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FOR COAL-FIRED UTILITY BOILERS

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1.0 INTRODUCTION

CombiNO_x is a NO_x reduction process which incorporates three individual NO_x control technologies: reburning, selective non-catalytic reduction (SNCR), and methanol injection. Gas reburning is a widely used technology that has been proven to reduce NO_x up to 60% on full-scale applications. Selective non-catalytic reduction (SNCR) is simply the injection of a XN carrier (ammonia, ammonium sulfate, urea, etc.) at appropriate temperature and stoichiometric conditions. Recent testing has indicated that reburning and SNCR may maintain a synergistic relationship. SNCR has been proven to be more effective in CO rich environments; this environment can be supplied as a consequence of reburning. The combination of reburning and SNCR has been named Advanced Reburning and is an EER patented technology. The third step in the CombiNO_x process, methanol injection, is intended to convert NO to NO₂. Methanol may also aid in the conversion of SO₃ to SO₂. NO₂ and SO₂ can then be removed in a conventional SO₂ scrubber.

The specific goals of the CombiNO_x project are:

- 70% NO_x reduction at 20% of the cost of selective catalytic reduction;
- NO_x levels at the stack of 60 ppm for ozone non-attainment areas;
- To demonstrate coal reburning;
- To identify all undesirable by-products of the process and their controlling parameters;
- To demonstrate 95% NO₂ removal in a wet scrubber.

Before integrating all three of CombiNO_x's technologies into a combined process, it is imperative that the chemistry of each individual process is well understood. Pilot-scale SNCR and Advanced Reburning tests and the corresponding computer modeling were studied in detail and discussed in the previous two quarterly reports. Also discussed in the last quarterly were the lab-scale methanol injection test results. This report will present results from the pilot-scale methanol injection tests performed on EER's Boiler Simulation Facility (BSF).

2.0 PILOT-SCALE METHANOL INJECTION TESTS

All of the pilot-scale methanol injection tests were performed on the Boiler Simulation Facility (BSF) located at EER's Santa Ana test site. The BSF, as displayed in Figure 2-1, is a 1 million Btu/hr, down fired furnace capable of burning both coal and natural gas. Methanol injection tests were performed while burning both natural gas and coal as primary and reburning fuels.

The specific goals of the methanol injection tests were to:

1. Determine the optimum methanol concentration for the desired NO to NO₂ conversion.
2. Identify a temperature window in which methanol injection is most effective.
3. Determine the effect of initial NO concentration on methanol performance.
4. Determine the effects of SO₂ on methanol performance.
5. Determine the effect of ammonia slip on methanol performance.
6. Determine by-products formation resulting from methanol injection.

A Spraying Systems 180° pressure atomizer nozzle with good atomization properties was used to inject the methanol. Pure methanol was injected as a vapor with a nitrogen carrier.

NO_x measurements were made with the newly developed NO_x sample conditioning system. This system, discussed in detail in Quarterly #5, was developed to measure NO_x when large levels of NO₂ are present. Measurements were taken at the downstream sample location displayed in Figure 2-1. Flue gas residence time between the methanol point of injection and sample port ranged from 1.3 to 2.5 seconds. This portion of the furnace is completely refractory lined, no steel exposure exists.

2.1 Methanol Chemistry

When methanol is injected into the flue gas at ideal conditions, a conversion of NO to NO₂ occurs by means of the following chemical process:

Figure 2-1. Boiler Simulation Facility (BSF).

It was of interest to determine at which conditions these reactions are most likely to occur. The variables taken into consideration were injection temperature, methanol concentration, and initial NO concentration. The effect of ammonia slip and SO₂ on methanol performance was also observed.

2.2 Natural Gas Fired Methanol Injection Tests

Past experiments have indicated that initial NO concentration and the presence of SO₂ may effect methanol performance. In order to quantify how these compounds effect performance, experiments were conducted while firing natural gas. Natural gas, being a "clean" fuel, provides baseline conditions in which both these compounds are very low or non-existent. By doping the flue gas with more NO or SO₂ and comparing the results to those of baseline, the effect of each compound on methanol performance can be determined. The results are as follows.

2.2.1 Effect of Initial NO Concentration on Methanol Performance

Past experiments performed for SNCR de-NO_x have demonstrated that NO reduction improves as initial NO concentration is increased. It was of interest to see if the same is true for methanol injection. Figure 2-2 summarizes the data as methanol injection temperature and initial NO concentration were varied. (An initial NO concentration of 200 ppm was obtained by straight firing with natural gas and varying the primary air swirl, or flame zone mixing. An initial NO concentration of 400 ppm was obtained by doping NH₃ into a natural gas flame at very high temperatures.) Figure 2-2 shows that the difference of 200 ppm in initial NO concentration does not affect methanol performance.

Figure 2-2. Effect of NOi on methanol performance.

