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Nitrous Oxide Emissions

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Nitrous Oxide Emissions

CONTRACT INFORMATION

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Period of Performance	July 1, 1990 - June 30, 1993

FY'92 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A	S
Pilot-Scale Testing													
Data Analysis													
Model Development													
Bench-Scale Testing													

OBJECTIVES

Information gathered during the initial phase of the project indicated that coal properties and operating temperatures probably have the greatest impact on the amount of N₂O formed during combustion. Other operating parameters are thought to have a minimal

impact on N₂O emissions. Many researchers have focused their approach on small, well-controlled bench reactors, and, as a result, a database is being established on the fundamentals of N₂O formation and destruction. Other researchers have been taking measurements from pilot- or full-scale systems. What appears to be lacking, however, is a good

bridge between the fundamental studies and what is occurring on the full-scale units.

The overall objective of this research is to take an integrated approach 1) to generate information necessary to develop a global engineering model for the prediction of N_2O emissions from fluidized-bed combustion, and 2) to develop abatement techniques.

BACKGROUND INFORMATION

The potential anthropogenic contribution of N_2O to global climate change has led to many recent studies of its emission from combustion systems using coal and allied materials. The concern over N_2O as a potential contributor to global climate change is due to its high strength as an infrared absorber, namely 200 times greater than that of carbon dioxide [1]. Current emphasis of investigation has shifted from conventional pulverized coal-fired boilers to advanced combustion technologies such as fluidized-bed combustors (FBCs), including circulating, bubbling, and pressurized systems. Typically, measured N_2O emissions from atmospheric FBCs can range from 40 to 200 ppm, depending on the coal properties and operational and design parameters. In contrast, pulverized coal-fired boilers emit very low levels (0-10 ppm) of N_2O .

The purpose of this paper is to report the effect of key operating parameters, the relative importance of coal type, and the potentially significant coal properties for producing N_2O emissions in an atmospheric circulating fluidized-bed combustor (CFBC) and pressurized bubbling fluidized-bed combustor (PFBC). The generation of N_2O emissions is quantified in an empirical model based on the experimental data.

PROJECT DESCRIPTION

Parametric testing has been undertaken at the Energy and Environmental Research Center (EERC) in a 1-MW_{th} pilot-scale CFBC. The test rig, having an internal diameter of 0.51 meters (20 inches) and a height of 12.8 meters (42 feet), contains a series of refractory-lined sections bolted together. Its operating conditions are a temperature range 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 (11.8 to 23 ft/s), and a coal size of -3.2 to -12.7 mm (120 to 35 mesh). The system is comprehensively described elsewhere [2]. Continuous in situ monitoring of O_2 , CO , CO_2 , SO_2 , NO_x , and N_2O was performed; in particular, N_2O was analyzed by a nondispersive infrared spectrometer (NDIR). A previously established [3] sampling protocol for N_2O analysis was used to minimize cross interferences from other gaseous species.

The Argonne National Laboratory PFBC consists of a refractory-lined carbon steel vessel with a nominal 15.2-cm inside diameter and can be operated at pressures up to 10 atm. Coal and dolomite are pneumatically fed from hoppers to the combustor with rotary feeders. The bed temperature is controlled by five hairpin-shaped, water-cooled, internal cooling loops. The flue gas from the combustor exits through a horizontal port located in the middle of the freeboard section and enters a primary hot cyclone. After being further cleaned of particulates by a secondary (cold) cyclone, the flue gas enters a metallic filter for a final knockdown of entrained ash fines and, finally, is vented.

Coals tested at the EERC include two lignites (one from Asia and one from North Dakota), one subbituminous coal (Black

Thunder), and two bituminous coals (Salt Creek and Blacksville). Data from ANL are presented from testing using bituminous coal (Kerr-McGee). The properties of the coals are listed in Table 1.

RESULTS

The coals were chosen from a wide range of geographical formations and ranks (Table 1). The partitioning of the coal nitrogen into the volatile matter and the char is also presented in Table 1. The char was produced at 1225 K using the standard ASTM proximate analysis technique for determining volatile matter. The significance of the distribution of nitrogen in the volatile matter and char is related to the reaction pathway in which fuel-bound nitrogen is converted to N_2O . The nonmatrix-bound nitrogen released with the volatile matter is free to react through homogeneous or heterogeneous reaction pathways to form nitrogen or nitrogen oxides (NO , NO_2 , N_2O). Matrix-bound char nitrogen will produce nitrogen oxides through heterogeneous oxidation reactions, but is believed to be a minor contributor to N_2O formation [4]. The char nitrogen can also devolatilize and react through gas-phase mechanisms.

