Nitric Oxide Emissions during Coal and Coal/Biomass Combustion under Air-Fired and Oxy-fuel Conditions

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Nitric oxide (NO) emissions are measured during the combustion of sub-bituminous Powder River Basin coal and coal/sawdust mixtures under air-fired and oxy-fuel conditions in a once-through laboratory-scale (30 kWth) unpiloted combustor. In this system, flame attachment to the burner appeared to be the most important parameter for obtaining the lowest possible NO emissions. Oxy-coal conditions in which air was replaced with a 30% O2/70% CO2 mixture in both the primary and secondary oxidizer streams resulted in a 20% reduction in NO. When the O2 concentration in the primary and secondary streams was varied, an optimum set of conditions resulting in minimal NO formation was found. Varying the adiabatic flame temperature by altering the secondary oxidizer gas composition had little effect on NO emissions, provided that the temperature was sufficient to maintain a burner-attached flame. Sawdust co-firing in one scenario resulted in flame instability and increased NO formation. When stable flame conditions were achieved, the effect of sawdust co-firing on NO emissions was dependent upon the sawdust particle size, with larger particles having little effect on NO emissions and smaller particles reducing NO emissions under air-fired conditions but not under oxy-fuel conditions.

Introduction

One of the most pressing environmental challenges facing our world is the threat of climate change because of the presence of excess greenhouse gases, such as carbon dioxide (CO2), in the atmosphere. As a major contributor to global CO2 emissions, coal-fired power plants are receiving enormous attention. One of the most promising methods to reduce CO2 emissions from coal power plants involves capturing the CO2 present in the exhaust gases for long-term geologic storage, enhanced oil recovery (EOR), or enhanced coal bed methane (ECBM) production. Under conventional air-fired conditions, the concentration of CO2 in the exhaust gases is relatively low (10–20%) because of the presence of N2 from air. At such low concentrations, CO2 capture requires post-combustion separation processes that consume a significant amount of energy with no potential benefit to the combustion process. However, oxy-coal combustion can produce exhaust gas CO2 concentrations of up to 95%, enabling capture by more direct methods while potentially improving combustion efficiency and reducing pollutant emissions.

Oxy-coal combustion involves replacing the oxidizer air with a combination of oxygen (≥95 vol % O2) and recycled flue gas (RFG). Since proposed as a means to produce CO2 for EOR, many laboratory-scale, pilot-scale, and computational studies investigating the design and operational issues of oxy-coal combustion have been performed, and a review of the work prior to 2005 is available by Buhre et al. Increased energy costs are anticipated in an oxy-coal power plant equipped for carbon capture and storage (CCS) in large part because of the parasitic load of the air separation unit and the CO2 compression and purification unit. Nevertheless, oxy-fuel combustion results in a reduced flue gas volume, enabling higher boiler thermal efficiencies, and has demonstrated the potential to reduce NOx emissions by as much as 60–75% and SOx emissions by as much as 27%, suggesting that postcombustion treatment equipment can be scaled back, improving the benefit/cost ratio.

A common low-NOx strategy for pulverized coal boilers is oxidizer staging. For wall-fired units, a burner is typically configured with two separate gas streams that supply insufficient air for complete combustion: a primary oxidizer (PO), in which the coal particles are entrained, and a secondary oxidizer (SO) that surrounds the PO and usually exits through swirl vanes to aid in flame stabilization and mixing. A third flow (overfire air or oxidizer) can be introduced some distance downstream to consume the remaining fuel (usually char) under fuel-lean conditions. This strategy results in a reducing region between the burner and the overfire oxidizer, where NOx can be converted to molecular nitrogen. The effectiveness

(2) Abraham, B. M.; Asbury, J. G.; Lynch, E. P.; Teotia, A. P. S. Coal—oxygen process provides carbon dioxide for enhanced recovery. Oil Gas J. 1982, 80 (11), 68–70, 75.
of staged combustion can be influenced by the level of oxidizer deficiency in the burner (i.e., the depth of staging), the flame stand-off distance, and the near burner temperature, which can influence the stand-off distance and the rate of coal devolatilization. Deeper staging in general is desirable for lower NOx emissions; however, if there is insufficient air in the near burner region, temperatures can become too low, leading to greater flame stand-off distances. This can lead to SO air entrainment and increased NOx formation, flame instabilities, late coal devolatilization, and reduced boiler efficiencies and char burnout.

Considering these factors, it has been recognized that oxy-fuel combustion provides opportunities for further reductions in NOx emissions because (1) molecular nitrogen has largely been removed from the system, (2) some NOx will be recycled through the flame region, where it will have additional opportunities to be reduced to N2; and (3) independent control of oxygen and RFG concentrations enables a decoupling of temperature and stoichiometry in the near burner and postflame regions.6–10

Early oxy-coal studies6–11 identified three pathways for NOx reduction enabled by flue gas recycle in oxy-fuel combustion, namely: (1) high CO2 concentrations may lead to more CO (because of either gasification of char, char + CO2 → 2CO, or thermal dissociation) available to reduce NOx to N2 via the reaction NO + CO = 0.5N2 + CO2, which can be catalyzed at the char surface; (2) recycled NOx may interact with nitrogen species released during devolatilization (volatiles N); and (3) recycled NOx may be reduced to N2 by hydrocarbon species released during devolatilization when passing through the flame zone. Okazaki and Ando6 investigated the relative influence of these mechanisms by simulating the effects of volatiles with CH4 and NH3 and char with anthracite in separate experiments. It was concluded that increased CO2 concentrations contributed to less than 10% of the observed NOx reduction, while reactions between recycled NOx and volatiles N accounted for 50–80%, and reactions between recycled NOx and hydrocarbon species in the flame accounted for 10–50% of the observed reduction.

