Effect of Volatile—Char Interaction on the NO Emission from Coal Combustion

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To clarify the effects of volatile—char interaction on the redistribution of fuel-N to N₂ during devolatilization and the reduction of NO through gas—solid reactions during combustion, two types of experiments were performed on a novel reactor. The separate combustion of volatile and char and the combustion of entrained pulverized coal, and the formation of NO was examined between 800 and 1100 °C by using four typical Chinese coals with different ranks. The effect of volatile—char interaction on fuel-N conversion to NO during combustion was elucidated through comparing the NO emissions from the two types of combustion experiments. The results show that the volatile—char interaction is more important in the redistribution of fuel-N to N₂ during devolatilization than in the reduction of NO over 900 °C, and a contrary conclusion is obtained below 850 °C for all used coals. A specific parameter has been proposed to characterize the relative importance of the volatile—char interaction in the redistribution of fuel-N to N₂ during devolatilization to the interaction in the reduction of NO to N₂ during simultaneous combustion of volatile and char. The results are of significance for minimizing the NO formation in industrial combustion processes.

1. Introduction

NO emissions from coal combustion are derived from both the coal nitrogen and the nitrogen in the combustion air. Three types of NO formation, thermal, prompt, and fuel, have been identified (1,2). Coal contains 0.5—2 wt % nitrogen integrated in the organic coal structure. This nitrogen, known as fuel-N, is partly converted to NO during combustion, and becomes the major source of NO in pulverized coal combustion, accounting for more than 80% of the total NO emission (3,4).

To optimize combustion and minimize NO formation, a good understanding of the fuel-N conversion is required. The combustion of coal can be conceptually divided into two steps, that is, the devolatilization of coal followed by the reaction of the volatile and char with oxygen (1). The devolatilization is the thermal decomposition of the fuel resulting from the heating of the coal particles. The products of devolatilization are char and volatile. Part of the nitrogen escapes as volatile-N in gas phase such as cyanic (CN) and amino (NH) compounds. The nitrogen retained in the residual char is called char-N. Thus, NO finally formed during coal combustion comes from the combustion of both volatile-N and char-N (5–7). However, char-N differs from volatile-N in the mechanism of NO formation during combustion. The NO from the combustion of volatile is formed through homogeneous reactions, whereas the NO formation from char-N involves a gas—solid heterogeneous oxidation and an important reduction step of NO back to N₂ (8).

One of the important objectives in coal combustion research is to develop a comprehensive model of NO formation. To do so, most investigators developed individual models for volatile-N and char-N and then their relative contributions to the total NO emission were evaluated (1,9–11). Therefore, it is a common practice that volatile and char are combusted separately to investigate their relative contributions to the total NO emission (2,9). However, separate combustion of volatile and char cannot represent the real process in industrial furnaces. Previous work has shown that volatile—char interaction can lead to drastic changes in char structure and properties during the pyrolysis of coal (13–15), and throughout the process of coal-N oxidation there are significant gas—solid reactions between volatile and char if they are not separated from each other. Therefore it is necessary to take into account the effect of volatile—char interaction to develop an even more exact prediction model of NO formation during coal combustion for the minimization of NO emission (16,17).

Currently, little is known about the effect of volatile—char interaction on the conversion of fuel-N to NO. Using a novel reactor, this study is focused on the relative contributions of volatile-N and char-N to the total NO emission and the effect of volatile—char interaction during the coal combustion. The results demonstrate that the volatile—char interaction has a drastic effect on the conversion of fuel-N during combustion through two ways: the fuel-N redistribution during devolatilization and the reduction of NO during the combustion of volatile and char.

