4.6 Nitrous Oxide Emissions

NITROUS OXIDE EMISSIONS

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by

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NITROUS OXIDE EMISSIONS

1.0 BACKGROUND

Due to growing scientific and public concern relating elevated CO_2 concentration to changes in the global climate, other trace gases including CH_4, chlorofluorocarbons (CFCs), and nitrous oxide (N_2O) have become suspect as contributors to the greenhouse effect and ozone depletion. N_2O is reportedly increasing in atmospheric concentrations at an estimated rate of 0.7 ppb per year (1) and was measured (1988) as present in the atmosphere at a concentration of 307 ppb (2).

Although the atmospheric concentrations of N_2O are low (1100 times less than CO_2), the relative strength of N_2O as an infrared absorber is reportedly 200 times more than CO_2 (2). In addition, N_2O, a stable compound, is transported to the stratosphere where it is photochemically oxidized to nitric oxide (NO), the major contributor to catalytic ozone depletion. The association and/or contribution of N_2O to the greenhouse effect and ozone reduction has led to considerable interest in determining the natural and man-made pathways to its formation and destruction.

The reported increase in atmospheric N_2O concentration over the last decade has prompted researchers to direct their attention toward anthropogenic sources of N_2O formation. These include biomass burning, fertilization, groundwater release through irrigation, and fossil fuel combustion. Pulverized coal combustion was first implicated as a major producer of N_2O emissions as a result of a sampling artifact. However, the established N_2O levels currently reported are typically less than 10 ppm, resulting in a negligible atmospheric contribution with respect to natural sources (1).

At present, attention has been focused upon advanced coal-combustion techniques currently becoming commercialized by the electric utilities industry. The most prominent of these are the fluidized-bed combustors (FBCs) and their variations (circulating, pressurized, or both). The main driving forces behind the use of fluidized-bed combustion have primarily been environmental concerns, fuel flexibility, and compatibility with low-cost fuels.

The role of the present project at the Energy and Environmental Research Center (EERC) is to determine the amount of atmospheric N_2O derived from coal combustion in FBCs. Additionally, the goal is to establish a comprehensive engineering model to assist in the prediction of N_2O emissions based upon operating and design considerations.

2.0 THREE-YEAR PROJECT OBJECTIVES

2.1 Task 1--Literature Survey

A literature survey will be 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 the formation of N_2O in FBC systems will be developed. Process variables to consider should include temperature, pressure, reactant types and concentrations, and residence time effects.

2.2 Task 2--Equipment Design and Test Plan Development

A detailed test plan will be developed based on the results of Task 1. The plan shall include, but not be limited to, the following: design of the experimental facility, the experimental facility operating characteristics, experimental operating procedures, required instrumentation, and planned model development.

The facility will, at a minimum, have the following capabilities: suitability for determining N_2O reactions and reaction rates; bubbling, circulating, and transport regimes; variable temperature up to 1800°F, variable pressure up to 20 atm (300 psi), and variable velocity up to 20 fps; and the required instrumentation for diagnostics and data acquisition.

Parameters will be measured to provide data to determine the reaction kinetics and should include the mass-flow rate of reactants and products, the physical and chemical composition of reactant products, and the reaction temperature and pressure.

Parametric testing will be planned that will 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.

2.3 Task 3--Facility Modification

The goal of this task is to construct a new reactor facility, or modify an existing facility, in accordance with the design approved by the Technical Monitor (TM) in Task 2.

2.4 Task 4--Experiments and Theory Development

The goal of this task is to perform the experimentation in accordance with the approved test plan developed in Task 2. Using this information, the global model, initiated in Task 1 to estimate the rates of N_2O reactions under FBC conditions, will be refined. The ultimate goal is to produce a simple global model for boiler designers to predict N_2O stack emissions and destruction in FBC systems.

2.5 Task 5--Analysis of Results and Final Report

The goal of Task 5 is to produce a final report which includes the following: reduced data for each test condition; parametric analysis and interpretation of data; a predictive model as a simple equation, otherwise as a compressed graphical representation and tabulations; and the original data in suitable format, i.e., a Lotus® spreadsheet.