The influence of the oxygen concentration (≥ 20 vol %), as enabled by independent control of oxygen and RFG, was demonstrated by Hu et al.17,18 at variable temperatures and equivalence ratios in an electrically heated furnace. Emissions of NOx on a mass basis were shown to be only slightly dependent upon oxygen concentrations ≥ 50 vol % and were comparable to results obtained in air when pure oxygen was used. Liu and Okazaki19 proposed a novel oxy-fuel scenario, in which the oxygen concentration was reduced relative to air (< 21 vol %) and combustion was sustained by recycling heat as well as flue gases. In an electrically heated furnace, it was demonstrated that reducing the oxygen concentration to 15 vol % while recycling 40% of the heat and 89% of flue gases could reduce the conversion ratio of fuel N to exhausted NO by a factor of 7.

In a larger scale system, Chatell-Pelage et al.20 indicated that higher temperatures in the fuel-rich near burner region induced by high oxygen concentrations can increase the rate of NO reduction to N2 as well as the rate of volatile nitrogen species conversion to N2. The results of Mackrory et al.15 appeared to support this phenomenon. Higher oxygen concentrations have also been used to promote shorter flame stand-off distances, resulting in less SO air entrainment and lower NOx,6 as well as deeper staging without the limitations encountered under air-firing.11 In addition, Anderson et al.21 and Normann et al.22 investigated the reduction of NOx at high temperature in oxy-fuel combustion and showed that NOx destruction by the reverse Zeldovich mechanism is possible. In addition to oxy-fuel combustion for CO2 mitigation and lower NOx emissions, increased use of biomass in both direct and co-firing scenarios is another technology receiving increased attention as electricity providers strive to meet regional and statewide renewable energy standards. Moreover, when combined with CCS, the co-firing of biomass fuels can result in a net decrease in atmospheric CO2. Many studies have examined the effects of co-firing biomass and fossil fuels under conventional air-fired conditions, with significant
contributions from Tillman and co-workers\(^\text{24}–\text{29}\) and reviews by Werther et al.\(^\text{30}\) and Sami et al.\(^\text{31}\) Nevertheless, on the basis of the current literature, biomass co-firing under oxy-fuel conditions is a nascent area of study with enormous potential. For example, air-fired studies by Brouwer et al.\(^\text{32}\) reported a 17% reduction in NO\(_x\) when 50% wood (on a thermal basis) containing 0.2 wt % nitrogen was co-fired with coal containing 1.6 wt % nitrogen during unstaged combustion. While these results are promising, the reduction in NO was not proportional to the reduced amount of fuel-bound nitrogen in the system. Moreover, when wood was co-fired directly with coal in a staged low-NO\(_x\) system, insignificant changes were observed until 70% wood (thermal basis) was co-fired. On the basis of these results, it was suggested that reductions in NO\(_x\) emissions when co-firing may not scale with the reduction in fuel-bound nitrogen because rapid biomass volatile release can result in increased near burner temperatures, leading to enhanced thermal NO\(_x\). However, under oxy-fuel conditions, N\(_2\) is removed from the oxidizer streams and, with all else being equal, NO\(_x\) formation should scale with the fuel N present in the system, leading to reduced NO\(_x\) when co-firing with a biomass having a lower nitrogen content. Furthermore, higher local temperatures induced by rapid biomass devolatilization could result in reduced NO\(_x\) formation because of the rate and residence time effects discussed by Mackrory and Tree\(^\text{16}\) or NO\(_x\) destruction via the reverse Zeldovich mechanism, as suggested by Andersson et al.\(^\text{22}\) and Normann et al.\(^\text{23}\). Sami et al.\(^\text{31}\) also noted that the increased fuel loading required to maintain the same thermal input when co-firing, because of the lower heating value of biomass, may alter the flame position, resulting in higher NO\(_x\). More specifically, larger PO stream gas flow rates may be required to convey the additional fuel when co-firing biomass at coal-only firing rates. This can impact NO\(_x\) emissions through changes in the flowfield and local stoichiometry, as demonstrated by Damstedt and co-workers.\(^\text{33}\) However, under oxy-fuel conditions, the PO and SO stream gas compositions can potentially be optimized to minimize adverse effects.