Effects of Operating Parameters and Coal Type

The effects of operating parameters, namely, temperature, excess air, limestone feed rate, and primary-to-total-air ratio on the formation of N_2O are shown for CFBC operation in Figures 1 through 4, respectively. The pilot-scale results show appreciably different N_2O emissions for the five coals, as shown in Figure 1. The bituminous coals yielded the highest N_2O emissions and the Black Thunder subbituminous the lowest. The dependence of N_2O emission on temperature

was strongest for the highest-ranked Blacksville bituminous coal and weakest for the Black Thunder subbituminous coal. Two temperature trends intimately related to coal rank are that the absolute N_2O emissions from the higher-ranked coals are greater than from the lower-ranked coals, and that the temperature dependence (slope of temperature versus emissions curve) of a given coal rank is of the same magnitude. Figure 1 shows that the bituminous, lignite, and subbituminous coals have distinctly different slopes.

Figure 2 presents the effect of excess combustion air on N_2O emissions with four different coals. Increasing excess air in CFB combustion yielded an increase in N_2O emissions when burning all four coals. Excess air and temperature also interact in relation to N_2O emissions: the effect of excess air level is stronger at lower temperatures than at higher temperatures. As can be seen in Figure 2, the Salt Creek coal shows a much stronger dependence on excess air at 1074 K than at 1153 K. The illustrated data points for the other coals were obtained at approximately 1115 K.

The effect of limestone feed rate on N_2O emissions is shown in Figure 3. The general trend for four of the five coals is a slight decrease in emissions with increasing sorbent feed. The opposing trend displayed for the Black Thunder subbituminous coal may be related to the low coal-sulfur content or to the ash composition of this Powder River basin coal.

The effect of primary air-to-total-combustion-air ratio for Blacksville and Salt Creek coals is displayed in Figure 4. The primary air effect appears to interact with temperature. At higher temperatures (~ 1140 K), the N_2O emissions tend to decrease very slightly with increasing primary air split, while

Table 1.
Analysis of Coals Tested in EERC 1-MW_{th} CFBC

	Salt Creek HVC Bit.	Blacksville HVA Bit.	Black Thunder Subbit. C	Center, ND Lignite	Asian Lignite	Kerr-McGee HVB Bit.
Proximate Analysis (as-received %)						
Moisture	7.65	2.37	27.57	37.26	17.03	6.18
Volatile Matter, VM	31.04	36.40	33.23	28.76	37.40	35.24
Fixed Carbon, FC	42.74	52.86	34.60	28.85	7.60	50.71
Ash	18.58	8.51	4.59	5.12	38.03	7.87
FC/VM Ratio	1.38	1.45	1.04	1.00	0.20	1.44
Ultimate Analysis (as-received %)						
Carbon	58.82	74.47	49.85	40.95	24.98	69.86
Hydrogen	4.98	5.21	6.61	6.98	4.25	4.52
Nitrogen	1.15	1.36	0.62	0.53	0.65	1.51
Sulfur	0.48	2.46	0.31	0.58	6.05	2.62
Oxygen	16.02	7.98	37.99	45.74	26.10	7.44
Ash	18.58	8.51	4.59	5.12	38.03	7.87
Nitrogen Distribution¹ (% of total N)						
Volatile Matter	43.45	35.57	27.10	24.90	87.86	NA
Char	56.55	64.43	72.90	75.10	12.14	NA
Heating Value (as-received MJ/kg)						
HHV	23.85	30.94	20.08	16.24	10.90	29.15

¹ Nitrogen was measured in coal and in char prepared according to ASTM proximate analysis specifications.
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 1. The Effect of Temperature on N_2O Emissions for Five Coals

Figure 2. The Effect of Excess Air on N_2O Emissions

Figure 3. The Effect of Limestone Feed Rate on N_2O Emissions

Figure 4. The Effect of Primary Air Split on N_2O Emissions

the opposite trend occurs at lower temperatures (1060 K). It is likely that S3 data (Salt Creek bituminous) at higher excess air are showing an interaction with primary air split, which may be the contributing factor for the greater slope for this curve.

