

EFFECTS OF DEEP OXYGEN-STAGING ON NO_x FORMATION DURING OXY-FUEL CO-COMBUSTION OF COAL-BASED SOLID FUELS

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ABSTRACT

Staged combustion and oxy-fuel combustion are both effective technologies to control NO_x emission for power plant. Besides, blending fuel is also widely used in power plants. In this paper, CHEMKIN software was used to simulate the NO_x formation characteristics. The co-combustion simulation of semi-coke and bituminous coal in this paper was under oxy-fuel atmosphere and deep oxygen-staging conditions. All of these combustion conditions were considered to explore the rule and reaction path of NO_x formation. The simulation results show that when the temperature of the main combustion zone is below 1400 °C, the conversion of NO to N₂ is promoted, while the condition is opposite at temperature above 1400 °C. Accelerating the NH₂ transforming to NH rather than HNO can promote the fuel-nitrogen transforming to N₂, reducing the generation of NO. This study can provide new insight into NO_x formation and reaction mechanism of boiler deep oxygen-staging oxy-fuel co-combustion.

Keywords: deep oxygen-staging combustion, NO_x, blending combustion, oxy-fuel combustion

1. INTRODUCTION

Deep oxygen-staging combustion and oxy-fuel combustion are both effective technologies to control NO_x emission for power plants [1]. Besides, blending fuel, such as semi-coke is also widely used to reduce the cost of electricity generation in power plants [2]. Semi-coke has a high char nitrogen fraction, so the high NO_x emission is an obvious defect for semi-coke [3]. CHEMKIN software can be used to simulate the formation process of nitrogen oxides during combustion. Recently, lots of scholars used CHEMKIN to explore the combustion problems. Sieradzka et al. [4] and Monika et al. [5] used CHEMKIN to predict coal pyrolysis, combustion, and gasification products. Hussein et al. [6]

used the PSR (perfectly Stirred Reactor) and PFR (Plug Flow Reactor) in CHEMKIN software to simulate the impacts of a new ammonia-hydrogen combustion device on NO_x emission reduction.

However, in O₂/CO₂ atmosphere and deep oxygen-staging conditions, there are few studies on NO_x formation mechanism of co-combustion, especially the co-combustion of semicoke and bituminous. Therefore, in this paper, the combustion model used three emission reduction strategies in the same time, including deep oxygen-staging, blending and oxy-fuel combustion to explore the rule and reaction path of NO_x formation. This study can provide guidance to the NO_x reduction in oxy-fuel combustion boilers.

2. MATERIAL AND METHODS

2.1 Model building

The PFR (Plug Flow Reactor) in CHEMKIN software was used as a simulation reactor. GRI-mech3.0, the standard methane oxidation mechanism of The American Institute for gas dynamics, consists of 5 reaction elements C, H, O, N and Ar, 53 chemical substances and 325 elementary reactions. Converting solid fuel to CH₄ in the simulation is helpful to simplify the problem. During pulverized coal combustion, a large amount of nitrogen conversion takes place in the gas phase. Hydrocarbons are the main components of the volatiles. It has differences with the actual pulverized coal combustion process, because the conversion of char nitrogen and the heterogeneous reduction of NO_x are not considered. This simplification results in a deviation from the actual direct prediction of NO_x formation [7]. In this study, although methane combustion simulation cannot fully reflect the nitrogen conversion in coal combustion, it can still explain the formation and reduction of NO_x during conventional combustion. Therefore, in this study, bituminous coal and semi-coke were both converted to CH₄, and the nitrogen in them

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were regarded as mixtures of HCN and NH₃. Due to the different chemical properties, HCN in bituminous coal accounts for 70%, and NH₃ accounts for 30%. HCN in semi-coke accounts for 90%, and NH₃ accounts for 10%. Fig. 1 shows the model in the CHEMKIN simulation.

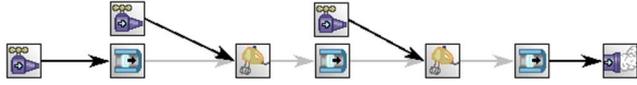


Fig 1 deep oxygen-staging combustion model

2.2 Parameter setting

The setting of the basic operating condition of the burning substances is shown in Table 1. The data in the Table1 are the volume flow rates for each substance, and Ncm³/min is selected as the unit. The setting of the basic conditions of the combustion physical parameters is shown in Table 2. The temperature of gases (including bituminous coal primary air, semi-coke primary air and burnout air) before entering the PFR reactor is indoor temperature, which is uniformly selected as 25 °C. When the gas enters the PFR reactor, it is heated by radiation and convection, and the primary gas begin to burn. The temperature in the furnace is set as 1400 °C, and the heat transfer coefficient is uniformly selected as 0.002 J/(cm²·K·s).