Recognizing the potential for improvements in NO\(_x\) reduction under oxy-fuel conditions and when co-firing biomass, this work explores a range of oxy-fuel and co-firing conditions to quantify their effects on NO\(_x\) concentrations in the exhaust gas in a once-through laboratory-scale combustor using no overfire oxidizer. When considering oxy-coal combustion in a retrofit scenario, it has been observed that approximately 30 vol % O\(_2\) is required to yield temperature and heat-transfer characteristics similar to conventional coal/air combustion mainly because of the higher specific heat of CO\(_2\).\(^\text{34}\) Given that the PO stream velocity must be sufficient to keep the coal particles in suspension and the replacement of coal delivery tubes for an oxy-coal retrofit is economically infeasible, the PO stream flow rate must be maintained. With this constraint, using a 30 vol % O\(_2\) stream as the coal carrier gas could potentially influence the formation of NO\(_x\) because of an increase in the local PO stoichiometric ratio

\[
\lambda_{\text{PO}} = \frac{m_{\text{air}, \text{PO}}}{m_{\text{air}, \text{st}}} = \frac{m_{\text{O}_2, \text{PO}}}{m_{\text{O}_2, \text{st}}} \tag{1}
\]

where \(m\) is the mass flow rate, the subscript st refers to the conditions required to meet stoichiometricity, and the subscript PO refers to the flow issuing from the PO stream. Under conventional coal/air conditions, \(\lambda_{\text{PO}}\) is typically in the range of 0.15–0.25, which translates to a range of 0.21–0.36 for oxy-coal conditions with the same volumetric flow rate and 30 vol % O\(_2\) in the PO. We note, however, that an oxy-coal system offers the potential for independent control of PO, SO, and tertiary (if applicable) oxidizer stream gas compositions. Thus, \(\lambda_{\text{PO}}\) can be reduced while maintaining the adiabatic flame temperature \((T_{\text{ad}})\) by (1) replacing oxygen with RFG in the PO to maintain the desired volumetric PO flow rate and (2) increasing the concentration of oxygen in the SO stream. In the data presented below, the effect of \(\lambda_{\text{PO}}\) on NO formation is investigated under air-fired conditions to provide a baseline for comparison to oxy-coal experiments, in which the PO and SO stream gas compositions are varied. We note that the high PO stream oxygen concentrations investigated in this work and others may pose a risk of fire or explosion in the delivery components of larger scale systems. Nevertheless, consideration should be given to schemes involving fuel transport by sufficiently inert gas streams with the addition and mixing of oxygen at or near the burner outlet to reduce the risk of early ignition. The effect of the temperature is also investigated. Furthermore, as discussed by Khare et al.,\(^\text{35}\) the higher O\(_2\) concentration requirement under oxy-coal retrofit conditions results in a reduced SO flow rate that can impact flame hydrodynamics. Additional hydrodynamic effects are also considered in this study by varying the percentage of SO swirl under both air-fired and oxy-fuel conditions. We then consider the effects of biomass co-firing on NO emissions under both air-fired and oxy-fuel conditions.

**Experimental**

Experiments were conducted under both air-fired and oxy-fuel conditions in a cylindrical, horizontally fired 30 kWth combustor. A schematic of the combustor is shown in Figure 1. Pulverized coal and sawdust were fed to the combustor using separate volumetric screw feeders (K-Tron and Schenk AccuRate, respectively) and were entrained with the PO stream using a Fox Valve Venturi eductor. Gas flows were controlled using

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\(^{(28)}\) Tillman, D. A. Biomass cofiring: The technology, the experience, the combustion consequences. *Biomass Bioenergy* 2000, 19 (6), 365–384.


calibrated rotameters, and none of the gas flows were preheated. Compressed air was dried and filtered prior to being metered and passed to the burner. Under oxy-fuel conditions, flue gases were not recycled; rather, industrial-grade CO\textsubscript{2} was used. The refractory-lined combustion chamber was sealed, and the eductor was contained within an enclosure to prevent air infiltration.

Although not considered in this study, air infiltration can be simulated using a separate stream of air in any of the burner inlets. The combustor was maintained at a slight negative pressure (ca. 10 Pa). The visible flame was largely contained within the first section of the combustor (14 cm inner diameter), and the second section (37 cm inner diameter) provided sufficient residence time for burnout of larger char particles and for the gas composition to become uniform.

The burner was constructed in-house and is shown in Figure 2. The coal delivery tube (PO tube) exits the eductor with an inner diameter of 1.1 cm such that, under standard operating conditions, the velocity is sufficient to maintain the fuel particles in suspension. Approximately 3 cm prior to entering the combustion chamber, the PO tube diverges gradually to 2.3 cm to reduce the PO exit velocity. There is an annulus between the 1.1 cm tube and the 2.3 cm inner diameter tube through which gaseous fuel may be introduced for lighting or flame stabilization purposes. In this study, all flames were stabilized without the aid of a pilot gas. The SO inlet is lined with 1.2 cm of refractory, resulting in an inner diameter of 9.5 cm. The SO stream can be introduced axially or through tangential ports to induce a swirling secondary flow. Brass wool and stainless-steel honeycomb fill the space between the inlet of the axial SO and the tangential SO to straighten the axial flow. Both the SO axial and tangential flows can be controlled independently, thereby providing the capability to vary the swirl intensity in real time. The amount of SO flow introduced tangentially (\(Q_{SO,tan}\)) relative to the total amount of SO flow (\(Q_{SO,total}\)) is defined as the SO inlet ratio (SIR) = \(Q_{SO,tan}/Q_{SO,total}\).