The effect of combustor operating pressure on N_2O emissions is of primary importance to most researchers due to the general lack of data, especially in the pilot- and full-scale size range. Three tests were performed at ANL at 0.9-m/s velocity, 855°C temperature, and 4.5% excess O_2 . Combustor pressure ranged from 3 to 120 psig. Figures 5 and 6 show the effects of pressure on N_2O and NO_x , respectively.

As seen in Figure 5, the error bars for pressure control are very small, showing good regulation. N_2O values, however, were highly variable when the combustor was above atmospheric pressure. This variability is believed to be due to the erratic coal feed that occurred during these tests as evidenced by bed temperature fluctuations during Tests 9 and 10. The effect of these coal feed interruptions on NO_x emissions was not evident, as shown in Figure 6. This may be explained by the differences in the analyzers used for measuring the respective gases. The NDIR N_2O analyzer is very susceptible to a methane cross interference that will not affect the NO_x analysis. Therefore, changes in coal feed may not influence NO_x analysis, but may add to errors in N_2O measurement. Recent experiments utilizing an on-line FTIR instrument showed that, for every surge of coal feed, a significant appearance of methane occurred that was detected by the in-line (series) NDIR N_2O analyzer.

In light of the past discussion and the low level of statistical certainty associated with the N_2O values, the interpretation of the results shown in Figure 5 for N_2O dependence on

pressure can only be speculative. Wallman and others [5] showed little increase in N_2O emissions with pressure using a lab-scale packed-bed reactor and a bituminous coal (with sulfated limestone bed) at temperatures common to FBC operation. However, until other data are presented, the trend indicates that pressure either has no effect or causes a small increase in N_2O emissions. Pressure would not be an effective abatement strategy for N_2O emissions. The data presented in Figure 6 clearly shows that increasing combustor pressure is an effective means of reducing NO_x emissions and is also consistent with observations made by Wallman.

Comparison Between Bubbling and Circulating FBCs

The ANL FBC was operated at atmospheric pressure to obtain N_2O emissions data as a function of operating conditions. This provided data to use for a comparison between bubbling and circulating atmospheric FBCs. Data for two similar coals taken from the EERC CFBC testing and the ANL bubbling bed testing are presented in Figure 7. These data show that at low operating temperatures, circulating FBCs tend to emit more N_2O than do bubbling beds. As the temperature increases, the difference between the two modes of combustion decreases. A similar trend was seen when comparing data from the EERC 8" x 8" bubbling bed to the CFBC when burning the same coal. Likewise, full-scale data indicate that bubbling beds may produce significantly less N_2O . Measurements taken at the TVA 160-MW Station showed N_2O emissions of about one-half that observed at the Colorado Ute 110-MW Nucla Station.

Figure 5. Effect of Combustor Pressure on N₂O Emissions for ANL's PFBC

Figure 6. Effect of Combustor Pressure on NO_x Emissions for ANL's PFBC

Figure 7. Comparison of N₂O Emissions from the EERC CFBC and ANL Bubbling FBC

Modeling from CFBC

For modeling purposes, it is necessary to remove the "coal type" as a discrete variable and replace it with a continuous measure of an interaction with temperature and N₂O emissions. The relation of several parameters, including coal nitrogen, oxygen, volatile matter, fixed carbon, and their ratios, was used to correlate with the temperature dependence of N₂O emissions shown in Figure 1. This approach provides an operating range of temperature/coal-type interactions which enables the accurate prediction of N₂O emissions.

Figures 8 through 13 show the correlations of the coal property parameters with the rate of change of N₂O emissions with temperature. The parameters VM, fuel ratio (FC/VM), and O/N ratio are shown in Figures 8 through 10, respectively. The coal properties determined by proximate and ultimate analyses were

normalized for heating value (kg of dry material/MJ of heat input). In effect, this quantity not only normalizes each coal for its heating value, but also is indicative of the actual flux of raw materials entering the combustor. It is seen that only the O/N ratio provides a relatively fair correlation when using a very diverse set of coals. The oxygen level in this ratio does not include oxygen from moisture. Figure 11 shows the relation of N₂O formation with the N/VM ratio. This figure shows a correlation very similar to that obtained for the O/N ratio, demonstrating a distinct separation of the lower- and higher-rank coals.

