NO emission during co-firing coal and biomass in an oxy-fuel circulating fluidized bed combustor

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HIGHLIGHTS

• Burning biomass alone has a higher NO emission than coal.
• Nitrogen conversion is in agreement with the H/N ratio in the fuel.
• In oxy-fuel combustion, lower NO emission has been observed.
• Oxygen staging combustion succeeds in controlling the NO emission.

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ABSTRACT

Co-firing biomass and coal under oxy-fuel combustion in a circulating fluidized bed combustor (CFBC) holds the potential for negative CO2 emission into the atmosphere and is a promising technology to realize atmospheric CO2 reduction. Experiments co-firing coal and three kinds of Chinese biomass, i.e. rice husk (RH), wood chips (WC) and dry wood flour (WF) under oxy-fuel condition were carried out in a 10 kWt CFBC. Results show that burning biomass separately produces higher NO emissions and a higher fuel nitrogen conversion ratio than burning coal without biomass addition due to the higher volatile matter content of the biomass; the fuel nitrogen conversion ratio is in agreement with the H/N ratio in the fuel under both air and oxy-fuel atmosphere. In oxy-fuel combustion, lower NO emission is observed than in air combustion, because CO2 replacing N2 reduces the yield of NO precursors like NH3 during the devolatilization process and enhances NO reduction via char/NO/CO reaction. NO emission increases as temperature, overall oxygen concentration and primary oxidant fraction increase during oxy-fuel combustion. Oxygen staging succeeds in controlling NO emission in a comparatively low level at high overall oxygen concentration condition. The results can be helpful for the design and operation of the oxy-fuel fluidized bed combustor.

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1. Introduction

Carbon capture and storage (CCS), is the process of capturing waste carbon dioxide (CO2) from its emission sources or atmosphere, transporting it to a storage site, and depositing it where it will not enter the atmosphere again. CCS technology now is the major and efficient way to slow down the global warming. Several CCS technologies such as post-combustion chemical absorption, integrated gasification combined cycle (IGCC), chemical looping combustion (CLC) and oxy-fuel combustion have been suggested and developed in the recent years to realize carbon capture from industrial emission resources. However, current technologies mainly focus on the reduction of CO2 emission into the atmosphere, which can only slow down the rising trend rather than bring down the CO2 concentration in atmosphere. The essential way for removing CO2 from the atmosphere seems to be direct capture of CO2 from air [1], which is technically challenging and expensive.

Biomas, as one of the renewable energy sources, has already captured worldwide attention in the context of greenhouse gas control even though fossil fuels retain their dominant role in the world energy supply in the coming decades. The use of biomass provides substantial benefits as far as the environment is concerned. Biomass absorbs carbon dioxide during growth, and emits it during combustion. Utilization of biomass as fuel for energy
production offers the advantage of a renewable and CO₂-neutral fuel [2]. As for co-combustion biomass and coal, since biomass in most cases contains considerably less sulfur than coal, an increasing biomass share in the thermal input decreases the SO₂ emission proportionally. In addition, SO₂ can be partly captured in the ash by the alkaline-earth components enriched in the biomass [3]. Due to the high volatile content in the biomass, low NO emission can be achieved by both air staging and reburning [3]. Also when co-firing biomass and coal was tested in a pilot circulating fluidized bed combustor, lower NO, N₂O and SO₂ in the dense bed was achieved due to the more reducing atmosphere [4].

Oxy-fuel combustion technology is a new promising combustion technology in coal-fired power plant in order to reduce the emission of CO₂, which is considered as technically feasible and economically competitive [5–7]. Burning biomass under oxy-fuel condition offers the option for negative CO₂ emission and also offers other advantages such as improving the ignition and burnout performance [8], reducing the pollutant emission [9] when co-firing with coal, etc. Circulating fluidized bed (CFB) technology has been recognized as a clean coal combustion technology owing to its advantages on fuel flexibility, low combustion temperature, long residence time of fuel in furnace, low cost of in-furnace desulfurization and low NOx emissions during combustion. CFB combustion under oxy-fuel atmosphere inherits the technical advantages of fluidized combustion and brings further advantages [10–12], especially negative CO₂ emission when burning biomass in oxy-fuel CFB combustor. Work by Jia et al. [10] suggested that fluidized bed combustion can burn biomass and fossil fuels at any given ratio, ranging from 0% to 100%, thus offering the possibility of using local and seasonally available biomass fuels in a “CO₂-negative” manner. Nevertheless, the recent studies on oxy-fuel combustion burning biomass focused mainly on pulverized coal style rather than fluidized bed combustion.

