

A Mechanistic Investigation of Nitrogen Evolution and Corrosion with Oxycombustion

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Objectives

Nitrogen evolution and corrosion potential will be investigated in oxy combustion conditions for three coals: Powder River Basin (PRB), sub-bituminous, Illinois 6, and Pittsburgh 8, bituminous. A flat-flame burner will be used to study nitrogen evolution in coal particle stream devolatilization experiments at elevated temperatures produced by high oxygen content flames. A laminar flow reactor burning coal in CO₂/oxygen streams will be used to collect NO_x and temperature axial profiles as well as ash deposits to evaluate the effects on NO_x formation and corrosion potential.

The objectives are: 1. To identify the mechanism producing NO_x reduction in Oxycombustion and 2. Identify changes in the oxycombustion reaction process which might produce a negative impact in corrosion.

Accomplishments to Date

The following tasks have been accomplished to date.

1. The multi-fuel reactor has been modified to produce a simulated oxycombustion event using compressed CO₂ and O₂ gas. The reactor has been instrumented to measure flow rates, wall temperatures, and axial gas sampling.
2. Axial gas sampling has been completed for two coals and three oxidizer composition for both staged and unstaged combustion.
3. Particle samples simulating deposits on boiler tubes have been collected for the unstaged combustion conditions. Some of the deposits samples have been analyzed by SEM imaging.

The most significant result to date is the demonstration of lower NO_x formation rates with oxycombustion even though flame temperature is held constant. This suggests that NO_x reductions seen in demonstrations are not just a result of reburning recycled NO_x from the exhaust stream.

Support for this conclusion can be seen in Figures 1 and 2, where NO_x axial profiles are shown for Illinois #6 coal. All of the NO_x data are reported on a fuel specific basis in order to separate out the dilution effects caused by varying amounts of diluent in the oxidizer (CO₂ or N₂). The data in Figure 1, were obtained with the coal burning under premixed conditions with enough primary air to keep the combustion process overall lean at all times. A normal air-fired condition is shown in comparison to two oxycombustion conditions where the oxidizer consists of 25 and 30 % O₂ added to CO₂. In the air case, NO_x is seen to form in the first 85 cm of the reactor before reaching a peak and then slowly decreasing. The peak in NO_x coincides well with peak wall temperatures indicating NO_x is formed throughout the volatiles combustion period. The nitrogen released in or with the volatiles appears to oxidize and produce large amounts of NO_x, the conversion being greater than 60%. After the volatiles burn, there is a net decrease in NO_x which may be caused by NO_x reacting with char or a decrease in NO_x in the direction of thermal equilibrium as the temperature decreases. The oxycombustion case with 25% O₂ produces a similar result to the air case. This was expected because the adiabatic reaction temperature is close to that of the air case although molar concentrations of O₂ are higher. The 30% oxygen case however produced very high NO_x levels with over 75% nitrogen conversion to NO_x which would appear to result because of higher reaction temperature and higher oxygen concentrations.

NO_x profiles for the same three oxidizer concentrations under staged conditions are shown in Figure 2. In these data, the coal and oxidizer are premixed but there is initially insufficient air to burn out the coal. Burnout air is added at 0.68 m. In all three cases, the NO_x levels are the highest at the first axial position and then drop as the gases pass downstream in the reactor. The air case clearly produces the highest nitrogen conversion to NO_x even though it has approximately the same adiabatic temperature as the 25% O₂ case. The contrast in these two cases demonstrate the

capacity of oxycombustion to reduce NO_x during the formation process in addition to other reductions which might be achieved because of reburning reactions or reduced equilibrium values. After forming, NO_x reduced in each case within the rich zone of the reactor before leveling off after the addition of burnout air. The reduction in NO_x within this rich product zone would appear to be caused by reburning reactions. One possible explanation for the lower NO_x formation levels seen with oxycombustion is that higher oxygen concentration preferentially increases the rate of hydrocarbon oxidation over nitrogen oxidation and consumes the available oxygen more rapidly. Thus at a given temperature, less NO_x is formed because there is less time to form NO_x before the oxygen is consumed. This hypothesis requires additional experimental and analytical support which is the focus of additional work.

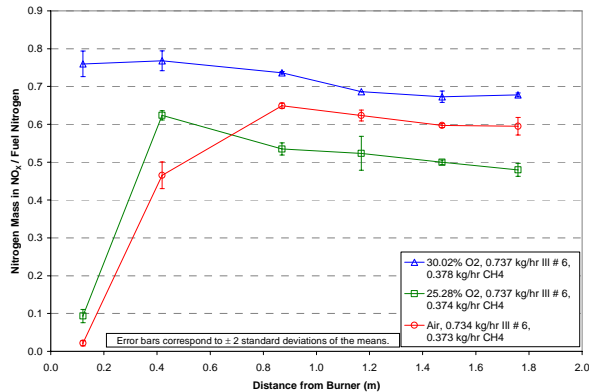


Figure 1. Fuel specific NO_x (Nitrogen in NO_x / Nitrogen in fuel) as a function of axial position in the multi-fuel reactor. Illinois # 6 coal, unstaged combustion.

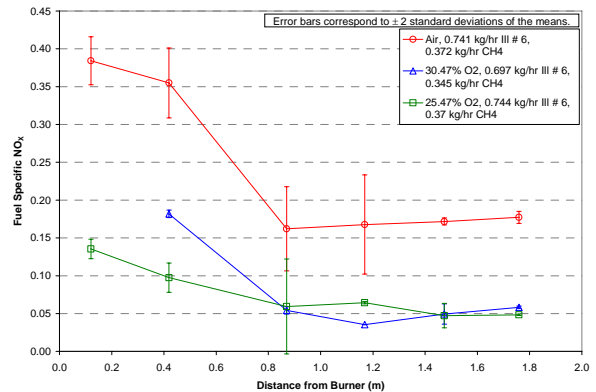


Figure 2. Fuel specific NO_x (Nitrogen in NO_x / Nitrogen in fuel) as a function of axial position in the multi-fuel reactor. Illinois # 6 coal, staged combustion.

Ash deposition samples for the oxycombustion and normal air combustion have thus far shown no significant differences between the two types of combustion related to corrosion potential. It is clear that oxycombustion will increase the concentrations of all gas species because of the absence of molecular nitrogen, but this increase aside, there is no evidence to date in our deposits to suggest that the composition of inorganic elements in the ash is changed.

Future Work

The following is a portion of activities planned for future work.

1. The oxycombustion cases measured in the reactor will be modeled using a full kinetic mechanism to determine if the oxycombustion reduction in NO_x formation can be predicted and is consistent with current kinetic theory.
2. Higher resolution measurements in the near burner region will be obtained to determine the true peak in NO_x and the rate of NO_x formation.
3. Additional nitrogen species will be measured including HCN and NH_3 using a FTIR gas analysis to improve our understanding of the nitrogen evolution from coal at the inlet to NO_x at the outlet.
4. Flat flame burner experiments will show the relative rate of devolatilization of oxycombustion and normal air combustion and will determine if the fraction of nitrogen between char and volatiles is affected.
5. Additional levels of staging will be investigated to determine if a minimum in NO_x formation can be achieved.

Publications

Mackrory, A. J., Lokare, S., Baxter, L. and Tree, D. L., "An Investigation of Nitrogen Evolution in Oxy-fuel Combustion," The 32nd Annual Conference on Coal Utilization and Fuel Systems, June 11-15, Clearwater FL, 2007.

Students

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