The heating value of the coals used in this test matrix, when evaluated on a moist, mineral-matter-free basis, should correlate to the approximate rank of the coal. If the trends are truly rank-dependent, then these rankings should correlate, in a broad sense, with the observed

Figure 8. The Change of N_2O Emissions with Temperature Versus Volatile Matter Feed Rate

Figure 9. The Change in N_2O Emissions with Temperature Versus the Fuel Ratio

Figure 10. The Change in N_2O Emissions with Temperature Versus the O/N Ratio

Figure 11. The Change in N_2O Emissions with Temperature Versus the Nitrogen-to-Volatile-Matter Ratio

Figure 12. The Change in N_2O Emissions with Temperature Versus the Moist, mmf Heating Value

Figure 13. The Change in N_2O Emissions with Temperature Versus the Distribution of Nitrogen in the Fixed Carbon and Volatile Matter

N₂O formation. Figure 12 shows the N₂O/temperature slopes as a function of corrected heating value. Except for the subbituminous coal, the ranking of the coals shows a strong relationship with N₂O formation.

An attempt at improving the correlation by involving the distribution of nitrogen between the volatiles and the produced char is shown in Figure 13. The simple relation of the sum of the ratios of nitrogen leaving the volatile matter (N_v) to that of the nitrogen remaining in the char (N_c) was used as a plausible explanation for the difference between N₂O emissions observed in the coal ranks. As presented in Figure 13, the N₂O formation correlated as well, using this relation, as with O/N, N/VM, and moist, mmf heating value. Again, the subbituminous coal is the outlier, and further information is required to enhance this model.

A statistical analysis of the experimental data was performed to 1) screen the operational parameters for significance, and 2) quantify these parameters for use in an empirically derived model. A 90% confidence level was chosen for the analysis, with two, three, and four variables inputted simultaneously. The results of the screening statistics were depicted graphically in Figures 1 through 4.

The predictive equation for N₂O emissions, as derived through linear multiple regression analysis, takes the simplest form as follows:

$$N_2O = A(\text{coal}) + B(\text{temp}) + C(\text{air}) + D(\text{sorbent}) + E(\text{primary})$$

where N₂O = ppm of N₂O at 3% O₂
 coal = effect of coal type
 temp = effect of temperature, K
 air = effect of excess combustion air, %
 sorbent = effect of limestone feed rate, kg/100 kg coal feed

primary = effect of primary-to-total-air ratio, %

A = a' + b'(fuel variable)

B = 1.27 - 51.6 (N_v/VM) - 121 (N_c/FC) ppm/K

C = 17.16 - 0.0148 (temp, K) ppm/% excess air

D = -0.85 ppm/(kg limestone/100 kg coal)

E = -0.6 ppm/%primary air

where a' and b' are constants being determined from additional experimentation.

FUTURE WORK

- Investigate the impacts of fuel effects on N₂O emissions to better define the mechanisms of formation and destruction. Use this fundamental information to help develop mitigating measures.
  - Study the effect of volatiles on N₂O emissions using the EERC coal pretreatment cell and doped natural gas, on both the lab and pilot scale.
  - Study the effect of char as compared to the parent coal on N₂O emissions on both the lab and pilot scale.
  - Study the effect of coal ash type on N₂O emissions by comparing washed and doped coal to the parent coal.
- Repeat tests performed on the CFBC on the pilot-scale bubbling and bench-scale pressurized FBCs.
  - Compare the effect of operating parameters and mode of operation on N₂O emissions.

- Compare the effect of coal properties and mode of operation on N₂O emissions.
  - Investigate measures for reducing N₂O emissions.
    - Optimize operating conditions to minimize N₂O emissions.
    - Test various additives such as hydrated lime.
    - Investigate innovative combustion techniques, such as the use of the coal pretreatment cell developed at the EERC.
    - Develop other control strategies based on results from the fundamental investigations of coal properties.
  - Improve the global empirical model for predicting N₂O emissions.
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