ENHANCED COAL REBURNING IN OXIDIZING ENVIRONMENTS

Final Technical Report

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SUMMARY

Conventional fuel rich coal reburning relies upon two primary mechanisms: 1) the reaction of coal volatiles with NO to form HCN, which can subsequently decay to molecular nitrogen (N₂) given sufficient residence time at a suitable temperature; and 2), additional NO reduction by reaction of NO with carbon on the coal char surfaces. Recent research has indicated the possibility of HCN release as an additional product during char oxidation, and under appropriate conditions this HCN could provide a third mechanism for reducing NO to N₂.

Lab-scale experiments and kinetic calculations were carried out to identify conditions that might lead to effective coal reburning under oxidizing conditions. The results of the kinetic calculations indicated that, depending on the temperature, oxygen concentrations in the range of 200 ppm to 1000 ppm (0.1%) would provide the greatest levels of gas phase reduction of NO using HCN, and that reductions between 60-80% are possible (in the absence of heterogeneous effects).

Experiments using pulverized coal in a laminar flow drop tube furnace demonstrated NO reduction levels as high as 40-50%; however, these experiments were shown to have limited gas/coal contacting. The two different experimental configurations used demonstrated a clear dependence of observed NO reduction efficiency on gas/coal loading. The laboratory results were thus extrapolated to gas/solid loadings more typical of a utility boiler, and this extrapolation indicated that greater levels of NO reductions may well be achievable in a coal-fired boiler application.

It was concluded that, given a knowledge of the location of high NO concentrations (obtained for example by CFD modeling), these regions could be targeted with coal injection under slightly oxidizing conditions to obtain NO reductions in excess of the 40-50% levels obtained in the lab-scale experiments. It is recommended that further testing under conventional pulverized coal combustion conditions be pursued to further verify this assertion.
INTRODUCTION

The control of NO\textsubscript{x} production during coal combustion constitutes a high priority since nitric oxides are acid rain and photochemical oxidant precursors. Fuel reburning is one of many promising technologies available for nitric oxide abatement, and the use of reburning constitutes a cost-effective method in which 10 to 30\% of the total fuel is injected upstream of the main oxidation zone, generating a region where nitric oxide is reduced.

Traditional reburning consists of injecting fuel into a slightly oxidizing zone downstream of the burners to create a fuel-rich zone, allowing time of the order of 0.4 seconds for the NO to be reduced, and then completing the combustion by injecting overfire or burnout air to bring the mixture to overall lean conditions in order to complete the combustion. In the case of coal, the reduction in the fuel rich zone occurs through two mechanisms, the reaction of nitric oxide with the hydrocarbons produced during coal devolatilization and the heterogeneous reduction of nitric oxide with char. A further modification of this technique has been proposed where the products from the fuel rich zone are cooled down to the selective non-catalytic reduction (SNCR) temperature window around 1250\degree K (ca. 1800\degree F) before the overfire air is injected so that fuel nitrogen species such as ammonia formed in the fuel rich zone can selectively reduce the NO\textsubscript{x} on oxidant addition [Chen et al., 1986].

An alternative approach considers fuel-lean reburning, in which no overfire air is used. The reburn fuel is added to very lean gases that have enough oxygen to not only consume the reburn fuel, but to provide for the desired excess oxygen level at the outlet. Lean reburning has been found effective with hydrocarbon injection [Miller et al., 1998]. However, there is limited experience of the effectiveness of coal use in lean reburning.

OBJECTIVES

The objective of this work was to explore the use of coal as a lean reburn fuel, taking advantage of recent findings that show enhanced NO reduction by coal char due to the evolution of nitrogenous species during char oxidation and that these nitrogenous species can reduce NO under certain temperature and stoichiometric conditions. This NO\textsubscript{x} reduction pathway could augment the traditional paths of reduction by volatiles and char.
Coal acts as a reburning fuel via the following three mechanisms of NO reduction: 1) NO reduction by volatiles; 2) NO reduction by char; and 3) NO reduction by nitrogenous species released by char under oxidizing conditions. The novelty of the University of Utah’s work is the focus on the third mechanism. Evidence of the release of nitrogenous species during char oxidation comes from the detection of HCN in significant amounts during the process of char oxidation, particularly when the homogeneous oxidation of HCN is suppressed, either by the use of radical quenching techniques such as iodine [Winter et al., 1996; Winter et al., 1999] or by placing the probe close to the char surface [Jones et al., 1995; Ashman et al., 1998; Ashman et al., 2000]. HCN has also been detected, though at lower concentrations, when the oxidation in the homogeneous phase was not suppressed [Ren et al., 2002; Molina et al., 2002]. The nitrogenous species evolved can then reduce the NO in the particle boundary layer.