2. Experimental Section

Radicals formed during devolatilization surrounding the char can greatly affect the reactions of char-N. Recent studies (13–15) have confirmed that volatile—char interaction during pyrolysis at elevated temperatures leads to a drastic change in the releases of fuel-N. It was believed that the volatile—char interaction would make more fuel-N release as N₂ during devolatilization through the gas—solid reactions (4,16–20). In addition, the reduction of NO could be enhanced by the volatile—char interaction during the simultaneous combustion of volatile and char (22,23). The fate of the fuel-N is schematically illustrated in Figure 1. Figure 1 implies that the volatile—char interaction could help reduce the NO formation through the redistribution of fuel-N to N₂ during devolatilization and the reduction of NO during the combustion that follows.

The conversion of fuel-N to NO without volatile—char interaction is assumed to be Xc. The conversion of fuel-N to NO with volatile—char interaction taking effect only during devolatilization is expressed by Xc, and the separate combustion of volatile and char can exemplify this conversion. Xc is assumed to denote the conversion of fuel-N to NO with volatile—char interaction taking effect only during combustion, and the combustion of entrained pulverized coal can exemplify this conversion.
$x_1$ and $x_2$ are defined as the volatile–char interaction coefficients to describe the effect of the interaction on NO abatement:

$$x_1 = \frac{X_0}{X_1}, \quad x_2 = \frac{X_0}{X_2}$$

(1)

Two types of experiments were designed in order to clarify the relative contributions of char-N and volatile-N to NO emission from the combustion of coal and the effect of volatile–char interaction on fuel-N conversion.

In the first type of experiment, NO emission from char-N and volatile are quantified separately. A novel setup was established for the experiments, as shown in Figure 2. The quartz reactor was located in the furnace. The electrical heating created approximately isothermal conditions. Temperature could be adjusted continuously. A 0.1 g coal sample was used throughout all experiments. The sample was loaded in the microfeeder (5) in advance, and the helium gas flow (800 mL/min) entrained the coal particles into the reactor that had been heated to a predetermined temperature within two minutes, as shown in Figure 2. The exiting tube was fixed and the sample tube could be pushed forward by a stepping motor to keep a given distance between the bottom of exiting tube and the surface of sample bulk, so that a constant feeding rate could be maintained. Quartz cotton of 3 cm thick was placed in the inner tube (9) at about 10 cm to its exit. Once coal particles entered the reactor volatiles were released and char was formed. The volatiles were able to pass through the quartz cotton and entered the outer tube of reactor, but the char was retained on the quartz cotton. When an experiment was started, the $O_2$ stream (200 mL/min) was switched to Line b in Figure 2 to oxidize the volatiles. The $O_2$ stream was switched to Line a in order to oxide the char formed as soon as devolatilization had been finished. Experiments continued until the complete combustion of char.

The purity of the $O_2$ and He used was more than 99.999%. The concentration of NO from the combustion of volatile and char was measured in succession by a GASMETTM DX4000 FT-IR gas analyzer.

The profile of NO emissions from the separate combustion of volatile and char is shown in Figure 3a. $T_s$ represents the time when $O_2$ is switched and char-N began to combust. The two peaks in the NO profile suggest that there should be two NO sources, the first arises from the nitrogen in the volatile matters, and the second arises from the fixed nitrogen in char. The char came from the same coal sample as volatiles, and it was combusted intact as it was prepared to keep the activity of char until being oxidized. Obviously, an interaction between volatile and char would exist in the inner tube during pyrolysis. However, since the volatile was separated from char and oxidized in a different place, there would be no interaction between the volatile and the char during this period. So the total NO emission in this type of experiments can be represented as

$$X_1 = \frac{X_0}{x_1}$$

(2)

$X_1$ is the total conversion of fuel-N to NO from both volatile and char.

