NO Reduction in Decoupling Combustion of Biomass and Biomass—Coal Blend

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Biomass is a kind of renewable energy. It is the fourth largest source of energy following coal, petroleum, and natural gas, and it accounts for about 14% of the total world energy consumption, even up to 40% for developing countries. Biomass is CO$_2$-neutral because its growth consumes CO$_2$ through photosynthesis. However, the supply of biomass energy is generally seasonal, and it is uneconomical to transport biomass too far away from the producing area; therefore, biomass—coal co-firing is a quite practical way to use biomass energy. Nonetheless, biomass contains N, which can form NO, during combustion. NO emissions per unit energy input from biomass combustion are even higher than those from coal combustion. Therefore, it is necessary to devise new biomass combustion technologies to reduce NO emissions.

Various technologies have been tested to reduce NO emissions from biomass combustion in previous work. Staiger et al. and Salzmann et al. reported that NO$_x$ emissions from biomass combustion can be reduced about 10–20% via air- and fuel-staging technologies. Selective catalytic reduction (SCR) of NO$_x$ was also applied to biomass combustion. Nonetheless, air- or fuel-staging technology often makes the system complex and reduces the efficiency in the furnace; therefore, they are difficult to be used in small-scale stoves or boilers. For SCR, its catalyst is easily deactivated by alkali metals present in biomass ash. Therefore, there is still no effective technology available for controlling NO$_x$ emissions in small-scale biomass stoves or boilers, which are actually the major tools for converting and using biomass energy in the countryside.

Decoupling combustion (DC) technology was originally developed to burn coal with suppressed smoke and low NO emission. It separates the combustion process into pyrolysis and combustion of char and pyrolysis gas, while the pyrolysis gas may be burnt out during its passage through the combusting char bed. Previous studies demonstrated that suppressed smoke in DC is mainly attributed to the complete combustion of pyrolysis gas in the combustion zone downstream of the pyrolysis zone, while low NO emission results mainly from the catalytic reduction of NO over hot char particles. Complete combustion of the pyrolysis gas in DC also led to low emissions of CO and soot, thus resulting in the higher combustion efficiency.

The present work is devoted to investigating the DC of biomass, especially the biomass combustion in the small-scale biomass stoves designed according to the DC technology. In the study, three kinds of biomass fuels and their blends with coal were first tested in a quartz dual-bed reactor to clarify the effect and mechanism of low NO emission via DC. Then, a 10 kW stove adopting the DC technology for co-firing rice
Table 1. Proximate and Ultimate Analyses of Fuels

<table>
<thead>
<tr>
<th></th>
<th>sawdust</th>
<th>rice husk</th>
<th>corn straw</th>
<th>coal</th>
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<tr>
<td>moisture</td>
<td>8.2</td>
<td>7.5</td>
<td>8.8</td>
<td>4.4</td>
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<td>volatile</td>
<td>78.1</td>
<td>64.2</td>
<td>74.0</td>
<td>25.3</td>
</tr>
<tr>
<td>fixed carbon</td>
<td>12.2</td>
<td>13.9</td>
<td>12.5</td>
<td>57.9</td>
</tr>
<tr>
<td>ash</td>
<td>1.6</td>
<td>14.5</td>
<td>4.7</td>
<td>12.5</td>
</tr>
<tr>
<td>Ultimate Analysis (Dry, wt %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>49.4</td>
<td>39.6</td>
<td>43.8</td>
<td>69.5</td>
</tr>
<tr>
<td>H</td>
<td>6.05</td>
<td>5.68</td>
<td>5.43</td>
<td>3.78</td>
</tr>
<tr>
<td>N</td>
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<td>0.98</td>
</tr>
<tr>
<td>S</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Q</td>
<td>42.6</td>
<td>38.4</td>
<td>44.6</td>
<td>12.1</td>
</tr>
<tr>
<td>VN</td>
<td>0.27</td>
<td>0.35</td>
<td>0.62</td>
<td>0.25</td>
</tr>
</tbody>
</table>

*a Estimated from element mass balance. b The product of volatile content and fuel-N content.*

Figure 1. Schematic diagram of the quartz dual-bed reactor.

husk–coal blend was manufactured and tested to demonstrate the realized low emissions.

2. Experimental Section

2.1. Fuels. Biomass fuels tested in the work were sawdust, rice husk, and corn straw from the Heilongjiang province of China. The bituminous coal from Datong, Shanxi province of China, was used to make the biomass–coal blend fuels. After all of the fuels were dried in air atmospheric pressure at 383 K for 2 h in an electric oven, they were ground and screened to the size of 0.45–0.90 mm. Table 1 summarizes the results of proximate and ultimate analyses of the fuels.

