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Nitrous Oxide Emissions

Topical
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TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES	iii
LIST OF TABLES	v
1.0 INTRODUCTION	1
2.0 PROJECT OBJECTIVES	1
2.1 Task 1 – Literature Survey	1
2.2 Task 2 – Equipment Design and Test Plan Development	2
2.3 Task 3 – Facility Modification	2
2.4 Task 4 – Experiments and Theory Development	2
2.5 Task 5 – Analysis of Results and Final Report	2
2.6 Task 6 – Protocol for Field Monitoring (Optional Task)	3
2.7 Task 7 – Field Monitoring of N ₂ O Emissions (Optional Task)	3
3.0 EXPERIMENTAL TECHNIQUES	3
3.1 1-MW _{th} CFBC	3
3.2 Bench-Scale Testing	4
3.3 Bubbling Fluidized-Bed Combustor	5
4.0 PILOT-SCALE DETERMINATION OF THE IMPACTS OF COAL PROPERTIES AND OPERATING CONDITIONS ON N ₂ O EMISSIONS	5
4.1 Effect of Temperature and Coal Rank	6
4.2 Effect of Combustion Scale	9
4.3 Effect of Excess Combustion Air	10
4.4 Effect of Sorbent Feed	10
4.5 Effect of Primary/Total Air Ratio	12
5.0 ROLE OF COAL CHAR ON N ₂ O FORMATION AND DESTRUCTION	13
6.0 HOMOGENEOUS VERSUS HETEROGENEOUS REACTIONS	15
7.0 MODELING OF N ₂ O EMISSIONS	20
7.1 CFBC Database	20
7.2 Modeling Assumptions and Techniques	28
7.3 Coding of Variables and Model Range	29
7.4 Model Selection	30
7.5 Modeling Results	31
8.0 ABATEMENT STRATEGIES	38
9.0 CONCLUSIONS	40
10.0 PUBLICATIONS AND PRESENTATIONS	40

TABLE OF CONTENTS (continued)

	<u>Page</u>
11.0 REFERENCES	42
APPENDIX A: PARAMETER ESTIMATES FOR PREDICTING N ₂ O EMISSIONS ..	A-1

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Schematic of the 1-MW _{th} EERC pilot-scale CFBC	4
2 Schematic of the coal pretreatment cell	6
3 Effect of temperature and coal rank on N ₂ O emissions	8
4 Effect of temperature and coal rank on NO _x emissions	9
5 Effect of excess air on N ₂ O emissions	11
6 Effect of limestone feed on N ₂ O emissions	11
7 Effect of primary air-to-total air ratio on N ₂ O emissions	12
8 Effect of coal rank and bed temperature on N ₂ O destruction	13
9 Effect of char preparation method on char reactivity	14
10 Effect of combustor temperature and fuel type on N ₂ O emissions	16
11 Effect of combustor temperature and fuel type on NO _x emissions	17
12 N ₂ O and NO _x conversions for BFB and CFB combustors firing selected fuels .	18
13 Conversion of fuel-nitrogen to N ₂ O for Center lignite coal, char, and volatiles in BFBC	19
14 Modeling of emissions from Center lignite coal, char, and volatiles	20
15 Actual versus predicted N ₂ O emissions (mg/MJ) using four fuel parameters: H ₂ O, Nc, VM, CaO	34
16 Actual versus predicted N ₂ O emissions (ppmv) using four fuel parameters: H ₂ O, Nc, VM, CaO	34
17 Actual versus predicted N ₂ O emissions (conversions of fuel-N) using four fuel parameters: H ₂ O, Nc, VM, CaO	35
18 Temperature versus N ₂ O emissions (mg N ₂ O/MJ) for actual CFBC combustion tests.	35
19 Temperature versus predicted N ₂ O emissions (mg/MJ) for predicted CFBC combustion tests.	36

LIST OF FIGURES (continued)

<u>Figure</u>		<u>Page</u>
20	Actual versus predicted N ₂ O emissions (mg N ₂ O/MJ) using three fuel parameters: H ₂ O, Nc, VM	36
21	Actual versus predicted N ₂ O emissions (mg N ₂ O/MJ) using two fuel parameters: N, VM.	37
22	Actual versus predicted N ₂ O emissions (mg N ₂ O/MJ) using one fuel parameter: H ₂ O	37
23	Actual versus predicted N ₂ O emissions (mg N ₂ O/MJ) using no fuel parameters	38

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Analysis of Coals Tested in EERC 1-MW _{th} CFBC	7
2	Nitrogen Balance for Combustion Tests Performed at 1120 K and 25% Excess Air	10
3	Properties of Fuels Tested in 1-MW _{th} CFBC	15
4	CFBC Operating Parameters	22
5	CFBC Flue Gas Emissions	24
6	Properties of CFBC Fuels	26
7	Variable Symbols and Limits Used for Coding	30
8	Statistical Analysis of Parameters used in N ₂ O Prediction Model	33
9	Effect of CFBC Operating Parameters Firing Salt Creek Coal	39

NITROUS OXIDE EMISSIONS

1.0 INTRODUCTION

Fluidized-bed combustion (FBC) has captured a significant portion of the manufacturing market where waste products or low-priced fuels are burned to produce process steam and/or electricity. More recently, FBC technology has been increased in scale to compete in the electric utility market, with the largest of the units capable of generating 160 MW of electricity in either the bubbling or circulating mode. The motivation to use fluidized-bed combustors in today's markets has evolved around environmental concerns and demands for fuel flexibility. Since these units operate at considerably lower temperatures (1120 K) than do pulverized coal-fired combustors, NO_x emissions are greatly reduced, and SO_x emissions can be controlled in situ by direct combustor sorbent injection.

As a consequence of operating FBCs at low temperatures to enhance the capture of SO_x and to reduce NO_x , the formation of nitrous oxide (N_2O) becomes prevalent. This observation has been documented on laboratory-, pilot-, and full-scale units by numerous researchers (1-10). Although N_2O is nontoxic as a trace pollutant, it is a greenhouse gas and a potential source of stratospheric nitric oxide (NO), a catalytic ozone destroyer. Regulations for the control of N_2O emissions do not currently exist, but may be promulgated as the greenhouse/ozone debate unfolds. Continued progress in the development of FBC technology may depend upon N_2O abatement through the understanding of N_2O chemistry and the effects of operational parameters.

Published N_2O emissions data for experimental studies examining large numbers of coals are generally scarce at the pilot-scale FBC level, although some data are available at the laboratory scale (11, 12). The primary objective of this study was to determine the atmospheric contribution of N_2O derived from coal combustion. Additionally, the goal was to establish a comprehensive engineering model to assist in the prediction of N_2O emissions based upon operating and design considerations.

2.0 PROJECT OBJECTIVES

To meet the overall objectives of determining the overall contribution of N_2O derived from FBC and developing an engineering model, seven tasks were originally proposed. The objective of each task as originally proposed and finally executed is presented here.

2.1 Task 1 – Literature Survey

A literature survey was performed to assess the current state of knowledge in the following areas: N_2O field measurements, measurement techniques, kinetics and reactions, and production of N_2O in FBC systems. Based on available information, an initial global model that predicts N_2O emissions in FBC systems was developed. Process variables considered included temperature, pressure, reactant types and concentrations, and residence time effects. As results of this effort, a review article was published in *Progress in Energy and Combustion Science*.

2.2 Task 2 – Equipment Design and Test Plan Development

A detailed test plan was developed based on the results of Task 1. The plan included the following: design of the experimental facility, the experimental facility operating characteristics, experimental operating procedures, required instrumentation, and planned model development.

Parametric testing was planned to include comprehensive testing on one coal and sorbent, testing on two additional coals to look at the effect of fuel-bound nitrogen, and testing on one additional sorbent for the effect of magnesium. Additional coals and sorbents were added to the test matrix, which currently includes seven coals, two petroleum cokes, and six sorbents.

2.3 Task 3 – Facility Modification

The goal of this task was to construct a new reactor facility, or modify an existing facility, in accordance with the design approved by the Performance Monitor (PM) in Task 2. Existing facilities at the EERC were found to be adequate for the proposed work; therefore, no construction or modification activities were required to perform this work.

2.4 Task 4 – Experiments and Theory Development

The goal of this task was to perform experimentation in accordance with the approved test plan developed in Task 2. This test plan was updated on a yearly basis. With this information, the global model, initiated in Task 1 to estimate the emissions of N_2O under FBC conditions, was refined. The ultimate accomplishment of this work is a global model for use by boiler designers and FBC operators to 1) predict N_2O stack emissions, and 2) facilitate the destruction of N_2O through changes in operating parameters..

2.5 Task 5 – Analysis of Results and Final Report

The goal of Task 5 was to produce a final report which includes the following: reduced data for each test condition; parametric analysis and interpretation of data; and a predictive model as a simple equation, otherwise as a compressed graphical representation and tabulations. Numerous reports regarding this work have been published (see Section 10.0 for a listing). This report summarizes the major results in five main areas:

- Results from pilot-scale circulating fluidized-bed combustion (CFBC) testing investigating the impacts of coal properties and operating conditions on N_2O emissions (Section 4.0)
- Results from bench-scale experiments investigating the role of char in formation and destruction mechanisms (Section 5.0)
- Pilot-scale studies on the influence of homogeneous versus heterogeneous reactions (Section 6.0)
- Modeling results (Section 7.0)
- A potential strategy for reducing N_2O emissions

2.6 Task 6 – Protocol for Field Monitoring (Optional Task)

The goal of this task was to develop a protocol for field monitoring, including the sampling plan, sampling locations, test conditions, process monitoring, and the duration of the test. Sites for testing were to be identified, with consideration given to the physical plant layout, access to sampling locations, combustor type, site access, and operational parameters. Two field tests were performed, one on Argonne National Laboratories' pressurized FBC and the second on Riley Stoker's hybrid FBC.

2.7 Task 7 – Field Monitoring of N_2O Emissions (Optional Task)

The goal of this task was to perform field monitoring in accordance with the sampling protocol established in Task 6. The two sampling trips mentioned in 2.6 were successfully completed.

3.0 EXPERIMENTAL TECHNIQUES

The experimentation performed as a part of this study was completed on three main test rigs. A 1-MW_{th} CFBC was the main tool for the work. Some fundamental char investigations were made on a small 2-inch reactor. A third test rig coupled a coal devolatilization cell with a pilot-scale bubbling bed. Each of these rigs is discussed briefly in this section with details provided in the noted references.

3.1 1-MW_{th} CFBC

Parametric testing was performed using a 1-MW_{th} pilot-scale CFBC. The test rig has an internal diameter of 0.51 meters and is 12.8 meters high. The combustor contains a series of refractory-lined sections bolted together and has been designed to operate over ranges in temperature of 1000 to 1200 K (1350° to 1700°F), excess air of 0% to 100%, superficial gas velocity of 3.6 to 7.0 m/s, and coal size of -3.2 to -12.7 mm (120 to 35 mesh). A schematic of this unit is displayed in Figure 1. Favorable comparisons have been made between results obtained from this pilot-scale facility and those from the full-scale 110-MW_e Colorado Ute Nucla Station (13). The effects of combustor scale on the size distribution of recirculating material, heat flux, combustion efficiencies, and flue gas emissions data were among the factors examined. The complete description of the pilot-scale CFBC and its operation can be found elsewhere (14).

During combustion testing, continuous flue gas monitoring of O_2 , CO, CO_2 , SO_2 , NO_x , and N_2O was performed, with N_2O analyzed by a nondispersive infrared spectrometer (NDIR). A previously established (15) sampling protocol for N_2O analysis was used to minimize cross interferences from other gaseous species.

Initially, experiments examining the effects of operational parameters on N_2O emissions were conducted using an 8-run fractional factorial design. This test matrix was used to screen the main parameters (effects) for significance: temperature (1075 and 1158 K), excess air (15% and 45%), limestone feed (1 and 3 alkali-to-sulfur ratio), and air

Figure 1. Schematic of the 1 MWth EERC pilot-scale CFBC.

split (50:50 and 70:30 primary:secondary air). Further experimentation concentrated on parameters shown to influence N_2O emissions. The N_2O emissions data are expressed on a $mg\ N_2O/MJ$ heat input basis. This effectively normalizes for combustor firing rate and allows fuel-component input rates to be placed on the same basis. Other bases, such as conversion of fuel nitrogen to N_2O or $ppm\ N_2O$ at 3% O_2 , assume a constant firing rate between tests as well as coals. Since firing rate can fluctuate with coals having high ash or moisture levels, we feel the firing rate basis will produce less error over the wide range of experimental conditions and coal ranks.

