BENCH AND PILOT SCALE PROCESS EVALUATION OF REBURNING FOR IN-FURNACE NOX REDUCTION

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This paper describes a combined experimental and theoretical study which was undertaken to quantify the impact of fuel and process parameters on reburning effectiveness and provide the scaling information required for commercial application of reburning under highly varied industrial conditions. Initially parametric screening studies were conducted in a 25 KW refractory-lined tunnel furnace. These studies were supported by large scale testing in a 3.0 MW pilot scale facility. The work at both scales focused on the importance and the fate of the reactive nitrogen species within the reburning zone.

The results of this study confirm the potential of the reburning process for significant NOx reductions, but they also demonstrate that a constant reburning effectiveness cannot be assumed under all conditions. The NOx reduction possible through reburning depends primarily on the NO concentration at the end of the primary zone; the stoichiometry, temperature, and residence time in the fuel-rich reburning zone; the mixing and stoichiometry of the reburning fuel jet; and the temperature in the final burnout zone. At the optimum reburning stoichiometry \( \text{SR}_{o} = 0.9 \) the exhaust emissions correlate linearly with the sum of the primary NOx and the equivalent reburning fuel nitrogen. Optimum effectiveness requires adequate primary zone residence time to insure complete combustion of the primary fuel. Reburning zone residence times of at least 400 ms are desirable and high temperatures favor molecular nitrogen formation. Rapid mixing of the reburning fuel enhances the effectiveness of the NOx destruction process but it can potentially detract from the overall process efficiency with coal reburning due to increased conversion of reburning fuel nitrogen unless the fuel is transported with an essentially inert gas stream. Extremely low exhaust emission levels can be achieved with coal reburning if the final burnout zone can be operated at a temperature low enough to promote in-situ thermal de-NOx.

Introduction

Reburning is a combustion modification technology which removes NOx from combustion products by using fuel as the reducing agent. This technology, which is alternately referred to as “in-furnace NOx reduction” or “staged fuel injection”, has been found to involve kinetic processes similar to those in staged combustion. The concept was originally developed by the John Zinc Company\(^1\) and Wendt et al.\(^2\) based on the principle of Myerson et al.\(^3\) that CH fragments can react with NO. More recently several investigators have conducted detailed investigations of the process\(^4-9\) and demonstrated its potential for large scale applications.\(^3,4,10,11\)

Conceptually the reburning process can be divided into three zones:

- **Primary Zone:** This main heat release zone accounts for approximately 80% of the total heat input to the system and is operated under fuel-lean conditions. The level of NOx exiting this zone is defined to be the input to the reburning process.
- **Reburning Zone:** The reburning fuel (normally 10 to 20% of the total fuel) is injected downstream of the primary zone to create a fuel-rich, NOx reduction zone. Reactive nitrogen enters this zone from two sources: the primary NOx and the fuel nitrogen in the reburning fuel. These reactive nitrogen species react with hydrocarbon fragments from the reburning fuel to produce intermediate species NH3 and HCN.\(^3,4,8\) Additionally some nitrogen is converted to N\(_2\) and some is retained as NO. If the reburning fuel is a solid, nitrogen may also leave this zone as char nitrogen.\(^3\)
- **Burnout Zone:** In this final zone, air is added to produce overall lean conditions and oxidize all remaining fuel fragments. The total
fixed nitrogen species (TFN = NH₃ + HCN + NO + Char N) will either be oxidized to NOₓ or reduced to molecular nitrogen.

This paper summarizes the results of a study which was undertaken to quantify the impact of fuel and process parameters on reburning effectiveness and provide the scaling information required for commercial application of the process under highly varied industrial conditions. Initially parametric screening studies were conducted in a 25 KW refractory-lined tunnel furnace. These studies were subsequently supported with testing in a 3.0 MW pilot scale facility and with finite rate kinetic modeling. The work at both scales focused on the importance and the fate of the reactive nitrogen species within the reburning zone. The experimental conditions were designed to directly simulate the 400—700 ms residence time available in a practical boiler between the burner zone and superheater tubes. Boiler heat transfer calculations suggest that the reburning fuel must be injected at 1400 ± 50°C and the reburning air at 1300 ± 50°C to insure complete burnout prior to the superheater.