TECHNICAL APPROACH

The kinetics of NO reduction by coal char were evaluated in a drop-tube reactor modified to allow for longer residence time of the char [Molina, 2002; Molina, et al., 2004]. Figure 1 illustrates the University of Utah’s drop–tube reactor. This reactor is designed to test reaction kinetics of heterogeneous systems at high temperatures. The drop tube is a laminar, entrained flow reactor, which allows testing at high temperature (up to 1750 K) under a wide range of atmospheres, ranging from inert to pure oxygen. It is ideal for studying fast reaction kinetics, with times up to one second, but can also be used over longer times for particles in the heated zone using a crucible. The energy is provided by an Astro model 1000A-3560 graphite-element furnace.

During this project, all of the experiments utilized Ohio coal and some coal property data is given in Table 1. The drop-tube reactor is typically operated as a continual-flow reactor, and several continual-flow experiments were performed with a residence time of 1.1 second. Because of this short residence time in the continual-flow configuration, much of the coal was not completely reacted. Therefore, the drop-tube reactor was modified into a batch reactor by adding a plug of glass wool, with a spreader feeding device at the inlet to disperse the coal uniformly across the plug. The coal remained on the glass wool while the gas-phase components flowed past the coal. Typical coal
residence times for the batch reactor were approximately 10 minutes to ensure complete burnout of the coal at very low oxygen concentrations.

**Table 1.** Ohio coal properties.

<table>
<thead>
<tr>
<th>Proximate wt%</th>
<th>Ultimate wt%</th>
<th>Ultimate wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>2.33</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>39.19</td>
<td>Carbon</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>48.78</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Ash</td>
<td>9.7</td>
<td>Sulfur</td>
</tr>
<tr>
<td>Heating Value</td>
<td>12,865</td>
<td>Chlorine</td>
</tr>
<tr>
<td>BTU/lb</td>
<td></td>
<td>Oxygen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ash</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BaO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Drop-tube reactor configured in flow reactor mode.

**Figure 2.** Drop-tube reactor configured in batch reactor mode.

The NO reduction by coal injection was investigated under both inert and oxidizing conditions. The inert conditions can provide information on the extent of NO reduction by char. The experiments under oxidizing conditions provide information on the enhancement of char reduction by the release of nitrogenous species, assumed to be HCN based on the references cited above. The results were compared to Chemkin simulations of the homogeneous aspects of coal reburning.

Under oxidizing conditions, char nitrogen oxidation occurs simultaneously with NO reduction by char. The two effects can be separated by varying the NO concentration in the inlet gas, since this will increase the NO/char reactions. The explanation for the increase in the rate of nitric oxide destruction by char under oxidizing conditions is related to the reaction of nitrogenous species evolved by the char along with nitric oxide
Other groups have also observed augmentation of the reduction of nitric oxides with coal when oxygen is present in the system [Jensen et al., 2000; Tomita, 2001]. This augmentation has been studied over a narrow temperature window and at 4 and 20% oxygen. These studies will help elucidate how reduction kinetics vary with stoichiometry over the two orders of magnitude difference between the inert and oxidizing conditions.

Therefore, the University of Utah performed experiments at different temperatures and stoichiometric ratios in order to determine the optimal conditions for fuel-lean coal reburning. Table 2 presents the preliminary experimental matrix. The optimal conditions are a trade-off between the ideal temperature and oxygen concentration required to obtain maximum NO reduction, and the one needed to guarantee complete char burnout. It is important in these experiments to consider the trade-offs between the following reactions:

- **NO/char kinetics.** These are favored by high temperatures, high char loadings, and oxidizing conditions.

- **Char nitrogen oxidation to NO.** This is favored by high temperatures and high oxygen concentrations.