Gas samples were extracted from the exhaust (Figure 1) at a rate of 200 cc/min using an uncooled ceramic 2 cm inner diameter probe and were filtered, dried, and diluted by a dilution probe system (Thermo Electron, Inc.). Pershing and Wendt\textsuperscript{36} reported no differences in NO measurements when using a water-cooled stainless-steel probe, a cooled quartz probe, or an uncooled quartz probe but noted that the measurements were taken after the exhaust had cooled below 800 K and at least 0.5 vol % O\textsubscript{2} was

present in the sample. In this work, the exhaust temperature at the sampling location was also below 800 K and 3 vol % O₂ was present. The concentrations of O₂, CO, and NO were monitored using a continuous emissions monitoring system (Thermo Electron, Inc.). Nitrogen oxide concentrations were measured using a chemiluminescence analyzer (Thermo Electron, model 42), and CO concentrations were measured using gas filter correlation (Thermo Electron, model 48).

To compare NO measurements under air-fired and oxy-fuel conditions, the measured concentrations must be normalized. In this work, the normalization is performed by first computing the product of the NO concentration and molar flow of dry products (W) in the exhaust, assuming complete combustion and using the molecular weight of the dry product mixture. This value is then multiplied by the species molecular weight (M) and divided by the thermal input, yielding NO emissions on a mass per unit energy basis (ng/J).

\[
\text{NO (ng/J)} = \frac{\text{NO (ppm)} \times M \text{ (mol/s)} \times W_{\text{SO}} \text{ (g/mol)} \times 10^3}{\text{thermal input (W)}} \quad (2)
\]

Note that the mass of NO produced per unit energy (ng/J or lb/MMBtu) is reported rather than the mass of NOₓ or NO₂. While the United States Environmental Protection Agency (EPA) NOₓ emission limits are regulated on a mass per unit energy basis, molar concentrations are also important when considering the design of the compression and purification unit for CCS-equipped power plants because NOₓ will be removed during compression and storage.

Sub-bituminous Powder River Basin (PRB) coal provided by a local power plant and waste sawdust obtained from a local sawmill, were used as fuels in this study. Sieve, proximate, and ultimate analyses were performed for both the coal and sawdust, and the results are provided in Table 1. Some variation in the coal particle size distribution was observed over the course of experiments, as indicated in the table. As obtained from the sawmill, the sawdust contained 21 wt % moisture, which led to feeding difficulties; however, after reducing the moisture content to 16 wt % by exposing the sawdust to laboratory room air for a period of time, successful feeding was achieved. Prior to combustion, the sawdust was also sieved through a 20 mesh screen. On the basis of a Rosin–Rammler size distribution, the mean size of the coal particles was approximately 55 μm, while the mean sawdust particle size was approximately 300 μm (after sieving). Measurements of the moisture content of both the coal and sawdust were taken daily prior to each set of experiments using a HI-Res TGA (TA Instruments, Inc.). The average moisture content in the coal was approximately 20 wt %.

Table 1. Fuel Properties

<table>
<thead>
<tr>
<th></th>
<th>PRB coal</th>
<th>sawdust</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV [MJ/kg, dry, ash free (daf)]</td>
<td>29.70</td>
<td>20.20</td>
</tr>
<tr>
<td>Proximate Analysis wt % (Dry)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ash</td>
<td>7.50</td>
<td>0.59</td>
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<tr>
<td>volatile matter</td>
<td>43.36</td>
<td>84.52</td>
</tr>
<tr>
<td>fixed carbon</td>
<td>49.13</td>
<td>14.89</td>
</tr>
<tr>
<td>Ultimate Analysis wt % (Dry)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>carbon</td>
<td>69.51</td>
<td>49.28</td>
</tr>
<tr>
<td>hydrogen</td>
<td>4.61</td>
<td>5.79</td>
</tr>
<tr>
<td>oxygen</td>
<td>17.02</td>
<td>44.14</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.97</td>
<td>0.15</td>
</tr>
<tr>
<td>sulfur</td>
<td>0.40</td>
<td>0.05</td>
</tr>
<tr>
<td>Sieve Analysis wt % Retained</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 mesh</td>
<td>&lt;0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>30 mesh</td>
<td>&lt;0.1</td>
<td>2.3</td>
</tr>
<tr>
<td>50 mesh</td>
<td>&lt;0.1</td>
<td>36.3</td>
</tr>
<tr>
<td>100 mesh</td>
<td>1.9–3.2</td>
<td>81.3</td>
</tr>
<tr>
<td>200 mesh</td>
<td>18–29</td>
<td>94.7</td>
</tr>
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</table>

Table 2. Summary of Experimental Operating Conditions

<table>
<thead>
<tr>
<th></th>
<th>(\dot{m}_{\text{coal}}) (kg/h)</th>
<th>(\dot{Q}_{\text{PO}}) (kW)</th>
<th>(\dot{P}_{\text{PO}}) (m³/h)</th>
<th>(\dot{Q}_{\text{SO}}) (m³/h)</th>
<th>SIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-Fired</td>
<td>20–49</td>
<td>0–35</td>
<td>20–30</td>
<td>21</td>
<td>17–30</td>
</tr>
<tr>
<td>Oxy-fuel</td>
<td>3.3–5.7</td>
<td>0–35</td>
<td>25–35</td>
<td>0–50</td>
<td>17–30</td>
</tr>
</tbody>
</table>

Figure 3. Nitric oxide measured in exhaust as a function of the thermal input under air-fired conditions with 16 vol % excess air and SIR = 1.