**Experimental Systems**

The process studies were conducted in the 2.5 m refractory-lined controlled temperature tower (CTT). This 25 KW furnace (Fig. 1) is 20.3 cm in diameter and the time/temperature profile can be adjusted using backfired heating sections within the refractory walls. The primary fuels were fired at 17.6 KW using two types of burners: a premixed burner for the gaseous fuel (propane) and pulverized coals, and a diffusion burner with twin fluid atomization for liquid fuels (oil and coal-water slurry). The reburning fuels were injected immediately downstream of a refractory choke with a 90° injector located at the centerline of the furnace. This injector allowed the reburning fuel, transported with nitrogen, to flow radially outward through four 0.5 cm holes and mix rapidly with the oncoming primary effluent. Another refractory choke was inserted downstream to isolate the fuel rich reburning zone from the final burnout zone. Burnout air was also injected radially.

The 3.0 MW, down-fired tower furnace (Fig. 1) used in the pilot-scale investigations was refractory-lined and water-jacketed with inside dimensions of 1.2 x 1.2 x 8.0 m. The four main diffusion burners each consisted of an inner pipe for axial primary fuel injection and an outer pipe, equipped with swirl vanes, for the main combustion air. This four burner array produced relatively uniform velocity and composition profiles at the primary zone exit.

The furnace contained seven rows of ports for reburning fuel and burnout air injection. The temperature profile was manipulated by insertion of cooling panels, positioned against the furnace walls. The reburning fuel and burnout air injectors were designed to maintain jet mixing similarity between the pilot-scale furnace and a full scale boiler based on empirical correlations for entrainment rate and jet penetration.

Exhaust gas samples were withdrawn through a stainless steel, water-jacketed probe and analyzed for NOₓ (chemiluminescence), O₂ (paramagnetic), CO/CO₂ (NDIR), and SO₂ (NDUV). Furnace thermal profiles were characterized with a suction pyrometer.

The fuels used in this study included natural gas (containing 90% CH₄, 6% C₂H₆ and 1% C₃H₈ by volume), propane, a low nitrogen (0.2%) Middle East residual oil, a high nitrogen (0.8%) residual oil from Kern County, California, a Yallourn predried Australian brown coal, a Beulah, N.D. lignite, a subbituminous coal from Colstrip, Montana, a Utah high volatile bituminous coal and a medium volatile bituminous coal from Rosa, Alabama. In addition, non-hydrocarbon fuels, hydrogen and CO, were used as reburning fuels and a coal-water slurry, which contained 30% water, was used as a primary fuel. Complete analyses of the oils and coals are available in the literature.

**Process Parameters**

**Available Reactive Nitrogen**

Figure 2 compares the effectiveness of different reburning fuels as the reburning zone stoichiometry (SR₂) was reduced from 1.1 (no
Fig. 2. Influence of Reburning Zone Stoichiometry on Exhaust Emissions for Various Reburning Fuels (Propane primary, $(NO_x)_p = 630$ ppm, $\tau_2 = 400$ ms, reburning fuel transport: $N_2$)

reburning) to 0.7 (ca. 36% reburning fuel). In these studies the primary zone $NO_x$, $(NO_x)_p$ was 630 ppm and the primary zone stoichiometric ratio $(SR_1)$ was 1.1. Propane and natural gas (not shown) are the most effective reburning fuels; hydrogen and CO (not shown) are the least. The hydrocarbon fuels rapidly form CH fragments which convert the primary $NO_x$ to HCN while CO and H$_2$ only form CH fragments through interactions with H$_2$O or CO$_2$ species. Detailed measurements at the end of the reburning zone indicated that HCN formation was significantly less with hydrogen or CO as the reburning fuel. The coals are also effective at reducing the $NO_x$ from the primary zone; however, they are less effective than propane because they add additional reactive fuel nitrogen. All of the hydrocarbon fuels exhibited an optimum stoichiometry at $SR_2 = 0.9$ because of a trade-off between the efficiency of primary $NO_x$ destruction and the formation of HCN. The fact that both propane and the solid fuels have the same optimum rich

zone stoichiometry suggests that fuel volatility is not of first order importance (so long as the rich zone residence time and stoichiometry are adequate to insure overall, fuel-rich conditions).