2.2. Apparatus and Method. Experiments for demonstrating the NO reduction via DC for biomass and biomass–coal blends were performed in a quartz dual-bed reactor heated by a two-zone electric furnace. Figure 1 shows the schematic diagram of the reactor. The reactor consisted of an outer tube (40 mm in inner diameter and 1380 mm in height), an upper-inner tube, and a lower-inner tube (each 26 mm in inner diameter and 820 mm in height; each had a quartz porous plate). The outer tube was fixed in the two-zone electrical oven. The upper-inner and lower-inner tubes could be moved out of the outer tube conveniently to place fuel samples on the two plates. There were five outlet/inlet ports in the dual-bed reactor, labeled as outlet/inlet (A–E) in Figure 1, which made it easy to model many types of combustion processes by changing the supply mode of reactant gas.

In the experiments using the dual-bed reactor, fuel was dispersed into quartz sand of 0.9–1.0 mm in size. Ar, instead of N2, was adopted as the inert reaction atmosphere. The mixing ratio of O2/Ar was 21:79, and the flow rate of the mixture gas was constantly kept at 3.0 L/min. The compositions of O2, NO, N2O, CO, and CO2 in gas flue were analyzed by an online flue gas analyzer (ABB-AO2020), and NO2 was measured by a MSI analyzer. Because N2O and NO2 in the gas flue were less than 10 ppm, they were suggested to be negligible and only the values of measured NO are reported in this study. Each experiment was carried out for about 10 min. When the concentration of CO2 in the flue gas was lower than 0.1%, the experiment was considered finished.

In the test of DC, Ar and O2/Ar entered the reactor from inlet B and inlet C, respectively, and the flue gas left the reactor from outlet D, while inlets A and E were closed. The flow rate of Ar fed from inlet B was 0.5 L/min, and the flow rate of Ar/O2 fed from inlet C was 2.5 L/min. The total flow rate in the lower-inner tube was 3 L/min, and the mixing ratio of O2/Ar was 21:79. Before each experiment of DC, 0.4 g of fuel was placed on the quartz porous plate of the lower-inner tube and was pyrolyzed in the atmosphere of Ar to make char, in which the flow rate of Ar was 0.5 L/min and the pyrolysis temperature was the same as the temperature of the upper-inner tube in the DC test. Then, the resulting char was left on the quartz porous plate of the lower-inner tube to be used in the succedent experiment of DC. In the DC test, the char made from 0.4 g of fuel was in the lower-inner tube and 0.4 g of fuel was loaded on the quartz porous plate of the upper-inner tube. Fuel in the upper-inner tube was only pyrolyzed in Ar atmosphere. The volatiles generated from the fuel pyrolysis in the upper-inner tube would flow downward to the lower-inner tube and burn out with char on the porous plate of the lower-inner tube by reacting with O2 fed from inlet C. In the test of DC, it was considered that 0.4 g of fuel was burned out because only the volatiles produced from the pyrolysis of fuel on the upper plate and the char on the lower plate were combusted, whereas the char particles generated in the fuel pyrolysis were left in the upper-inner reactor under the protection of Ar.

In the test of traditional combustion (TC), 0.4 g of fuel was placed only on the porous plate of the lower-inner tube. A stream of O2/Ar was conducted into the reactor from inlet C, and the gases exited from outlet D, leading to the fuel burning merely in the lower-inner tube. In the test of TC, inlets A, B, and E were closed.

2.3. Data Treatment. The integrated total NO emission, denoted as [NO] in mg/g, from burning a fuel sample in a time period from t1 to t2 was estimated as follows:

\[ [NO] = \frac{M_{NO}}{2.24 \times 10^4} \int_{t1}^{t2} \nu C_{NO} \, dt \]

where \( C_{NO}, \nu, M_{NO}, \) and \( m \) represent the NO concentration (ppm) in the reacted gas, reacted gas flow rate (N m\(^3\)/s), molar mass of NO (g/mol), and mass of the fuel sample (g), respectively. The conversion \( \alpha_{NO} \) of fuel-N to NO can be determined as

\[ \alpha_{NO} = \frac{[NO]_{mol}}{[N]_{mol}} \times 100\% \]

where \([NO]_{mol}\) (mol/g) is the moles of NO from burning 1.0 g of fuel sample and \([N]_{mol}\) (mol/g) is the moles of fuel-N with 1.0 g of fuel.

