogen can be converted to N_2. By contrast, during the conventional PC combustion process without preheating, coal-N was released and converted under fuel-lean condition. Thus, temperature would pose reverse impact on NO formation. A higher temperature accelerated the volatile-N oxidation and the NO formation under an oxidizing atmosphere, whereas a higher temperature favors the NO reduction under a reducing atmosphere. Thereby, NO emission for that with and without preheating differed more pronounced at higher preheating temperatures.

In a fuel-rich zone, hydrocarbon (C_iH_j) also plays as a major factor in NO reduction, especially under high temperatures (Taniguchi et al., 2010). The reaction between NO and C_iH_j could be

expressed in a simplified global reaction, as shown in R2. Yields of C_iH_j from coal preheating have also been predicted using the CPD model (Tian et al., 2001). Fig.3b specifically indicated that the concentration of C_iH_j increased with the raised temperature. Yields of C_iH_j at 1600 K were almost twice that of 1000 K. The 'other' in Fig.3 b) means the hydrocarbon species other than CH_4 in volatile, including C_2H_4, C_2H_6. Besides, temperature would not only accelerate the yields of C_iH_j during devolatilization but also the reaction rate between C_iH_j and NO (Hu et al., 2019; Taniguchi et al., 2010). Finally, high preheating temperature promoted the conversion of NO_x precursor to N_2, thus reducing the final NO emission.

$$NO + C_iH_j \rightarrow HCN + ... \quad \text{(R2)}$$



a) coal-N distribution b) light gas distribution

Fig.3 Effects of preheating temperatures on devolatilization products predicted by the CPD model.

3.2 Effects of residence times in preheating zone on NO emission

Fig.4 shows the effects of residence times in preheating chamber on NO emission under different preheating and combustion temperatures. It was observed that the measured NO showed a remarkable decrease as the residence time increase. The NO dropped from 593 $mg \cdot m^{-3}$ to less than 379 $mg \cdot m^{-3}$ as the residence time increased from 0.1 s to 0.45 s (EAR_p=0.2, T_p=1573 K and T_c=1473 K). This meant that the preheating time for an actual boiler should be prolonged as much as possible

to reduce NO_x formation during the preheating-combustion process. However, it should be noted that, in our experiment, the curve became flat when the residence time continued to increase after a rapid decline at T_p=1673 K, T_c=1473 K and EAR_p=0.3. This indicated that a NO reduction threshold existed when the residence time was sufficiently long. This threshold value appeared earlier with the elevated preheating temperature and EAR_p.

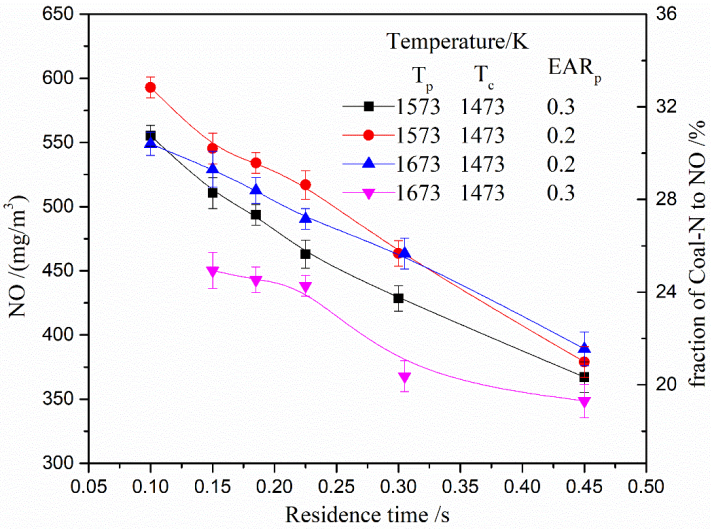


Fig.4 Effects of residence times in the preheating zone on NO emission.