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

The EERC will proceed with work under Task 6 only after receiving written direction from the TM. The goal of this task is to develop a protocol for field monitoring. This will include the sampling plan, sampling locations, test conditions, process monitoring, and the duration of the test. Sites for testing will be identified, with consideration given to the physical plant layout, access to sampling locations, combustor type, feasibility to site access, and operational parameters. The willingness of the boiler operator to participate in the sampling and allow release of the data must also be considered. The cost of each site visit will also be determined. The sampling protocol will be submitted to the Morgantown Energy Technology Center (METC) TM for approval before any sampling begins.

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

EERC will proceed with work under Task 7 only after receiving written direction from the TM. The goal of this task is to perform field monitoring in accordance with the sampling protocol established in Task 6.

3.0 RESULTS FROM CIRCULATING FLUIDIZED-BED COMBUSTOR TESTING AT THE EERC

Testing was continued using the 1-MW_{th} circulating fluidized-bed combustor (CFBC) to assess the effect of operating parameters and fuel specifications on N_2O emissions. A schematic of the combustor and ancillary equipment is shown in Figure 1. The main combustor has an internal diameter of 0.5 m and is 12.5 m tall. It is refractory-lined and has heat exchange panels located throughout the combustor to control heat removal. A cyclone is used to collect and recirculate solids through an external heat exchanger that is combined with the loop seal. A detailed description of the unit and operating procedures can be found elsewhere (3).

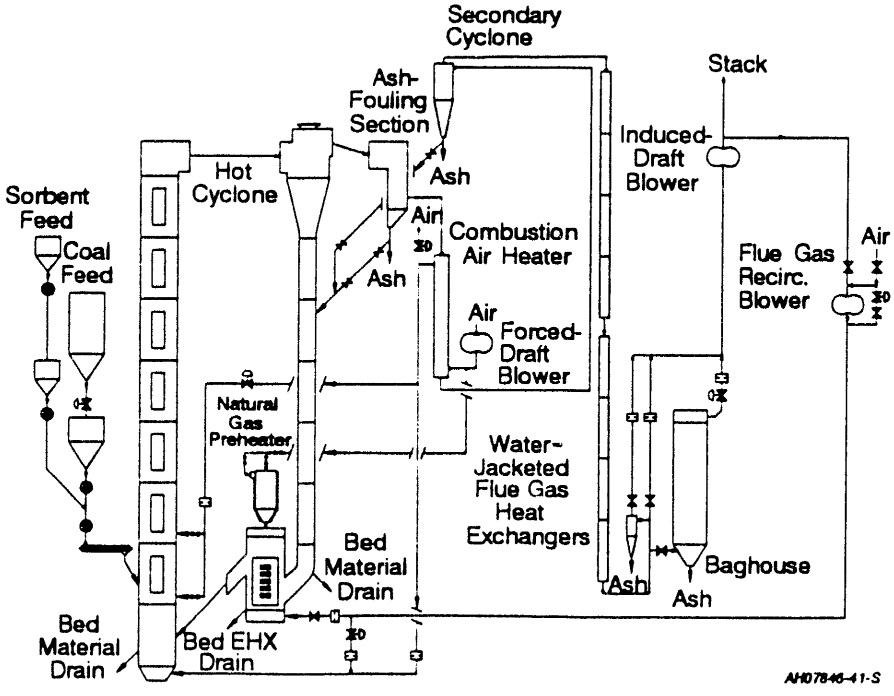


Figure 1. Schematic of the 1-MW EERC pilot-scale CFBC.

Since the last reporting period, two additional coals, a New Mexico bituminous and a second Wyoming subbituminous, were fired in the pilot-scale CFBC. These combustion tests were performed under private contracts; therefore, the data were limited to studying the effects of operating temperature and coal rank. The data from these additional coals will be summarized and presented against the trends established with previously reported data.

The proximate, ultimate, and heating value analyses are shown in Table 1 for the complete database of seven coals. Coal ash analyses for these coals are presented in Table 2. The last two coals added to the database (Powder River subbituminous and New Mexico bituminous) have no notable differences in ash composition when compared to the other coals of similar rank. The Powder River Basin coal exhibited the typical high-calcium ash associated with these coals. The partitioning of the coal-nitrogen into the volatile matter and the char is also presented in Table 1. The distribution of the 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 7 min at a temperature of 1225 K in crucibles covered with lids.