A summary of the range of experimental conditions considered in this study is provided in Table 2. In all air-fired and oxy-fuel experiments, conditions were set such that the exhaust gas contained 3 vol % O₂ and no overfire oxidizer was used. Under these conditions, the CO measured in the exhaust was near the lower detectable limit of the CO monitor for all experiments. Thus, CO concentrations are not reported. Loss-on-ignition for fly ash samples was also determined to be less than 1%. Several experiments were replicated multiple times and on different days to determine repeatability and experimental uncertainty for the NO measurements. For replicate data points, the error bars shown represent 1 standard deviation. For experimental conditions repeated less than 3 times, the uncertainty was estimated on the basis of a sensitivity analysis, which revealed that the uncertainty is largely due to variations in the coal particle size.

Results and Discussion

Air-Fired. As discussed above, operating under oxy-fuel conditions with 30 vol % O₂ in the PO stream will increase the stoichiometric ratio in the PO stream (\(\lambda_{\text{PO}}\)) when the PO volumetric flow rate is maintained. To produce a set of baseline air-fired data, the effect of varying \(\lambda_{\text{PO}}\) on NO emissions was investigated in two different scenarios shown in Figures 3 and 4. In Figure 3, the thermal input was varied from 20 to 30 kW at a constant PO flow rate (\(\dot{Q}_{\text{PO}} = 5.3\) m³/h), resulting in \(\lambda_{\text{PO}}\) values ranging from 0.29 at 20 kW to 0.18 at 30 kWth, with all SO flow introduced tangentially (i.e., SIR = 1). Here, it can be observed that NO emissions remained relatively constant, at approximately 86 ng/J (0.2 lb/MMBtu), when varying the thermal input (and consequently the stoichiometric ratio in the PO).

In Figure 4, the PO flow rate was varied at a constant thermal input (30 kW), resulting in \(\lambda_{\text{PO}}\) values ranging from 0.14 to 0.26. Here, the open-faced symbols designate flames having only axial SO flow (i.e., SIR = 0), and the closed-faced symbols designate flames in which the SIR = 1. For the SIR = 0 flames, the NO emissions began to increase significantly when the PO flow rate was increased beyond...
SIR = 1 flames for PO flow rates < 7 m$^3$/h. Increasing the PO flow rate at a constant thermal input can influence the NO emissions in three ways, namely: (1) increase turbulent mixing as characterized by the PO Reynolds number, (2) increase local stoichiometric ratio, and (3) increase flame stand-off distance resulting in SO air entrainment. The nominal changes in NO emissions observed for the flames with SIR = 1 as a function of the PO flow rate suggest that the rate of PO mixing and the local stoichiometric ratio PO are not primary factors influencing NO formation for the flames studied.

Visual observations through a view port clearly indicated that, at higher PO flow rates, the flame stand-off distance increased for the SIR = 0 flames, which would result in SO air entrainment. Moreover, it is well-known that swirl aids in flame stabilization by enhancing the recirculation of hot products in the near burner region, resulting in more rapid coal devolatilization.37–39 Pohl and Sarofim40 indicated that an increased temperature in the devolatilization zone results in higher volatile yields in the fuel-rich zone and reduced char N in the fuel-lean regions downstream. That is, by enhancing devolatilization in the fuel-rich zone, the amount of char N available to be converted to NO downstream, where more oxygen is available, is reduced. Thus, both SO air entrainment and delayed devolatilization could contribute to the increased NO emissions in the SIR = 0 flames.

After we recognized from Figure 4 that the influence of $\lambda_{PO}$ on NO emissions is swirl-dependent in this system, the effect of varying the SIR was explored next. In Figure 5, the closed-face triangles represent air-fired conditions at 30 kWe under variable SIR conditions. The oxy-coal data in Figure 5 will be discussed in the next section. Under air-fired conditions, it can be observed that NO emissions increased sharply when reducing the SIR from 1 to approximately 0.25. Below SIR = 0.25, however, NO emissions increased sharply, reaching a peak near SIR = 0.17. It was observed that the conditions producing peak NO emissions corresponded to a visible change in flame appearance, as seen through the axial view port. Specifically, at the condition of peak NO emissions, the mean flame position fluctuated dramatically, possibly because of the resonant interaction between the axial and tangential SO flows.