The distribution of fuel-nitrogen into the char and volatile matter was determined by performing ultimate analyses on coal and coal-derived chars produced using ASTM (D3175) procedures for determining volatile matter. The quantity of nitrogen in the volatile matter was thus determined by difference. In this ASTM procedure, dried coal samples are heated for seven minutes at a temperature of 1225 K in crucibles covered with lids.

3.2 Bench-Scale Testing

The relative reactivities of coal chars as a function of temperature and coal rank were examined using a fluidized-bed reactor (FBR). The reactor was constructed from a 1-m length of 38-mm-ID Schedule 40 stainless steel pipe and is externally heated using a tube furnace. The distributor plate is supported in a central location in the furnace where the bed temperature can be regulated to a maximum of 930°C.

Coal chars were prepared in a fluidized-bed coal pretreatment cell (CPC) at a temperature of 650°C for use in the FBR. Center lignite and Powder River subbituminous coals were successfully pyrolyzed to produce -6-mm coal chars, while successive attempts with New Mexico bituminous coal failed because of the swelling/caking nature of the high-rank coal. Therefore, the bituminous coal char had to be produced in a muffle furnace purged with nitrogen. In addition, and simultaneously, Center lignite coal char was produced in the muffle furnace to assess the mode of char production on reactivity.

A char size fraction of 150 to 250 microns and a superficial bed velocity of 0.3 to 0.5 m/s were chosen for all char tests. At these velocities, the reactor closely simulated a packed-bed reactor with minimal fluidization occurring at temperatures in excess of 540°C. The bed inside the FBR consisted of 250 g of #16 (1.2 mm) silica sand and 5 g of a char sample, yielding a 2% (w/w) char loading. Nitrogen was used in the FBR as the inert fluidizing gas, and N₂O was blended into the nitrogen in a manifold below the distributor plate. Temperatures in the bed were continuously increased at a rate of 5°C/min from room temperature to 900°C. Data for time, bed temperature, and N₂O emissions were recorded at approximately 16-second intervals using a computer-based data acquisition system.

3.3 Bubbling Fluidized-Bed Combustor

To separate the effects of homogeneous and heterogeneous N₂O reactions, tests were conducted using an integrated system comprising the coal pretreatment cell and the 8" x 8" bubbling fluidized-bed combustor (BFBC). The coal pretreatment cell was used to generate char and volatiles under fluidized-bed conditions for combustion tests. Figure 2 shows the schematic of the coal pretreatment cell. Center lignite coal was used to produce char at 1200°F. The volatile components eluted from the coal pretreatment cell were burned in the BFBC at various bed temperatures. Bed temperatures were selected and controlled by in-bed heat exchangers. The char was collected and burned separately in the BFBC.

4.0 PILOT-SCALE DETERMINATION OF THE IMPACTS OF COAL PROPERTIES AND OPERATING CONDITIONS ON N₂O EMISSIONS

The test matrix included two lignites (one from Asia and one from North Dakota), two subbituminous coals (Wyoming), and three bituminous coals (Pennsylvania, Colorado, and New Mexico). The properties of the coals are listed in Table 1. As this table shows, coals were chosen from a wide range of geographical formations and ranks. The partitioning of the coal-nitrogen into volatile matter and char is also presented in Table 1. The significance of the distribution of nitrogen in the coal is related to the reaction pathway in which fuel-bound nitrogen is converted to N₂O. The non-matrix-bound nitrogen released with the volatile matter is free to react early in the combustion process through homogeneous or heterogeneous reaction pathways to form nitrogen or nitrogen oxides (NO, NO₂, N₂O). In the case of CFB combustion, matrix-bound char nitrogen will produce nitrogen oxides through heterogeneous oxidation reactions throughout the combustor, but is believed to be a minor contributor to N₂O formation (16). The char nitrogen may also be gasified and react through homogeneous mechanisms (16, 17).

Figure 2. Schematic of the coal pretreatment cell.

4.1 Effect of Temperature and Coal Rank

The effect of temperature and coal rank on N_2O emissions is presented in Figure 3. The pilot-scale results show appreciably different N_2O emissions for the seven coals tested. For a given temperature, the N_2O emissions were greatest for the higher-ranked New Mexico bituminous coal and the least for the Powder River subbituminous coal. Two obvious temperature trends appear intimately related to coal rank. The first is that the absolute N_2O emissions from the higher-ranked bituminous coals are greater than those from the lower-ranked coals. The second trend indicates that the temperature dependence (slope of temperature versus emissions curve) of a given coal rank is of similar magnitude. The latter trend probably corresponds to differences in coal composition or physical characteristics loosely associated with rank. As Figure 3 shows, the bituminous, lignite, and subbituminous coals have distinctly different slopes.

Further examination of Figure 3 shows that the effect of coal rank on N_2O emissions is not a continuous relationship. At lower CFBC operating temperatures (< 1120 K), bituminous coals yielded the highest N_2O emissions, followed by the lignites and then the subbituminous coals. It is also interesting to note that the temperature dependence of the lower-ranked lignite coals falls into a range between the higher-ranked bituminous and subbituminous coals. These results imply that either the chemistry of these subbituminous coals is unique or that the coal rank classifications are much too simplistic to accurately predict N_2O emissions. Alternately, if these trends extend to a larger database, i.e., if most lignites and subbituminous coals follow the prescribed trends, then the magnitude of N_2O emissions may be predicted with some certainty from rank.

TABLE 1

Analysis of Coals Tested in EERC 1-MWth CFBC

Coal: Rank: Location:	Salt Creek HVC Bit. (Colorado)	Blacksville HVA Bit. (Pennsylvania)	Black Thunder Sub. C (Wyoming)	Center Lignite (N. Dakota)	Asian Lignite (Asia)	New Mexico HVA Bit. (New Mexico)	Powder River Sub. C (Wyoming)
<u>Proximate Analysis, as-received, wt%</u>							
Moisture	7.6	2.4	27.6	37.3	17.0	2.1	29.9
Volatile Matter (VM)	31.0	36.4	33.2	28.8	37.4	33.0	32.6
Fixed Carbon (FC)	42.7	52.9	34.6	28.8	7.6	52.5	33.0
Ash	18.6	8.5	4.6	5.1	38.0	12.4	4.5
FC/VM Ratio	1.38	1.45	1.04	1.00	0.20	1.59	1.01
<u>Ultimate Analysis, as-received, wt%</u>							
Carbon	58.8	74.5	49.8	41.0	25.0	73.7	48.8
Hydrogen	5.0	5.2	6.6	7.0	4.2	4.9	6.7
Nitrogen	1.2	1.4	0.6	0.5	0.6	1.4	0.7
Sulfur	0.5	2.5	0.3	0.6	6.0	0.5	0.4
Oxygen	16.0	8.0	38.0	45.7	26.1	7.0	39.0
Ash	18.6	8.5	4.6	5.1	38.0	12.4	4.5
<u>Nitrogen Distribution^a, % of total N</u>							
Volatile Matter	43	36	27	25	88	36	31
Char	57	64	73	75	12	64	69
<u>Heating Value, as-received, MJ/kg</u>							
HHV	23.85	30.94	20.08	16.25	10.90	30.09	19.66

^a Nitrogen was measured in coal and char prepared according to ASTM proximate analysis. Nitrogen in volatile matter was determined by difference.

Note: All proximate, ultimate, and heating values are a result of averaging several samples for each coal.

Figure 3. Effect of temperature and coal rank on N_2O emissions.

designations alone. In any case, an understanding of the fundamental chemistry of the Wyoming subbituminous coals may prove beneficial in reducing N_2O emissions.

In addition to N_2O , the formation of nitric oxide (NO) emissions from fuel-nitrogen is highly dependent upon temperature and, to a lesser extent, coal rank. Figure 4 displays NO_x emissions as a function of temperature and coal rank for the same combustion tests presented in Figure 3 for N_2O emissions. These data clearly show that NO_x emissions increase with temperature, a trend opposite that displayed for N_2O . It is also apparent that the scatter of the NO_x data points is greater than that for N_2O . This is largely due to enhanced sensitivity (relative to that of N_2O), excess air, limestone feed rate, and primary-to-secondary air ratio (air staging). This sensitivity is exemplified by the Center lignite tests where two sets of points are presented, those for excess air levels of 57% and 20%. The line in Figure 4 for Center lignite coal is drawn between these two levels of excess air, representing a median point of 38% excess air. It should be noted that these are the same points plotted in Figure 3 for N_2O emissions showing a lesser effect of excess air on this specific coal.

The data in Figures 3 and 4 indicate that the effects of temperature on N_2O and NO_x emissions are inversely related. The preference for one nitrogen oxide over the other results in a total nitrogen oxide conversion that remains mostly constant for a given coal over the normal CFBC operating temperature range. This effect has been quantified in a bench-scale bubbling fluidized-bed reactor by Pels and others (16) for numerous coals covering lignite through anthracite ranks. Pels found that the amount of N_2 formed from fuel-nitrogen is largely independent of temperature, is rank-dependent, and may be the

Figure 4. Effect of temperature and coal rank on NO_x emissions.

result of sharing a common precursor for NO_x and N_2O formation. Table 2 presents the nitrogen balance for combustion tests performed in the present study at approximately 1120 K and 25% excess air. These data points are represented in Figures 3 and 4. As seen from Table 2, the fuel-nitrogen conversion to N_2O is greater in the bituminous coals, while the conversion to NO_x is favored for the low-rank coals. The low conversion value for NO_x observed with the Asian lignite may be related to the high ash content of this coal. It should be noted that the majority of fuel-nitrogen is converted to N_2 , and this level remains mostly constant along the lines of similar rank, which is consistent with the referenced bench-scale study (16).

4.2 Effect of Combustion Scale

In the present study, the validation of scaling effects on N_2O emissions is based upon tests performed using Salt Creek bituminous coal. Correlations between these tests and data observed for the 110-MW_e Colorado Ute Station burning the same coal show that the N_2O temperature dependence is in good agreement (13). The magnitude of the N_2O emissions, however, was found to be 30% lower in the full-scale unit, which is one discrepancy noted when increasing scale. This effect is probably due to decreased residence time, increased wall effects, and improved mixing seen in the smaller pilot-scale units. Other flue gas emissions, including NO_x , were shown to be comparable in magnitude to those at the Nucla Station. Because pilot-scale CFBCs produce greater N_2O emissions, the estimated level of N_2O in full-scale CFBCs will be conservative in nature. This fact should make pilot-scale experimentation acceptable for developing N_2O mitigating strategies.

TABLE 2

Nitrogen Balance for Combustion Tests Performed at 1120 K and 25% Excess Air

Coal	Rank	% Conversion of Fuel-Nitrogen ^a		
		N ₂ O	NO _x	N ₂
New Mexico	HVA Bit.	11.3	2.88	85.8
Blacksville	HVA Bit.	10.7	6.17	83.1
Salt Creek	HVC Bit.	14.1	4.28	81.7
Black Thunder	Sub. C	4.94	10.7	84.3
Powder River	Sub. C	3.42	8.34	88.2
Center	Lignite	2.25	9.80	87.9
Asian	Lignite	3.51	3.82	92.7

^a Conversion expressed as mole emission-N per mole fuel-N.

4.3 Effect of Excess Combustion Air

Figure 5 presents the effect of excess combustion air on N₂O emissions with four different coals. All data points have been corrected to 1115 K using slopes from Figure 5. Increasing excess air in CFB combustion showed an increase in N₂O emissions when burning all coals. This apparent trend extends across all coal ranks tested and could be used to reduce N₂O emissions to a limited extent by using a minimal amount of excess air for combustion. The disparity in slope between the various coals possibly indicates a correlation between coal rank and excess air, but is not conclusive from the limited data available. There is also an interaction between excess air and temperature in relation to N₂O emissions: the effect of excess air level is greater at lower temperatures than at higher temperatures. This can be seen in Figure 5 for the Salt Creek coal data, which show a much stronger dependence on excess air at 1074 K than do the data acquired at 1153 K. The data points for the other coals in this figure were obtained at approximately 1115 K.

4.4 Effect of Sorbent Feed

The effect of limestone feed on N₂O emissions is shown in Figure 6. Sorbent feed in this figure is expressed on a grams per megajoule heat input basis. This places all coals on the same basis, unlike the Ca/S ratio, which is only meaningful for comparing fuels having similar sulfur contents and heating values. The general trend for four of the five coals presented in this figure is a decrease in N₂O emissions with increasing sorbent feed. The opposing trend displayed for the Black Thunder subbituminous coal is not readily understood. The data for the bituminous coals suggest a potential N₂O emissions control strategy of increasing the sorbent feed rate. Unfortunately, the use of a limestone sorbent

Figure 5. Effect of excess air on N₂O emissions.