- **Char burnout.** This is favored by high temperatures and high oxygen concentrations.

Table 2. Initial test matrix (flow reactor configuration).

<table>
<thead>
<tr>
<th>NO ppm</th>
<th>O2%</th>
<th>Coal use (g)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0, 1, 2.5, 4, 12, 20</td>
<td>0.16-0.27</td>
<td>1650</td>
</tr>
<tr>
<td>100</td>
<td>0, 1, 2.5, 4, 12, 20</td>
<td>0.16-0.25</td>
<td>1650</td>
</tr>
<tr>
<td>400</td>
<td>0, 1, 2.5, 4, 12, 20</td>
<td>0.12-0.27</td>
<td>1650</td>
</tr>
<tr>
<td>700</td>
<td>0, 1, 2.5, 4, 12, 20</td>
<td>0.08-0.38</td>
<td>1273, 1473, 1650</td>
</tr>
</tbody>
</table>

It is expected that optimum lean reburn conditions will be favored by a low oxygen concentration, low enough that NO formation by reaction 2 is suppressed, but sufficiently high to permit char burnout and to take advantage of the enhanced NO/char kinetics. Based on this knowledge and from the results of the initial text matrix, we selected an initial NO concentration of 700 ppm and a temperature of 1650ºK and focused on O2.
concentrations below 1%. Tables 3 and 4 present the test matrices for the additional flow reactor experiments and the batch reactor experiments.

Table 3. Second flow reactor test matrix (initial NO concentration 700 ppm).

<table>
<thead>
<tr>
<th>O2 %</th>
<th>Coal use (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Run 1</td>
</tr>
<tr>
<td>0</td>
<td>0.631</td>
</tr>
<tr>
<td>0.05</td>
<td>0.558</td>
</tr>
<tr>
<td>0.1</td>
<td>0.863</td>
</tr>
<tr>
<td>0.15</td>
<td>0.279</td>
</tr>
<tr>
<td>0.2</td>
<td>0.826</td>
</tr>
<tr>
<td>0.3</td>
<td>0.277</td>
</tr>
</tbody>
</table>

Table 4. Batch test matrix (initial NO concentration 700 ppm).

<table>
<thead>
<tr>
<th>O2 %</th>
<th>Coal use (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Run1</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0245</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0253</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0227</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0221</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0221</td>
</tr>
</tbody>
</table>

KINETIC MODELING OF HOMOGENEOUS COAL REBURN REACTIONS

Approach

Insights on possible homogeneous reburn behavior were obtained through use of gas phase kinetic modeling. Clearly, coal reburning will also involve heterogeneous effects; however, since the hypothesis of this work involved the impact of HCN released into the gas phase during coal/char oxidation, homogeneous calculations were pursued to isolate the effects of evolved HCN alone. The kinetic simulations were obtained by the use of
the CHEMKIN simulation package (Kee et al., 1989; Lutz et al., 1990). CHEMKIN is a set of software tools for solving complex chemical kinetics problems, which allows users to predict the chemical conditions of their system based on variable reactor parameters and inlet gas compositions. The plug flow or SENKIN module was used in these calculations to approximate reaction behavior in the laminar flow drop tube experiments. The simulations focused on temperatures and oxygen concentrations that included and bounded the experimental conditions to be tested (Table 5). The simulations also utilized a simplified reaction scenario where the initial gas-phase composition in the reactor was 1000 ppm NO, 1000 ppm HCN, and 200 ppm – 5% O₂, with the balance argon (Ar), and the temperature ranged from 1273-1873 K. The matrix presented in Table 5 was carried out using both the GRI-Mech 3.0 [Smith et al., 2004] and Glarborg 98 [Glarborg et al., 1998] kinetic mechanisms, and these mechanisms are described below.

Table 5. Kinetic simulation matrix.