NO formation from the combustion of preheated PC can be attributed to two main sources: the homogeneous reaction of volatile-N and the heterogeneous reaction of char-N (Molina et al., 2009). This study therefore centered on two aspects of the reduction in NO formation with an improvement in preheating time: the N_2 formation from volatile N and the association of char-N and other nitrogen-containing gasses to mitigate the NO formation during char combustion. Attributing to long residence time in preheating zone, the gas phase reaction became more complete, resulted in more formation of N_2 and less existence of reactive nitrogen containing species (such as HCN) in outlet of preheating chamber. Therefore, NO emission from oxidation of preheated gas dropped down. Besides, some researchers have shown that HCN and its precursors could interact considerably with char to form N_2 (Molina et al., 2009; Wu et al., 2019). With a prolonged residence

time in oxygen deficient atmosphere, nitrogen containing sites on the char surface may have greater potential to react with nitrogen containing gases, such as HCN to convert into N_2. This suggested that with prolonged preheating time, a portion of char-N continues to interact with nitrogen containing species and convert to N_2, resulted in less nitrogen exists in char (Ma et al., 2019; Ulusoy et al., 2019). Consequently, less char-N reduces the potential of NO formation during the oxidation of preheated char, benefiting the final reduction of NO emission during preheating-combustion process.

3.3 Effects of the stoichiometric ratio in the preheating zone on NO emission

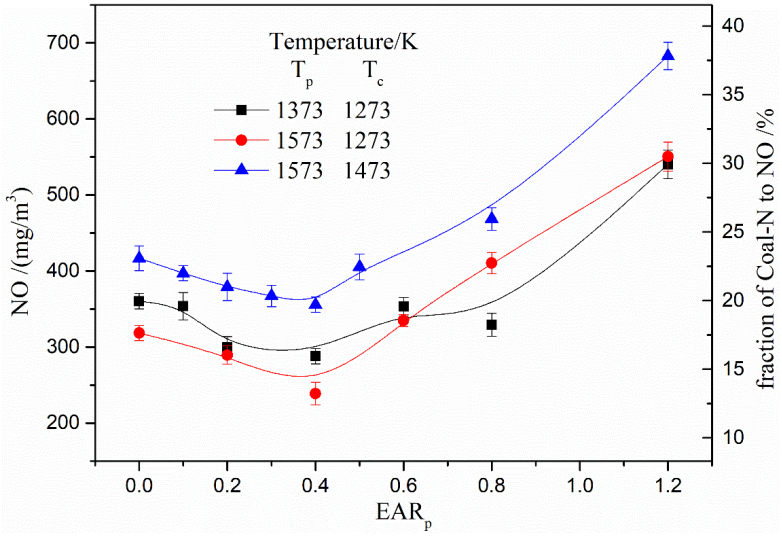


Fig.5 The influence of EAR_p on NO emission

Fig.5 shows the effects of EAR in the preheating zone on NO formation under different preheating and combustion temperatures. It was obvious that NO emission decreased first and then increased with the increase of EAR_p, even under different preheating temperatures and combustion temperatures. the NO emission achieved its lowest value when EAR_p was around 0.4.

For the experiments conducted in the single preheating chamber, the lowest NO in the outlet of preheating zone was achieved in EAR_p=0.1 (Wang, S. et al., 2020). However, for the preheating-combustion process, the lowest NO in the outlet of combustion chamber was achieved in EAR_p=0.4.

The shift of the optimized EAR_p to a higher level indicated that the optimization for NO formation in single preheating process would not work in the whole preheating-combustion process. The main reason was the continue conversion of nitrogen containing species in preheated fuel. The overall EAR was kept constant as 1.2. Thus, the newly provided oxidizer for combustion of preheated fuel of EAR_p=0.2,0.4,0.6 was EAR_c=1.0,0.8,0.6, respectively. When preheated fuel got into combustion chamber, it met the combustion air and the nitrogen containing species continued to convert. Especially for the condition of EAR_p=0.2, the remained HCN in preheated gas was oxidized quickly once encountering oxygen. Thus, the chance to form NO from HCN and char-N in lower EAR_p would be greater than that in high EAR_p due to the higher partial pressure of oxygen. Max et al. (Weidmann et al., 2016) also indicated that the contribution of NO from char-N and HCN increases with increasing available oxygen. In this study, the final NO achieved its lowest value at EAR_p=0.4, with NO reduction efficiency of 60.38%. Under such condition, volatile-N was mainly converted in the preheating stage under an oxygen deficient atmosphere (Wang, S. et al., 2020). Thus, the conversion of char-N will contribute nearly 40% of NO. This is in line with the findings of Glarborg (Glarborg et al., 2003; Glarborg et al., 2018) and Pohl (Pohl and Sarofim, 1977). Both reported that 60-80% of NO during bituminous coal combustion could be attributed to the conversion of volatile-N, whereas the other 20-40% of NO is typically from char-N. Therefore, it can be concluded that preheating-combustion process can effectively control NO emission from volatile-N (Ouyang et al., 2020). Moreover, the combustion of preheated fuel can be integrated with other technologies, such as air staging and MILD combustion, to further reduce the NO from char-N (Liu et al., 2015a; Liu et al., 2014; Liu et al., 2015b).