The difference in the minimum $NO_x$ levels achieved are directly related to differences in the fuel nitrogen contents of the various hydrocarbon fuels as illustrated in Fig. 3. Here the exhaust $NO_x$ emissions are plotted on a molar basis as a function of the total available reactive nitrogen (primary zone $NO_x$ plus fuel nitrogen in the reburning coal) for all of the stoichiometries and fuels shown in Fig. 2. In addition data from tests with various primary $NO_x$ levels have been added. Applications of reburning causes the emissions to fall onto operating lines where the source of the reactive nitrogen becomes indistinguishable: at $SR_2 = 0.9$ primary zone $NO_x$ and reburning fuel nitrogen are equivalent in terms of their impact on exhaust $NO_x$ emissions. Thus, in systems with already low primary emissions (less than 600 ppm) reburning fuel nitrogen can become very significant. (The nitrogen associated with reburning using 20% Utah coal at 1.5% fuel nitrogen is equivalent to 780 ppm of primary $NO_x$.)

The slope of the operating line under these baseline conditions corresponds to 25% conversion of the total available nitrogen. Figure 3 indicates that this slope is not strongly dependent on reburning fuel type; however, it does depend on the combustion conditions as will be discussed in the following sections.

Figure 4 summarizes data from a test sequence in which propane, three coals, two oils, and a coal-water slurry were alternately used as the primary fuel; the reburning fuel was always natural gas. (These experiments are the reverse of those shown in Fig. 3 where the primary fuel was always gas and the reburning fuel was
In this case the data can be simply correlated in terms of primary NO$_x$ because it is identically equal to the total available reactive nitrogen; the natural gas reburning fuel contains no reactive nitrogen. Thus these experiments allow the primary NO$_x$ and the reburning fuel nitrogen effects to be decoupled. The data from the wide spectrum of primary fuels correlate well with the solid line (doped propane primary) again indicating that the total available reactive nitrogen is the only composition variable of major importance under normal operating conditions.

In the summary the reactive nitrogen studies indicate that the reburning zone stoichiometry should be fuel-rich to achieve optimum emissions reductions. If the reburning fuel is nitrogen free, stoichiometries $\geq 0.9$ are essentially equal in effectiveness; with heavy oils and coals $SR_2 = 0.9$ is an optimum stoichiometry because further decreases in $SR_2$ add additional reactive nitrogen through the reburning fuel and result in higher exhaust NO$_x$ emissions. Under optimized reburning conditions exhaust NO$_x$ is directly related to the sum of the primary NO$_x$ and the reburning fuel nitrogen and the two nitrogen sources are essentially equivalent in terms of conversion to exhaust NO$_x$. Thus, if the initial NO$_x$ emissions are very low (e.g. 100 ppm) reburning with a high nitrogen coal can actually increase exhaust NO$_x$.

System Parameters

This section of the paper focuses on the bench scale studies conducted to optimize the system design parameters, specifically the location of the reburning fuel injection, the location of the final burnout air injection and the optimum thermal environment.

Figure 4 also shows data which were obtained with a short primary residence time (70 ms). Here the reburning fuel was injected close to the main burner to establish the impact of overlapping zones in practical systems where inadequate total residence time is available prior to the convective passages. (The final burnout air injection was also moved correspondingly to maintain the 400 ms rich zone residence time in each experiment.) In principle reducing the primary zone residence time should help reburning effectiveness because it increases the rich zone temperature; however, these data indicate that with all of the coals tested (including the coal-water slurry) decreasing the primary zone residence time from 330 ms to 70 ms had a significant detrimental impact on the effectiveness of the reburning concept. Internal measurements indicated that this was primarily because the effective reburning zone stoichiometry ($SR_2$) was significantly increased due to incomplete combustion in the primary zone. The oxygen concentration at the primary exit was 6% with the Rosa coal and 9% with coal-water slurry; the oxygen concentration with complete primary combustion would have been 2.1%. Thus, if the primary zone residence time is not adequate to insure almost complete consumption of the available oxygen, the primary fuel will continue to oxidize through much of the reburning zone under oxygen rich conditions. These data emphasize the importance of avoiding significant zone overlap in practical combustion systems. Primary zone residence times of at least 300 ms are clearly desirable.