Figure 6. Effect of limestone feed on N₂O emissions.

as a means of reducing N_2O emissions has been shown to result in a comparable increase in NO_x emissions (4). Therefore, the net result of this activity would be the conversion of N_2O to NO .

4.5 Effect of Primary/Total Air Ratio

The effect of combustion air staging into the primary and secondary zones was studied with Blacksville and Salt Creek bituminous coals. Figure 7 shows the effect on N_2O emissions of increasing the primary combustion air distribution in the combustor as a function of temperature and excess air level. As seen in this figure, the N_2O emissions appear to be affected by an interaction between primary air and temperature. At higher temperatures (1140 K), the N_2O emissions tend to decrease very slightly with increasing primary air split, while the opposite trend occurs at lower temperatures (1060 K). Increasing excess air from 20% to 45% when firing Salt Creek bituminous coal increased N_2O emissions in accordance to the prescribed trend shown in Figure 5. These subtle effects displayed in Figure 7 may be manifested by changes in the dense-bed velocity and temperature profiles and are, therefore, indications of the interdependence of the operating parameters.

Figure 7. Effect of primary air-to-total air ratio on N_2O emissions:
 $\square$ Salt Creek, $\circ$ Blacksville.

5.0 ROLE OF COAL CHAR ON N_2O FORMATION AND DESTRUCTION

The results of the char reactivity tests are presented in Figure 8 for the blank experiment (no char) and for the chars derived from Center lignite, Powder River subbituminous, and New Mexico bituminous coals. In these tests, nominal N_2O concentrations of 220 ppm were passed through the bed. The result of the blank test shows that at the maximum temperature of 900°C, N_2O was reduced from 220 ppm to 168 ppm, or only a 24% reduction by thermal decomposition. Figure 8 shows a significant difference exists between the low- and high-rank coals. The bituminous coal shows N_2O destruction beginning at 540°C, while the low-rank coals begin destruction at 290°C. Closer examination of the bituminous char data shows distortion in the curve at approximately 650°C, the temperature at which the char was produced in the muffle furnace. Additional devolatilization occurred, causing a cross interference in the N_2O analyzer. The lower-ranked coals did not show this behavior, possibly indicating that the majority of the coal devolatilization occurred at or before 650°C.

Figure 9 shows a comparison between the reactivity of Center lignite char prepared in a fluidized-bed and a muffle furnace. It is noted that preparing char in the muffle furnace shifted the curve by only 30°C, but otherwise it mirrored the overall trend of the char prepared in fluidized-bed CPC. This shift to slightly higher temperatures may be

Figure 8. Effect of coal rank and bed temperature on N_2O destruction.

Figure 9. Effect of char preparation method on Center lignite char reactivity.

related to surface area development. Since surface areas are generally much greater in the low-rank coals than in the high-rank coals, their surface area development should also be more sensitive to the pyrolysis environment.

Surface areas were measured for chars prepared in a furnace according to the ASTM proximate analysis method. Surface areas for Center lignite, Powder River subbituminous, and New Mexico bituminous coal chars were determined to be 450, 220, and 50 m²/g, respectively. If the differences in N₂O destruction shown in Figure 8 were due strictly to surface area, we would expect greater separation between the subbituminous and the lignite coal chars. The difference in reactivity is probably related to a combined effect of surface area, composition, and surface structure.

The data presented in Figure 8 suggest that lower-rank coals should produce lower N₂O emissions by virtue of the char reactivity at FBC operating temperatures. This trend has been shown to be true in our database of coals fired in the CFBC (17), although this result may not be related to just the char reactivity. The composition of the volatiles is probably the most dominant factor for establishing the magnitude of flue gas N₂O emissions. Results depicted in Figures 8 and 9 were from experiments performed in an inert atmosphere where there was no competition for active sites by oxygen. Consequently, these data cannot be directly extended to the atmosphere of the dense bed region, although this region will have zones of reducing or low oxygen where N₂O destruction can occur. Because of the N₂O destruction capability of the low-rank coal chars, the net emissions released from these coals may be controlled by heterogeneous mechanisms.

The results of this study show that compared with bituminous coal char, the low-rank coal chars will destroy N_2O at much lower temperatures. Although FBCs operate at temperatures of $850^\circ C$, where significant N_2O destruction occurs even with the bituminous coals, the more active low-rank coal chars will reduce N_2O levels at greatly reduced bed-char concentrations.

6.0 HOMOGENEOUS VERSUS HETEROGENEOUS REACTIONS

A variety of fuels were selected to determine the role of homogeneous and heterogeneous reactions on the emission of nitrogen oxides. Selected properties of fuels tested in the 1-MWth CFBC are shown in Table 3. The distribution of fuel nitrogen into the char and volatile matter was determined by performing ultimate analyses on coal and coal-derived chars produced using ASTM (D3175) procedures for determining volatile matter. The quantity of nitrogen in the volatile matter was thus determined by difference. As this table shows, the quantity of nitrogen in the fuels varies substantially on a percentage basis, but is less variable when normalized for the heating value. The heating value basis is indicative of the actual nitrogen consumption rate. Interestingly, when the fluid coke was devolatilized for the proximate analysis, a minimal amount of nitrogen was liberated, even though nearly 10% of the mass was released as volatile matter.

Figure 10 presents N_2O emissions as a function of the CFBC temperature for each fuel listed in Table 3. Emissions of N_2O from the high-rank coal and the petroleum cokes were seen to be higher than those of the low-rank coals. The data in Figure 10 indicate that the fuels with the highest fuel ratio (FC/VM) will generate the greatest N_2O emissions, which would appear to conflict with gas-phase homogeneous N_2O production through volatile matter. Particularly notable is that for fluid coke, less than 1% of the nitrogen is released with the volatile matter when heated to 1225 K (Table 3), yet it is the

TABLE 3

Properties of Fuels Tested in 1-MWth CFBC

	Fluid Coke	Delayed Coke	New Mexico	Black Thunder	Center
Type	Pet. Coke	Pet. Coke	HVA Bit.	Sub. C	Lignite
N, as-received	1.66	1.37	1.38	0.62	0.53
N, g/MJ	48.8	39.9	45.9	30.9	32.6
Nv, %	< 1	17	36	27	25
Nc, %	99+	83	64	73	75
FC/VM	9.38	6.08	1.59	1.04	1.00
HHV, MJ/kg	33.99	34.30	30.09	20.08	16.25

Figure 10. Effect of combustor temperature and fuel type on N₂O emissions.

greatest emitter of N₂O. The mass balance for the test performed at 1060 K using this coke showed conversions approaching 24% of the total available nitrogen. There are two possible explanations for this result: the char-nitrogen is being oxidized to form the required N₂O, or alternatively, the petroleum coke, being a solidified liquid, is burned partially by vaporization rather than by a shrinking sphere diffusion-controlled combustion. The vaporized liquid may contribute to the homogeneous-phase nitrogen pool, although the data in Table 3 suggest that this is unlikely at the temperatures where the highest N₂O emissions occur. Additionally, many high-volatile bituminous coals transform through a plastic state when caking occurs, leaving a relatively low surface area. This transformation may be akin to that of petroleum coke, resulting in the high N₂O emissions typically seen with bituminous coals.

Figure 11 presents the NO_x emissions data for the same combustion tests shown in Figure 10. Here the NO_x emissions tend to be higher from the low-rank coals at lower combustion temperatures, but have a similar dependence on temperature displayed by the high-rank coals. Most interesting with respect to NO_x emissions is again the fluid coke fuel. This fuel has almost negligible NO_x emissions and is largely unaffected by temperature. At the lower combustion temperature of 1060 K, only 0.6% of the fuel nitrogen is converted to NO_x. This result is unusual compared to high-rank coals where up to 60% of the char can be converted to NO (18). This could imply that the coke is not behaving as a char when burned and would support homogeneous conversion to NO_x or that the surface is well designed for NO reduction and char-nitrogen oxidation by NO.

Figure 11. Effect of combustor temperature and fuel type on NO_x emissions.

The effect of fluidization mode was assessed by comparing results from tests performed on the 1-MW_{th} CFBC with those obtained from a 0.1-MW_{th} BFBC for three coals of different ranks. These results are shown in Figure 12, where the NO_x and N_2O levels are expressed as % conversion of total fuel nitrogen. It is clear from this figure that the conversion of nitrogen is a function both of rank and of the fluidization mode. With the exception of lignite coal, the conversion to N_2O was approximately half that seen for circulating mode, while NO_x conversion doubled when coals were burned in bubbling mode.

The N_2O formation mechanisms may be related to the differences between fluidizing modes utilized by the combustors. The two major differences between the CFBC and the BFBC are 1) the CFBC entrains the fuel/ash beyond the dense-bed zone and 2) the CFBC utilizes staged combustion. Clearly, in CFB combustion, NO_x is reduced by staged combustion, but the final N_2O levels were shown by Kilpinen and Hupa (19) to remain mostly unaffected unless the final air stoichiometry remained at 1.0. This suggests that the difference between CFBC and BFBC N_2O formation is dependent upon the heterogeneous char reactions occurring in the dilute phase after the addition of secondary air, where the gas velocity is sufficient to entrain this material. Gas profile measurements taken by Amand and Leckner (10) in the riser of a CFBC indicated that approximately 50% of the N_2O was formed in the dense-bed region, with the remaining N_2O being formed along the riser. Likewise, a major portion of the NO was destroyed in the bed, with significant reduction of NO also occurring in the riser. This finding is consistent with the current results seen in Figure 12 for the BFBC, where NO conversions are higher due to the lack of entrained carbon and staged combustion, and N_2O

Figure 12. N_2O and NO_x conversions for BFB and CFB combustors firing selected fuels. (FC = fluid coke, DC = delayed coke, NM = New Mexico, BT = Black Thunder, CL = Center Lignite.)

conversions lower, probably due to the char being burned in the dense bed where significant catalytic activity and high CO levels retard N_2O formation.

To further explore the heterogeneous and homogeneous N_2O formation mechanisms, experiments were performed using the BFB where Center lignite coal, char, and volatiles were fed separately to the bed of the combustor. The entire closed system roughly simulates staged combustion, where 50% of the combustion air was used to heat the devolatilization cell by consuming a portion of the coal, while the remaining oxygen entered the BFB under the bed (secondary air). The volatiles and nitrogen eluted from the devolatilization cell contained no residual oxygen from the primary air supply. The volatiles supply was introduced into the bed of the BFB where they were burned with secondary air to maintain the flue gas oxygen between 2%-6%. Separate tests were then conducted with the char produced and also with the original coal. Initial attempts at separating volatiles from a bituminous coal failed because of severe caking. Figure 13 presents the BFB combustion data for volatiles, char, and the parent Center lignite coal normalized as a percentage of the total nitrogen available in the original coal. The volatile combustion data show greater scatter due to the complexity of controlling the integrated system. At low excess air conditions, the volatiles and the char are converted

Figure 13. Conversion of fuel-nitrogen to N_2O for Center lignite coal, char, and volatiles in BFBC.

equally to N_2O . The sum of these two conversions accounts for about 80% of that seen for the original coal. As the excess air is increased, the char remains unaffected while the volatiles conversion increases. Likewise, the coal conversion increases with excess air. A comparison of these results shows that excess air mostly affects volatile nitrogen conversion to N_2O . This result would be consistent with diffusion-limited combustion of the char in the bed. At the higher excess air conditions, the overall closure of the nitrogen balance is seen to be 85%-90%, based on the summation of the volatile and char components.

Regressions of the data shown in Figure 13 for excess air and temperature effects on N_2O conversion were used to predict the normalized N_2O emissions from the mass balances. Points were plotted for the predicted values of the missing points. These data are presented in Figure 14. This figure shows that the relative contribution from the char and volatiles to N_2O emissions is nearly independent of temperature at low excess air (3% O_2). At high excess air (5% O_2), the contribution to N_2O emissions increases from the volatiles and decreases from the char as temperature increases. The latter trend suggests that at higher temperatures, the destruction of N_2O from the volatile phase is less than that of the char. This may not be unreasonable for a lignite coal char, where the surface area is approximately 400 m^2/g and contains large quantities of finely dispersed, catalytically active mineral matter.

