Computational Modeling and Experimental Studies on NO_x Reduction Under Pulverize Coal Combustion Conditions

Technical Progress Report
Ninth Quarter
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INTRODUCTION

During this quarter efforts were made to conduct reburning experiments with coal. Our efforts met with partial success but there arose persistent problems with the operation of the coal feeder. This entire quarter has been the most challenging time for the research team in terms of solving the problems and carrying out the intended experiments. Discussed below are some of the results as well as challenges. We hope to overcome the problems in due time. At the writing of this report, some parts of the coal feeder are being rebuilt by MK Fabrication.

PARTIAL SUCCESS

The research team selected DECS-23, a high volatile A bituminous Pittsburgh coal (Washington county sample obtained in1994) from the PennState Coal Sample Databank for the preliminary testing. As outlined in the last quarter, the coal feeder assembly was incorporated in the experimental setup; and the experimental conditions for methane reburning were set. The nitric oxide level was set at 1000 ppm as in all the previous experiements. A continuous coal feeding was verified and the Nox reduction was checked. No significant impact of the presence of coal was seen initially so long as the methane was not introduced. This indicates that coal is effective only under reducing conditions. Hence, methane was introduced without the feeding of the coal and the reduction was achieved. As expected from the knowledge of prior reburning experiments, the reduction was slight (6%)

at SR2=1.0 and quite considerable (55%) at SR2=0.95. When coal was introduced (uniformly) along with methane, further reduction was observed: the reduction was very significant (98%) at SR2=0.95, although slight reduction (8%) was achieved at SR2=1.0 as well. Table 1 lists the Nox readings for these preliminary tests.

Table 1. Nox reading during reburning with methane and coal (DECS-23 sample), ppm

Initial Nox set at 1000 ppm.

SR2	With methane only	With methane and coal
1.0	940	917
0.95	450	18

The trend has been very encouraging in terms of our attempt to reduce Nox and we have planned several tests DECS sample 25 (lignite A coal, Pust seam)..

CHALLENGES

The attempt to vary the coal feeding rate was limited by the length of the solid piston rod and in time the piston rod was replaced. However, it was observed that the coal feeder was not feeding properly. Seeing the bending of the feeder, it was decided to drill larger holes at both ends of the carriage mechanism where the coal feeder is mounted. The wing nut would still do the locking. It seemed to work well preventing deflection when the carriage mechanism moved up and down. Soon came the problem of broken plexi-glass chamber in which the piston and the feed tube are housed. Two pieces of the plexi-glass chamber were purchased through MK Fabrication. Assembling the coal feeder mechanism again, the coal feeder was tested for its operation. The motor was turned on and rotation was observed at the love-joy coupling but the driving mechanism was not moving up and down. Expecting the coupler inserts were not acting properly, they were replaced and the feeder mechanism was tested. Even the collar shaft was replaced. After a lot of trials to fix the coal feeder mechanism, it was determined that the coal feeder had a defective part only the builder could repair. The nut fitting had been malfunctioning and the threaded shaft moving the coal feeder mechanism up and down was getting deformed. Hence the coal feeder was not feeding properly. The feeder has been sent to MK Fabrication for repair.

EXPECTATIONS

It is expected that the team will be busy in the summer (1997) to conduct reburning experiments with several coal samples and move toward surface catalysed reburning studies with calcium carbide and calcium sulfide.

RECENT PAPERS

Enclosed in the following pages is the paper presented at and published in the proceedings of the Fifth HBCU/MI Fossil Energy Technology Transfer Symposium held in Baton Rouge, LA during March 3-5, 1997. The highlight was that the undergraduate research student, Mr. Tyrus L. Hodges presented the results before other researchers and the U.S. DOE officers attending the conference.