Figure 5 summarizes similar results on the importance of reburning zone residence time. The data (obtained with propane reburning at two different primary NO$_x$ concentrations) indicate that increasing the rich zone residence time from 140 ms (corresponding to the observed length of the reburning flame) to 400 ms significantly increases the effectiveness of the reburning process at high primary NO$_x$ concentrations but has little effect at low primary NO$_x$ concentrations. Little additional reduction was achieved by extending the reburning residence time beyond 400 ms in either case.

A simplified model was used to simulate the reburning process and assist with the interpretation of the results shown in Fig. 5. The reburning zone was assumed to consist of two parts: a flame zone, lasting 200 ms where half of the primary NO$_x$ was converted to HCN with the rest remaining as NO and a post flame zone where the NO$_x$ and HCN decayed according to the Fenimore mechanism. H$_2$ and H$_2$O were assumed to be equilibrated and a fourth order Runge Kutta integration was used to solve the simultaneous differential equations for species concentrations. The empirical correlation based
The work of Chen and coworkers, originally developed to model the formation of NO\textsubscript{x} emissions in the final lean stage of a staged coal combustor, was used to approximate the conversion of NH\textsubscript{3}, HCN, and NO in the final burnout zone since no validated detailed mechanism currently exists:

\[
(\text{NO}_{\text{x}})_{\text{ex}} = 0.81 \times R_{\text{z}} \times \text{NO}^{0.36} [\text{HCN} + \text{NH}_{3}] + 0.0024 [\text{HCN} + \text{NH}_{3}] + 53
\]

where all concentrations are ppm dry corrected to 0% O\textsubscript{2}.

Model predictions are shown as the solid lines in Fig. 5; no adjustments have been made to improve the agreement between the data and model (other than the arbitrary assumption of a 50% NO\textsubscript{x} conversion to HCN in the reburning flame zone).

The model agrees reasonably well with the experimental measurements suggesting that, within the temperature and residence time range considered practical for reburning, the Fenimore mechanism and rates are adequate to approximately describe the reactions occurring in the post flame zone. This agrees with the observation of Glass and Wendt\textsuperscript{21} who successfully predicted the behavior of NO, NH\textsubscript{3}, and HCN in the post flame region of a 2 kg/hr bituminous coal flame using the Fenimore mechanism.

Figure 6 illustrates the impact of thermal history with both gas and coal reburning at (NO\textsubscript{x})\textsubscript{ex} = 630 ppm. In these experiments cooling coils were added to the lower half of the fuel-rich reburning zone, reducing the temperature at the exit of this zone from 1200 °C to 930 °C. With propane reburning this resulted in an increase NO\textsubscript{x} emissions and detailed measurements indicated that this was directly attributable to an increase in TFN species exiting the fuel rich zone. Reducing the temperature in the fuel rich zone slowed the decay of HCN, NO and NH\textsubscript{3} and this is consistent with previous staged combustion results on gas and liquid fuel firing.\textsuperscript{17} Conversely with Beulah coal reburning, adding additional cooling dramatically reduced the exhaust NO\textsubscript{x} emissions. Previous work with this coal (a N. Dakota lignite) has indicated that it produces large amounts of NH\textsubscript{3} under fuel-rich conditions\textsuperscript{22} and these results suggest that this ammonia is selectively reacting with NO\textsubscript{x} in the final burnout zone to produce N\textsubscript{2} and thus reduce NO\textsubscript{x} emissions. Chen and coworkers\textsuperscript{19} documented a similar effect where in-situ "de-NO\textsubscript{x}" as defined by Lyon\textsuperscript{23} occurred in the final burnout zone of a heavily cooled staged, coal-fired system. Thus, it is possible to achieve very low emission levels (less than 100 ppm) with coal reburning if the final burnout zone can be practically operated at the conditions required (ca. 1000 °C) for selective NO\textsubscript{x} reduction by NH\textsubscript{3}.