2.2.2 Effect of Methanol Injection Temperature on Methanol Performance

Figure 2-2 shows that methanol injection produces 50% or better conversion between the temperatures of 1050° and 1350°F. Optimum injection temperatures range from 1150° to 1300°F, producing up to 82% NO to NO₂ conversion.

2.2.3 Effect of Methanol Concentration on Methanol Performance in a Gas Fired System

Methanol performance was found to improve by 31% as methanol concentration was increased from 0.68 to 1.8. Figure 2-3 demonstrates this improvement in performance, as well as the increase in CO that occurs as a result of methanol injection. It should be noted that, even though methanol concentrations above MSR's of 1.1 do not improve the NO to NO₂ conversion by much, CO production continues to increase. Appropriate amounts of methanol should be carefully considered to avoid unnecessary formation of CO.

2.2.4 Effect of SO₂ Doping on Methanol Performance

In the past it was observed that methanol injection is less effective in coal fired systems than in natural gas. It was of interest to see how much of this performance decrease can be contributed to the high SO₂ levels found when firing coal. Tests were performed while injecting 3000 ppm of SO₂ into the natural gas fired furnace; NO conversion was found to suffer, but not as much as expected. Figure 2-4 shows the effect of SO₂ on NO conversion.

During the development of the new NO_x sampling system it was discovered that the SO₂ effect on methanol performance was only a sampling artifact (see Quarterly #5). The following test was performed to determine whether SO₂ was affecting the methanol chemistry, or interfering somewhere within the sample conditioning system:

While firing natural gas, methanol was injected at optimum conditions producing adequate amounts of NO₂. SO₂ was doped immediately upstream of the sample probe, well after any methanol conversions in the furnace would have taken place. The methanol-formed NO₂ was found to re-convert back to NO as soon as the SO₂

Figure 2-3. Effect of MSR on methanol performance and CO production.

Figure 2-4. The effect of SO_2 on methanol injection NO-to- NO_2 conversion.

was injected (the SO_2 was converting NO_2 back to NO somewhere between the probe inlet and the NO_x analyzer).

It is therefore believed that the SO_2 interference is a sampling artifact and not an interference in the methanol chemistry. Further research has shown that under acidic aqueous conditions, NO_2 has the tendency to convert to NO . It is highly possible that the condensed moisture within the ice bath water trap has become acidic due to the high concentrations of SO_2 in the flue gas. NO_2 may be converting to NO within the water trap, resulting in artificially high NO readings.

N_2O measurements were also found to be affected by the presence of SO_2 . N_2O readings increased as methanol performance improved, however only in the presence of high SO_2 concentrations. This N_2O production has been attributed to the same sampling artifact as the NO measurements. When NO_2 and SO_2 are simultaneously present, NO_2 converts to N_2O as well as NO within the acidic, aqueous environment of the chiller water trap.

Unfortunately these sampling artifacts were not discovered until the end of the BSF tests. All data taken during high SO_2 testing (i.e., coal firing tests) will include error bars to account for this sampling error.

2.2.5 Formaldehyde Formation as a Result of Methanol Injection

Formaldehyde is an intermediate product of the methanol injection chemistry, therefore the possibility of increasing its emission through methanol injection is a concern. Figure 2-5 shows results obtained from methanol studies performed at bench-scale (discussed in detail in Quarterly #4). Displayed are the formaldehyde emissions as a function of injected methanol concentration. A reference to the corresponding NO conversion is also made. Until 600 ppm of methanol is injected ($\text{MeOH}/\text{NO}_i = 6$), formaldehyde formation never increases above 2 ppm. When greater than 700 ppm of methanol is injected, formaldehyde increases to 12 ppm.

The pilot-scale tests at the BSF showed very low formaldehyde emissions when injecting methanol. Two tests were performed in which formaldehyde was measured with Dragor indicating tubes while methanol was injected at optimum conditions. Formaldehyde readings were lower than 1 ppm for both cases, assuring that if injected at appropriate conditions, methanol injection will not result in elevated formaldehyde emissions.

Figure 2-5. Formaldehyde formation from MeOH injection at lab-scale.

2.3 Coal Fired Methanol Injection Tests

Several tests were performed to characterize methanol performance while firing a Illinois high sulfur coal. The results are as follows.

2.3.1 Effect of Methanol Injection Temperature on Performance

Methanol injection temperature was varied while coal firing at a final stoichiometry of 1.2. Results are displayed in Figure 2-6. Error bars are included to account for the SO₂ bias discussed earlier. Optimum temperature for methanol induced conversion of NO to NO₂ is approximately 1180°F.