The present study adds to the growing database of evidence supporting the significant contribution of heterogeneous N_2O formation in CFB combustion. Comparison of data between bubbling and circulating mode combustors suggests that the volatiles

Figure 14. Modeling of emissions from Center lignite coal, char, and volatiles.

contribution to N_2O emissions dominates in the dense-bed region, while char oxidation and NO reduction occur in the dilute phase. The data presented in this section and in the selected references show that the overall contribution to total N_2O emissions from the char can be as high as 40%-50%. This level could be slightly higher if the dense-bed region of the CFBC can be shown to contribute to the total N_2O emissions through heterogeneous char reactions.

7.0 MODELING OF N_2O EMISSIONS

The primary objective of this project was to 1) define significant FBC operating parameters and their effect on N_2O emissions and 2) incorporate these pilot-scale test results into an empirical model to concisely describe these results from an engineering perspective. This model would be applicable to preliminary FBC design for estimating prospective N_2O emissions based upon the fuel selected and the operating conditions employed. Alternatively, because of the difficulty in accurately measuring N_2O emissions without the required sampling and treatment protocol, the model may be applied to existing facilities for estimating N_2O emissions where the necessary equipment is unavailable. The latter scenario would be applicable to most installations since, at present, there are no regulations mandating N_2O control.

7.1 CFBC Database

The complete CFBC database including flue gas emissions, fuel properties, and operational parameters were recompiled to check for errors and assure accuracy of

calculations. Prior to modeling, six combustion tests that had been performed without the use of an external heat exchanger for load control were removed from the database. This was done because of the inherent differences in combustor operation. For example, the use of an external heat exchanger to control load maintains the combustor at near isothermal conditions at the expense of velocity or excess air. The nonisothermal mode of operation used for the other six tests relied on reductions in temperature and velocity to achieve the same result. Other uncontrolled combustion tests not related to the N₂O project were also edited from the database.

The complete database used for modeling is presented in Tables 4-6 for CFBC operating parameters, flue gas emissions, and fuel properties, respectively. A total of 57 combustion tests representing nine fuels, including seven coals and two petroleum cokes, were used in the modeling computations. Symbols used for coals in the database are as follows: L = Center Lignite, S = Salt Creek, A = Asian, B = Blacksville, T = Black Thunder, P = Powder River, N = New Mexico, D = delayed coke, and F = fluid coke. Operating conditions explored through parametric testing are presented in Table 4 and include excess air (EA), temperature (Temp.), combustor superficial gas velocity (Vel.), primary air split (PA), and limestone sorbent feed rate (LF). The alkali-to-sulfur ratio (A/S) and sulfur retention (SR) values are also presented for comparison to limestone feed. The measured flue gas emissions (responses) resulting from the preselected operating parameters are shown in Table 5. The N₂O and NO_x emissions are presented on three different bases to facilitate modeling of the data in molar volume, firing rate, or conversion of fuel-nitrogen units.

Table 6 presents the fuel properties used for modeling the fuel-related effects on N₂O emissions. Specifically, fuel properties were used to replace the discrete "fuel" variables with continuously measurable parameters. As seen in Table 6, proximate, ultimate, selected ash constituents, and nitrogen partitioning in the fuel were used as modeling inputs. These data were placed on a firing rate basis to represent the actual flux of these materials entering the combustor. The firing rate basis was required because of the vast differences in heat content and moisture levels of the selected fuels. The hydrogen and oxygen values reported in this table do not include any contribution from inherent moisture.

The distribution of fuel-nitrogen into the char and volatile matter was determined by performing ultimate analyses on coal and coal-derived chars (ASTM D3176). The chars were produced using ASTM proximate procedure D3175 for determining volatile matter. In this ASTM procedure, coal samples are heated for 7 minutes at a temperature of 1225 K in crucibles covered with lids. The quantity of nitrogen in the char and volatile matter was thus determined by difference using the following calculations:

$$\%N_{FC,coal} = \frac{\%N_{coal}(daf)}{100 - VM_{coal}(daf)} \times 100 = \frac{\%N_{coal}(daf)}{FC_{coal}(daf)} \times 100 \quad [\text{Eq. 1}]$$

$$\%N_{FC,char} = \%N_{char}(daf) \quad [\text{Eq. 2}]$$

TABLE 4

CFBC Operating Parameters

Coal	Test	EA, %	Temp., K	Vel., m/s	PA, %	LF, g/MJ	A/S Molar Ratio	SR, %	Coal feed kg/hr
L	0	22	1103	5.30	56	0.00	1.6	6	151.0
L	1	25	1119	5.06	56	3.63	5.1	63	136.5
L	2	55	1019	4.11	60	0.83	2.4	84	100.2
L	4	95	1109	4.24	67	1.10	2.3	47	78.5
L	5	57	1101	4.60	62	1.75	2.0	62	106.6
L	6	22	1127	5.03	60	1.04	2.0	44	128.8
S	1	20	1148	5.03	51	0.00	0.6	6	102.9
S	2	21	1152	4.94	47	1.67	2.6	66	107.9
S	3	23	1121	4.24	61	1.38	1.8	74	92.1
S	5	43	1075	4.88	65	1.38	2.0	68	96.1
S	6	17	1076	4.75	47	1.04	1.3	59	117.0
S	7	18	1161	4.91	67	1.65	2.2	57	106.1
S	8	40	1152	5.00	51	1.84	1.9	63	94.8
S	9	45	1142	5.09	69	3.32	5.2	95	94.8
S	10	20	1154	5.03	47	2.08	3.3	82	110.7
S	11	17	1080	4.91	67	2.38	4.1	91	119.7
S	12	45	1072	4.79	47	2.32	4.7	92	97.5
A	1	24	1125	5.55	60	31.87	2.1	90	221.3
A	2	23	1072	5.06	55	32.70	2.2	88	217.2
A	3	23	1172	5.76	60	33.39	2.1	86	217.2
A	4	26	1124	5.91	59	0.00	0.6	70	217.2
B	1	28	1121	4.91	60	0.00	0.1	14	78.9
B	2	24	1113	4.82	59	6.65	2.8	91	78.9
B	3	30	1050	4.63	60	6.06	2.7	70	79.8
B	4	19	1122	5.61	70	6.19	2.6	89	97.1
B	5	53	1119	5.61	50	8.64	3.7	76	77.6
B	6	30	1199	5.00	60	7.87	3.4	26	74.8
B	7	20	1131	4.15	50	4.63	2.1	70	66.7
B	8	50	1108	4.15	67	2.34	1.0	81	60.3
B	14	41	1139	4.88	60	8.94	3.9	59	72.1
B	15	28	1120	4.88	60	4.23	1.8	70	79.8
B	16	21	1129	4.75	60	6.09	2.7	74	87.5
B	17	29	1118	4.91	60	7.56	2.9	85	78.5
B	18	32	1127	4.88	60	0.00	0.1	16	85.3
T	1	32	1130	4.91	47	0.00	1.8	15	113.4
T	2	26	1115	4.91	50	1.27	3.9	81	123.8
T	3	23	1060	4.88	49	0.00	1.7	99	136.5
T	4	9	1106	4.82	48	2.37	5.5	74	142.9
T	7	23	1109	3.96	64	0.87	2.9	78	103.9

TABLE 4 (cont.)

Coal	Test	EA, %	Temp., K	Vel., m/s	PA, %	LF, g/MJ	A/S Molar Ratio	SR, %	Coal feed kg/hr
T	8	42	1111	4.91	48	1.41	3.9	97	111.6
T	9	30	1165	5.15	49	2.74	6.3	91	123.4
P	1	27	1156	4.48	50	2.09	4.3	90	107.0
P	2	16	1086	4.24	50	0.45	2.1	87	122.0
P	3	21	1116	4.36	50	1.38	3.4	92	116.6
P	5	23	1142	4.45	50	1.64	3.7	92	113.8
N	1	18	1145	4.79	50	2.63	5.7	82	81.6
N	2	20	1073	4.51	50	0.71	2.2	85	80.7
N	3	19	1118	4.60	50	1.77	4.2	88	78.0
N	5	20	1145	4.69	50	1.66	4.0	86	83.4
D	1	23	1147	5.21	60	10.64	1.6	90	87.1
D	2	20	1117	5.03	60	12.67	2.2	91	93.0
D	3	23	1184	5.18	60	11.70	2.0	89	87.1
D	4	18	1155	4.21	60	10.33	1.7	92	73.0
D	5	17	1160	4.24	70	11.59	1.9	93	70.7
D	6	18	1152	4.21	60	10.12	1.6	93	66.7
F	0	18	1064	4.30	60	12.90	4.4	73	73.0
F	1	19	1114	4.42	60	8.39	3.0	87	72.6
F	4	19	1107	4.45	60	5.96	1.7	91	71.7

note that in the above calculations, the dry, ash-free basis (daf) reduces the proximate analysis to a binary system, namely, volatile matter (VM) and fixed carbon (FC). In addition, Equation 1 places the coal-N on a volatile-matter-free basis. After the moisture and volatile matter are removed from the coal, the ultimate nitrogen analysis of the char on a dry, ash-free basis is numerically on the same basis as the original coal analysis, $\%N_{FC,coal}$. If all of the coal-N remained in the char after heating to remove moisture and volatile matter, then:

$$\%N_{FC,char} = \%N_{FC,coal} \quad [\text{Eq. 3}]$$

If any of the original coal-N was released with the volatile matter, this percentage of the total coal-N would then equal:

$$\%N_{VM} = \frac{\%N_{FC,coal} - \%N_{FC,char}}{\%N_{FC,coal}} \times 100 \quad [\text{Eq. 4}]$$

TABLE 5
CFBC Flue Gas Emissions

Coal	Test	O ₂ %	----- Corrected 3% O ₂ -----					N ₂ O, mg/MJ	N ₂ O, %conv.	NO _x , mg/MJ	NO _x , %conv.
			N ₂ O, ppm	NO _x , ppm	CO ₂ , %	CO, ppm	SO ₂ , ppm				
L	0	3.78	48	141	17.0	16	760	26.5	5.18	80.84	7.61
L	1	4.25	22	202	17.7	11	327	11.9	2.32	110.08	10.08
L	2	7.57	126	122	17.4	56	132	70.1	13.70	68.37	6.58
L	4	10.30	54	278	17.2	16	438	29.7	5.81	158.24	15.00
L	5	7.67	49	233	17.3	18	315	26.8	5.24	129.86	12.50
L	6	3.77	21	183	17.1	12	456	11.5	2.25	101.48	9.80
S	1	3.65	150	143	16.5	12	530	83.9	11.10	80.84	5.28
S	2	3.76	143	158	16.4	10	179	80.0	10.60	90.73	5.82
S	3	3.95	190	116	17.2	14	127	106.2	14.10	63.64	4.28
S	5	6.44	310	93	16.5	15	168	174.6	23.10	52.89	3.40
S	6	3.11	219	32	15.8	26	211	123.0	16.20	18.92	1.16
S	7	3.35	115	115	16.3	11	227	64.1	8.49	66.65	4.28
S	8	6.12	146	194	16.7	9	196	81.7	10.80	108.79	7.24
S	9	6.65	169	272	16.9	9	26	95.0	12.60	150.50	10.10
S	10	3.60	124	145	16.5	8	94	69.7	9.23	83.42	5.34
S	11	3.10	223	56	16.1	19	41	125.6	16.60	32.25	2.06
S	12	6.63	291	154	16.3	18	34	163.4	21.60	88.58	5.73
A	1	4.06	60	130	17.8	80	1569	32.8	3.51	77.40	3.82
A	2	4.05	115	85	17.9	87	1966	63.2	6.76	51.60	2.50
A	3	4.03	33	151	18.5	21	2306	18.1	1.94	86.00	4.47
A	4	4.37	81	106	17.3	102	4770	44.7	4.78	64.50	3.09
B	1	4.73	168	121	15.2	137	1703	94.2	13.70	73.10	4.90
B	2	4.22	145	94	16.7	88	201	84.3	12.20	51.60	3.97
B	3	4.95	265	35	17.0	233	666	148.4	21.50	18.92	1.41
B	4	3.50	123	122	16.6	124	239	66.7	9.70	67.51	4.93
B	5	7.40	153	228	17.0	49	526	84.7	12.30	123.84	9.25
B	6	4.94	52	264	17.1	78	1637	28.9	4.19	141.04	10.70
B	7	3.64	115	78	17.6	34	698	64.1	9.27	40.85	3.16
B	8	7.19	167	174	17.2	106	436	92.9	13.40	92.45	6.99
B	14	6.22	90	144	16.3	72	914	50.3	7.33	78.26	5.89
B	15	4.75	145	135	16.3	63	632	81.3	11.80	76.11	5.49
B	16	3.77	108	130	16.7	42	574	60.2	8.75	71.38	5.27
B	17	4.88	132	153	16.6	12	329	74.0	10.70	84.71	6.17
B	18	5.19	141	156	15.6	18	1698	79.1	11.50	92.45	6.34
T	1	5.15	25	246	16.7	3	372	13.7	2.84	138.03	14.05
T	2	4.44	43	183	16.2	11	84	23.9	4.93	107.07	10.73
T	3	4.06	62	166	16.6	18	4	33.9	6.70	95.03	9.41
T	4	1.72	30	128	16.7	10	119	16.4	3.39	72.67	7.21

TABLE 5 (cont.)