3. Results and Discussion

3.1. NO Emissions from Different Fuels. The NO emission and conversion of fuel-N to NO at 1173 K are compared between TC and DC in Figure 2. In TC, the NO emissions from all of the tested biomass fuels were lower than that from coal on an equal-mass basis (Figure 2a). Notwithstanding, the conversion of fuel-N to NO was generally higher for biomass, as shown in Figure 2b. Biomass has a higher volatile content, which allows for more fuel-N to be distributed into volatiles and to act as volatile-N.13 It should be responsible for the higher

conversion of fuel-N to NO because volatile-N is easier to be oxidized into NO in comparison to char-N during combustion.\(^{14}\)

In DC, the NO emissions from the tested sawdust, rice husk, and coal were all significantly lower than those in TC, whereas the corresponding conversions of fuel-N to NO of biomass were not higher than that of coal. This result verified the low NO emission characteristics of DC, and it also suggested that biomass char, which had good activity for NO reduction, played a crucial role in reducing NO via DC, as was early observed for coal char in fluidized-bed combustion.\(^{15-17}\) In DC, the unburned volatiles from the upper-inner tube would burn during its passage through the char bed on the quartz porous plate of the lower-inner tube. This would allow for the gas and char to interact with each other to implement a series of oxidation and reduction reactions. For example, the NO produced from gas burning could be reduced into N\(_2\) over char, and the NO produced in burning char may also be converted into N\(_2\) via the reduction of volatile gas. However, in TC, the gases went out of the reactor without reacting with char, and there was no contact between char and gases. NO emissions were higher in TC than those in DC because of the lack of contact with char in TC.

As an exception in Figure 2b, little difference was detected in NO emissions of corn straw between DC and TC. To make clear the NO reduction of corn straw via DC, NO emissions of corn straw in TC and DC were compared at different temperatures, e.g., at 973 and 1173 K. The results are presented in Figure 3. The NO emission in TC at 973 K was much higher than that at 1173 K, and the obvious decrease of NO emission via DC can be obtained at 973 K. There was a small influence of temperature on NO emissions in DC. It has been reported that N-containing species (e.g., NH\(_3\) and HCN) in volatiles acted as either NO precursors or NO reductants, and the temperature and O\(_2\) partial pressure had an effect on the fate of N-containing species, leading to the so-called “temperature window” phenomenon.\(^{14}\) The fuel-N content in corn straw is higher than that in the other biomass fuels, so that the concentration of N-containing species was higher in the volatiles of corn straw and the “temperature window” phenomenon occurred more easily. When the combustion temperature increased from 973 to 1173 K in TC tests, the increase of the heating rate would result in the decreased yields of HCN and NH\(_3\) and the fast pyrolysis of straw corn. The higher amounts of volatiles would decrease the O\(_2\) partial pressure, which was favorable to make N-containing species act as reductants. Thus, the decreases of N-containing species and O\(_2\) partial pressure were the main reasons for low emission in the TC test at 1173 K. At 973 K, the corresponding low heating rate would increase the yields of HCN and NH\(_3\) and decrease the pyrolysis rate of corn straw, which would make O\(_2\) partial pressure in the reactor higher than that at 1173 K. The N-containing species were thus easier to be oxidized into NO, making the NO emission at 973 K higher than at 1173 K in TC tests. However, in DC, NO emission depended upon not only the temperature and O\(_2\) partial pressure but also the contact of char and gases. NO in gases can be reduced into N\(_2\) when gases go through the char bed on the lower plate. The higher the NO concentration in gases, the more NO would be reduced over the char. Thus, there was not an obvious change of NO emissions in DC tests at different temperatures for corn straw.

3.2. NO Emissions from Biomass—Coal Blends. Figure 4 compares the NO emissions from burning biomass—coal blends between TC and DC at 1173 K, where the biomass percentages in blends are 0, 25, 50, 75, and 100% on a mass basis. With an increasing biomass amount in the blend, the NO emission in TC first slightly increased (especially in Figure 4c) and then decreased. The maximum NO emission occurred at different blending ratios for different biomass fuels, which were 25% for sawdust (Figure 4a) and rice husk (Figure 4b) and 50% for corn straw (Figure 4c), respectively. For the tested blends, the conversion of fuel-N to NO in TC increased with increasing biomass percentage, except for corn straw, and was generally higher than that of coal.

Essentially, NO emission in combustion is closely related to the fuel-N and volatile contents of the fuel. Table 1 shows that the product of volatile and fuel-N contents, denoted as VN, of the blend fuel becomes higher with increasing biomass percentage. In an oxygen-rich atmosphere, a high VN value can facilitate fuel-N to convert into NO, whereas in an oxygen-lean atmosphere, the high VN value makes more fuel-N act as NO reductants. A higher percentage of biomass and the corresponding increase in volatile matter content would lead to lower oxygen partial pressure in the reactor, and the NO emission as well as the conversion of fuel-N to NO in TC would decrease with increasing the biomass percentage. However, when burning blends with low biomass percentage, the oxygen partial pressure in the reactor is higher, which would facilitate the conversion of volatile-N to NO. Thus, NO emission increased with an increasing biomass content in the blend for a low percentage of biomass, as shown in Figure 4. For the corn straw-coal blend, which had the highest VN value, the NO emission and the conversion of fuel-N to NO in this case exhibited the most obvious increase and then decrease with an increasing amount of corn straw in the blend (Figure 4c).