**Oxy-coal.** In Figure 5, the NO emissions as a function of SIR from two oxy-coal flames are shown. For these flames, both the PO and SO streams were composed of 30 vol % O$_2$. The closed-faced circles designate the oxy-coal flame, in which the PO flow rate is equivalent to that of the coal/air flame, and the open-faced circles designate the oxy-coal flame, in which the PO flow rate has been reduced by 20%. It can be seen here that replacing the combustion air with a mixture of 30 vol % O$_2$ and 70 vol % CO$_2$ did not reduce NO emissions when the PO stream flow rate was equivalent to that of the air-fired case, even though N$_2$ was removed from the system, presumably eliminating the potential for thermal NO. In fact, NO emissions actually increased relative to the air-fired case when the SIR was between approximately 0.17 and 0.90 for this oxy-coal scenario. The almost immediate increase in NO emissions for this flame for SIR < 1 suggests that insufficient swirl may be the cause of the higher than expected NO emissions because of the flame stand-off and SO oxidizer entrainment or delayed devolatilization resulting in more char N available to form NO in fuel-lean regions, as discussed previously. When the PO flow rate was reduced to 4.2 m$^3$/h (open circles in Figure 5), conditions were achieved in which NO emissions were relatively insensitive to changes in the SIR between approximately 0.60–1. Furthermore, a 20% reduction in NO emissions was observed relative to the air-fired case at SIR = 1, and we note that this result compares well to that of Liu et al.34 and is reasonable when considering the work of Pershing and Wendt,36 who demonstrated that the thermal component of the total NO produced in coal combustion is around 20%. As with the coal/air case, maximum NO emissions occurred when the SIR was between 0.17 and 0.20 for both oxy-coal cases.

The effect of varying the oxygen concentration in the SO stream while maintaining a 30/70 volumetric mix of O$_2$ and CO$_2$ in the PO stream on NO emissions is shown in Figure 6. The flames were produced with a PO volumetric flow equivalent to the coal/air case (i.e., 5.3 m$^3$/h), SIR = 0, and sufficient SO flow to yield 3 vol % oxygen in the exhaust. As a point of reference, the adiabatic flame temperature was calculated. The lower heating value of the PRB coal was used, and complete combustion was assumed. Excess oxygen
was treated as inert, and for simplicity, the products were assumed to be CO2 and H2O(g) only (no dissociation). Temperature measurements were taken in the near burner region using an unsheathed type-K thermocouple with a bead diameter of 750 μm. The thermocouple was inserted through the ignition port until the bead was approximately 2 mm downstream of the PO tube exit and was translated until a maximum temperature was observed. The ignition port is at an angle of 45° from the burner head. Because radiation corrections were not made, these measurements provide only a qualitative indication of changes in the local temperature. As can be seen along the upper abscissa, the SO oxygen concentration was varied from 27 to 39 vol %, resulting in adiabatic flame temperatures ranging from 1950 to 2500 K. The vertical dashed line separates the conditions at which burner attached flames and lifted flames were observed through the ignition view port as shown in Figure 7.

A minimum amount of NO was produced with 33 vol % oxygen in the SO at an adiabatic flame temperature of 2220 K. When O2 in the SO was decreased below ca. 30 vol % (Tad < 2100 K), the flame was completely detached and the near burner region appeared dark, as demonstrated by the photograph in Figure 7b. The decreasing temperature and increasing NO emissions also suggest that a transition occurred near this condition. The modest changes observed for the flames with adiabatic flame temperatures greater than 2100 K are consistent with the results of Pershing and Wendt,36 who found for a variety of coals that the fuel NOx mechanism is relatively insensitive to temperature changes over the range of temperatures considered here. Conversely, Hu et al.17 observed a significant increase in NOx emissions with increasing temperature in an electrically heated furnace under oxy-fuel conditions.

The effect of varying the PO and SO gas compositions under oxy-fuel conditions is shown in Figure 8. For these flames, the thermal input was held at 30 kW, the adiabatic flame temperature was maintained at 2100 K, and the percent O2 in the exhaust was maintained at 3 vol %. The adiabatic flame temperature was held constant when reducing the PO oxygen concentration by increasing the oxygen concentration in the SO. For all three cases shown in Figure 8, the amount of NO produced is non-monotonically a function of the oxygen concentration in the PO stream. Minimum NO emissions were observed in the high PO flow non-swirling flame at 30 vol % oxygen in the PO stream.

For both the low and high PO flow flames with SIR = 1, the minimum NO emissions were observed when the PO oxygen concentration was ~20 vol %. We note, however, that the observed changes between 0 and 30 vol % O2 in the PO stream lie within the experimental uncertainty.

For the high PO flow flames with no SO swirl, the NO emissions were on average approximately 25% greater than the NO emissions from the swirling flames with the same PO flow rate when the PO oxygen concentration was 30 vol % or less. When the PO oxygen concentration was increased to 40 vol %, the NO produced in these two cases was similar. Moreover, it was observed that, at 40 vol % O2 in the PO stream, the non-swirling flame was firmly attached to the burner in a similar fashion to the swirling flame. This result suggests further that the enhanced stability of the swirling flame plays a dominant role in preventing SO stream entrainment and elevated NO emissions.6

In the high PO flow non-swirling flame, the increasing NO observed when the oxygen concentration was reduced below 30 vol % was attributed to slight flame detachment and SO entrainment but delayed devolatilization could have also contributed. The latter effect may have been responsible for the increased NO emissions in the low and high PO flow swirling flames when decreasing the oxygen concentration below 20 vol % as well, given that the maximum temperatures measured in the region of the PO tube exit (as described previously) decreased from ~1450 K at 30 vol % oxygen in the PO to ~1000 K at 4 vol % oxygen in the PO.