Experiments of the second type involved the combustion of entrained pulverized coal. The gas for feeding coal particles was switched from pure He to He–$O_2$ mixture. Volatile and char undergo simultaneous combustion. The profile of NO emission for the second type of experiments is shown in Figure 3b. The volatile was oxidized as soon as it was released from coal particles because of sufficient oxygen. But, there

![FIGURE 2. Schematic experimental setup: 1 compressed gas; 2 steady flow valve; 3 pressure valve; 4 flow meter; 5 microfeeder; 6 three-way valve; 7 electrical furnace; 8 feeding tube; 9 inner tube; 10 outer tube; 11 quartz cotton; 12 gas analyzer.](image-url)
was little chance for the volatile to react with char under this condition, and the effect of volatile–char interaction on the fuel-N redistribution during devolatilization could be ignored. Nevertheless, the NO formed from volatile-N could be reduced by char through the gas–solid heterogeneous reactions, so that the volatile–char interaction was ineluctable during the combustion of volatile and char, and the NO emission can be represented as follows:

\[ X_c = \frac{X_{\text{NO}}}{X_{x_i}} \tag{3} \]

The total NO emission during experiments is the integral of NO concentration within a certain length of time. If \( X_{\text{NO}} \) is used to represent the ratio of nitrogen converted to NO during combustion process within \( \Delta t \) to the nitrogen contained in the sample, then

\[ X_{\text{NO}} = \frac{\int_{t_0}^{t_0+\Delta t} F \times C_{\text{NO}} \times 10^{-6} \times dt/22.4}{M \times N_d / 14} \times 100\% \tag{4} \]

where \( F \) = volumetric flow, L/s; \( t_0 = \) time at which measurement begins; \( \Delta t = \) measurement duration, s; \( M = \) sample weight, g; \( N_d = \) nitrogen content in sample, % db; and \( C_{\text{NO}} = \) NO concentration in flue gas, \( \mu\text{L}/\text{L}. \)

Four Chinese coals used for experiments were Jiaozuo, Tongchuan, Hejin, and Shenmu, which are denoted respectively as JZ, TC, HJ, and SM hereinafter. All the coal samples were air-dried at 105 °C for 24 h, then ground and sieved to a size of less than 150 µm. The ultimate and proximate analyses are listed in Table 1. Table 2 shows the ash and metal contents in the used coals.

### 3. Results and Discussion

#### 3.1. NO Emissions from the Separate Combustion of Volatile and Char

Figure 4 shows the NO emissions from the separate combustion of volatile and char, that is, the emissions from the experiments of the first type, and the total conversion of fuel-N to NO (expressed by \( X_i \)) is \( X_{\text{NO}} \) from volatile plus that from char. The results show that the total NO emission from separate combustion of volatile and char is greater at lower temperatures, and reaches the highest at 800 °C for all samples. Some previous investigators reported that the total NO emission increased with increased temperature (22, 23), but their experiments were performed under the condition of simultaneous volatile and char combustion. It has been reported that there was abundant N2 release from coal during devolatilization, and the conversion of fuel nitrogen to N2 increased almost linearly with temperature (16–20). As such, the total NO emission in this study inevitably decreases because of the more conversion of fuel nitrogen to N2 at higher temperatures. It seems that the volatile–char interaction has more significant effect on the redistribution of fuel-N to N2 during devolatilization at higher temperatures, resulting in less NO emission. It can also be seen from Figure 4 that there is an obvious dependence of \( X_i \) on \( X_{\text{NO}} \) from char, since \( X_{\text{NO}} \) from volatile varies very insignificantly with temperature, especially when the temperature is over 1000 °C. It has been indicated that higher conversion of nitrogen to N2 is always associated with lower conversion to char-N, and \( X_{\text{NO}} \) from volatile is independent of temperature when the temperature is high enough (19, 20, 24). The experimental results show that for HJ and TC coals the total NO emission \( X_i \) and \( X_{\text{NO}} \) from char is increased remarkably at 1100 °C relative to the values at 1000 °C. As we know, various minerals in coal can exert an influence on the conversion of char-N to NO (25–27). It is assumed that the catalytic effect of minerals in HJ and TC coals on the conversion of char-N to

<table>
<thead>
<tr>
<th>TABLE 1. Fuel Characteristics</th>
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<tbody>
<tr>
<td>coal code</td>
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<tr>
<td>Shenmu SM</td>
</tr>
<tr>
<td>Hejin HJ</td>
</tr>
<tr>
<td>Tongchuan TC</td>
</tr>
<tr>
<td>Jiaozuo JZ</td>
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\( a \) O determined by difference.