Coal	Test	O ₂ %	----- Corrected 3% O ₂ -----					N ₂ O, mg/MJ	N ₂ O, %conv.	NO _x , mg/MJ	NO _x , %conv.
			N ₂ O, ppm	NO _x , ppm	CO ₂ , %	CO, ppm	SO ₂ , ppm				
T	7	4.00	39	198	17.8	7	112	20.4	4.21	105.35	10.60
T	8	6.34	41	254	17.3	5	12	22.3	4.60	139.32	14.30
T	9	4.88	24	254	16.8	6	42	13.5	2.79	143.62	14.40
P	1	4.52	29	200	16.4	1	55	15.6	2.91	115.24	10.10
P	2	2.93	39	118	16.9	12	77	21.3	3.99	66.65	6.08
P	3	3.73	33	164	16.9	18	50	18.3	3.42	91.59	8.34
P	5	3.94	19	177	16.3	6	48	10.4	1.95	102.77	9.15
N	1	3.25	93	171	17.1	204	84	52.5	7.30	93.31	6.70
N	2	3.57	205	38	16.2	120	64	115.2	16.00	21.93	1.49
N	3	3.42	145	74	17.0	92	55	81.3	11.30	40.42	2.88
N	5	3.59	93	96	16.9	32	63	52.0	7.28	52.89	3.76
D	1	4.02	90	136	17.0	37	349	49.5	7.88	51.00	5.95
D	2	3.57	143	112	16.9	51	372	78.7	12.50	41.90	4.89
D	3	3.97	57	280	15.7	22	440	31.4	5.01	105.00	12.30
D	4	3.18	95	213	18.8	13	261	52.5	8.32	80.20	9.35
D	5	3.13	91	226	17.6	24	242	50.3	7.99	84.80	9.90
D	6	3.18	93	217	18.8	16	261	51.2	8.13	81.80	9.53
F	0	3.29	314	16	18.2	72	596	181.5	23.70	6.16	0.59
F	1	3.38	211	21	17.6	38	271	122.1	15.90	8.26	0.79
F	4	3.38	207	17	18.3	35	195	119.1	15.50	6.53	0.62

The percentage of the coal-N that remains in the char after the coal is devolatilized must then be:

$$\%N_{char} = 100 - \%N_{VM} \quad [\text{Eq. 5}]$$

The actual addition rates of nitrogen in the volatile matter and char, N_v and N_c , respectively, are calculated from the original nitrogen flux (firing rate basis) and the nitrogen partitioning values using the following two relations:

$$N_v = \frac{\%N_{VM}}{100} \times N \text{ (g/MJ)} \quad [\text{Eq. 6}]$$

$$N_c = \frac{\%N_{char}}{100} \times N \text{ (g/MJ)} \quad [\text{Eq. 7}]$$

TABLE 6

Properties of CFBC Fuels

Coal	Test	HHV, MJ/kg	VM, g/MJ	FC, g/MJ	N, g/MJ	O, g/MJ	C, g/MJ	H, g/MJ	S, g/MJ	Ash, g/MJ	H ₂ O, g/MJ	CaO, g/MJ	Fe ₂ O ₃ , g/MJ	MgO, g/MJ	NaO, g/MJ	Coal, kg/hr	Nc, g/MJ	Nv, g/MJ
L	0	16.31	17.75	17.70	0.33	7.86	25.07	1.78	0.40	3.11	22.75	0.699	0.500	0.317	0.115	151.0	0.24	0.09
L	1	16.31	17.75	17.70	0.33	7.86	25.07	1.78	0.40	3.11	22.75	0.699	0.500	0.317	0.115	136.5	0.24	0.09
L	2	16.31	17.75	17.70	0.33	7.86	25.07	1.78	0.40	3.11	22.75	0.699	0.500	0.317	0.115	100.2	0.24	0.09
L	4	16.31	17.75	17.70	0.33	7.86	25.07	1.78	0.40	3.11	22.75	0.699	0.500	0.317	0.115	78.5	0.24	0.09
L	5	16.31	17.75	17.70	0.33	7.86	25.07	1.78	0.40	3.11	22.75	0.699	0.500	0.317	0.115	106.6	0.24	0.09
L	6	16.31	17.75	17.70	0.33	7.86	25.07	1.78	0.40	3.11	22.75	0.699	0.500	0.317	0.115	128.8	0.24	0.09
S	1	23.89	12.99	17.89	0.48	3.86	24.62	1.73	0.20	7.78	3.20	0.117	0.235	0.117	0.018	102.9	0.35	0.13
S	2	23.89	12.99	17.89	0.48	3.86	24.62	1.73	0.20	7.78	3.20	0.117	0.235	0.117	0.018	107.9	0.35	0.13
S	3	23.89	12.99	17.89	0.48	3.86	24.62	1.73	0.20	7.78	3.20	0.117	0.235	0.117	0.018	92.1	0.35	0.13
S	5	23.89	12.99	17.89	0.48	3.86	24.62	1.73	0.20	7.78	3.20	0.117	0.235	0.117	0.018	96.1	0.35	0.13
S	6	23.89	12.99	17.89	0.48	3.86	24.62	1.73	0.20	7.78	3.20	0.117	0.235	0.117	0.018	117.0	0.35	0.13
S	7	23.89	12.99	17.89	0.48	3.86	24.62	1.73	0.20	7.78	3.20	0.117	0.235	0.117	0.018	106.1	0.35	0.13
S	8	23.89	12.99	17.89	0.48	3.86	24.62	1.73	0.20	7.78	3.20	0.117	0.235	0.117	0.018	94.8	0.35	0.13
S	9	23.89	12.99	17.89	0.48	3.86	24.62	1.73	0.20	7.78	3.20	0.117	0.235	0.117	0.018	94.8	0.35	0.13
S	10	23.89	12.99	17.89	0.48	3.86	24.62	1.73	0.20	7.78	3.20	0.117	0.235	0.117	0.018	110.7	0.35	0.13
S	11	23.89	12.99	17.89	0.48	3.86	24.62	1.73	0.20	7.78	3.20	0.117	0.235	0.117	0.018	119.7	0.35	0.13
S	12	23.89	12.99	17.89	0.48	3.86	24.62	1.73	0.20	7.78	3.20	0.117	0.235	0.117	0.018	97.5	0.35	0.13
A	1	9.07	41.28	8.38	0.72	12.05	27.56	2.60	6.67	41.94	18.78	8.340	5.703	1.368	0.117	221.3	0.09	0.63
A	2	9.07	41.28	8.38	0.72	12.05	27.56	2.60	6.67	41.94	18.78	8.340	5.703	1.368	0.117	217.2	0.09	0.63
A	3	9.07	41.28	8.38	0.72	12.05	27.56	2.60	6.67	41.94	18.78	8.340	5.703	1.368	0.117	217.2	0.09	0.63
A	4	9.07	41.28	8.38	0.72	12.05	27.56	2.60	6.67	41.94	18.78	8.340	5.703	1.368	0.117	217.2	0.09	0.63
B	1	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	78.9	0.28	0.12
B	2	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	78.9	0.28	0.12
B	3	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	79.8	0.28	0.12
B	4	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	97.1	0.28	0.12
B	5	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	77.6	0.28	0.12
B	6	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	74.8	0.28	0.12
B	7	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	66.7	0.28	0.12
B	8	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	60.3	0.28	0.12
B	14	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	72.1	0.28	0.12
B	15	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	79.8	0.28	0.12
B	16	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	87.5	0.28	0.12
B	17	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	78.5	0.28	0.12

continued . . .

TABLE 6 (cont.)

Coal	Test	HHV, MJ/kg	VM, g/MJ	FC, g/MJ	N, g/MJ	O, g/MJ	C, g/MJ	H, g/MJ	S, g/MJ	Ash, g/MJ	H ₂ O, g/MJ	CaO, g/MJ	Fe ₂ O ₃ , g/MJ	MgO, g/MJ	NaO, g/MJ	Coal, kg/hr	Nc, g/MJ	Nv, g/MJ
B	18	30.87	11.37	17.42	0.40	1.89	24.09	1.63	0.78	2.67	0.93	0.151	0.444	0.031	0.019	85.3	0.28	0.12
T	1	20.12	16.52	17.20	0.31	6.69	24.78	1.76	0.15	2.28	13.70	0.557	0.146	0.180	0.011	113.4	0.18	0.13
T	2	20.12	16.52	17.20	0.31	6.69	24.78	1.76	0.15	2.28	13.70	0.557	0.146	0.180	0.011	123.8	0.18	0.13
T	3	20.12	16.52	17.20	0.31	6.69	24.78	1.76	0.15	2.28	13.70	0.557	0.146	0.180	0.011	136.5	0.18	0.13
T	4	20.12	16.52	17.20	0.31	6.69	24.78	1.76	0.15	2.28	13.70	0.557	0.146	0.180	0.011	142.9	0.18	0.13
T	7	20.12	16.52	17.20	0.31	6.69	24.78	1.76	0.15	2.28	13.70	0.557	0.146	0.180	0.011	103.9	0.18	0.13
T	8	20.12	16.52	17.20	0.31	6.69	24.78	1.76	0.15	2.28	13.70	0.557	0.146	0.180	0.011	111.6	0.18	0.13
T	9	20.12	16.52	17.20	0.31	6.69	24.78	1.76	0.15	2.28	13.70	0.557	0.146	0.180	0.011	123.4	0.18	0.13
P	1	19.70	16.55	16.77	0.34	6.31	24.80	1.70	0.19	2.28	15.17	0.550	0.125	0.161	0.027	107.0	0.23	0.11
P	2	19.70	16.55	16.77	0.34	6.31	24.80	1.70	0.19	2.28	15.17	0.550	0.125	0.161	0.027	122.0	0.23	0.11
P	3	19.70	16.55	16.77	0.34	6.31	24.80	1.70	0.19	2.28	15.17	0.550	0.125	0.161	0.027	116.6	0.23	0.11
P	5	19.70	16.55	16.77	0.34	6.31	24.80	1.70	0.19	2.28	15.17	0.550	0.125	0.161	0.027	113.8	0.23	0.11
N	1	30.15	10.94	17.37	0.46	1.70	24.44	1.54	0.18	4.11	0.71	0.353	0.262	0.082	0.032	81.6	0.29	0.17
N	2	30.15	10.94	17.37	0.46	1.70	24.44	1.54	0.18	4.11	0.71	0.353	0.262	0.082	0.032	80.7	0.29	0.17
N	3	30.15	10.94	17.37	0.46	1.70	24.44	1.54	0.18	4.11	0.71	0.353	0.262	0.082	0.032	78.0	0.29	0.17
N	5	30.15	10.94	17.37	0.46	1.70	24.44	1.54	0.18	4.11	0.71	0.353	0.262	0.082	0.032	83.4	0.29	0.17
D	1	34.28	3.91	23.80	0.40	0.33	24.26	0.93	1.90	1.03	0.44	0.020	0.141	0.013	0.002	87.1	0.33	0.07
D	2	34.28	3.91	23.80	0.40	0.33	24.26	0.93	1.90	1.03	0.44	0.020	0.141	0.013	0.002	93.0	0.33	0.07
D	3	34.28	3.91	23.80	0.40	0.33	24.26	0.93	1.90	1.03	0.44	0.020	0.141	0.013	0.002	87.1	0.33	0.07
D	4	34.28	3.91	23.80	0.40	0.33	24.26	0.93	1.90	1.03	0.44	0.020	0.141	0.013	0.002	73.0	0.33	0.07
D	5	34.28	3.91	23.80	0.40	0.33	24.26	0.93	1.90	1.03	0.44	0.020	0.141	0.013	0.002	70.7	0.33	0.07
D	6	34.28	3.91	23.80	0.40	0.33	24.26	0.93	1.90	1.03	0.44	0.020	0.141	0.013	0.002	66.7	0.33	0.07
F	0	33.99	2.79	26.20	0.49	0.16	26.96	0.48	0.91	0.18	0.25	0.020	0.010	0.007	0.001	73.0	0.49	0.00
F	1	33.99	2.79	26.20	0.49	0.16	26.96	0.48	0.91	0.18	0.25	0.020	0.010	0.007	0.001	72.6	0.49	0.00
F	4	33.99	2.79	26.20	0.49	0.16	26.96	0.48	0.91	0.18	0.25	0.020	0.010	0.007	0.001	71.7	0.49	0.00

7.2 Modeling Assumptions and Techniques

The effects of CFBC operating parameters on N_2O emissions that were documented in Section 4 of this report lend insight into the basic form of the model. As a result of this work, and the general consensus of the available literature addressing N_2O emissions, the following assertions and assumptions have been made for the development of a model to predict N_2O emissions:

- 1) Increasing temperature decreases N_2O emissions.
- 2) Increasing excess air increases N_2O emissions.
- 3) Increasing limestone feed rate decreases N_2O emissions.
- 4) The effect of excess air on N_2O emissions is enhanced at lower combustor temperatures.
- 5) Fuel type dictates the magnitude of N_2O emissions.
- 6) Fuel type effects the slope in the temperature versus N_2O emissions curve.
- 7) Fuel type may affect the slope of the excess air versus N_2O emissions curve.
- 8) Other parameters, including combustor gas velocity and air staging, have a minimal (nonsignificant) impact on N_2O emissions over the experimental ranges used in this study.