As mentioned previously, when oxygen concentrations in the primary were greater than 30 vol %, non-swirling and swirling flames were firmly attached to the burner. Thus, the increased
NO emissions at higher oxygen concentrations were attributed to the stoichiometric ratio, $\lambda_{PO}$, exceeding a critical value. This critical value is near the conditions where sufficient oxygen is supplied in the primary for stoichiometric combustion of the coal volatiles. Because (1) NO emissions from the air-fired experiments did not exhibit a strong dependence on $\lambda_{PO}$ and (2) NO emissions for the low PO flow swirling flame that had 40 vol % oxygen in the primary did not increase substantially when compared to the emissions observed at 20 and 30 vol% O$_2$, this point requires further analysis.

Returning to the air-fired experiments of Figure 4 with SIR = 1 and variable PO flow rate, $\lambda_{PO}$ ranged from 0.14 to 0.26, with minimal changes in NO emissions observed. The $\lambda_{PO}$ of the 4.2 m$^3$/h flow rate oxy-fuel flame in Figure 8 at 40 vol % oxygen in the PO is 0.27. This is near the upper bound of the conditions considered in the air-fired experiments of Figure 4, and as seen in Figure 8, a small increase in NO was observed. However, for the 5.3 m$^3$/h PO flow oxy-fuel flame with 40 vol % O$_2$ in the PO, $\lambda_{PO}$ is 0.34. This may be near a critical value because the amount of NO is rising rapidly with $\lambda_{PO}$. To provide additional evidence for this hypothesis, NO emissions from four additional flames were measured. First, a coal—air flame was produced at a thermal input of 22 kW with the SIR = 1 and a PO flow rate of 7.7 m$^3$/h, resulting in a stoichiometric ratio in the PO of 0.34. Under these conditions, the NO emissions increased approximately 100 ng/J when compared to the coal—air flame produced with a PO flow rate of 5.3 m$^3$/h. Three additional non-swirling oxy-coal low PO flow flames at the same adiabatic flame temperature were also generated with 40 vol % O$_2$ in the PO stream at thermal inputs of 25, 33, and 35 kW and sufficient excess oxygen to yield 3 vol % O$_2$ in the exhaust. The NO measured in the exhaust for these three flames along with the non-swirling 30 kWth flame with 40 vol % O$_2$ in the PO from Figure 8 are shown in Figure 9.

While the influence of enhanced mixing in the high PO flow rate coal—air flame may play a role in the increased NO emissions, a critical value of $\lambda_{PO}$ has been identified in Figure 9. It can be seen that NO emissions were 30% higher in the 25 kWth flame, having a stoichiometric ratio in the PO stream of 0.42, when compared to the 30 kWth flame, having a stoichiometric ratio in the PO of 0.34. Upon increasing the thermal input to 33 kW, which reduced $\lambda_{PO}$ to 0.31, the NO emissions dropped only 7%. Finally, at thermal input of 35 kW and a stoichiometric ratio in the PO of 0.29, the NO emissions were unchanged. Considering that the PRB coal used in this study contains ~43 wt % volatiles, a $\lambda_{PO}$ of 0.42 would correspond to near stoichiometric conditions for volatile combustion. Thus, the critical $\lambda_{PO}$ may be related to the stoichiometric ratio of the volatiles.

Co-firing. The effect of co-firing sawdust on NO emissions is shown in Figure 10. All flames were produced with SIR = 1 and 3 vol % O$_2$ measured in the exhaust. Under air-fired conditions at 20 kWth, the flame stand-off distance increased as the percentage of sawdust co-fired was increased, which may have been a consequence of the lower SO swirl associated with the 20 kWth flames, resulting in weak recirculation of hot combustion products and/or the larger average size of the sawdust particles compared to the PRB coal. Robinson and co-workers$^{41}$ noted that biomass devolatilization times can be longer than coal because of “intra-particle temperature gradients in the relatively large biomass particles”. Longer devolatilization times for the larger sawdust particles would result in ignition of volatiles farther downstream and, thus, increase flame standoff distances. We note that, when co-firing 30 wt % sawdust or more at 20 kWth, a dark near-burner region was observed through the ignition port, as shown in Figure 7b. Consequently, increasing the amount of sawdust led to higher NO emissions, likely because of increased flame standoff distances.

When co-firing sawdust at a thermal input of 30 kW under air-fired conditions, the flame remained attached to the burner; however, it can be seen in Figure 10 that the NO emissions were not reduced, even though the nitrogen content of the sawdust was 0.15 wt % compared to the 0.97 wt % nitrogen content in the coal. Measurements of the maximum temperature in the region near the PO tube exit indicated a reduction of approximately 100 K when going from 100% coal to co-firing 40 wt % sawdust, which could influence the rate of volatile release.