Fuel nitrogen conversion and NOx emission characteristics in conventional air combustion have been widely investigated by a number of researchers in the past twenty years for both coal and biomass. The representative studies by Li and Tan [13], Tan and Li [14,15] and Chang et al. [16] revealed the NOx precursor’s formation mechanism during pyrolysis process of coal and biomass in a very detailed and convinced manner. As well, the operational dependence of NOx emission in circulating fluidized bed combustion has been well summarized by Winter [17]. In this paper, a 10 kWt oxy-fuel CFB combustor was used to study NO emission characteristics and the operational parameter effects were emphasized.

2. Experimental

The experimental system includes a CFB combustor, a screw feeder to convey fuel, a gas supply train to supply O₂/CO₂ mixture or air to the combustor, an electrical external heating and temperature controlling system to help maintaining the desired temperature, a heat exchanger to cool down the flue gas before measurement and a flue gas in-situ measurement line, as shown in Fig. 1.

The inner diameter of the CFB combustor is 65 mm with the riser height of 2300 mm. The air was supplied by an air compressor in the air combustion test. In oxy-fuel combustion test, O₂ and CO₂ gases with purity of 99.9% from gas cylinders were premixed in two separate oxidant manifolds, a primary one and a secondary one, before being fed into the furnace. All the gas flows were measured by rotameters. In the experiments, three different kinds of biomass including rice husk (RH), wood chips (WC), dry wood flour (WF) and a bituminous coal were used. These were fed into the furnace by a pre-calibrated screw feeder. The mass percentage of biomass in the fuel blend was set at 0%, 10%, 20%, 50% and 100% respectively for a certain test run. The composition of exhaust gases, including O₂, CO, CO₂, SO₂, NO and NO₂, were measured on-line on a dry basis by a multiple flue gas analyzer (NGA2000 type, Emerson, USA), which was calibrated before each test. The selected particle sizes of raw coal, RH, WC and WF were 0–3 mm, 0–2 mm, 0–2 mm and 0–150 μm respectively, and the particle size of the quartz sand bed material was in the range of 0.25–0.9 mm. Table 1 shows the proximate analysis and ultimate analysis of fuel samples. C + RH, C + WC and C + WF are used as the abbreviation of coal/rice husk blend, coal/wood chips blend and coal/dry wood flour blend.

3. Results and analysis

3.1. NO emission during burning biomass and coal alone at different atmospheres

Fig. 2 shows NO emission burning single fuel during air combustion and oxy-fuel combustion at different units, i.e. mg/Nm³ in Fig. 2(a) and mg/MJ at Fig. 2(b). All the tests were operated with the same parameters, i.e. bed temperature: 850 ± 10 °C, oxygen to fuel stoichiometric ratio: 1.05, primary oxidant fraction: 0.7. It can be seen from Fig. 2 that different fuel has a different NO emission ranging from 56–195 mg/Nm³ and 16–58 mg/MJ, mainly determined by the nitrogen content in the fuel and regardless of the atmosphere, indicating that NO emissions during fluidized bed combustion originate from fuel nitrogen only. Bituminous coal has the lowest NO emission even though it contains comparatively higher fuel nitrogen. The reason is that bituminous coal has the lowest volatile matter, while the nitrogen in biomass is mainly volatile nitrogen which is easier to convert to NO. For biomass, RH has the biggest NO emissions in both air and oxy-fuel combustion due to the highest nitrogen content in it, while WC has the lowest NO emissions because it has only 0.39% nitrogen. Both coal and biomass have lower NO emissions in oxy-fuel combustion compared with their emissions in air combustion, which is consistent with the former studies on coal [10,18]. The probable reason is that CO₂ changes the fuel nitrogen transformation routine during the pyrolysis process [16,19], as well as the enhanced NO reduction by the potential high CO emission [18] in the dense bed. Li and Tan [13,16] has found that CO₂ substituting Ar can suppress HCN and NH₃ formation by consuming the N-sites or H radicals on the char surface, whereas HCN and NH₃ are the main NO precursors during
combustion process. At the same time, taking consideration of the fact [18] that high CO₂ concentration in the primary zone retards the coal combustion as well as the potential occurrence of the CO₂-char gasification, higher production of CO will occur in oxy-fuel combustion, which promotes the char/NO/CO heterogeneous reaction for NO reduction.