EXPERIMENTAL STUDIES ON NOX REDUCTION BY REBURNING WITH METHANE, METHANE AND ACETYLENE, AND METHANE AND AMMONIA

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INTRODUCTION

Having predicted favorable NOx reduction by modeling the simulated flue gas reburning in a constant pressure, adiabatic reactor using CHEMKIN supercomputing package routines, we have sought to verify the findings experimentally at Rust College bench facility. The composition of the simulated gas reflects the flue gas at the end of the coal combustion primary zone (stoichiometric ratio, SR1=1.1) treated with reburn fuel at various stoichiometric ratios (SR2=0.75-1.0). The experiments center around reburning with three fuel types- 100% methane, a combination of methane and acetylene (e.g. 90/10) and a combination of methane and ammonia (e.g. 98/2). The experiments are conducted at various SR2 conditions for a variety of reburn fuel compositions.

EXPERIMENTAL FACILITY

Seven gas cylinders (He pure, 20.1% O_2/balance He, CO_2 pure, 20.1% CH_4/ balance He, 2.19% C_2H_2/ balance He, 0.352% NO/ balance He, 0.36% NH_3/ balance He), fitted with respective pressure regulators were safely chained to the walls. The pressure regulators, valves and fittings for ammonia and nitric oxide had to be stainless steel due the corrosive nature of the gases. A quarter inch Teflon tubing was employed for all connections. Using the proper Swage-lok fittings and ferrules, the gas cylinders were connected to the inlet of respective flow meters. The flow meters employed were of K-74 series purchased from King Instrument Company. The float valves for oxygen and NO flow were made of stainless steel, the valves for CO_2 and helium were made of sapphire and the others were made of carboloy. All these were chosen to suit the desired flow rates through the respective flow meters. All the gases, upon leaving the respective flow meters enter into the stainless steel manifold. However, in order to ensure homogeneous mixing, the gas mixture is drawn into a stainless steel chamber from the manifold. This chamber acts as the buffer vessel where proper mixing takes place. The gas mixture is then led to the reactor inlet through Teflon tubing. The Teflon tubing of 0.25" dia is fitted onto the 1" OD ceramic reactor with adaptors on both ends of the reactor. The inlet adaptor has two ports, one for the gas flow and another for future use of coal feeding. The adaptor for the exhaust end of the ceramic reactor has been accommodated with two ports as well: the 1/4" fitting was set for the gas flow and the 3/16" fitting for thermocouple insertion. The Omega high temperature probe measures the gas temperature in the reactor about 3" inside the furnace. The ceramic reactor which is 26" long, is enclosed by a 1200 C Thermolyne furnace (15.5") in its middle portion. Presently the reactor-furnace assembly is stationed horizontally for convenience. It will be held vertically for heterogeneous reactions with coal reburning. The temperature probe is connected to a HH12 digital thermometer.

The gas at the exhaust end of the reactor is led to the NOx analyzer via gas dryer. The dryer ensures removal of moisture. Teflon tubing of sufficient length was used to allow the cooling of gas mixture to the temperature range acceptable for the operation of the analyzer thus ensuring protection of the NOx analyzer. The analyzer needs oxygen supply for the ozonator which is accommodated from the same oxygen cylinder used in the reburning experiments by employing a T connection. The gas, upon analysis, leaves the analyzer and vents through the exhaust hood of the building.

REBURNING WITH METHANE

As many as 15 runs were conducted on nitric oxide reburning with methane. First, the furnace was turned on and with its temperature set point control, a particular furnace temperature was set. Slowly, helium, oxygen and carbon dioxide cylinders were opened and the flow levels calculated for a particular reburning stoichiometric ratio (SR2) were set. Oxygen simultaneously flowed through NOx analyzer. The analyzer was turned on and allowed to warm up. The parameters on the analyzer were checked until they reached the normal operating conditions. Then, the nitric oxide flow was adjusted so as to read 1000 ppm on the NOx analyzer digital readout. The Omega probe measured the gas temperature inside the reactor which was digitized on the thermometer readout. When all the flow parameters were stable and the desired gas temperature was reached, methane was introduced according to the calculated flow rate for the particular SR2 in question. Instantly, the NOx output decreased and once it reached a steady value, the reading was recorded. A constant check on gas leaks was crucial to the success of the experiments. When the furnace was set at 1130 C, the gas temperature 3" inside the reactor read 1092 C. The experiment was performed for five SR2 values, namely, 0.8, 0.85, 0.9, 0.95 and 1.0.