3.4 Kinetic modeling studies of NO formation during preheating-combustion

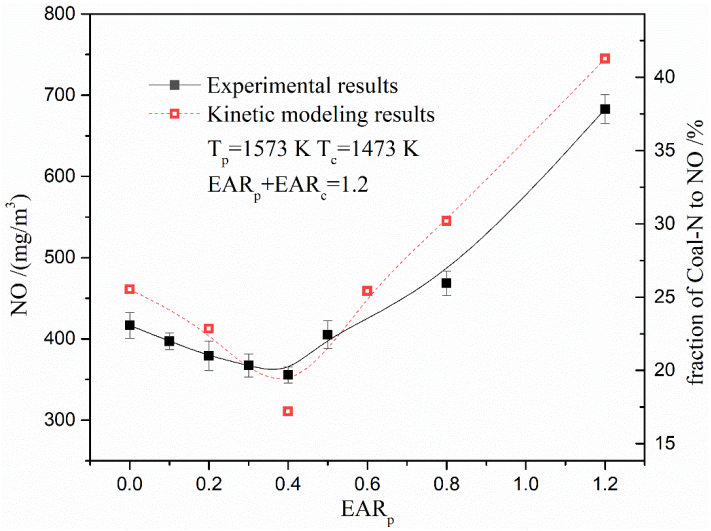
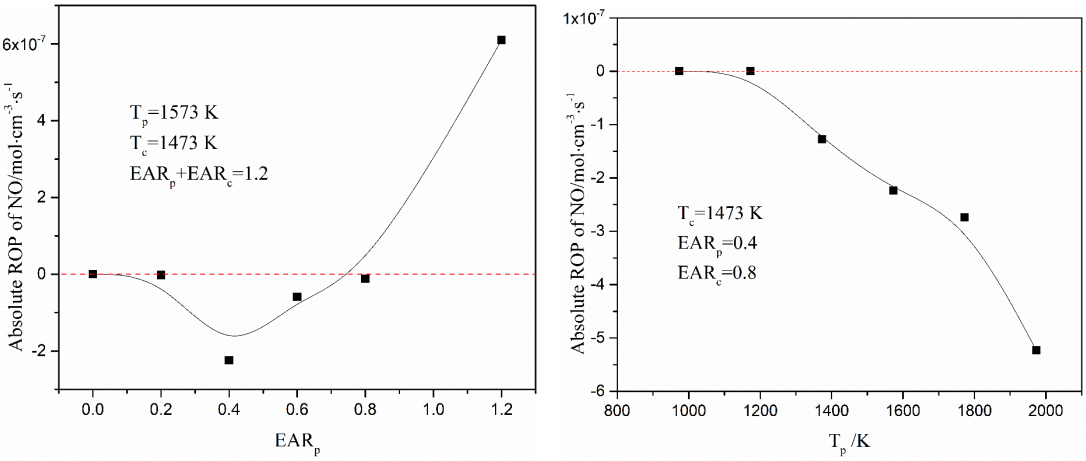


Fig.6 Comparison of experimental and modeling results

Fig.6 shows a comparison between the experimental data and modeling values. Compared with the experimental data, the kinetic modeling of preheating-combustion process gave a well reproduction on the NO emission. Although some slight derivation existed between experimental and kinetic modeling results, the interesting fact was that both the experiment and simulation of preheating-combustion achieved the lowest NO emission at EAR_p=0.4.



a) Effects of EAR_p b) Effects of T_p

Fig.7 Absolute ROP of NO at 0.2 s

To explain the dependence of NO on the preheating temperature and EAR_p, rate of production (ROP) analysis of NO was also performed. As shown in Fig. 7, the lowest absolute ROP of NO was achieved with EAR_p=0.4, and the ROP of NO decreases rapidly when the preheating temperature

increased under oxygen deficient conditions.