The significance of the distribution of nitrogen in the coal 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 early in the combustion process through homogeneous or heterogeneous reaction pathways to form nitrogen or nitrogen oxides (NO, NO_2, N_2O). 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 N_2O formation. The char nitrogen may also be gasified and react through homogeneous mechanisms.

3.1 Effect of Operating Parameters on N_2O Emissions from CFBC

The effects of CFBC operating parameters on N_2O emissions are shown in Figures 2 through 5. These parameters include temperature, excess air, sorbent-feed rate, and air staging. The N_2O emissions data in these figures are expressed on a mg N_2O/MJ heat input basis. This effectively normalizes for fuel or nitrogen input rate as well as the combustor firing rate. 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.

3.1.1 Effect of Temperature and Coal Rank

The effect of temperature and coal rank on N_2O emissions is presented in Figure 2. 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

TABLE 1

Analysis of Coals Tested in EERC 1-MW CFBC

Coal:	Salt Creek	Blacksville	Black Thunder	Center	Asian	New Mexico	Powder River
Rank:	HVC Bit	HVA Bit	Sub C	Lignite	Lignite	HVA Bit	Sub C
Location:	Colorado	Pennsylvania	Wyoming	N. Dakota	Asia	New Mexico	Wyoming
Proximate Analysis, as-received wt%							
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
Ultimate Analysis, as-received wt%							
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
Nitrogen Distribution,[1] % of total N							
Volatile Matter	43	36	27	25	88	36	31
Char	57	64	73	75	12	64	69
Higher Heating Value, as-received MJ/kg	23.85	30.94	20.08	16.25	10.90	30.09	19.66

[1] Nitrogen was measured in coal and in char prepared per 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.

TABLE 2

Analysis of Ash From Coals Tested in EERC 1-MW CFBC

Coal: Rank: Location:	Asian Lignite A Asia	Center Lignite A N. Dakota	Black Thunder Sub. C Wyoming	Salt Creek HVC Bit. Colorado	Blacksville HVA Bit. Pennsylvania	Powder River Sub. C Wyoming	New Mexico HVA Bit. New Mexico
Ash Composition, wt% of ash as oxides							
Silica, SiO_2	31.8	14.8	28.5	59.9	43.7	31.5	48.6
Aluminum, Al_2O_3	12.8	9.0	16.4	30.9	22.9	14.9	24.7
Ferric, Fe_2O_3	13.5	14.2	6.4	3.0	16.8	5.4	6.4
Titanium, TiO_2	0.2	0.4	1.4	1.1	0.7	1.2	0.9
Phosphorus, P_2O_5	0.5	0.8	1.3	0.4	0.4	1.2	1.8
Calcium, CaO	18.6	22.4	24.3	1.5	5.4	25.3	8.5
Magnesium, MgO	3.3	9.6	7.9	1.5	1.2	7.1	2.0
Sodium, Na_2O	0.3	5.2	0.5	0.2	0.7	1.2	0.8
Potassium, K_2O	1.2	0.5	0.9	1.0	1.5	0.3	0.5
Sulfur, SO_3	17.5	22.1	12.4	1.0	6.5	13.1	5.8
Ash Composition, wt% of coal as oxides							
Silica, SiO_2	12.1	0.8	1.3	11.1	3.7	1.4	6.0
Aluminum, Al_2O_3	4.9	0.5	0.8	5.7	1.9	0.7	3.1
Ferric, Fe_2O_3	5.1	0.7	0.3	0.6	1.4	0.2	0.8
Titanium, TiO_2	0.1	0.0	0.1	0.2	0.1	0.1	0.1
Phosphorus, P_2O_5	0.2	0.0	0.1	0.1	0.0	0.1	0.2
Calcium, CaO	7.1	1.1	1.1	0.3	0.5	1.1	1.1
Magnesium, MgO	1.3	0.5	0.4	0.3	0.1	0.3	0.2
Sodium, Na_2O	0.1	0.3	0.0	0.0	0.1	0.1	0.1
Potassium, K_2O	0.5	0.0	0.0	0.2	0.1	0.0	0.1
Sulfur, SO_3	6.7	1.1	0.0	0.2	0.6	0.6	0.7

the Powder River subbituminous coal. Two obvious temperature trends appear to be intimately related to coal rank. The first is that the absolute N_2O emissions from the higher-ranked bituminous coals are greater than 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 seen in Figure 2, the bituminous, lignite, and subbituminous coals have distinctly different slopes.