Table 1 Basic conditions of combustion substances

Volume flow rate of different components (Ncm ³ /min)	Bituminous coal primary gas	Semi-coke primary gas	Burnout gas
CH ₄	180.0	180.0	/
NH ₃	0.4823	1.660	/
HCN	1.126	0.184	/
O ₂	324.0	324.0	216.6
CO ₂	1218.9	1218.9	814.8

Table 2 Basic conditions of combustion physical parameters

	Main combustion zone	Burnout zone
Excess air coefficient α	0.9	0.3
$T/^\circ\text{C}$	1400	1100
Heat transfer coefficient of furnace $\theta/\text{J}/(\text{cm}^2\cdot\text{K}\cdot\text{s})$	0.002	0.002
L/mm	500	500
Semi-coke blending proportion		50%
Blending location/mm	100	/

2.3 NO_x conversion rate calculation

According to the basic principle of atomic conservation, the calculation of NO_x conversion rate is to calculate the percentage of N atoms of HCN and NH₃ converted into then of NO_x. NO_x is mainly NO and NO₂. The specific calculation is as follows:

$$\text{NO}_x \text{ conversion rate} = \frac{C(\text{NO} + \text{NO}_2) \text{ in the outlet}}{C(\text{HCN} + \text{NH}_3) \text{ in the inlet}}$$

2.4 Sensitivity analysis

Sensitivity analysis is a method to study the response of system to small disturbance [8]. For the chemical reaction system, the influence degree of the reaction rate constant change on the production concentration change is sensitivity. The sensitivity coefficient can quantitatively reflect the influence of each reaction on the calculation results of each component. The greater the absolute value of the sensitivity coefficient, the greater the influence of the reaction on the generation or reduction of NO. By analyzing the sensitivity coefficients of each reaction, the elementary reactions closely related to NO reduction can be obtained. The expression of sensitivity coefficient can be referred in previous publication [8]. In this paper, the sensitivity coefficient was obtained directly from CHEMKIN.

2.5 Model validation

As shown in Fig. 2, the NO_x conversion curve calculated based on this model is similar to the variation trend in reference [7] and [9].

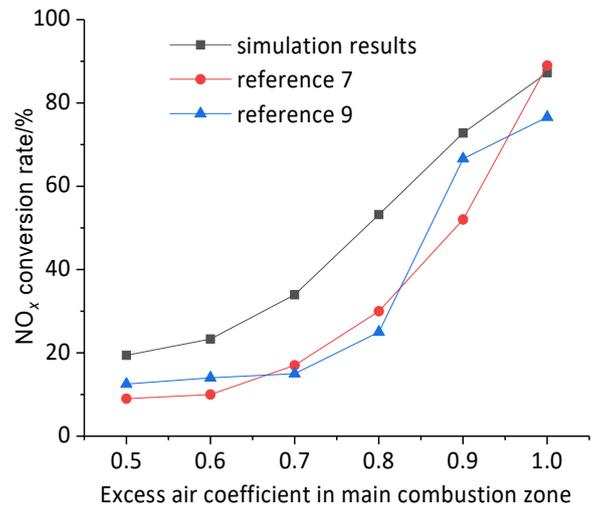


Fig 2 NO_x conversion rate at different excess oxygen coefficients of main combustion zone when the main combustion temperature is 1500 °C

The data in the reference [7] are from simulations and the data in the reference 9 are from experiments, so

it can be considered that the law is similar. Due to different parameters set under different conditions, the specific value has a little difference. Therefore, the numerical approach in this paper is valid.

