

RESULTS FROM A MODELING AND EXPERIMENTAL EVALUATION OF THE COMBINO_x PROCESS

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INTRODUCTION

Control of emissions of oxides of nitrogen, or NO_x, from fossil-fuel fired combustion systems is becoming of increasing interest due to the role of atmospheric nitrogen oxide species in the formation of acid rain and photochemical oxidant or smog. High levels of NO_x removal are typically only achievable with expensive post-combustion technologies employing catalyst beds. This paper describes a process, called "CombiNO_x", which is capable of achieving high levels of NO_x reduction at costs significantly below those of catalytic technologies. The CombiNO_x process consists of three NO_x control technologies—reburning, selective non-catalytic reduction ("agent injection"), and NO₂ scrubbing—which have been integrated and optimized in a manner which takes advantage of the chemical reactions involved in each process to achieve NO_x reduction approaching 90 percent.

The CombiNO_x process has been studied experimentally using two pilot-scale furnaces. The first series of tests were conducted in a one million Btu/hr down-fired furnace. At this facility, each component of the CombiNO_x process was parametrically evaluated. Results from these studies have been reported elsewhere [1]. Pilot-scale tests at 10 million Btu/hr were also conducted to address process scale-up issues. This paper presents selected results of both series of experimental studies as well as kinetic modeling studies performed to aid in interpretation of the experimental results.

BACKGROUND

The technologies involved in the CombiNO_x process have been extensively studied in small scale combustion tests and demonstrated in a wide range of industrial applications. In general, the global chemical mechanisms involved in the processes are considered relatively well-known. The three technologies used in the CombiNO_x process are described in the following.

Reburning. The reburning concept was first investigated nearly two decades ago [2]. This process consists of injecting a portion of fuel downstream of the primary combustion zone to drive the flue gas stoichiometry slightly fuel rich. In this "reburning zone", the NO_x generated in the primary zone is reduced to molecular nitrogen. Downstream of the reburning zone, additional air is injected to complete combustion of the unburnt products from the reburning zone. Bench and pilot scale studies have identified the general requirements for applying the process to industrial combustion systems [3-4]. Recently, demonstrations of the reburning process employing natural gas as a reburning fuel have been performed on coal-fired utility boilers [5-6].

Agent Injection. Selective non-catalytic reduction, or agent injection, technologies consist of the injection of amine-producing agents into post-combustion flue gases. Typical agents include ammonia

and urea. These agents must be injected into a narrow temperature window generally centered about 1850°F. Injection of the agent at too high of a temperature can cause oxidation of the agent resulting in increased NO_x emissions, while injection of the agent at too cold of a temperature can lead to excessive by-product emissions, such as unreacted NH₃. The fundamentals of the process have been described in the literature [7-8]. Reagent injection for NO_x control has been applied to full-scale utility boilers [9-10]. The results of these and similar tests have shown that the process is extremely sensitive to the gas temperature and that broad temperature distributions at the point of injection of the agent can limit performance.

NO₂ Scrubbing. Studies have shown that it is possible to scrub NO₂ with conventional SO₂ scrubber solutions provided that the solution is slightly modified [11]. The CombiNO_x process exploits this phenomena by injecting methanol into the flue gas downstream of the reburning and agent injection processes to convert any remaining NO to NO₂ and then scrubbing the NO₂ in a conventional wet limestone SO₂ scrubber operating with a modified scrubbing liquor. Although methanol injection has been evaluated at full utility boiler scale as a means of reducing ammonia slip from SNCR systems [12], the integrated NO₂ scrubbing process has yet to be demonstrated in a practical system.

ADVANCED REBURNING

In practice, agent injection performance is extremely sensitive to flue gas temperature at the injection point. However, in the presence of oxidizing CO, the dependence of the process on injection temperature is significantly reduced [12]. The CombiNO_x process furnishes oxidizing CO by injecting reburning fuel upstream of the reducing agent. The EER patented combination of reburning and agent injection, called Advanced Reburning, comprises the first two steps of the CombiNO_x process.

Figure 1 shows schematically how Advanced Reburning was experimentally evaluated. A high-volatile bituminous coal was used as the primary fuel, while natural gas was used as the reburning fuel. The process can be divided into three zones: the region between the top of the furnace and the reburn fuel injectors is referred to as the primary zone, the region between the reburn fuel injectors and the burnout air ports is the reburning zone, the region downstream of the burnout air ports is referred to as the burnout zone. In these experiments, urea was injected within the reburning zone. The Advanced Reburning parameters evaluated included: reburning zone stoichiometry (or CO level), urea injection temperature, and burnout air injection location.