<table>
<thead>
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<th>TABLE 2. Ash and Metal Contents</th>
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<tr>
<td>ash (wt%, dry)</td>
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<td>sample</td>
</tr>
<tr>
<td>SM</td>
</tr>
<tr>
<td>HJ</td>
</tr>
<tr>
<td>TC</td>
</tr>
<tr>
<td>JZ</td>
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<table>
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<tr>
<th>sample</th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
<th>Na</th>
<th>Ti</th>
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<tr>
<td>SM</td>
<td>7.9</td>
<td>4.18</td>
<td>1.31</td>
<td>0.46</td>
<td>1.06</td>
<td>0.10</td>
<td>0.02</td>
<td>0.23</td>
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<tr>
<td>HJ</td>
<td>24.09</td>
<td>11.69</td>
<td>8.44</td>
<td>0.88</td>
<td>1.08</td>
<td>0.18</td>
<td>0.20</td>
<td>0.22</td>
</tr>
<tr>
<td>TC</td>
<td>27.00</td>
<td>13.21</td>
<td>8.74</td>
<td>1.81</td>
<td>0.94</td>
<td>0.15</td>
<td>0.04</td>
<td>0.76</td>
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<tr>
<td>JZ</td>
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<td>6.26</td>
<td>0.81</td>
<td>0.89</td>
<td>0.15</td>
<td>0.24</td>
<td>0.19</td>
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Figure 3. NO emissions from the separate combustion of volatile and char (a) and the combustion of entrained pulverized coal (b).
NO becomes predominant at 1100 °C, resulting in more $X_{NO}$ from char, hence more $X_1$.

Figure 5 shows the contribution of char-N to total NO emission, i.e., the ratio of the NO emission from char to the total NO emission. Obviously, the NO emission from char of SM coal (bituminous) is less than the NO emission from volatile during 800–1100 °C, since it is always less than 35%. As for JZ coal (anthracite), char-N becomes the primary source of NO emission and the contribution of char-N is greater than 56% at all temperatures. Both HJ and TC are lean coals, and the contributions of char-N for these two coals are greater than SM but less than JZ. It can be concluded that the contribution of char-N to NO emission is greater for higher rank coals.

In addition to coal rank, temperature can have a profound effect on the contribution of char-N to NO emission. At low temperatures (900 °C or below), char-N is the main source of NO emission, except for the coal with very high volatile content (SM coal for instance). As temperature increases, volatile-N becomes more important. At high temperatures, volatile nitrogen conversion is generally greater than that of char nitrogen, which is in agreement with previous work. It has been reported that the NO emission from volatile can be as high as 60–80% of the total fuel NO emission under the conditions typical for pulverized coal systems (2). Besides, mineral matters in coal can change the redistribution of fuel-N between char and volatile and catalyze the oxidation of char, which has been verified by our demineralized
3.3. NO Emission from the Combustion of Entrained Pulverized Coal. It is well-known that the oxidation of fuel-N to NO and the reduction of NO occur simultaneously during coal combustion. Consequently, the NO emission is determined by the competition of the two processes. NO emission increases if the formation rate of NO is greater than its reduction rate, and vice versa.

The conversion of fuel-N to NO during the combustion of entrained pulverized coal, i.e., the second type of experiment, is shown in Figure 6. It can be seen that the fuel-NO emission does not increase with increased temperature monotonously. The conversion of fuel-N to NO reaches its maximum at 900 or 1000 °C, and decreases beyond that temperature, which is attributable to more NO reduction over 1000 °C (28). In this type of experiment, the volatile—char interaction affects the NO formation only through enhancing the gas—solid reaction on the surface of char. The experimental results show that the effects of volatile—char interaction on the NO reduction can be significantly elevated at 1000 °C, so that the reduction rate of NO increases more quickly than the oxidation rate of fuel-N to NO.