Later, the furnace temperature was adjusted to the maximum, that is, 1200 C, which in turn, maintained the gas mixture in the reactor at a temperature of 1153 C. Five runs were conducted at this set temperature for the flow rates mentioned above (five SR2 conditions). Similar procedure was repeated for another temperature setting with furnace temperature of 1050 C and a corresponding reaction temperature of 1010 C. All the results are summarized in Table 1.

Table 1. Experimental results on NO reburning with methane

Reburning SR2	Furnace T 1200 C Gas T 1153 C		Furnace T 1130 C Gas T 1092 C		Furnace T 1050 C Gas T 1010 C	
	NO in	NO out	NO in	NO out	NO in	NO out
0.8	998	5	1012	14	914	89
0.85	963	**3.7**	1018	10.3	922	72
0.9	960	**2**	1012	**6**	941	55
0.95	955	449	956	270	944	352
1.0	45	777	1018	852	1027	830

NO concentrations are measured in ppm.

It is apparent from Table 1 that the SR2 in the neighborhood of 0.9 is optimum for nitric oxide reduction and this trend is in line with the predictions reported earlier. Similarly, the reaction temperature of about 1100 C as reported in the numerical simulation results is verified to be an optimum for NO reduction. The reduction at 1092 C as well as 1153 C is significant compared to reduction at 1010 C. In fact, these experimental results indicate better reduction than the numerically predicted values; for e.g., a maximum reduction to 46 ppm from 1000 ppm was predicted through computer projection at SR2=0.9 for NO reburning with methane at 1100 C while the experiment shows nitric oxide reduction to 6 ppm from 1012 ppm at 1092 C for the same SR2. These results were encouraging and support(ed) further investigation on reburning effectiveness of various fuels, in both homogeneous and heterogeneous reaction setting.

EXPERIMENTAL RESULTS WITH METHANE/ACETYLENE

The experimental procedure employed for nitric oxide reburning with methane/acetylene was very similar to the one outlined for reburning with methane. The experimental results for four combinations of methane/acetylene, namely, 95/5, 90/10, 85/15 and 80/20 are shown in Table 2. The results for NO reburning with 100% methane are also tabulated for the purpose of comparison.

Table 2. Experimental results on NO reburning with various combinations of methane and acetylene

Gas Temperature 1100 C

SR2	100/0	95/5	90/10	85/15	80/20
0.75	-	1000/7	1000/8	-	-
0.8	1012/14	1000/7	1000/5	1000/5	1000/5
0.85	1018/10.3	1000/8	1000/6	1000/6	1000/6
0.9	1012/6	1000/8	1000/7	1000/4	1000/5
0.95	956/270	1000/453	1000/452	1000/410	1000/372
1.0	1018/852	1000/785	1000/753	-	-

NO in/out Concentrations are measured in ppm.

It can be seen from Table 2 that for the case of 100% methane as reburn fuel, NO reduction increases with increase in SR2 ratio until the optimum SR2 value of 0.9. The reduction is not as high for the cases of SR2 > 0.9. For the case of 95% methane and 5% acetylene, a similar reduction is observed. The inlet concentration of NO (1000 ppm) reduces to mere single digits for the lower SR2 values (0.75-0.9), thus yielding a wider SR2 window that favors NO reduction. The reduction is 55% at SR2=0.95 and only 21% at SR2=1.0. Again, the experimental results of NO reduction with a combination of methane and acetylene follow the same trend predicted computationally.

It can be noticed also that NO reduction is almost the same for various methane/acetylene combinations. It means that a slight addition of acetylene is enough to strengthen the reductive effectiveness of methane. In effect, the addition of acetylene will enhance the operating window considerably from a narrow 0.85-0.9 SR2 range for methane to 0.75-0.9 SR2 range for all combinations of methane and acetylene.