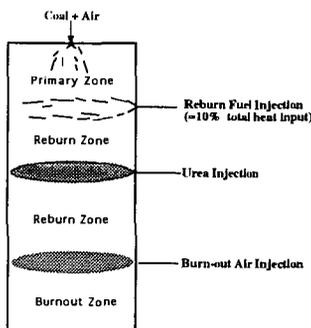
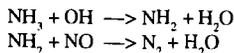
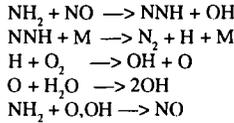


Figure 1. Advanced reburning pilot scale testing schematic.

The effect of reburn zone stoichiometry on urea performance was evaluated to determine the impacts of CO oxidation on the optimal temperature window and achievable NO_x reductions. The chain branching de-NO_x reactions of importance are summarized below [13]:





The rate limiting step is the oxidation of ammonia to form NH_2 . The reducing agent needs to be injected at high enough temperatures to allow the reaction to proceed fast enough to generate sufficient radicals to oxidize NH_3 . If temperatures are too hot, the reaction intensity will be too high, and NH_2 will be oxidized rather than react with NO to form molecular nitrogen. If temperatures are too low, the ammonia will not oxidize, and will show in the emissions as ammonia slip. Therefore, there is an optimum agent injection temperature. At temperatures above and below approximately 1850°F, NO reduction efficiency drops off.

The addition of CO has been shown to shift the reaction window to lower temperatures because carbon monoxide oxidizes and generates additional radicals [13] that support further oxidation of NH_3 in the process. Figure 2 shows predicted NO reduction versus injection temperature using a chemical kinetic model which incorporates a plug flow/stirred reactor algorithm [15]. The plot compares injection of urea without CO to injection of urea with the equivalent of 3000 ppm CO for a stoichiometric ratio (SR) of 1.2. The addition of CO generates additional radicals, which shifts the cold side of the window to lower temperatures. The hot side of the window also shifts to the left, but to a lesser degree because the incremental amount of OH radicals contributed by this small amount of CO is not as great as that from ammonia alone. The net result of these effects is a broader reaction window.

Figure 2 also shows the predicted effect of co-injecting urea with the equivalent of 3000 ppm CO into two different stoichiometric environments. At higher stoichiometries, CO will oxidize more readily and generate more radicals, improving urea performance at lower temperatures, but worsening performance at higher temperatures. At the lower stoichiometry, fewer additional radicals are generated and the curve is not shifted as far to cooler temperatures. An interesting point is that the SR=1.2 curve is broader at the bottom, but rises more steeply as injection temperature increases than the SR=1.02 curve. The explanation may be that the increase in radicals at the high temperature side is relatively less for the SR=1.02 case than for the SR=1.2 case, resulting in relatively less oxidation of NH_2 .

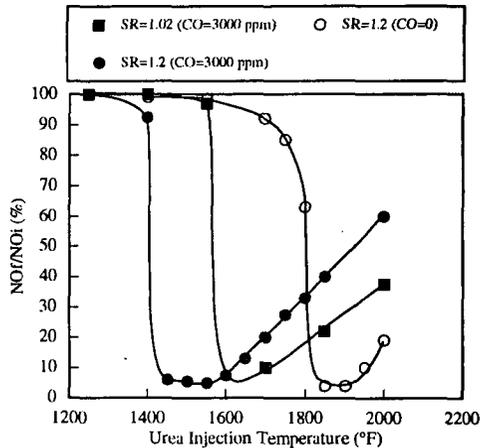


Figure 2. Predicted effect of CO on urea injection performance.

The design and operating conditions of a particular actual combustion system will significantly influence the amount of CO produced at a given stoichiometry. In the pilot-scale tests, the reburning zone stoichiometry was varied to evaluate the impact of reburning zone CO and O₂ levels on urea performance. Figure 3 shows the effect of reburn zone stoichiometry on the urea temperature window for the small (one million Btu/hr) pilot-scale tests. As the reburn zone stoichiometry drops, CO increases and O₂ decreases and the temperature window broadens with the optimum injection temperature at 1850°F. For a reburn zone stoichiometry of 1.02, the window not only broadens, but deepens as well, indicating that this unique combination of CO and O₂ provides an optimum amount of radicals. When SR₂ was more fuel-rich than this optimum, the curve shifted to the left rather than broadening. This result is believed to be due to an overabundance of radicals at the high temperature level.