Based upon these assumptions, the form of the model must contain, at a minimum, the following parameters using a linear regression modeling procedure:

$$N_2O = a + (-b)(T) + (c)(EA) + (-d)(LF) + (-e)(T \times EA) + (f)(FT) + (g)(T \times FT) \quad [\text{Eq. 8}]$$

where,

N_2O = concentration of N_2O in exiting flue gas, mg/MJ

T = temperature, K

EA = excess air, %

LF = limestone feed, g limestone/MJ

FT = fuel type, dimensionless

and,

a = intercept, mg N_2O /MJ

b = slope, (mg N_2O / MJ) / T

c = slope, (mg N_2O / MJ) / EA

d = slope, (mg N_2O / MJ) / LF

e = slope, (mg N_2O / MJ) / ($T \times EA$)

f = slope, (mg N_2O / MJ) / (FT)

g = slope, (mg N_2O / MJ) / ($T \times FT$)

are the coefficients determined for the model that minimize the error for the prediction of N_2O . Additionally, the term $(h)(EA \times FT)$ could be added to the equation, based upon the weak relation indicated in Item 7 listed above.

Since the fuel type defined in this equation is actually a discrete variable with quantitized levels, an additional function must be defined to transform this quantity into a continuous variable of the form:

$$FT(C1, C2, C3, C4) = a' (C1) + b' (C2) + c' (C3) + d' (C4) \quad [Eq. 9]$$

where:

$FT(C1, C2, \dots, Cn) = \text{flux of fuel components (Cn) into combustor, g Cn / MJ}$

$a' = \text{slope, FT / (g C1 / MJ)}$

$b' = \text{slope, FT / (g C2 / MJ)}$

$c' = \text{slope, FT / (g C3 / MJ)}$

$d' = \text{slope, FT / (g C4 / MJ)}$

Equation 9 implies that all coal properties used to model the fuel type (FT) must be present in each of the terms represented in Equation 8 if the initial assumptions (1-8) are correct. Even if this were true, it is still possible for the coefficients of individual coal property terms to approach zero, or a term to become insignificant (such as higher order interactions), in which case certain coal properties associated with that term would be rejected. In any case, Equation 9 is an arbitrary linear function chosen for simplicity. This decision is based on the probability that the combined errors of experimentation exceed the gains derived from more complex relations. Specialized functions would be warranted if fundamental guiding theory were used to form those relations.

To further justify the use of simple relations, we see from Table 6 that there are 16 fuel properties used as input variables. Each of these fuel properties is also combined with interactions with temperature and excess air to form 32 additional variables (see Equation 8). Higher-order interactions, quadratic terms, and interactions with other operating parameters were neglected. Interaction terms between all operating parameters were considered in the model selection, and in total, approximately 64 variables were used for model inputs.

7.3 Coding of Variables and Model Range

Before any statistical analysis of the data were performed, the variable inputs were coded to normalize the data to values between -1 and $+1$. This is done for two reasons, 1) to minimize correlations between variables, and 2) to place the magnitude of the parameter estimates (coefficients in model) on the same basis. The latter reason allows one to assess the contribution of a given variable to the entire model. The coding equation is given by:

$$X_c = \frac{X - (X_{\max} + X_{\min})/2}{(X_{\max} - X_{\min})/2} \quad [Eq. 10]$$

where:

X_c is the coded value of variable X

X is the variable quantity to be coded

X_{max} is the maximum value of variable X
 X_{min} is the minimum value of variable X

Table 7 presents the minimum and maximum values of each variable used to calculate the coded-variable equation parameters. The values in the table also indicate the usable range of variable inputs that the model describes. Extrapolation beyond these limits could provide erroneous results. It is noteworthy to mention that the coding procedure provides for a model limit check, since values outside of the range -1 to $+1$ will in most cases violate the model limits.

TABLE 7
Variable Symbols and Limits Used for Coding

Variable	Symbol	X_{min}	X_{max}
Operating Parameters			
Excess Air, %	EA	9	95
Comb. Temperature, K	T	1019	1199
Comb. Velocity, m/s	VEL	3.96	5.91
Primary Air, %	PA	47	70
Heating Value, MJ/kg	HHV	9.07	34.28
Limestone Feed, g/MJ	LF	0	33.4
SO ₂ , ppmv (3% O ₂)	SO ₂	4	4770
Coal Properties, g/MJ			
Volatile Matter	VM	2.79	41.28
Fixed Carbon	FC	8.38	26.2
Nitrogen	N	0.31	0.72
Oxygen	O	0.16	12.05
Carbon	C	24.09	27.56
Hydrogen	H	0.48	2.60
Sulfur	S	0.15	6.67
Ash	ASH	0.18	41.94
Moisture	H ₂ O	0.25	22.75
CaO	CaO	0.020	8.34
Fe ₂ O ₃	Fe ₂ O ₃	0.010	5.70
MgO	MgO	0.007	1.37
NaO	NaO	0.001	0.117
Nitrogen (char)	Nc	0.087	0.490
Nitrogen (VM)	Nv	0.000	0.633

7.4 Model Selection

The number of variables used in the model were systematically reduced using the REG multiple linear regression procedure from the SASTM statistical software library. The most significant variables were identified using Stepwise, Forward, and Maxr model selection procedures. Fuel variables were grouped with their temperature interaction terms to force both variables into the model simultaneously. In this way, the most promising fuel properties were separated from nonsignificant terms, and the model was formulated to match Equation 8. The reduced set of variables were examined using the Minr and Rsquare model selection procedures, the latter of which provides all possible subsets of these variables based on the criteria of maximizing the correlation coefficient. Further reduction in variables were made, based on statistical analysis and the following criteria:

- 1) The probability of significance of individual parameters in the model (T-statistic) was greater than or equal to the 95% confidence level.
- 2) The sign of the parameter estimates (slope coefficients) was in relation to the observed trends for temperature, excess air, and limestone feed rate.
- 3) The terms in Equation 8 were represented in the model. Interactions of fuel properties with excess air were optional.
- 4) A maximum of four different fuel properties would be allowed in the model.

The last criteria is an arbitrary designation based on the number of fuels in the database. Since the composition of the fuels cannot be properly statistically designed, it is difficult to determine the actual degrees of freedom allowed for modeling the fuels. Expansion of the limits to six coal properties did not appreciably improve the quality of the prediction for N_2O emissions.

7.5 Modeling Results

Initial modeling efforts showed that the limestone feed rate (LF) was not a significant operating parameter. This was disconcerting since the qualitative assessment of decreasing N_2O emissions with increasing limestone feed rate had been noted by many researchers. In actuality, the effect of limestone feed on N_2O is significant for coals of similar heating values and coal-S concentrations. This is due to the fact that coals of similar coal-S levels will require equivalent sorbent feed rates to capture sulfur. If, for example, an equivalent limestone feed rate from a high-sulfur coal were used firing a low-sulfur coal, a large excess of unreacted sorbent would accumulate in the CFBC. Since CaO is catalytically active for N_2O destruction, and not $CaSO_4$, N_2O destruction would be greater with the low-sulfur coal.

A possible solution to modeling the effect of the limestone feed on N_2O emissions is to quantify the level of free CaO available for reacting with N_2O . Amand et al. (20) demonstrated the influence of the SO_2 concentration in the flue gas on homogeneous NO/N_2O chemistry, as well as the dependence of heterogeneous N_2O destruction on available CaO surface. In CFBC experiments, they found that an increase in N_2O emissions would occur by artificially increasing SO_2 concentration in the flue gas. This

effect could be seen with or without limestone feed. In addition, as the SO_2 concentration approached zero, the accumulating CaO in the bed was shown to reduce N_2O emissions linearly. This latter result has also been seen in work performed at EERC using a bubbling FBC.

As a result of these observations, the SO_2 concentration in the flue gas was substituted for the limestone feed rate as a main operating parameter for modeling. Unlike the limestone feed, the SO_2 concentration was shown to be a significant modeling variable, displaying trends consistent with those previously referenced. The reason for the improved correlation is probably the result of the SO_2 concentration reflecting the level of sulfation of the sorbent. This can be rationalized by the fact that as sulfur concentrations in the coal decrease, less sorbent is required for a given level of SO_2 capture, but the utilization of available sorbent tends to decrease. The overall effect is to produce greater quantities of free CaO surface as the absolute SO_2 concentration approaches zero, regardless of initial coal-S levels. Also, as the CFBC temperature increases above ~ 1100 K, an increase in SO_2 will generally occur for all coal ranks as a result of reduced utilization by the sorbent. A subsequent increase in the sorbent feed is required to attain the original SO_2 capture, adding to the free CaO surface. In this way, the absolute SO_2 concentration tends to mirror the effects of the sorbent rather than quantifying the sorbent flux. In any case, the SO_2 concentration in the flue gas serves as a parameter for predicting N_2O emissions by directly or indirectly modeling the interaction between the sorbent and sulfur.

The best four-fuel-parameter model for predicting N_2O emissions ($\text{mg N}_2\text{O/MJ}$) is shown in Table 8. The parameter estimates (coefficients) for the model and the associated T-statistics are presented in the table. The parameter estimates in this model are scaled for use with coded-variable inputs to obtain the proper prediction of N_2O emissions. The magnitude of the coefficients have to be interpreted with respect to the range of each individual parameter (Table 7). Based upon the magnitude of the parameter estimates, it can be seen that temperature has a greater effect than either excess air or limestone (SO_2), which is consistent with the previously reported trends. Likewise, the main effects of the fuel parameters were ranked in this order: $\text{N} > \text{CaO} > \text{O} > \text{H}_2\text{O}$. The fuel property, oxygen, was expressed as an interaction with temperature, with no main effect entered into the model. At this time it is not known if these fuel properties can be interpreted for prospective mechanisms. It is possible that these fuel properties are indirect measurements of related parameters such as coal rank or hybrids between direct fuel effects and indirect measures of the physical processes occurring in the CFBC.

Complete statistical analyses of N_2O emissions models structured with four, three, and two fuel properties entered into the equation are presented in Tables A-1–A-9 in Appendix A. In addition, N_2O emissions are presented, using three different bases (mg/MJ , ppmv , and $\%\text{conversion of fuel-N}$). In all of these models, the operating parameters indicated in Equation 8 are forced into the equation, with fuel properties selected according to best fit. It should be noted that for all models, coded-variable inputs must be used in the equations. The coded equations can be determined by substituting the values in Table 7 into Equation 10 for the respective variable.

TABLE 8

Statistical Analysis of Parameters used in N₂O (mg/MJ) Prediction Model

Variable	DF	Parameter Estimate	Standard Error	T for H ₀ : Parameter = 0	Prob > T
INTERCEPT	1	77.7	5.34	14.6	0.0001
T	1	-94.8	6.85	-13.8	0.0001
EA	1	27.8	7.99	3.48	0.0011
SO ₂	1	31.6	4.97	6.37	0.0001
T x EA	1	-54.8	10.5	-5.19	0.0001
EA x LF	1	-27.4	5.12	-5.34	0.0001
H ₂ O	1	-8.67	2.89	-3.00	0.0043
N	1	119.1	8.15	14.6	0.0001
T x N	1	-36.9	5.61	-6.58	0.0001
EA x N	1	50.6	10.2	4.99	0.0001
CaO	1	-105.6	7.66	13.8	0.0001
T x O	1	49.0	4.96	9.88	0.0001

Figures 15-17 show the actual N₂O emissions versus the predicted N₂O emissions, for three different bases of N₂O measurement. The models in these figures used four coal properties to describe the fuel interaction with the operating parameters. In each of the figures, data from 57 combustion tests are plotted, with each fuel type being designated by the letter symbols used in Tables 4-6. The r-square statistics for the predicted values show that the models reasonably characterize the data set within experimental error. The respective errors of the prediction for the three models indicated in Figures 15-17 are ± 7 mg N₂O/MJ, 12 ppmv N₂O, and 1% conversion of fuel-N.