When the amounts of coal and biomass were equal in the blend, the NO emission of the biomass-coal blend in DC was obviously lower than that in TC, while it also tended to decrease linearly with an increasing biomass percentage. The conversion of fuel-N to NO in DC was lower than that in TC, regardless of what biomass was used. Lower conversions of fuel-N to NO were also shown for the blended fuels in comparison to coal. Although the conversion of fuel-N to NO decreased with an increasing biomass percentage in the blends for both TC and DC, the conversion in DC had the obvious decrease. Similar to the analysis made in section 3.1 for biomass burning, the decreased NO emission in DC was a result of the heterogeneous NO reduction over char particles. The higher the biomass percentage in the blend, the fewer the char particles on the quartz porous plate of the lower-inner reactor. However, the NO emission for DC maintained its decrease with the increase of the biomass percentage in the blend because biomass char is more active in reducing NO.

3.3. Study on the DC Stove of Biomass—Coal Blends. The results in sections 3.1 and 3.2 demonstrated that DC of biomass and its blends with coal can definitely lower NO emission in comparison to TC. For further demonstration of this in practical applications, a 10 kW stove incorporating the DC technology was manufactured to co-fire rice husk and coal, as illustrated in Figure 5a. A bulkhead divided the furnace into a pyrolysis zone and a combustion zone, and both zones were connected via a burner port. A sloping grate was used to move fuel automatically via gravity. Ash was taken out through a rotary valve.

The combusted fuel was a blend of 50% rice husk and 50% coal (Datong coal) on a mass base. The fuel consumption rate was 4.5 kg/h. The fuel was supplied into the hopper every 30 min. It moved downward and pyrolyzed in the pyrolysis zone. The resulting volatiles and char further moved into the combustion zone and both zones were connected via a burner port. A sloping grate was used to move fuel automatically via gravity. Ash was taken out through a rotary valve.

To compare emissions between stoves adapting the DC and TC method, a TC stove (7 kW), in which the grate can be moved intermittently by shaking a handle, was employed to burn the same fuel. The sketch of this TC stove is shown in Figure 5b. In the TC stove, the fuel was supplied from the top of the furnace every 15 min and the air was introduced from the air chamber under the grate. By shaking the handle connected with the grate intermittently, the grate would move and ash on the grate could be removed from the furnace. The fuel consumption rate and total air feeding rate of this TC stove were 3.0 kg/h and 20 m³/h, respectively, so that the excess air ratio in the TC stove was the same as in the DC stove.

Figure 6 compares the measured NO and CO emissions for the two stoves. It is clearly shown that the NO emission from the DC stove was lower than that from the TC stove. The average NO emission was about 130 ppm in the DC stove, while this value increased to about 160 ppm in the TC stove. There was a relative NO reduction of 19% via DC. As expected, Figure 6 also shows that the CO emission from the

![Figure 4. NO emission and the conversion of fuel-N to NO of the biomass—coal blend in TC and DC.](Image)
In summary, the technical superiorities of the DC stove, e.g., low NO emission and high combustion efficiency, mainly come from its dividing the fuel combustion process into fuel pyrolysis and combustion of char and pyrolysis gas and from its arrangement of the gas burning with the char, so that char and volatile gas can interact with the gaseous products. In TC stove, fuel pyrolysis occurs above the char bed and the resulting volatiles exhaust without experiencing the high temperatures in the char bed. Thus, CO emission in the TC stove is often high because of incomplete combustion, and NO emission is not low because there is little NO reduction over char.

4. Conclusions

The possibility and mechanism for NO reduction in DC of biomass and biomass–coal blends were investigated in a quartz dual-bed reactor. A set of comparative experiments were also carried out using TC. The results demonstrated that the NO emission and the corresponding conversion of fuel-N to NO in DC of biomass and biomass–coal blends were obviously lower than those in TC. A decrease of the conversion of fuel-N to NO was found when increasing the biomass percentage in the biomass–coal blends, but this phenomenon was more pronounced in DC. In a DC stove co-firing rice husk and coal, there was a decrease of about 19% of NO emission in comparison to that in a TC stove. The results in the DC stove also exhibited much lower CO emission, more stable combustion, and much easier operation. This study confirmed that the DC is effective for controlling NO and CO emissions in biomass combustion.

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