<table>
<thead>
<tr>
<th>O₂ concentration (%)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>1273, 1473, 1698, 1773, 1873</td>
</tr>
<tr>
<td>0.05</td>
<td>1273, 1473, 1698, 1773, 1873</td>
</tr>
<tr>
<td>0.1</td>
<td>1273, 1473, 1698, 1773, 1873</td>
</tr>
<tr>
<td>0.2</td>
<td>1273, 1473, 1698, 1773, 1873</td>
</tr>
<tr>
<td>0.3</td>
<td>1273, 1473, 1698, 1773, 1873</td>
</tr>
<tr>
<td>1</td>
<td>1273, 1473, 1698, 1773, 1873</td>
</tr>
<tr>
<td>2.5</td>
<td>1273, 1473, 1698, 1773, 1873</td>
</tr>
<tr>
<td>5</td>
<td>1273, 1473, 1698, 1773, 1873</td>
</tr>
</tbody>
</table>

**Mixture:** 1000 ppm HCN, 1000 ppm NO, variable O₂, bal. Ar

*Description of Mechanisms Used*

**GRI Mech 3.0**

GRI-Mech 3.0 is an optimized mechanism designed to model natural gas combustion, including NO formation and reburn chemistry. It is the successor to version 2.11, and another step in the continuing evolution of the mechanism, although there are currently
no plans for a subsequent update. Propane and C2 oxidation products have been added to this version, and new formaldehyde and NO formation and reburn targets included. Higher hydrocarbons that appear as minor constituents were approximated by additional use of propane.

The conditions for which GRI-Mech 3.0 was optimized, limited primarily by availability of reliable optimization targets, are roughly 1000 to 2500 K, 10 Torr to 10 atm, and equivalence ratio from 0.1 to 5 for premixed systems. A few aspects of natural gas combustion chemistry are not described by GRI-Mech 3.0; these include soot formation and the chemistry involved in selective non-catalytic reduction of NO. The latter may be important in natural gas reburning at lower temperatures. GRI-Mech has been optimized for methane and natural gas as fuel.

Glarborg 98

For the sake of comparison, the calculations were also performed using the Glarborg 98 mechanism. The aim of this mechanism was to describe the low-temperature nitrogen oxide chemistry during C1 and C2 hydrocarbon oxidation in plug flow. The hydrocarbon part of this mechanism is based on compilations and recommendations by Tsang and Hampson (NIST) and by Baulch (CEC). A number of updates in this version reflect new kinetic data, especially in vinyl and ketyl radical reactions. The nitrogen chemistry was mainly based on the mechanism by of Miller and Bowman [1989], with significant revisions in the description of interactions between hydrocarbons and nitrogen-containing species. The mechanism has been validated against a simulated reburning process in a plug flow reactor over the range 800 K < T < 1500 K. It is because of this reburning emphasis that this mechanism was also utilized as a comparison with GRI Mech.

Homogeneous Modeling Predictions

Chemkin modeling was carried out to show the effects of temperature and O2 concentration on NO reduction in the presence of stoichiometric HCN. The results for the GRI Mech 3.0 and Glarborg 98 mechanisms are shown in Figures 3 and 4, respectively.

The modeling results indicate that temperature changes the oxygen concentration at which maximum NOx reduction can be achieved. At lower temperatures, there appears
to be an optimal oxygen concentration where maximum NO reduction can be achieved. As temperatures increase, this optimum shifts to lower oxygen concentrations (note that oxygen is plotted on a logarithmic scale). This optimum is due to a tradeoff between NO reduction by HCN and oxidation of HCN to NO. At high temperatures, the oxidation becomes more dominant and reduction efficiency decreases.

This trend, however, appears to reverse at very low oxygen concentrations, when oxygen is no longer in excess of stoichiometric, and higher reductions are achieved at higher temperatures. This effect is more clearly illustrated in Figure 5, which provides greater resolution of simulation results for the low oxygen conditions, and also includes results obtained for the case of no initial oxygen. Thus, depending on the reaction temperature, predictions for homogeneous NOx reduction with HCN reach a maximum between 200-1000 ppm O₂.
Figure 3. Plug flow modeling of NO reburning in the presence of HCN for various temperatures and oxygen concentrations (Mechanism: GRI Mech 3.0).
Figure 4. Plug flow modeling of NO reburning in the presence of HCN for various temperatures and oxygen concentrations (Mechanism: Glarborg 98).
EXPERIMENTAL RESULTS AND DISCUSSION

The gas phase simulations indicated that very low oxygen concentrations are required to achieve significant homogeneous NO reduction under oxidizing conditions. The release of HCN during heterogeneous oxidation of char will also be a function of oxygen (and temperature); however, the optimal release of HCN from char may not occur at the same oxygen concentration as maximum gas phase NO reduction. In addition, heterogeneous reduction of NO by char is occurring simultaneously, and thus net effect of these processes must be evaluated. Therefore, experimental trials were carried out under a range of temperature and oxygen concentrations, as described previously, to identify the combined effects of these various mechanisms.