As described in Section 4, the effect of the fuel-temperature interaction on N₂O emissions is the most prominent among the operating parameters, and is therefore the critical parameter to model accurately. To better visualize the model capabilities, the actual and predicted values of N₂O emissions for the temperature versus N₂O data are shown in Figures 18 and 19, respectively. Figure 18 is similar to Figure 3, with the addition of two petroleum cokes to the database. The predicted values presented in Figure 19 show good agreement with the magnitude of the actual data, and especially with regard to depicting the trends and slopes for the given fuels. The major weakness to the model appears to be that with the Powder River Basin coals (P and T). With these coals the temperature dependence is accurately predicted, but the magnitude of the Black Thunder coal (T) is over predicted while the Powder River coal is slightly under predicted. The reason for this is unclear, but may be a result of experimental error or insufficient representation by the fuel properties selected in the model.

Figure 15. Actual versus predicted N_2O emissions (mg/MJ) using four fuel parameters: N, CaO, O, H_2O .

Figure 16. Actual versus predicted N_2O emissions (ppmv) using four fuel parameters: N, CaO, O, H_2O .

Figure 17. Actual versus predicted N₂O emissions (conversions of fuel-N) using four fuel parameters: N, CaO, O, H₂O.

Figure 18. Temperature versus actual N₂O emissions (mg N₂O/MJ) for CFBC combustion tests. L = Center Lignite, S = Salt Creek, A = Asian, B = Blacksville, T = Black Thunder, P = Powder River, N = New Mexico, D = delayed coke, and F = fluid coke.

Figure 19. Temperature versus predicted N_2O emissions (mg/MJ) for CFBC combustion tests. L = Center Lignite, S = Salt Creek, A = Asian, B = Blacksville, T = Black Thunder, P = Powder River, N = New Mexico, D = delayed coke, and F = fluid coke.

Figures 20-23 present actual versus predicted N_2O emissions on a mg N_2O /MJ basis for models using respectively three, two, one, and no fuel properties in the equation. The figures show the degradation of the models for predicting N_2O emissions as the number of fuel properties is reduced. The three-fuel parameter model is interesting, in that the overall quality of the model is not greatly reduced, only a slight change in the temperature dependence with the Center lignite coal. In addition, the fuel property that is removed from the four-parameter model to make the three-fuel parameter model is the H_2O term. The term had the smallest coefficient in the model and consequently had the least impact on the overall model when removed. Figures 21-23 clearly show that models using less than three fuel properties to simulate the fuel type create too much uncertainty in the prediction of N_2O emissions.

8.0 ABATEMENT STRATEGIES

Data presented in this report show that the operating parameters can have a significant effect on N_2O emissions and that the fuel specification controls the absolute magnitude of the emissions when the combustor is operated under similar conditions. In order to assess the relative contribution of individual operating parameters and fuel type on N_2O emissions, a comparison was made among these factors when firing Salt Creek bituminous coal. Since the operating parameters have been shown to interact with the fuel, this quantitative analysis cannot be extended to include other coals. Table 9 shows the effect of changing parameters relative to a reference nominal base condition of 40% excess air, 1116 K combustor temperature, 50% primary air split, and 63% sulfur retention by coal ash and sorbent (1.85-g sorbent/MJ). As seen in Table 9, when based upon a unit change in the respective parameter ($\Delta N_2O/\Delta \text{parameter}$), sorbent feed will

Figure 20. Actual versus predicted N_2O emissions (mg N_2O /MJ) using three fuel parameters: N, CaO, O.

Figure 21. Actual versus predicted N_2O emissions (mg N_2O /MJ) using two fuel parameters: N, CaO.

Figure 22. Actual versus predicted N₂O emissions (mg N₂O/MJ) using one fuel parameter: Nc.

Figure 23. Actual versus predicted N₂O emissions (mg N₂O/MJ) using no fuel parameters.

TABLE 9

Effect of CFBC Operating Parameters Firing Salt Creek Coal

Operating Parameters	Nominal Base	Change in Excess Air	Change in Sorbent Feed	Change in Primary Air	Change in Temperature	Change of Coal
Temperature, K	1116	1116	1116	1116	1172	1116
Excess Air, %	40	20	20	20	20	20
Primary Air Ratio, %	50	50	50	67	50	50
Limestone Feed, g/MJ	1.85	1.67	2.08	1.65	1.67	1.39
N ₂ O Emissions, mg/MJ	110	104	102	98	60	16
ΔN_2O , mg/MJ	0	-6	-2	-6	-44	-88
Δ Parameter	0	20%	0.41 g/MJ	17%	56 K	---
$\Delta N_2O/\Delta$ Parameter	---	-0.30	-4.88	-0.24	-0.75	---

produce the greatest change in N₂O emissions, followed by temperature, excess air, and primary air. If switching to a Powder River subbituminous coal were a viable option, N₂O emissions could be reduced by 85% relative to firing Salt Creek coal under similar operating conditions.

In actual CFBC operation, the order of importance of the operating parameters affecting N₂O emissions may vary due to practical design limitations and operating costs. For example, the reduction of excess air will result in lower N₂O emissions, but a practical lower limit exists for which combustion efficiency will be affected. Likewise, increasing excess air beyond 40% becomes prohibitively expensive for operation. For this reason, the impacts of the operating parameters and fuel type are best correlated by the net change in N₂O emissions (ΔN_2O , mg/MJ in Table 9) for reasonable changes in operating conditions. A 45% reduction was realized using operating parameters as a control strategy, and another 40% reduction was achieved by switching fuels. Total N₂O emissions were reduced from 110 mg/MJ to 16 mg/MJ. The operating ranges depicted in Table 9 are subjective and must be interpreted from this perspective. Based on the values presented in Table 9, the relative order of importance is as follows: temperature > excess air/primary air split > sorbent feed rate for Salt Creek coal.

The abatement approach discussed above combines two different strategies:

- 1) minimization of N₂O emissions through improvements in operating conditions and
- 2) sacrificing emissions on one or more pollutants (NO_x and SO₂) for the sake of low emissions of the other (N₂O), combined with adopting special measures to reduce excessive levels of the selected pollutant. Another way to apply this approach would be to minimize SO₂ and NO_x emissions by applying current FBC technology. This would produce high levels of N₂O. The N₂O must then be destroyed, using either high temperatures in the

freeboard of the cyclone or by some catalytic additive. The use of gas reburning has been suggested by other researchers (1, 5). It was demonstrated that a 40% reduction in N_2O could be realized by burning natural gas in an amount equivalent to 10% of the total energy input. No detrimental effects were seen on NO_x , and CO emissions were reduced. The impact on SO_2 emissions was not investigated in the gas reburn study.

To date, little work has been done looking at catalytic additives. This type of additive could be used either in the combustion system itself or as a postcombustion technique. The EERC proposes to investigate both types of catalysts in a future research program.

9.0 CONCLUSIONS

Considerable information was obtained from studies conducted to determine the effect of FBC operating parameters on N_2O emissions. The data, documented in Section 4, indicated that the influential parameters, including combustor operating temperature, excess air, and limestone feed rate can be used to control N_2O emissions. The manipulation of operating parameters as a method for N_2O reduction was quantified for a Salt Creek bituminous coal in Section 8. This information suggested a potential CFBC design strategy consisting of a combustor optimized for operation at low excess air (15%) and higher temperatures (1175 K). The optimization of this system would be fuel-specific, with allowances made for increases in NO_x and SO_2 emissions that accompany increases in temperature. The complete destruction of N_2O probably would not occur until a temperature of 1225 K is reached in the combustor.

The usefulness of applying these controls is highly dependent on fuel selection, but more importantly on potential regulation requirements. If, for example, reductions in N_2O emissions by only 20% are required for a specific fuel, then the most economical approach may be to change operating parameters to effect this change. If greater control is required, then significantly more research is required to develop abatement strategies.

The insight gained from pilot-scale CFBC experiments led to the successful development of a global model describing the response of a CFB (N_2O emissions) to changes in the operating parameters. The models developed from this database depict several of the best-fits based on the criteria used to define the form of the equation. If the database is further expanded, any bias obtained in the model by intentionally maximizing the fit parameters (r-square) will decrease and the "true" variable parameters will surface. This does not imply that these models are wrong, but that more information may be required to obtain the complete picture. In any case, the models offered are first generation, and further refinement or use of other approaches to a model solution would be encouraged.

10.0 PUBLICATIONS AND PRESENTATIONS

During this research program, the following papers have been submitted and/or presented.

Mann, M.C.; Collings, M.E. "Mini-Workshop on N₂O Emissions from FBCs," presented at Morgantown Energy Technology Center, May 20, 1991.

Collings, M.E.; Weber, G.F.; Mann, M.D. "N₂O Measurement in Coal-Fired Flue Gas," presented at the Seventh Annual Coal Preparation, Utilization, and Environmental Control Contractors' Conference, Pittsburgh, PA, July 15-18, 1991.

Mann, M.D.; Collings, M.E.; Botros, P.E. "Effect of Operating Parameters on N₂O Emissions in a 1-MW CFBC," presented at the Eighth Annual International Pittsburgh Coal Conference, Oct. 14-18, 1991.

Mann, M.D.; Collings, M.E.; Botros, P.E. "Nitrous Oxide Emissions in Fluidized-Bed Combustion: Fundamental Chemistry and Combustion Testing," *Progress in Energy and Combustion Sciences* **1992**, *18*, 447-461.

Collings, M.E.; Mann, M.D.; Young, B.C. "Nitrous Oxide Emissions in the Fluidized-Bed Combustion of Coal," presented at the 1992 Spring Meeting of the Western States Section of the Combustion Institute, March 23-24, 1992.

Mann, M.D.; Collings, M.E. "Mini-workshop on Nitrous Oxide Emissions from Fluidized-Bed Combustion," presented at Morgantown Energy Technology Center, April 2, 1992.

Young, B.C.; Collings, M.E.; Mann, M.D. "Pilot-Scale Studies on N₂O Emissions, Coal Properties, and Conditions in a Circulating Fluidized-Bed Combustor," presented at the Fifth International Workshop on Nitrous Oxide Emissions, Tsukuba, Japan, July 1992.

Mann, M.D.; Collings, M.E.; Young, B.C.; Botros, P.E. "Predicting N₂O Emissions from Circulating Fluidized-Bed Coal Combustion," presented at the Ninth Annual Pittsburgh Coal Conference, Pittsburgh, PA, Oct. 1992 (Best Poster Paper Award).

Mann, M.D.; Collings, M.E.; Young, B.C. "Nitrous Oxide Emissions," presented at the METC Coal-Fired Heat Engines, PFBC, and Gas Stream Cleanup Systems Contractors' Review Meeting, Morgantown, WV, Oct. 1992.

Collings, M.E.; Mann, M.D.; Young, B.C.; Botros, P.E. "The Effect of Coal-Fuel Properties on N₂O Emissions in Fluidized-Bed Combustion," presented at the Twelfth International FBC Conference, May 1993 (Best Paper in Category Award).

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Young, B.C.; Collings, M.E.; Mann, M.D. "Formation and Destruction of N₂O in Fluidized-Bed Combustion," to be presented at the Seventh International Conference on Coal Science, Banff, Alberta, Canada, Sept. 1993.

Young, B.C.; Mann, M.D.; Collings, M.E. "Formation of NO_x and N₂O in the Fluidized-Bed Combustion of High- and Low-Rank Coals," to be presented at the Fifth International Conference on Processing and Utilization of High-Sulfur Coals, Lexington, KY, Oct. 1993.