Further examination of Figure 2 shows that the effect of coal rank on N_2O emissions is not a continuous relation. 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 in 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 for predicting 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 based on rank designations alone. In any case, a fundamental understanding of the chemistry of the Wyoming subbituminous coals may prove beneficial in reducing N_2O emissions.

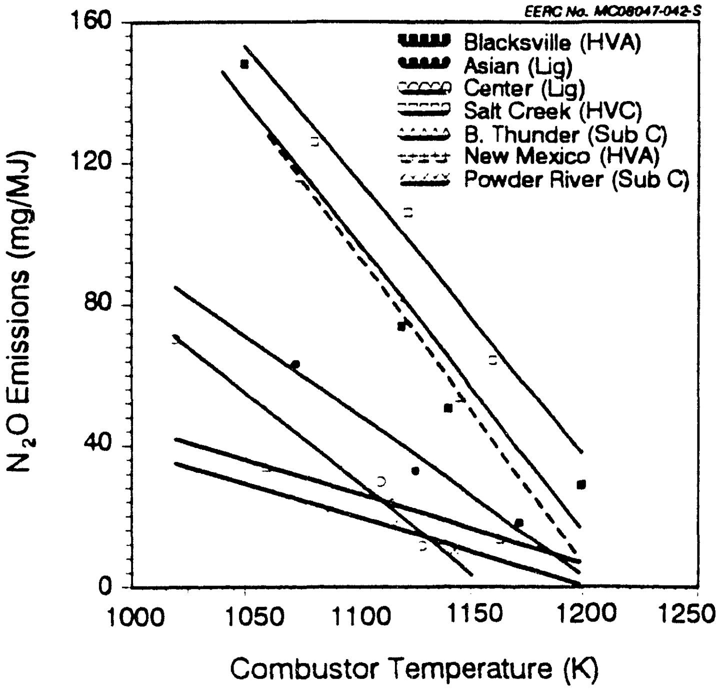


Figure 2. The effect of temperature and coal rank on N_2O emissions.

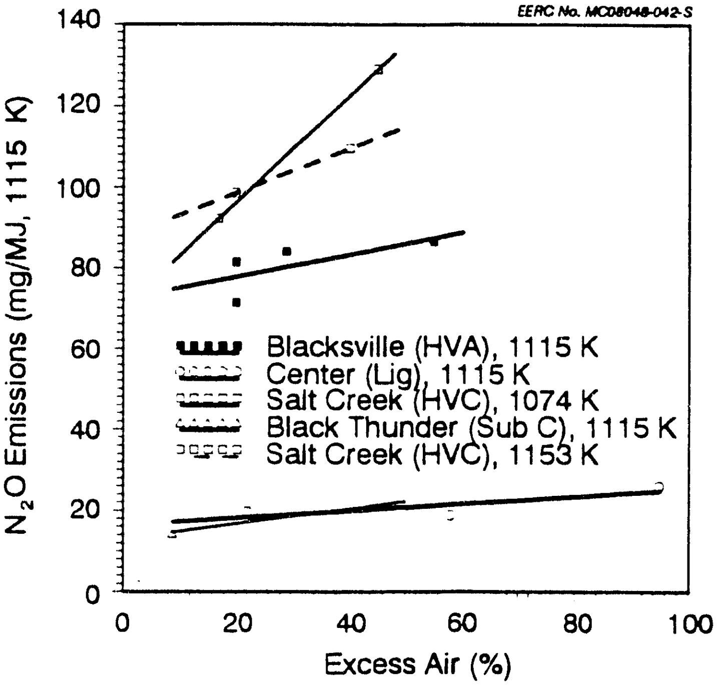


Figure 3. The effect of excess air on N_2O emissions.