Fuel nitrogen conversion ratio are calculated and presented in Fig. 3. The fuel nitrogen conversion ratio of all kinds of biomass is higher than that of coal, again due to the higher volatile matter content. WC leads the nitrogen conversion ratio. On the one hand, fuel with lower nitrogen content has more complete nitrogen conversion, as summarized by Winter [17]. On the other hand, WC has the largest H/N ratio among the biomass and is expected to generate more NH₃ during the pyrolysis process, which is the main precursor for NO formation. Higher H/N ratio means more H or H-related radicals are available during pyrolysis process, and other N-contained species such as HCN, HNCO can be further converted to NH₃ by them. NH₃ has been found to produce more NO than HCN, which may mainly convert to N₂O [20]. As shown in Fig. 4, fuel nitrogen conversion ratio increases as H/N ratio increases. The effect of H/N weight ratio from 8.1 to 14.7 diminishes compared with that seen when H/N is 8.1 or below, because too many H-radical weakens its contribution. Comparing the difference between oxy-combustion and air combustion curves, it can be seen that the suppression effect of replacing N₂ with CO₂ on fuel nitrogen conversion is stronger at higher H/N ratio, validating the suggestion [16] that CO₂ prevents H-radical from contacting with the N-sites in the coal matrix during the combustion process.

### 3.2. Effect of mixing ratio on NO emission

Effects of the biomass mixing ratio with coal on NO emission are shown in Fig. 5(a) and (b). NO emission increases as the biomass share increases for all the three biomass under both air and oxy-fuel conditions. This is because NO emission and fuel nitrogen conversion ratio when burning biomass alone are higher than when burning coal, as discussed above. And of course, a higher biomass share will cause higher NO emissions. In both atmospheres,
NO emission increases slightly when the biomass mixing ratio increases from 0% to 20%, while from 20% to 100%, it increases tremendously. In oxy-combustion, adding 50% coal into biomass substantially reduces the NO emission as shown in Fig. 5(b), and the reduction is larger than that in air atmosphere as shown in Fig. 5(a).

To further investigate whether there is an interactive effect on NO emission by burning blended fuel, a comparison between experimental values and theoretical values was undertaken. The theoretical value is calculated as the sum of the measuring value burning single fuel multiplying its mass ratio. The results with a biomass mixing ratio at 20% are shown in Fig. 6. In air and oxy-fuel combustion, experimental values are always smaller than the theoretical values, supporting the hypothesis of the existence of interactive reactions. The adding of coal into biomass provides the nascent char in dense bed and results in higher CO concentration due to the slower burnout characteristic of coal. The char and CO, as reducing agent, will reduce the NO via the char/NO/CO heterogeneous reaction, as we previously found [18]. In oxy-fuel combustion, the interactive effect seems more obvious than in air combustion, again due to the high concentration of CO, which has been demonstrated by Wang et al. [21] in a lab scale quartz reactor. The potential char-CO₂ gasification will produce more CO and the formation of a fuel-rich zone in the vicinity of the fuel particle’s surface can more effectively reduce NO.

3.3. Effect of temperature on NO emission

The effect of bed temperature on NO emissions under oxy-combustion atmosphere with a mixing ratio of 20% is shown in Fig. 7. NO emission increases as temperature increases, different from the situation burning pure biomass in air combustion, where NO emission peaks at around 800 °C for several kinds of biomass, as reported in Ref. [20]. It is easy to understand that as temperature goes up to 800 °C, NO emission increases because of the more complete nitrogen conversion at the higher temperature. As temperature goes further up to 900 °C, NO can be further reduced to N₂ by NH₃ when burning pure biomass, through the similar path of SNCR process as the author argued [20]. And as we know, the SNCR reaction has an optimal temperature window around
900 °C. But in the context of co-firing under oxy-fuel conditions, highly concentrated CO₂ will extend the fuel nitrogen release time by reducing the temperature of the char particles. Further, the nitrogen derived from coal char is difficult to convert completely at low temperatures. NO emissions during co-firing will not reach their maximum at 800 °C due to the incomplete burnout under oxy-fuel conditions. High temperatures will open more nitrogen sites in the coal matrix during the char combustion stage and enhance the fuel nitrogen conversion ratio. It has also been found [20] that during char combustion the nitrogen conversions to N₂O, HCN, and NH₃ were generally low, with only NO being formed in significant amounts. Therefore, NO emission increases as temperature increases from 800 °C to 950 °C in this study.