In summary, the system parameter studies indicate that for optimum performance the reburning fuel should be injected after the primary zone combustion is complete (τ\textsubscript{1} = 300 ms) and the residence time in the fuel-rich reburning zone (τ\textsubscript{2}) should be at least 400 ms. High temperatures favor N\textsubscript{2} formation in the reburning zone, but with solid fuels it is possible to achieve significant additional N\textsubscript{2} formation in the final burnout zone if it can be practically operated at the temperature (ca. 1000 °C) required for selective NO\textsubscript{x} reduction by NH\textsubscript{3}.

Scaling Effects: The Impact of Mixing

The previous sections have focused on chemical (fuel composition) and thermal his-
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tery effects; however, for scale up of the reburning technology to be consistently successful, the impacts of finite rate mixing must be quantified. Mixing effects are potentially important because they control: 1) the dispersion of the reburning fuel and, hence, its ability to incinerate primary zone NOx; 2) the overall conversion of any reburning fuel nitrogen to NOx; and 3) the oxidation of any gas or solid phase nitrogen species leaving the fuel-rich reburning zone. In full scale systems adequate mixing is difficult to achieve because of the small volumetric flow rates of the reburning fuel (especially with natural gas reburning) and final burnout air and the large distances across which mixing must occur.

Figure 7 summarizes pilot scale data obtained to quantify the importance of reburning fuel mixing. Natural gas was used as the reburning fuel so that the results would represent strictly the influence of fuel dispersion; oxidation of reburning fuel nitrogen was not a factor in these experiments. The results indicate that the effectiveness of the reburning process depends strongly on the dispersion of the reburning fuel. With 700 ppm of primary NO, natural gas reburning only produced a 40% reduction in overall exhaust emissions when the reburning fuel was added as a single axial jet; however, when a line source injector containing 14 holes of 0.3 cm diameter was used to create rapid, complete fuel dispersion, an emission reduction of almost 60% was achieved. An intermediate reduction was achieved with four reburning fuel jets as expected. Similar results were obtained in the small scale testing by switching the reburning fuel injection system from axial to radial injection. Effective incineration of primary zone NOx can only be achieved if the reburning fuel is widely dispersed prior to its complete oxidation; the NOx species must contact CH radicals.

Similar small scale testing indicated that effectiveness of the reburning process was relatively insensitive to the mixing of the final burnout air so long as the burnout air was not directed backwards into the fuel-rich NOx reduction zone (thereby reducing the effective residence time in the rich zone). Large scale testing in the pilot scale furnace as part of this study also confirmed the insensitivity to the rate of burnout air mixing. Tests were conducted with eight opposed 9 cm jets, four 9 cm jets, four 15 cm jets, and one 22 cm jet and the results were essentially indistinguishable.

Figure 8 summarizes the results obtained in the pilot scale furnace with a Utah bituminous coal as both the primary and reburning fuel. These data focus on the complex impact of reburning fuel mixing on both primary zone NOx incineration and reburning fuel nitrogen oxidation. In these tests the primary zone NO was approximately 350 ppm at SR1 = 1.1 and the reburning fuel was alternately injected through four 7 cm jets and one 22 cm reburning jet. The reburning zone stoichiometry (SR2) was held constant at 0.9 and the stoichiometry of the reburning fuel jet (oxygen content relative to the combustible material) was varied by using mixture of FGR and air as the transport medium.

When the reburning jet stoichiometry (SR2) was low (e.g. 0.2) no significant difference was observed between the four jet system (designed to produce more rapid mixing of the reburning fuel with the primary zone exhaust gases) and the single jet. At high reburning jet stoichiometries the single jet system produced significantly lower emissions. These results demonstrate that, with a reburning fuel which contains significant nitrogen, there exists a trade off between high dispersion rates to achieve effective incineration of the primary NOx and low reburning jet mixing rates to minimize the conversion of reburning fuel nitrogen. Overmoe et al.24 and Myamae et al.10 have demon-

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**Fig. 7. Importance of Reburning Fuel Mixing—Natural Gas Reburning**

**Fig. 8. Influence of Reburning Jet Stoichiometry and Mixing—Coal Reburning**
strated that an inert transport medium (e.g. N\textsubscript{2} or FGR) enhances the performance of the reburning process relative to air as the transport medium because the inert medium decreases the conversion of reburning fuel nitrogen. The data shown in Fig. 8 suggest that mixing produces the same trade-off. Thus, in practical systems utilizing a reburning fuel with significant nitrogen, the reburning injection system should be designed to provide rapid dispersion of the reburning fuel but the fuel must be transported with an inert carrier so that the reburning fuel is not oxidized in a large excess of O\textsubscript{2}.