Under oxy-fuel conditions when co-firing sawdust at 30 kWth, the flame also remained attached; however, as observed for the air-fired 30 kWth flames, co-firing sawdust under these specific oxy-fuel conditions had no effect on the production of NO. Moreover, these results provide additional evidence in support of the 20% reduction in NO emissions achieved under oxy-fuel conditions discussed previously. Assuming as before that the thermal NO mechanism makes no contribution to NO production under oxy-fuel conditions, co-firing sawdust had no effect on the amount of NO produced because either more coal-bound nitrogen is

converted, sawdust-bound nitrogen is converted to NO more efficiently than coal nitrogen, or some combination of both effects exists. The effect of elevated local temperatures, because of the higher volatile content of the sawdust, leading to increased thermal NO under air-fired conditions as previously discussed, would not contribute here.

To understand the potential impact of biomass particle size on NO emissions, the sawdust particles larger than approximately 300 μm were removed by additional sieving prior to co-firing. The results of co-firing the smaller sawdust with coal under air-fired and oxy-fuel conditions at 30 kWth are shown in Figure 11. Nitric oxide emissions decreased by approximately 20% when co-firing 60 wt % of the smaller sawdust particles under air-fired conditions. However, under oxy-fuel conditions, NO emissions were unchanged. One possible explanation for this phenomenon may be that the devolatilization and/or combustion of the smaller sawdust particles may be influencing the thermal NO pathway. Thus, under air-fired conditions, reduced NO is observed, while under oxy-fuel conditions, the thermal pathway is unavailable, given that N₂ has been removed from the system.

Conclusions

Measurements of NO concentrations in the exhaust gas during unstaged coal and coal/sawdust combustion in an unpiolated laboratory-scale 30 kWth combustor were performed under a variety of air-fired and oxy-fuel conditions. Experiments examined the effects on NO emissions of the PO stream stoichiometric ratio, adiabatic flame temperature, PO and SO gas composition, and sawdust co-firing under air-fired and oxy-fuel conditions. The following conclusions can be made: (1) In this burner, the primary influence of secondary swirl on NO emissions appears to be through flame stabilization. Moreover, interactions between the tangential swirling flow and the axial flow at reduced swirl (17–20% of total SO flow) resulted in unsteady flames and increased NO emissions for both air-fired and oxy-fuel conditions. (2) When operating under swirling oxy-fuel conditions in which the oxidizer air was replaced with a mixture of 30 vol % O₂ and 70 vol % CO₂ and the PO stream volumetric flow rate was equivalent to the baseline air-fired scenario, NO emissions were not reduced relative to the baseline air-fired case. When the PO volumetric flow rate was maintained, as would likely be required under a retrofit scenario for existing utility boilers, the SO flow rate was reduced by 38%, likely resulting in conditions promoting increased flame stand-off distances and SO oxidizer entrainment, and delayed coal devolatilization, leaving more nitrogen in the char to be converted to NO in fuel-lean regions. When the PO volumetric flow rate was reduced by 20% while the SO flow rate was increased to maintain constant total O₂, a 20% reduction in NO emissions was observed similar to the work of Liu et al. Such a reduction in the PO flow rate is not likely to be an option for current boilers given that a minimum velocity of approximately 17 m/s is required to keep the pulverized coal in suspension. (3) Increasing the flame temperature under oxy-fuel conditions by changing the oxygen concentration in the SO stream with a 30 vol %/70 vol % mixture of O₂ and CO₂ in the PO stream resulted in negligible changes in NO emissions when the flame remained attached to the burner. These results indicate that the fuel NO mechanism may not be strongly dependent upon the temperature, as discussed by Pershing and Wendt. Thus, increasing the oxygen concentration in the SO may be valuable for improving flame stability without increasing NO formation under oxy-coal conditions. Reducing the adiabatic flame temperature below ca. 2100 K resulted in a detached flame, as observed visually and via near burner thermocouple measurements, and flame detachment resulted in higher NO emissions. (4) Varying the PO and SO gas compositions at constant adiabatic flame temperature (i.e., low O₂ in PO with high O₂ in SO and high O₂ in PO with low O₂ in SO) resulted in non-monotonic NO emissions as a function of the PO stream oxygen concentration. Minimum NO emissions were observed when the PO oxygen concentration was between 20 and 30 vol %. Low oxygen concentrations in the PO reduced the maximum near burner flame temperature and presumably caused delayed devolatilization, resulting in higher NO. (5) At high oxygen concentrations in the PO, a critical stoichiometric ratio was identified, at which NO emissions increased sharply. Thus, if elevated oxygen concentrations are to be used in the PO stream for flame stability, the stoichiometric ratio in the PO must be kept below a critical value, which is most likely coal-dependent. (6) Co-firing sawdust can reduce flame stability, resulting in flame detachment and increased NO emissions, even though the sawdust contained 84% less fuel N on a mass basis (50% less fuel N on a thermal basis) than the PRB coal. When co-firing this same sawdust under stable flame conditions up to 40 wt % sawdust (33% thermal), NO emissions were not reduced under air-fired or oxy-fuel conditions (i.e., more fuel N was converted to NO). Co-firing sawdust with a smaller mean particle size resulted in reduced NO emissions under air-fired conditions and no changes under oxy-fuel conditions. Further investigations will be required to understand this phenomenon.

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