The comparison between the conversion of fuel-N to NO from the combustion of entrained pulverized coal (expressed by $X_2$) and that from the separate combustion of volatile and char ($X_1$) is shown in Figure 7. It can be seen that $X_2$ is less than $X_1$ at 800 °C and greater than $X_1$ at 900 °C or above. That is to say, more NO release from the combustion of entrained pulverized coal than from the separate combustion of volatile and char when the temperature is greater than 900 °C. The effects of temperature on $X_1$ and $X_2$ are different. $X_1$ decreases with increased temperature below 1000 °C, and increases beyond 1000 °C for some coals. $X_2$ increases with increased temperature below 1000 °C, and decreases beyond 1000 °C for all used coals. $X_1$ may be equal to $X_2$ between 800 and 900 °C. The effect of volatile—char interaction on the reduction of NO is at least at 1000 °C and elevated at 1100 °C. The effect of volatile—char interaction on fuel-N redistribution to N2 during devolatilization increases with increased temperature when the temperature is lower than 1000 °C, but it might decrease beyond 1000 °C.

### 3.3. Effect of Volatile—Char Interaction.

As mentioned above, $x_1 = X_0/X_1$ and $x_2 = X_0/X_2$. We define
\[ r = \frac{x_1}{x_2} = \frac{X_1}{X_2} = \frac{X_0}{X_1} \]  

(5)

\( r \) indicates the relative importance of the volatile–char interaction in the redistribution of fuel-N to N\(_2\) during devolatilization to the interaction in the reduction of NO to N\(_2\) during the combustion of volatile and char.

The calculated results of \( r \) are shown in Figure 8. Obviously, coal rank has a profound effect on the NO formation. It seems that the volatile–char interaction during devolatilization is stronger as the coal rank increases between 900–1000 \( ^\circ\)C, but JZ coal is an exception. Beyond that temperature range, coal rank has a more complex effect on the value of \( r \). It can be deduced that nitrogen content, nitrogen functionalities, mineral matters, etc., could have an effect on the interaction. More work is needed to clarify these effects.

While \( r \) is greater than 1.0, the volatile–char interaction is more significant in the fuel-N redistribution to N\(_2\) during devolatilization than in the NO reduction through gas–solid reactions during combustion. A greater value of \( r \) means a more significant interaction during devolatilization as the first step of coal combustion. In fact, NO emission would decrease when combustion is conducted under conditions of departure from stoichiometry, for example in the case of bias combustion or staged combustion. Theoretically, while \( r \) is greater than 1.0, NO emission would be decreased to the greatest extent if the two steps of coal combustion can be distinctly separated and an adequate devolatilization process can be ensured. For example, NO emission can be decreased if coal is gasified first and the formed gas and residual char are sent to furnace at different points to complete combustion separately.

If \( x_0 \) is less than \( x_1 \), i.e., \( r \) is less than 1.0, the volatile–char interaction is more significant in the reduction of NO during combustion than in the redistribution of fuel-N to N\(_2\) during devolatilization. So that, combustion was expected to be performed under stoichiometric conditions to decrease the conversion of fuel-N to NO when \( r \) is less than 1.0. In practice, stoichiometric excess and uniform air distribution are necessary to control NO emissions, and bias combustion or staged combustion are not recommended to decrease NO emissions in this case.

According to the above discussions and Figure 8, it can be concluded that 1000 \( ^\circ\)C is the most suitable temperature for controlling the NO emission from coal combustion under conditions of departure from stoichiometry (oxygen deficiency) for these four coals. For example, bias combustion or staged combustion technology can be applied over 900 \( ^\circ\)C. Stoichiometric excess and uniform air distribution are necessary to control NO emission below 850 \( ^\circ\)C because \( r \) is less than 1.0 for all coals.

**Acknowledgments**

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