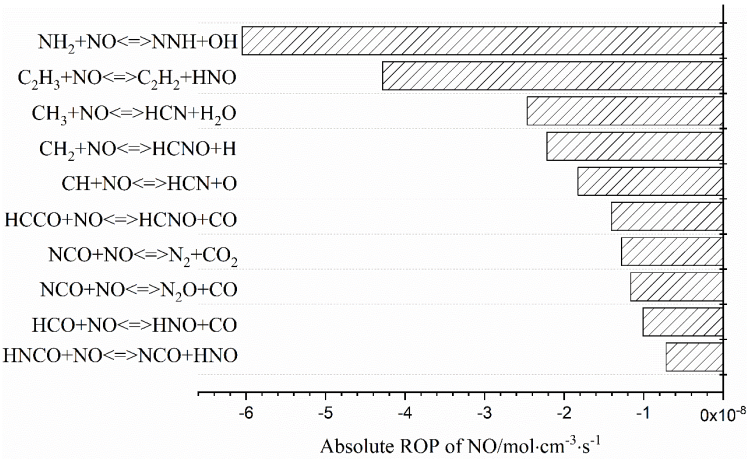


Fig.8 Absolute ROP of NO for different radicals at 0.2 s (T_p=1573 K, T_c=1473 K, EAR_p=0.4, EAR_c=0.8)

Furthermore, the ROP analysis could illuminate the main reactions and species that played a major role in NO formation and destruction. The analysis showed that NH_2 played a dominate role in NO destruction, accounting for nearly 30%, as presented in Fig.8. In addition, a significant part of NO was consumed by hydrocarbon radicals (C_iH_j), such as CH_3+NO, CH_2+NO and CH+NO, which was consistent with the results of experiment conducted by Degaut (Dagaut and Lecomte, 2003). Other nitrogen-containing compounds, such as NCO and HNCO, could also reduce NO, but the influence was slight.

4. Conclusion

In this work, NO emission characteristics during PC preheating-combustion process were investigated using two series connected drop tube furnaces, and kinetic modeling of this process was also conducted to better understand NO formation and destruction. The main conclusions are as follows:

1) Increasing the temperature and prolonging the residence time in the preheating zone were beneficial to the release and reduction of coal-N and the interaction between char-N and nitrogen containing gases, which enhances the NO reduction potential of preheating-combustion process.

2) With an increase of excess air ratio (EAR) in the preheating zone, the NO emission first decreased and then increased. An optimal EAP in preheating zone was identified at 0.4,

correspondingly, the lowest NO emission was 223 $mg \cdot m^{-3}$.

3) The results of kinetic modeling, which considered both homogeneous and heterogeneous effects, showed an ability to reproduce the experimental results. Rate of production analysis indicated that the importance of main radicals on NO destruction followed the sequence: NH_2> C_iH_j> HCCO>NCO>HCO.

Acknowledgements

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Supplementary file

Experimental and kinetic studies on NO emission during pulverized coal preheating-combustion process with high preheating temperature

Shuai Wang [a], Guangqing Zhu [a], Yanqing Niu [a,*], Yiyu Ding [b], Shi'en Hui [a]

[a] State Key Laboratory of Multiphase Flow in Power Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China

[b] Department of Energy and Process Engineering, Faculty of Engineering, NTNU — Norwegian University of Science and Technology, Trondheim, Norway

Input conditions for kinetic modeling in Chemkin-Pro were provided for the reproduction of the numerical results in this paper in Table S1.

Table S1 Detailed input parameters for Chemkin-Pro

species	input value ($L \cdot min^{-1}$)	
	Inlet I	Inlet II
N_2	4.86;4.815;4.771;4.727;4.683;4.595;4.507;4.332 (EAR_p=0; 0.1; 0.2; 0.3; 0.4; 0.6; 0.8; 1.2)	4.473;4.517;4.439;4.605;4.648;4.737;4.824;5 (EAR_c=1.2; 1.1; 1.0; 0.9; 0.8; 0.6; 0.4; 0)
O_2	0;0.043;0.878;0.132;0.176;0.263;0.351;0.527 (EAR_p=0; 0.1; 0.2; 0.3; 0.4; 0.6; 0.8; 1.2)	0.527;0.483;0.561;0.395;0.351;0.263;0.176;0 (EAR_c=1.2; 1.1; 1.0; 0.9; 0.8; 0.6; 0.4; 0)
HCN	0.004052	0
CO	0.015321	0
CH_4	0.038375	0
H_2O	0.055556	0
CO_2	0.008886	0
C_2H_6	0.0182	0
Char	0.000704	0