Figure 9 illustrates the results of matched bench and pilot scale experiments designed to provide directly comparable scaling data under optimized, commercially acceptable reburning conditions with the Utah bituminous coal as the reburning fuel. The exhaust emissions are shown as a function of the NO\textsubscript{x} concentration exiting the primary combustion zone. (In both cases variations in primary NO\textsubscript{x} were achieved by doping the natural gas to the main burner with pure NO.) These studies were conducted with a primary zone stoichiometry of 1.1, 20% reburning fuel (SR\textsubscript{2} = 0.9) transported with FGR (SR\textsubscript{1} = 0.26), a 500 ms fuel-rich reburning zone and 1430 C at the inlet of the reburning zone. The bench scale tests (25 KW) were conducted with radial reburning fuel and final burnout air injection; the pilot scale tests (3.0 MW) were conducted with four 7.0 cm reburning fuel jets and four 15 cm final burnout air jets both injecting from one wall. In both cases the jets were designed to produce rapid mixing.

Figure 9 demonstrates that a 10\textsuperscript{2} scale-up is possible without loss in process effectiveness if the critical stoichiometry, fuel, thermal environment, and reburning fuel dispersion parameters are matched. At normal primary NO\textsubscript{x} levels, 20% reburning produced a 50% reduction in the exhaust emissions in agreement with previous studies;\textsuperscript{4,7} however, at low primary NO levels the percentage reduction decreased due to the oxidation of the reburning fuel nitrogen. The results discussed previously have shown that reburning efficiencies as large as 85% are possible by reducing the burnout zone temperature (e.g. Fig. 6) or reducing SR\textsubscript{1} below 1.1; however, these conditions will not be possible in some commercial applications.

In summary the mixing studies indicate that there exists a trade-off between rapid reburning fuel dispersion to achieve effective incineration of primary zone NO\textsubscript{x} and minimization of the contact between the reburning fuel nitrogen and high local oxygen concentrations. If the reburning fuel is natural gas, the fuel injection system should be designed to maximize dispersion; if the reburning fuel contains significant nitrogen, the fuel should be transported with a basically inert medium or dispersion must be retarded.

**Conclusions**

The results of this study confirm the potential of the reburning process for significant NO\textsubscript{x} reductions. Process effectiveness depends strongly upon the stoichiometry, temperature, and residence time in the fuel-rich reburning zone; the NO\textsubscript{x} and O\textsubscript{2} concentrations at the end of the primary zone; mixing and stoichiometry of the reburning fuel jet; and the temperature of the final burnout zone. The only reburning fuel parameters which appear to be of first order importance are (1) fuel nitrogen content and (2) the ability of the fuel to form CH fragments. At the optimum reburning stoichiometry (SR\textsubscript{2} = 0.9) the exhaust emissions correlate with the sum of the primary NO\textsubscript{x} and the reburning fuel nitrogen. CO and H\textsubscript{2} are significantly less effective than hydrocarbon fuels. Reburning zone residence times of at least 400 ms are desirable and high temperature favor molecular nitrogen formation. Reburning effectiveness decreases with high primary O\textsubscript{2} produced by excessive SR\textsubscript{1}, or inadequate primary zone residence time. Rapid mixing of the reburning fuel enhances the effectiveness of the incineration process but it can potentially detract from overall process efficiency with coal reburning due to reburning fuel nitrogen oxidation unless the fuel is transported with an essentially inert gas stream. Extremely low exhaust NO\textsubscript{x} levels can be achieved with optimized reburning, low SR\textsubscript{1}, and very low final burnout zone temperatures (to produce in-situ de-NO\textsubscript{x}).
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REFERENCES