Figure 5. Low oxygen range for plug flow modeling of NO reburning in the presence of HCN (Mechanism: Glarborg 98).
Flow Reactor Experiments

Initial experiments were carried out using the Flow Reactor configuration of the drop tube furnace. Figure 6 shows an example of the gas-phase concentrations measured during a flow reactor experiment. The main gas stream was fed into the reactor with an initial NO concentration of 900 ppm, an initial O₂ concentration of 0.3%, and the balance being molecular nitrogen (N₂). Once the temperature and gas concentrations were stabilized, pulverized coal was injected and the drop in NO concentration due to coal reburning for the current conditions was recorded.

As shown in the figure, upon coal injection, the NO concentration decreased initially and then leveled off, while the CO increased and the O₂ decreased to new average levels. The fluctuations noted in the gas phase concentrations are due to perturbations in the pulverized coal feed rates. The fluctuations are generally not as apparent when using higher oxygen concentrations; however, the data in Figure 6 are for an average oxygen concentration of approximately 0.1% when feeding coal.

The NO reduction is calculated from the average of the NO concentration during the coal feed and the initial NO concentration as follows:

\[
\text{\%NOreduction} = \left(1 - \frac{NO_{\text{reburn}}}{NO_{\text{initial}}} \right) \times 100
\]

Because nitrogen (N) can be released from the coal used in these experiments (1.37 wt.% N, c.f. Table 1) and can be oxidized to NO, and thus have an effect on the measured outlet NO of the flow reactor, we needed to determine the relative impact of coal N oxidation on exhaust emissions. Such a determination was important because it was difficult to fully oxidize the residual coal char in the drop tube furnace at low oxygen concentrations. The residence time for the coal under flow reactor conditions was simply not long enough to completely burn out all the fuel at low O₂ levels. Thus, to make comparisons of the reduction of NO by coal at various oxygen levels, it was important to assess the contribution of coal NO to the exhaust emissions measured in this experiment.
Figure 6. Flow reactor experiment at 900 ppm NO (initial) concentration, 0.3% O2 (initial) and a temperature of 1473K.

By use of the ideal gas law, and with knowledge of the volume and flowrate of the drop-tube reactor, the amount of nitrogen released from the coal could be calculated by assuming that all of the coal N was converted to NO. This assumption is a conservative estimate for the purposes of this calculation, since typical coal N conversion to NO will be less than 1.

The results of this analysis showed that the increase in exit NO concentration due to oxidation of the coal ranged from 1 ppm to 20 ppm, for the various conditions explored in the flow reactor studies, with 20 ppm representing conditions where a very high feed rate of coal was used. Thus the impact of coal NO on exhaust NO emissions is less than 3% of the initial NO concentration of 700 ppm used for the majority of these experiments. For experiments carried out at very low initial NO concentrations, the contribution of coal N to overall NO values was still less than 10%. Therefore, the effect of incomplete combustion on NO reduction values was ignored in the flow reactor studies, although it was explored more fully in subsequent batch reactor tests where long residence times with low oxygen concentrations were possible.
**Batch Reactor Experiments**

The batch reactor experiments provided longer residence times of approximately 10 minutes and thus allowed sufficient time for char oxidation to proceed to a high level of conversion, even at very low oxygen concentrations. Figure 7 shows an example of a batch experiment. The main gas flow was initiated with known NO and O$_2$ concentrations, as with the flow reactor experiments, but then a fixed quantity of pulverized coal (typically 5-25 mg) was rapidly injected into the furnace and dispersed over a plug of quartz wool. The coal would then undergo the processes of devolatilization and char oxidation, in parallel with the various coal reburn reactions described earlier in this report. NO, CO and O$_2$ concentrations were measured over the course of the experiment to quantify the transient behavior. The NO concentration initially dropped as the NO reacted with coal volatiles and char, and then slowly increased as the char was consumed by oxidation. The NO level returned to its initial level once the char had been completely oxidized.