REBURNING EXPERIMENTS WITH METHANE/AMMONIA

The experiments were conducted (in a similar procedure to the above) for various SR2 values (0.8-1.0) as well as for two reburn fuel combinations of methane and ammonia (98/2 and 96/4). The model results steered the choice of input conditions in this experimental study on the reburning effectiveness of methane/ammonia.

It can be seen from Table 3 as well as Table 4 that for the case of methane only as reburn fuel, NO reduction increases with increase in SR2 ratio until the optimum SR2 value of 0.9. The reduction is not as high for the cases of SR2 > 0.9. This behavior was documented in the previous report and is consistent with the numerical predictions carried out earlier in the program.

For the case of 98% methane and 2% ammonia (Table 3), a significant NOx reduction is observed. The inlet concentration of NO (1000 ppm) reduces to lower twenties in the ppm level for the SR2 values upto 0.9. The reduction is 73% at SR2=0.95 and only 16.2% at SR2=1.0. These experimental results of NO reduction with a combination of methane and ammonia follow the same trend predicted computationally.

Table 3. Experimental results on NO reburning with reburn fuel of 98% methane and 2% ammonia
Gas Temperature 1100 C

SR2	NO in	NO_{out}^{*} methane only	NO_{out} CH_4 and NH_3	NO_{out}^{*} ammonia only
0.8	1020	43	**24**	885
0.85	1010	37	**24**	860
0.9	990	31	**22**	845
0.95	1022	310	**275**	934
1.0	1080	940	**905**	1045

Table 4. Experimental results on NO reburning with reburn fuel of 96% methane and 4% ammonia
Gas Temperature 1100 C

SR2	NO_{in}	NO_{out}^{*} methane only	NO_{out} CH_4 and NH_3	NO_{out}^{*} ammonia only
0.85	994	38	**34**	697
0.9	1012	32	**22**	789
0.95	1000	431	**352**	861
1.0	1014	928	**865**	929

NO in/out Concentrations are measured in ppm.
[*] Not representative of SR2 value. Based on cutting off one or the other reburn fuel from the reaction mixture.

It can be noticed from Table 4 that NO reduction is similar (to the above trend) for 96/4 combination of methane/ammonia. The maximum reduction occurs at SR2=0.9. The reduction is less at higher SR2 ratios: 64.8% at 0.95 and only 14.7% at 1.0. However, comparing the levels with the introduction of methane only, it can be inferred that a slight addition of ammonia favors the NOx reduction further by strengthening the reductive effectiveness of methane. It can be further observed from Tables 3 and 4 that the additional effect of ammonia on NOx reduction is more pronounced at SR2 > 0.9 than SR2 < 0.9, the reason being methane-NOx reaction is not close to the equilibrium in the former case than the latter case.

Also shown in Tables 3 and 4 is the exit concentration of NO when methane feed was cut off and only ammonia was used as the reburn fuel. This was deliberately planned to see the performance of ammonia as a primary reburn fuel. The reduction of nitric oxide was not much, a maximum of 14.6% for 98/2 run and about 22% for 96/4 run. Thus it was concluded that the use of ammonia in small quantities is helpful in NOx reduction chiefly as a reburn fuel additive to methane.

SIGNIFICANCE AND CONCLUSIONS

The above findings are significant in terms of industry needs. With methane as a reburn fuel, the narrow operating window calls for precise cascade control between the primary zone combustion feed inlet, the reburning zone methane inlet and the NOx analyzer in order that the NOx emissions be within permissible limits. However, with C_2H_2 or NH_3 addition to methane as reburn fuel, the NOx emissions will be within permissible limits as long as a set point control is given to the CH_4/C_2H_2 or CH_4/NH_3 reburning feed inlet not to exceed the SR2 of 0.9. With the latter case, the operation is easier to keep the NOx emissions within limits even if there arise some changes in the primary zone combustion feed inlet.