3.4. Effect of oxygen concentration on NO emission

NO emission increases substantially as oxygen concentration increases when co-firing biomass and coal with a mixing ratio of 0.2 in oxy-fuel combustion, as shown in Fig. 8. In oxy-fuel combustion, the flue gas volume with the same heat input decreases substantially as oxygen concentration increases. Therefore NO emissions will certainly increase. NO emissions for different blended fuel show no significant difference due to the small share of biomass in the blended fuel. To further highlight the effect of oxygen concentration, nitrogen conversion ratios at different oxygen concentrations are presented in Fig. 9. Increasing oxygen concentration improves the nitrogen conversion ratio to NO for all three kinds of fuel blend. As oxygen concentration increases from 21% to 40%, an approximately 1.5% increase in fuel nitrogen conversion can be observed. As the partial pressure of oxygen increases in the atmosphere, more O and OH radicals will be produced which are the main intermediates to oxidize precursors such as NH₃ and HCN to NO. Meanwhile, the char will burn more completely and less CO will be produced in high oxygen concentration, thus reducing the chance of char/NO/CO reduction.

3.5. Effect of primary oxidant fraction on NO emission

The effect of primary oxidant fraction on NO emission co-firing under oxy-fuel condition is shown in Fig. 10. NO emission increases as the primary oxidant fraction increases, which is similar to the situation in air combustion and burning coal alone. The principle of this is the same as air staging combustion, and it has been well explained in our previous study [18]. With reducing the primary oxidant fraction, the environment in the dense bed where production of NO mainly takes place can be better controlled as reducing, which is beneficial for nitrogen conversion to N₂. With the high oxygen concentration conditions in oxy-fuel combustion, the primary oxidant fraction should not be operated at a sufficiently high percentage to avoid defluidization. For example, when burning coal and wood chips in 21%O₂ atmosphere, the fluidization velocity in the primary zone is approximately 3.53 m/s with the primary oxidant ratio at 0.6 and temperature at 850 °C. As oxygen concentration increases to 30%, the fluidization velocity will drop to 2.56 m/s if other conditions are unchanged. Fluidization velocity will drop further to 1.99 m/s as the oxygen concentration increases to 40%, which will likely cause defluidization with normal bed material in a commercial CFB combustor. One solution for oxy-fuel combustion with high oxygen concentration is oxygen staging, which means keeping the oxygen/fuel stoichiometric ratio at a low level for NO reduction and increasing the CO₂ (flue gas) flow as the primary oxidant to ensure good fluidization. In other words, the primary zone in a dense bed with oxygen staging will be maintained with low overall oxygen concentration, while it will largely increase the oxygen concentration in the secondary stream. Fig. 11 presents the effect of oxygen staging on NO emissions for three blended fuels. At 21% O₂ concentration, the primary oxidant fraction is 0.6. To maintain the same fluidization velocity and stoichiometric oxygen/fuel ratio with 21% O₂ concentration, the primary oxidant fraction was fixed at 0.84 for the overall oxygen concentration of 30%. As can be shown in Fig. 11, at oxygen concentration of 30%, NO emission is slightly higher than at 21% oxygen concentration, as a result of oxygen staging. The reason for the slight increase is that lower secondary oxidant flow with higher oxygen concentration weakens the gas–solid mixing in the secondary air zone and may cause local high temperatures, which is unfavorable for NO reduction. However, compared with the results shown in Fig. 8, oxygen staging can contribute to better control of NO.
emission at high overall oxygen concentration, and with the major advantage of avoiding defluidization.

4. Conclusions

NO emission tests were carried out on a lab-scale CFB facility during co-firing biomass and coal under oxy-fuel condition, and results show that:

(1) Burning biomass alone has a higher fuel nitrogen conversion than coal due to the high volatile matter content in biomass;
(2) fuel nitrogen conversion ratio is in agreement with the H/N ratio in parent fuel;
(3) in oxy-fuel combustion, lower NO emission has been observed compared with that in air combustion;
(4) oxygen staging combustion succeeds in controlling NO emission during oxy-fuel combustion at higher oxygen concentration.

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