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APPENDIX A

**PARAMETER ESTIMATES
FOR PREDICTING
N₂O EMISSIONS**

TABLE A-1

Predicting N₂O Emissions on a mg/MJ Basis Using Four Fuel Properties

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	11	103803.91812	9436.71983	219.233	0.0001
Error	46	1980.03733	43.04429		
C Total	57	105783.95545			
Root MSE		6.56081	R-square	0.9813	
Dep Mean		64.79517	Adj R-sq	0.9768	
C.V.		10.12547			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEPT	1	77.683914	5.33927097	14.550	0.0001
T	1	-94.829986	6.85354449	-13.837	0.0001
EA	1	27.839639	7.99102408	3.484	0.0011
SO2	1	31.646035	4.96928515	6.368	0.0001
T x EA	1	-54.789047	10.54890876	-5.194	0.0001
EA x LF	1	-27.377135	5.12300882	-5.344	0.0001
N	1	119.142319	8.15135028	14.616	0.0001
T x N	1	-36.928384	5.61149582	-6.581	0.0001
EA x N	1	50.644717	10.15016967	4.990	0.0001
H2O	1	-8.672278	2.88798826	-3.003	0.0043
CAO	1	-105.598418	7.65766533	-13.790	0.0001
T x O	1	49.002408	4.96199007	9.876	0.0001

TABLE A-2

Predicting N₂O Emissions on a ppmv (3% O₂) Basis Using Four Fuel Properties

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	11	320525.96738	29138.72431	219.688	0.0001
Error	46	6101.28865	132.63671		
C Total	57	326627.25603			
Root MSE	11.51680	R-square	0.9813		
Dep Mean	115.71552	Adj R-sq	0.9769		
C.V.	9.95269				

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEPT	1	142.279550	9.37251316	15.181	0.0001
T	1	-168.750024	12.03065667	-14.027	0.0001
EA	1	55.197415	14.02737916	3.935	0.0003
SO2	1	53.613530	8.72304304	6.146	0.0001
T x EA	1	-98.999883	18.51746928	-5.346	0.0001
EA x LF	1	-45.540031	8.99288833	-5.064	0.0001
N	1	209.825972	14.30881448	14.664	0.0001
T x N	1	-64.558568	9.85037447	-6.554	0.0001
EA x N	1	92.936416	17.81752589	5.216	0.0001
H2O	1	-17.006473	5.06955128	-3.355	0.0016
CAO	1	-180.162424	13.44220391	-13.403	0.0001
T x O	1	84.094630	8.71023731	9.655	0.0001

TABLE A-3

Predicting N₂O Emissions on a Conversion of Fuel-N Basis Using Four Fuel Properties

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	11	1699.42227	154.49293	175.800	0.0001
Error	46	40.42472	0.87880		
C Total	57	1739.84699			
Root MSE		0.93744	R-square	0.9768	
Dep Mean		9.32397	Adj R-sq	0.9712	
C.V.		10.05412			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEPT	1	10.493092	0.76290203	13.754	0.0001
T	1	-13.637797	0.97926909	-13.927	0.0001
EA	1	3.205025	1.14179792	2.807	0.0073
SO2	1	4.392187	0.71003659	6.186	0.0001
T x EA	1	-8.998051	1.50728142	-5.970	0.0001
EA x LF	1	-4.041453	0.73200140	-5.521	0.0001
N	1	12.875249	1.16470614	11.055	0.0001
T x N	1	-3.353714	0.80179890	-4.183	0.0001
EA x N	1	6.042164	1.45030756	4.166	0.0001
H2O	1	-1.621243	0.41265036	-3.929	0.0003
CAO	1	-13.059842	1.09416594	-11.936	0.0001
T x O	1	5.925355	0.70899423	8.357	0.0001

TABLE A-4

Predicting N₂O Emissions on a mg/MJ Basis Using Three Fuel Properties

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	10	103415.77575	10341.57757	205.244	0.0001
Error	47	2368.17970	50.38680		
C Total	57	105783.95545			
Root MSE		7.09837	R-square	0.9776	
Dep Mean		64.79517	Adj R-sq	0.9728	
C.V.		10.95508			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEPT	1	75.936785	5.74233690	13.224	0.0001
T	1	-91.619316	7.32429030	-12.509	0.0001
EA	1	24.284022	8.55031870	2.840	0.0066
SO2	1	38.166182	4.83604428	7.892	0.0001
T x EA	1	-49.574903	11.25754187	-4.404	0.0001
EA x LF	1	-34.634925	4.88713134	-7.087	0.0001
N	1	134.177874	6.95928005	19.280	0.0001
T x N	1	-36.098077	6.06389118	-5.953	0.0001
EA x N	1	57.629036	10.68960574	5.391	0.0001
CAO	1	-125.343505	4.24638342	-29.518	0.0001
T x O	1	46.759988	5.30740005	8.810	0.0001

TABLE A-5

Predicting N₂O Emissions on a ppmv (3% O₂) Basis Using Three Fuel Properties

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	10	319033.33378	31903.33338	197.455	0.0001
Error	47	7593.92226	161.57281		
C Total	57	326627.25603			
Root MSE	12.71113	R-square	0.9768		
Dep Mean	115.71552	Adj R-sq	0.9718		
C.V.	10.98481				

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEPT	1	138.853402	10.28287164	13.503	0.0001
T	1	-162.453849	13.11569460	-12.386	0.0001
EA	1	48.224795	15.31115838	3.150	0.0028
SO2	1	66.399642	8.65996258	7.667	0.0001
T x EA	1	-88.774866	20.15901542	-4.404	0.0001
EA x LF	1	-59.772672	8.75144478	-6.830	0.0001
N	1	239.310932	12.46206636	19.203	0.0001
T x N	1	-62.930323	10.85868277	-5.795	0.0001
EA x N	1	106.632775	19.14200537	5.571	0.0001
CAO	1	-218.882850	7.60404979	-28.785	0.0001
T x O	1	79.697209	9.50402501	8.386	0.0001

TABLE A-6

Predicting N₂O Emissions on a Conversion of Fuel-N Basis Using Three Fuel Properties

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	10	1685.85723	168.58572	146.760	0.0001
Error	47	53.98976	1.14872		
C Total	57	1739.84699			
Root MSE		1.07178	R-square	0.9690	
Dep Mean		9.32397	Adj R-sq	0.9624	
C.V.		11.49492			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEPT	1	10.166474	0.86703581	11.726	0.0001
T	1	-13.037577	1.10589505	-11.789	0.0001
EA	1	2.540319	1.29101315	1.968	0.0550
SO2	1	5.611099	0.73019463	7.684	0.0001
T x EA	1	-8.023291	1.69977695	-4.720	0.0001
EA x LF	1	-5.398264	0.73790827	-7.316	0.0001
N	1	15.686078	1.05078213	14.928	0.0001
T x N	1	-3.198492	0.91558731	-3.493	0.0011
EA x N	1	7.347851	1.61402424	4.553	0.0001
CAO	1	-16.751097	0.64116170	-26.126	0.0001
T x O	1	5.506145	0.80136466	6.871	0.0001

TABLE A-7

Predicting N₂O Emissions on a mg/MJ Basis Using Two Fuel Properties

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	6	97279.38053	16213.23009	97.227	0.0001
Error	51	8504.57492	166.75637		
C Total	57	105783.95545			
Root MSE	12.91342	R-square	0.9196		
Dep Mean	64.79517	Adj R-sq	0.9101		
C.V.	19.92960				

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEPT	1	77.406463	10.29974370	7.515	0.0001
T	1	-60.502747	4.66976271	-12.956	0.0001
EA	1	42.878503	14.61795212	2.933	0.0050
SO2	1	22.089729	8.14324564	2.713	0.0091
N	1	130.956225	12.45489312	10.514	0.0001
EA x N	1	44.717045	18.88271103	2.368	0.0217
CAO	1	-105.616249	6.38860068	-16.532	0.0001

TABLE A-8

Predicting N₂O Emissions on a ppmv (3% O₂) Basis Using Two Fuel Properties

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	6	300916.57555	50152.76259	99.484	0.0001
Error	51	25710.68048	504.13099		
C Total	57	326627.25603			
Root MSE		22.45286	R-square	0.9213	
Dep Mean		115.71552	Adj R-sq	0.9120	
C.V.		19.40350			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEPT	1	141.017020	17.90840460	7.874	0.0001
T	1	-106.447061	8.11942534	-13.110	0.0001
EA	1	79.892723	25.41657431	3.143	0.0028
SO ₂	1	38.588114	14.15885112	2.725	0.0088
N	1	233.240655	21.65561316	10.770	0.0001
EA x N	1	83.641693	32.83181009	2.548	0.0139
CAO	1	-184.993127	11.10800900	-16.654	0.0001

TABLE A-9

Predicting N₂O Emissions on a Conversion of Fuel-N Basis Using Two Fuel Properties

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	6	1579.15954	263.19326	83.534	0.0001
Error	51	160.68744	3.15073		
C Total	57	1739.84699			
Root MSE		1.77503	R-square	0.9076	
Dep Mean		9.32397	Adj R-sq	0.8968	
C.V.		19.03729			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > T
INTERCEPT	1	10.352582	1.41576471	7.312	0.0001
T	1	-8.485802	0.64188833	-13.220	0.0001
EA	1	5.196992	2.00932969	2.586	0.0126
SO2	1	3.160979	1.11934046	2.824	0.0068
N	1	14.925050	1.71200359	8.718	0.0001
EA x N	1	4.775612	2.59554769	1.840	0.0716
CAO	1	-13.731922	0.87815344	-15.637	0.0001

1. Program/Project Identification No. DE-FC21-88MC10637	2. Program/Project Title Nitrous Oxide Emissions (4.6)	3. Reporting Period 7-1-83 through 9-30-83
4. Name and Address Energy & Environmental Research Center University of North Dakota P.O. Box 9018, Grand Forks, ND 58202-9018 (701) 777-5000		5. Program/Project Start Date 7-1-80
		6. Completion Date 12-31-83

7. FY	8. Months or Quarters	1992												1993																																																											
92/93	Quarters	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN																																																												
9. Cost Status		a. Dollars Expressed in Thousands												b. Dollar Scale																																																											
10. Cost Chart																																																																									
Fund Source		Quarter				Cum. to Date	Total Plan																																																																		
		1st	2nd	3rd	4th																																																																				
DOE	P	86	73	73	72	304	304																																																																		
	A	86	12	79	18	304																																																																			
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	A																																																																								
	Total P	86	73	73	72	304	304																																																																		
	Total A	86	121	79	18	304																																																																			
	Variance	0	(48)	(6)	54	0																																																																			
		P = Planned A = Actual																																																																							
Total Planned Costs for Program/Project		<table border="1"> <tr> <td>Planned</td> <td></td><td></td><td>86</td><td></td><td></td><td>159</td><td></td><td></td><td>232</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>304</td> </tr> <tr> <td>Actual</td> <td></td><td></td><td>86</td><td></td><td></td><td>207</td><td></td><td></td><td>286</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>304</td> </tr> <tr> <td>Variance</td> <td></td><td></td><td>0</td><td></td><td></td><td>(48)</td><td></td><td></td><td>(54)</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>0</td> </tr> </table>																		Planned			86			159			232								304	Actual			86			207			286								304	Variance			0			(48)			(54)								0
Planned			86			159			232								304																																																								
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12. Remarks	
13. Signature of Recipient and Date	14. Signature of DOE Reviewing Representative and Date

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Nitrous Oxide Emissions (4.6)		3. Reporting Period 7-1-93 through 9-30-93	
4. Name and Address Energy & Environmental Research Center University of North Dakota P.O. Box 9018, Grand Forks, ND 58202-9018 (701) 777-5000				5. Program/Project Start Date 12-31-90	
				6. Completion Date 9-30-93	
Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
Task A	PFBC Testing				
A.1	Literature Survey	10-31-92	10-15-92		
A.2	Testing on Bench-Scale PFBR	4-15-93 ¹			
Task B	Impacts of Fuel Properties on N ₂ O				
B.1	Effect of Volatiles	11-30-92	2-27-93		
B.2	Effect of Char	12-31-92	2-27-93		
B.3	Effect of Coal Ash	2-28-93	3-31-93		
Task C	Impacts of Mode of Operation				
C.1	Repeat CFBC Tests on Bubbling Bed	4-30-93	3-15-93		
C.2	Quantify Effect of Mode of Operation	5-15-93	3-15-93		
Task D	Bench-Scale Testing				
D.1	Evaluation of Homogeneous vs. Heterogeneous Reactions	6-30-93	6-30-93		
Task E	Investigate Mitigating Measures				
E.1	Optimization of Operating Conditions	3-15-93	3-15-93		
E.2	Additives Testing	4-30-93	4-30-93		
E.3	Innovative Combustion Techniques	6-30-93	6-30-93		
Task F	Improve Global Empirical Model				
F.1	Update Global Empirical Model	6-30-93	6-30-93		
¹ Construction of the PFBR was delayed; therefore, it was not available for N ₂ O testing.					

DATE

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END