Even when the error bars are taken into account, the performance of methanol on the coal fired system is not as good as that for the natural gas fired system. In addition to the sampling artifact due to SO₂, it was discovered that coal ash on a sample filter creates a sampling error. The following experiment was performed which helped deduce this hypothesis:

While injecting methanol at optimum conditions, NO and NO_x were measured with the new NO_x sampling system while using a clean sample filter. The methanol was showing to be fairly successful at its intended purpose of converting NO to NO₂. The sample filter was then coated with a thick layer of coal ash collected from the baghouse. Without making any variations in the methanol injection set-up, a substantial change in the NO to NO₂ conversion was detected, showing a decrease in methanol performance.

It is believed that the unburned carbon in the ash is responsible for converting NO₂ back to NO, just as the purpose of a carbon converter found inside some NO_x analyzers. During the last two days of tests, experiments were conducted using a clean sample filter within the new NO_x sample conditioning system. However, ash still exists within the furnace ducts and within the sample probe, NO₂ to NO conversions are probably still taken place in these sections. It is believed that, if it were not for these sampling artifacts present when firing coal (high SO₂ and ash presence), that methanol performance would measure as successful for a coal system as it does for natural gas.

BSF, 1/92
 Coal Firing: .724MBtu/hr
 Natural Gas reburn to achieve
 NO_x = 400 ppm
 No urea injection
 MeOH/NO_x = 1.2
 SR1 = 1.13
 SR2 = 1.02
 SR3 = 1.20
 Burnout air injected at 1550°F.

NO measurements taken with old
 sample system. Error bars are
 included because of SO₂ bias within
 this system when NO₂ is present.
 (Refer to Quarterly #5)

Figure 2-6. Effect of methanol injection temperature on NO to NO₂ conversion while firing coal.

2.3.2 Effect of Methanol Concentration on Methanol Performance in a Coal Fired System

While firing coal as the main fuel, and natural gas as the reburning fuel, methanol concentration was increased from 1.5 to 2.0 (Figure 2-7). As expected, NO conversion improved with increasing methanol concentration; 54% NO conversion occurred at 1150°F with a methanol-to-NO ratio of 2. Data shown in this Figure were obtained using the new NO/NO_x sampling system described in detail in Quarterly #5, the error bars are included to account for the SO₂ sampling interferences.

2.3.3 Effect of Ammonia Slip on Methanol Performance

It was of interest to see if the presence of ammonia in the flue gas would have an effect on methanol performance. To achieve this, 150 ppm of ammonia was injected at 1300°F; a temperature cool enough to prevent the ammonia from burning. NO to NO₂ conversion suffered by as much as 19% when ammonia was present. Although it is conceivable that high ammonia levels may result from non-optimized advanced reburning, our data show that when the Advanced Gas Reburning process is optimized, very little ammonia slip is produced. Therefore, as long as the advanced reburning step is working successfully, the methanol injection step will not be affected by high ammonia concentrations.

2.3.4 CO Trends During Methanol Injection

Referring to the methanol chemistry, there is indication that elevated levels of CO may result from methanol injection (1 CO for every NO to NO₂ conversion). Figure 2-8 shows a coal firing, natural gas reburning case in which only methanol (no urea) is injected. The NO measurements were made with the old NO/NO_x sampling system; the error bars are included to account for the SO₂ bias that occurs within the system. This figure verifies that CO increases from approximately 100 to 530 ppm as the methanol performance improves.

Figure 2-7. The effect of methanol concentration on NO to NO₂ conversion in a coal fired system.

Figure 2-8. CO trends during methanol injection.

3.0 THE COMPLETE COMBINO_x PROCESS

All three of the CombiNO_x NO_x control technologies were performed simultaneously for the first time. Tests were performed while firing coal as the primary fuel, and natural gas and coal as reburn fuels.

The results for the complete CombiNO_x process for coal firing and natural gas reburning are displayed in Figure 3-1. NO/NO_x measurements were taken with the new sample system. The filter and line were cleaned periodically throughout testing to avoid ash build-up; ash has also been shown to convert NO₂ to NO.

Reduction due to natural gas reburning was 54% with burnout air injected at a downstream location of approximately 1600°F. Advanced Gas Reburning produced a 79% reduction (although it is suspected that better reduction would have been possible if injection resolution in the furnace allowed the urea to be injected at a more optimum temperature of 1850°F). The methanol injection step converted 45% of the existing NO to NO₂, achieving an overall CombiNO_x NO reduction of 89%.

The coal reburning CombiNO_x test results are displayed in Figure 3-2. Results are similar to those obtained for natural gas reburning. Reduction due to urea injection was better while reburning with coal than for natural gas, probably due to the more optimum urea injection temperature. The methanol injection step converted 40% of the NO to NO₂, similar to the 45% NO conversion that occurred for natural gas reburning. An overall CombiNO_x NO reduction of 93% was achieved, resulting in a final NO concentration of 61 ppm at 3% O₂.

Figure 3-1. CombiNOx
 Coal Firing, Natural Gas Reburning

Figure 3-2. CombiNOx
 Coal Firing, Natural Gas Reburning

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