As with the flow reactor experiments, the batch reactor runs could be carried out at different oxygen concentrations to determine the overall amount of NO reduction for each condition. An example of this is shown in Figure 8, which indicates batch reactor results for two different oxygen concentrations. The NO traces could each be integrated to determine the total amount of NO that exited the reactor, and compared with the total amount of NO that would have exited if no reduction had occurred. In this way, a fractional reduction could be computed for each run. Essentially, the relative area of the ‘dip’ in NO concentration indicates the amount of NO reduced. The batch reaction results clearly show that lower O$_2$ levels improve NO removal.
Figure 7. Batch experiment with 1% (initial) O$_2$, 700 ppm NO (initial), and performed at 1650 K.

Figure 8. NO/NO initial for the final batch runs.
Effect of NO concentration

Experiments were carried out using the flow reactor configuration with a range of initial NO concentrations, to evaluate the impact of initial NO on lean coal reburn reduction efficiency. These experiments also covered a wide range of oxygen concentrations, and the NO reduction values obtained are shown in Figure 9. Error bars representing one standard deviation are included when multiple experimental runs were available. It is clear that the effect of oxygen is consistent at all NO levels investigated, in terms of increasing NO reduction for decreasing levels of O\textsubscript{2}, and that O\textsubscript{2} levels in excess of a few percent oxygen will result in very limited NO reduction, or even a net increase in NO, for all initial NO levels. The sensitivity to oxygen concentration appears to be greatest for the lowest initial NO level (100 ppm), and this is in part due to a greater influence of the NO originating from the coal. At higher NO levels, 400 and 700 ppm, there seems to be little influence of initial NO except under inert conditions (0% oxygen).

In addition, at a nominal NO concentration of 100 ppm, initial NO levels fluctuated somewhat because of difficulty in maintaining a constant low flowrate for the NO-containing gas stream that was mixed with N\textsubscript{2} and O\textsubscript{2} streams to obtain the final desired mixture. Initial NO concentrations of 400 and 700 ppm, however, produced fairly stable results. Therefore, the majority of subsequent experiments were performed with an initial NO concentration of approximately 700 ppm in order to maintain stable flows and to also minimize the relative contribution of NO from coal.
Additional experiments were carried out to focus on the effect of oxygen concentration using the flow reactor configuration, but with a greater emphasis on the very low oxygen concentrations where NO reduction was presumed to be the highest, based on the gas phase reduction calculations. These oxygen results are shown in Figure 10, with average values and error bars (denoting a standard deviation of one) plotted when there were multiple data points. Note that the oxygen concentration in Figure 10 is plotted on a logarithmic scale to provide greater resolution of the results with lower oxygen values.

For these tests, the initial NO concentration of the main gas flow was 700 ppm to minimize variations in the initial NO level, as well as the relative contribution of NO originating from the coal.

The experimental results illustrate the same trend of increasing NO reduction as with decreasing O₂ concentration, and the relationship appears to be logarithmic in oxygen.
concentration, as illustrated by the good correlation with a log-linear regression relationship.

The kinetic calculations indicated that very low oxygen concentrations were required to achieve the maximum homogeneous reburn effect. Experiments at very low oxygen concentrations in the flow reactor configuration resulted in limited combustion of the coal in the residence time available; therefore, the lower oxygen concentrations were explored in more detail with the batch reactor setup.

The low O$_2$ concentration experiments with the batch reactor setup are presented in Figure 11. The NO reduction values obtained in the batch configuration were lower overall than those in the flow reactor configuration, but the reduction still appeared to have a logarithmic dependence on O$_2$ concentration. The lower reduction levels are potentially due to the reduced amounts of coal used in the batch experiments, and this dependency on coal flowrate was explored in additional experiments.

\[
y = -6.2639 \ln(x) + 11.023
\]

\[R^2 = 0.9659\]

\[0.01 \quad 0.1 \quad 1 \quad 10 \quad 100\]

\[0 \quad 10 \quad 20 \quad 30 \quad 40 \quad 50 \quad 60\]

\[\text{NO reduction (%)} \quad \text{O2 concentration (%)}\]

**Figure 10.** Comparison of NOx reduction versus O$_2$ concentration for the flow reactor runs. The error bars denote one standard deviation. Note that the X-axis is plotted on a log scale.
Figure 11. Comparison of NOx reduction versus initial O₂ concentration for low O₂ levels in the batch reactor configuration.