3. RESULTS AND DISCUSSION

3.1 Characteristics of NO_x formations in different temperatures of main combustion zone

In the co-combustion model of semi-coke and bituminous coal, a total of three PFR reactors participated in combustion, and the temperature of the first and second reactors was changed at the same time, while the other conditions were kept as unchanged. Thus, the formation of NO_x with different temperatures could be obtained. As can be seen from Fig. 3, that NO_x conversion increases from 1200 °C to 1400 °C and then decreases from 1400 °C to 1600 °C in the main combustion zone in O₂/CO₂ combustion atmosphere. The NO_x conversion rate is the highest at 1400 °C. The main reactions of producing NO can be analyzed by the rate of production analysis (ROP method). The generation rates of 325 elementary reactions are given in CHEMKIN software, and the reaction rate of each elementary reaction can be checked after the simulation completed. Through the formations of intermediate products such as NH₂, HNO, NH and HOCN, NH₃ and HCN are further transformed into NO. The main reaction equations are shown in equations 1 to 8:

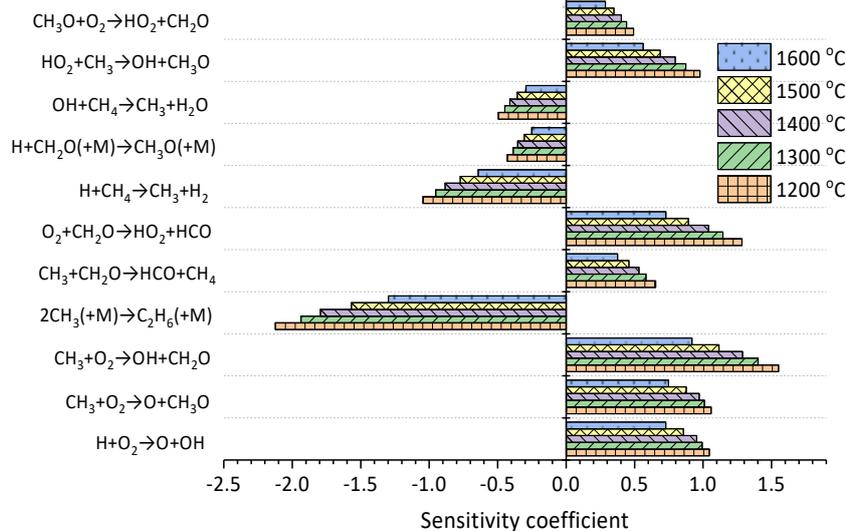
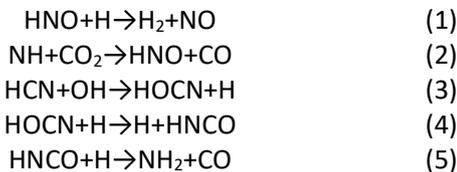


Fig 4 Sensitivity analysis of N₂ at different temperatures of main combustion zone



As shown in Fig. 4, there are more elementary reactions that promote N₂ generation than those inhibit N₂ generation. When the temperature of the main combustion zone increases, the sensitivity coefficient of each elementary reaction to N₂ promotion and inhibition formation decreases. Therefore, when the temperature increased, both the reactions promoting N₂ generation and inhibiting N₂ generation were strengthened, and there was a competitive relationship between them. When the sensitivity coefficient is positive, more N elements are converted to N₂, reducing the generation of NO. Combined with Fig. 4, it could be predicted that the reaction sensitivity coefficient of inhibiting N₂ generation increases faster at 1200-1400 °C, while the condition is opposite at temperature above 1400 °C.

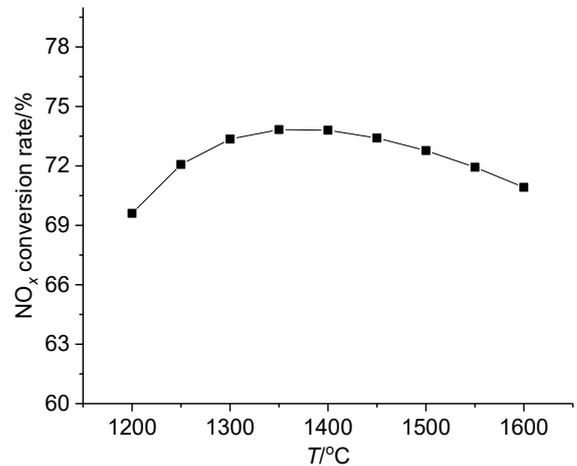


Fig 3 NO_x conversion rate at different temperatures of main combustion zone

3.2 Characteristics of NO_x formations in different excess oxygen coefficients at the main combustion zone

As shown in Fig. 5, the NO_x decreases first and then increases with the increasing of excess oxygen coefficient in the main combustion zone. Because the excess oxygen coefficient is less than 1, the main combustion area is in reducing atmosphere after high intensive combustion, and the lower the excess oxygen coefficient is, the stronger the reducing atmosphere is. Although the NO generates little in the main combustion zone when the excess oxygen coefficient is 0.5. When the over-fire gas flow of the oxidizing atmosphere passes into the furnace, the nitrogenous substance is oxidized to NO again. Therefore, the NO_x conversion is really high in the low excess oxygen coefficient.