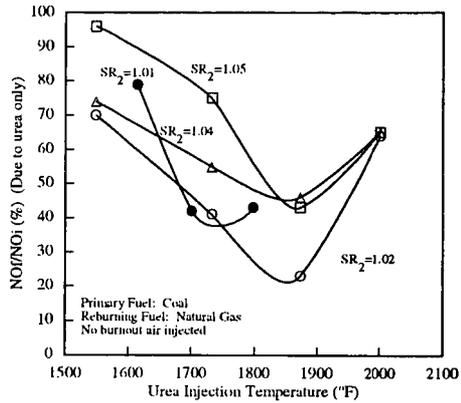


Figure 3. Effect of local CO concentration (SR) on urea performance at small pilot scale.

Because the flue gas flow in the small pilot-scale furnace is laminar, the mixing properties are not representative of a boiler. Also, flue gas temperature quench rates are much lower than on an actual full-scale boiler. Therefore, the 10 million Btu/hr tests were designed to provide information on advanced reburning performance in the presence of large scale turbulent mixing phenomena and at more realistic quench rates. Urea was injected at various temperatures for reburning zone stoichiometries from 1.05 to 0.99, which produced CO concentrations in the reburning zone ranging from 1,500 to 15,000 ppm, respectively. These results are presented in Figure 4. Contrary to the small pilot-scale results, the stoichiometry of the reburning zone did not appear to have a large effect on either the optimum injection temperature or NO reduction. It is hypothesized that the CO enhancement relies on mixing to distribute OH radicals to the SNCR agent uniformly. At large scale, bigger pockets of CO and O₂ co-exist, yielding non-uniform concentrations of radicals, and ultimately failing to promote the deNO_x chemistry as well. It may be stated however, that the SR =

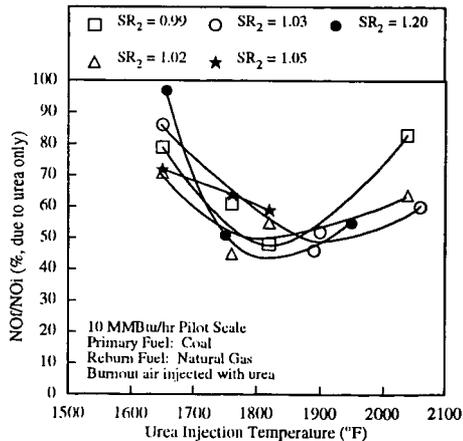


Figure 4. Effect of reburn zone stoichiometry on urea performance at large pilot scale.

1.20 case where no reburning is performed (no CO promotion) upstream of urea injection yielded the narrowest temperature window.

The final Advanced Reburning parameter of interest is the location of burnout air injection to complete combustion of the reburning fuel. Figure 5 shows overall NO_x reduction (due to reburning and urea injection) as a function of burnout air injection temperature (location) for optimum reburn zone stoichiometry and urea injection temperature. At small pilot-scale, NO_x reduction improves as the burnout air is moved away from the urea injection point. This is probably because downstream air prolongs the urea residence time in the "optimum" radical environment. Also shown in the figure are the large pilot-scale data. NO_x reduction did not vary with burnout air location at large scale. From an application standpoint, this is important in that it is less expensive to retrofit Advanced Reburning to a boiler if the burnout air and reduction agent can be injected through the same openings.

Figure 6 presents Advanced Reburning NO_x reduction levels as a function of reburn zone stoichiometry and urea injection temperature at large pilot-scale. Compared to traditional agent injection, the Advanced Reburning process offers a wider range of urea injection temperatures and significantly improved reduction performance up to 84 percent.

METHANOL INJECTION

The third step of the Combi NO_x pro-

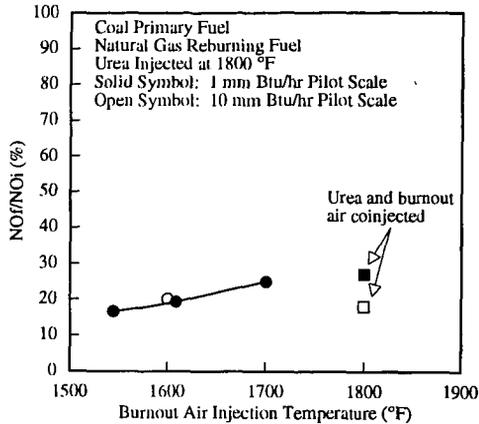


Figure 5. Effect of burnout air injection temperature on Advanced Reburning performance.