Effect of Coal Feed Rate

The effect of coal feed rate and the total amount of coal fed were explored in both the flow reactor and batch reactor scenarios. These results are shown in Figure 12, where it is clear that the NO reduction is dependent upon the coal feed rate, as would be expected. The effect of oxygen is also evident in the figure, as the three different O₂ levels appear to be grouped separately. A similar dependence on coal fed is evident for the batch experiments, as shown in Figure 13. In this figure, NO reduction is plotted versus total coal fed (instead of feed rate), since it is a batch experiment.
Figure 12. Comparison of NOx reduction versus coal feedrate with the flow reactor configuration at three different O2 levels.

Figure 13. Comparison of NOx reduction versus coal feedrate with the batch reactor configuration at several different O2 levels.
Discussion of Experimental Results and Model Predictions

The previously discussed modeling results indicated that a maximum NO reduction could be observed at very low oxygen concentrations. That analysis, however, only considered NO reduction due to the homogeneous reaction of HCN with NO. Although it is clear that NO/char reactions will also be present, the homogeneous results provide some insight on their relative contribution to the overall NO reduction.

Figure 14 provides a comparison between the homogeneous model predictions and the experimental results for the flow and batch reactor studies. The model predictions cover the range of temperatures most likely to reflect the bulk gas conditions in the drop tube furnace. A range of experimental results are represented at several different oxygen concentrations by an average value and error bars as shown in the figure. The range shown primarily represents NO reduction values obtained over a range of coal feed rates.

It is clear from the figure that at low oxygen concentrations, the experimental results are significantly lower than the homogeneous predictions. As stated earlier, such a comparison is not entirely fair since heterogeneous effects are not included in the model predictions. However, the purpose of this comparison is to provide a qualitative view of the trends of the experimental results and model predictions.

The experiments did not appear to demonstrate the clear optimum predicted by the gas phase calculations for oxidizing conditions; however, the maximum NO reductions were achieved at the lowest oxygen concentrations. The magnitude of the reductions observed at low oxygen concentrations, although significant, could be easily achieved or even superseded under conventional fuel rich coal reburning conditions. Thus, it would seem that there would be limited benefit to carrying out coal reburn under mildly oxidizing conditions. It should be noted, however, that both experimental configurations (flow and batch) were limited in the amount of the NO-laden gas that was in contact with the coal.

For the flow reactor configuration, a thin stream of coal was injected down the center of the drop tube furnace, and then the reactant gas was introduced in a laminar flow stream inside of the 2.5 inch diameter tube. Thus, the amount of NO-bearing gas that was in contact with the coal was somewhat limited. For the batch reactor configuration, the coal was dispersed across the cross-section of the reactor; however, the amount of coal
injected was still relatively small, and thus only a fraction of the gas would have been in contact with the coal particles.

![Graph showing NO reduction versus O2 concentration](image)

**Figure 14.** Experimental data and homogeneous kinetic calculations.

**IMPLICATIONS FOR FULL SCALE OPERATION**

The magnitude of the results of these laboratory tests would seem to indicate that there is limited potential for applying coal reburning under oxidizing conditions to real systems. As was mentioned previously, however, the laboratory tests were limited in terms of the amount of simulated flue gas that was treated. In particular, the difference between the flow reactor and batch results, highlights this issue of fuel to gas ratios.

The batch reactor tests demonstrated consistently lower NO reductions than the flow reactor tests, and one difference between the two scenarios that might explain this discrepancy is the volume of gas treated per mass of coal in the system. If the two reactor scenarios are compared on a normalized basis, Mass of Gas Treated per Mass of Coal, the results seem more consistent. A plot of NO reduction versus Gas/Coal mass ratio is shown in Figure 15, where “Gas” in this case represents the purge gas used in the drop tube experiments (primarily N\textsubscript{2}, with small amounts of NO and O\textsubscript{2}).
The data points shown represent experimental results in the oxygen concentration range of 0-0.1%. The batch reactor results are grouped near a value of 10,000, and the flow reactor results are shown in the range of 100-1000 (note that it is a log scale). The data from both experiments seem to correlate quite well with Gas/Coal ratio.