It can be seen in Fig. 6, NH_3 is first converted into NH_2 . Under the oxidizing atmosphere, the free radical N and NH react with O_2 , which proceeds in the direction of forming NO, while NO reacts with the free radical N and NH to form N_2 . This means that the N and NH react in the two directions at the same time. Controlling the reaction atmosphere can help more reactions in the direction of NO reduction. On the basis of the analysis of the reaction rate, HNO is the main source which transformes into NO. NH in the subsequent partly transformes to NO, and another transformes into N_2 . Therefore, accelerating the NH_2 transforming to NH rather than HNO, can also promote the fuel-nitrogen transformes to N_2 , and declining the generation of NO.

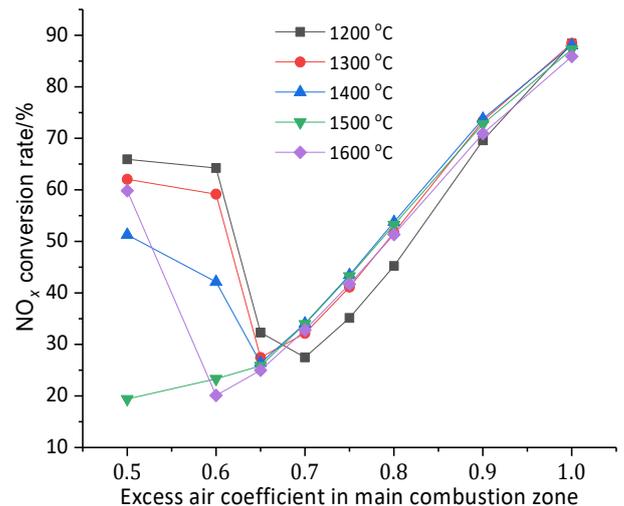


Fig 5 NO_x conversion rate at different excess oxygen coefficients of main combustion zone

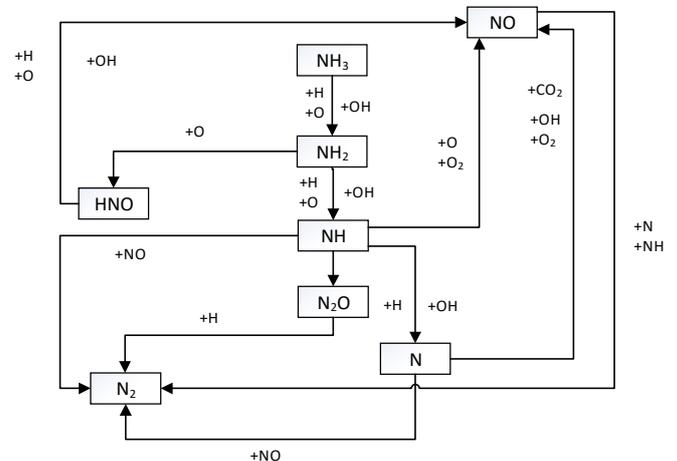


Fig 6 The migration path of N element during the transformation of NH_3 to NO in the main combustion zone

4. CONCLUSIONS

In this paper, a three-stage PFR was used to construct a bituminous coal and semi-coke blending combustion model in oxy-fuel combustion with deep oxygen-staging. The regulation of NO_x formations under the simulation conditions was obtained. Reaction kinetics analysis was conducted on the phenomena of various influencing factors using the sensitivity analysis method. The main conclusions are as follows:

- (1) When the temperature of the main combustion zone is below 1400 °C, the conversion of NO to N_2 is promoted, while the condition is opposite at temperature above 1400 °C.
- (2) Accelerating the NH_2 transforming to NH rather than HNO can promote the fuel N transforming to N_2 , and inhibiting the generation of NO.

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