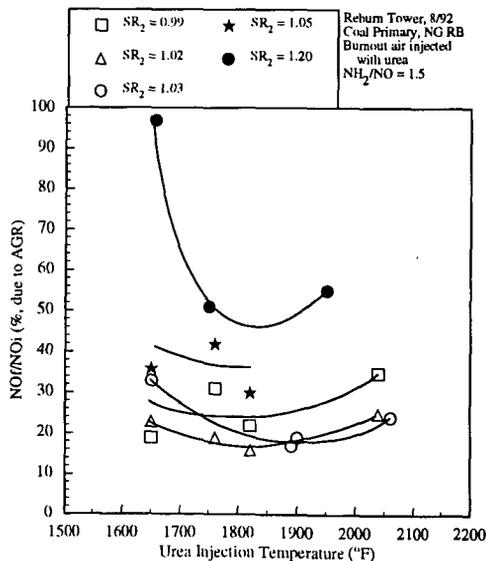


Figure 6. Large pilot scale Advanced Gas Reburning performance

cess, methanol injection, is performed downstream of the Advanced Reburning process. The methanol is intended to convert the NO remaining after Advanced Reburning to NO_2 . Since NO_2 is very water soluble, it can subsequently be removed in wet SO_2 scrubber operating with modified liquor. Based on previous kinetic studies, the reaction mechanism for the methanol step is [16]:

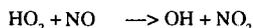
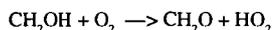
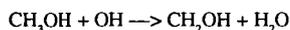


Figure 7 summarizes the effect of methanol injection temperature on the conversion efficiency of NO to NO_2 . Depending on residence time and temperature, the model predicts an optimum injection temperature of between 1500 °F and 1800 °F. Complete conversion was shown to be theoretically possible, with an optimum injection temperature of 1550 °F and a residence time of 0.1 seconds.

Experiments were conducted to verify the modeling results at bench- and one million Btu/hr pilot-scale. At bench-scale, a simulated flue gas was combined with vaporized methanol and introduced into a quartz tube reactor. The reactor temperature and residence times were varied to evaluate their impact on NO conversion. At pilot-scale, methanol was injected into natural gas combustion products at various locations (temperatures) and the resulting NO and NO_x levels were recorded. The residence time at the optimum injection temperature ($\pm 50^\circ\text{F}$) is approximately 600 msec. Figure 8 shows that the pilot-scale result for natural gas combustion products and the bench-scale data for the same residence time agree quite well.

The experimentally-determined opti-

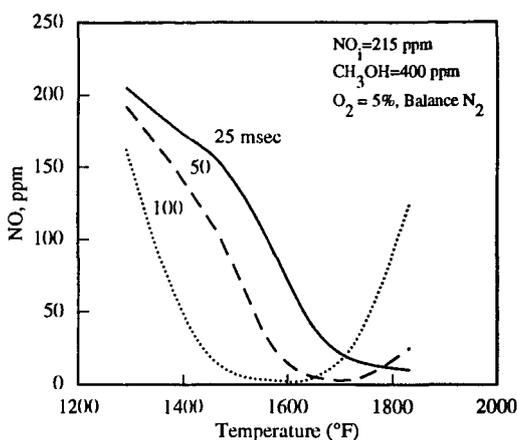


Figure 7. Predicted effect of temperature and residence time on methanol performance.

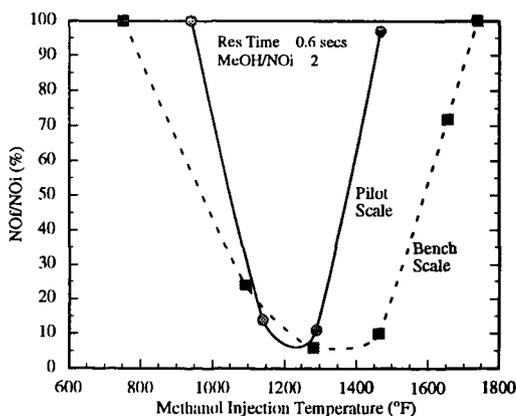


Figure 8. Bench vs Pilot scale methanol performance.

imum methanol injection temperature ranged from 1150°F to 1300°F, which is significantly lower than that predicted by the model. However, the experimental data were obtained at a residence time of 0.6 second residence time, while the predictions were performed for 0.1 second residence time. Additional modelling is planned to determine if increasing the residence time available for methanol reactions shifts the optimum injection temperature to lower levels.

CONCLUSIONS

These studies have shown the influence of the main parameters controlling performance of the Advanced Reburning process. Close coupling of the CO level in the reburning zone and the temperature at which the agent is injected is needed to optimize NO_x reduction. Studies of the methanol injection step in bench and pilot-scale reactors have shown that conversion of the NO remaining from the Advanced Reburning process to NO₂ is feasible.

In conclusion, the CombiNO_x process, consisting of Advanced Reburning and methanol injection combined with NO_x scrubbing, is a promising retrofit technology for coal fired utility boilers. The Advanced Reburning portion has been demonstrated at 10 millionBtu/hr pilot scale to reduce NO_x emissions by 84 percent. The complete process has the potential to reduce NO_x emissions by 90 percent.

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