If one assumes that this relationship, which ranges over 3 decades of Gas/Coal ratios, will extrapolate to lower Gas/Coal ratios, we can estimate what the performance of coal reburn under oxidizing conditions might be for Gas/Coal ratios more typical of a utility boiler. The highest values for this ratio are for transporting coal, in which Air/Coal mass ratios are typically 1.5-2.0. Such values are seen at the exit of coal nozzles in either the burner zone, or in a coal reburn zone. A stoichiometric value for Air/Coal mass ratio is of order 10 for a number of coals, and this value would represent particle loading in a burner zone operating at very low excess oxygen (near stoichiometric). A quick calculation of conventional coal reburn conditions, using a coal reburn rate of 10% of total thermal input, would indicate particle loadings on the order of 100 if one assumes that the reburn coal is perfectly mixed with all of the combustion products from the burner zone, as well as the transport air for conveying the reburn coal.

In a practical reburn application, one would thus expect to see gas/particle loadings that span this entire range, from approximately 1-100, depending upon local mixing behavior. The extrapolation would indicate that local NO reduction values could range from 45 to over 80%. A uniformly mixed scenario would represent the limiting case of 45%. The more realistic non-uniform mixing would provide higher levels of NO reduction on a localized basis, but some of the combustion products could pass through the reburn zone with contacting coal. Thus, the overall reduction would be the net effect of some regions of higher reduction, and some regions of no reduction, which could be greater or less than 45% depending upon conditions.

This qualitative analysis would seem to indicate, however, that under slightly oxidizing conditions, carefully targeted injection of coal into regions of highest NO concentration, could provide higher particle loadings than using a uniform dispersion of reburn coal, and would thus yield greater reductions in overall NO emissions. The design of such a system could be greatly facilitated by the use of computational-fluid-dynamics (CFD)-based coal
combustion simulations, such that regions of high NO concentration in the reburn zone could be identified, and different injection strategies evaluated.

Clearly, well-controlled coal reburning experiments under conventional Air/Coal conditions need to be performed to determine if such reductions are feasible. In addition, the practicality of controlling oxygen concentrations to such a narrow range of low values, as well as the sensitivity to oxygen concentration under conventional boiler conditions, would need to be addressed to enable successful implementation of this technology.

Figure 15. NO reduction versus Air/Coal ratio for Flow Reactor and Batch Reactor drop tube testing, with extrapolations to conventional boiler conditions.
CONCLUSIONS

Previous research indicated the potential for HCN, released during char oxidation, to provide an additional pathway for NO reduction during coal reburning. Lab-scale experiments and kinetic calculations were carried out to identify conditions that might lead to effective coal reburning under oxidizing conditions. A wide range of oxygen concentrations were explored, in addition to initial NO levels and coal feed rates. Two reactor configurations were tested: a flow reactor configuration with a continual feed of coal and NO-containing gas, and a batch reactor configuration where a fixed amount of coal was injected onto a bed of quartz wool and allowed to burn to completion in situ in the presence of the NO gas stream.

The results of the kinetic calculations indicated that, depending on the temperature, oxygen concentrations in the range of 200 ppm to 1000 ppm (0.1%) would provide the greatest levels of gas phase reduction of NO using HCN, and that reductions between 60-80% are possible (in the absence of heterogeneous effects).

Experiments using pulverized coal in a laminar flow drop tube furnace demonstrated NO reduction levels as high as 40-50%; however, these experiments were shown to have limited gas/coal contacting. The two different experimental configurations used demonstrated a clear dependence of observed NO reduction efficiency on gas/coal loading. The laboratory results were thus extrapolated to gas/solid loadings more typical of a utility boiler, and this extrapolation indicated that greater levels of NO reductions may well be achievable in a coal-fired boiler application.

It was concluded that, given a knowledge of the location of high NO concentrations (obtained for example by CFD modeling), these regions could be targeted with coal injection under slightly oxidizing conditions to obtain NO reductions in excess of the 40-50% levels obtained in the lab-scale experiments. It is recommended that further testing under conventional pulverized coal combustion conditions be pursued to further verify this assertion.
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