3.1.2 Effect of Excess Combustion Air

Figure 3 presents the effect of excess combustion air on N_2O emissions with four different coals. Increasing excess air in CFBC showed an increase in N_2O emissions when burning all coals. This apparent trend extends across all coal ranks tested and could be used to reduce N_2O emissions, to a limited extent, by using a minimal amount of excess air for combustion. There is also an interaction between excess air and temperature in relation to N_2O emissions--the effect of excess air level is stronger at lower temperatures than at higher temperatures. This can be seen in Figure 3 for the Salt Creek coal, which shows a much stronger dependence on excess air at 1074 K than for the data acquired at 1153 K. The data points for the other coals in this figure were obtained at approximately 1115 K. The disparity in slope between the various coals possibly indicates an interaction of coal rank with excess air, but is not conclusive from the limited data available.

3.1.3 Effect of Sorbent Feed

The effect of limestone feed on N_2O emissions is shown in Figure 4. Sorbent feed, in this figure, is expressed on a grams per MJ heat input basis. This places all coals on the same basis, unlike 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 N_2O emissions with increasing sorbent feed. The opposing trend displayed for the Black Thunder subbituminous coal is not readily

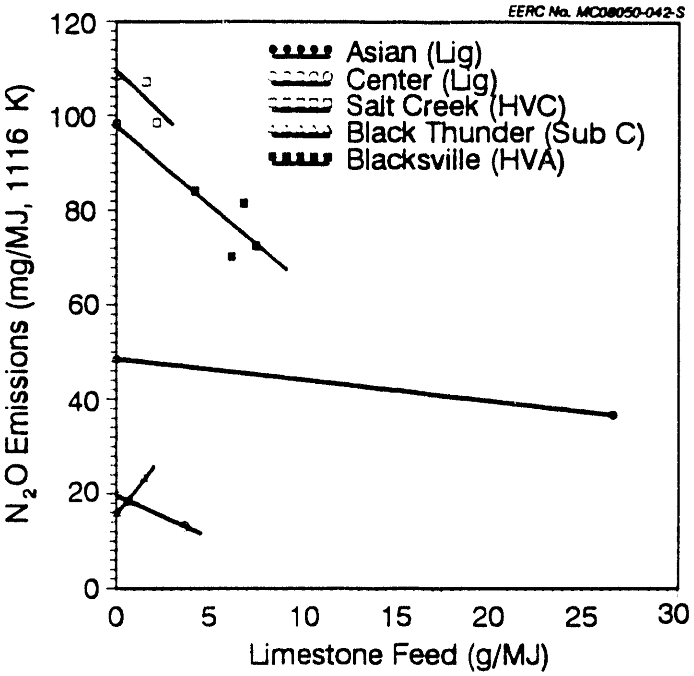


Figure 4. The effect of limestone feed on N_2O emissions.

understood. This trend may be related to the composition of the coal or coal ash, since, from the data displayed in Figure 4, it is evident that interactions exist between sorbent feed and coal selection. The data for the bituminous coals suggest a potential N_2O emissions control strategy by increasing the sorbent feed rate. Unfortunately, the use of a limestone sorbent as a means of reducing N_2O emissions has been shown to result in a comparable increase in NO_x emissions. Therefore, the net result of this activity would be the conversion of N_2O to NO.

3.1.4 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 5 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). The effect of higher excess air for S3 data points (Salt Creek bituminous) indicates an interaction with primary air split, which contributes to the greater slope for this curve. These subtle effects, displayed in Figure 5, may be caused by changes in the dense-bed velocity and temperature profiles and are, therefore, indications of the interdependence of the operating parameters. Due to the limited data points defining the curves, these results are considered preliminary until a better perception of the experimental error is established.

3.2 Impact of Coal and Operating Parameters

Figures 2 through 5 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 for 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 3 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 3, sorbent feed will produce the greatest change in N_2O emissions, followed by temperature, excess air, and primary air, when based upon a unit change in the respective parameter. If switching to a Powder River subbituminous coal were a viable option, N_2O 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 in affecting N_2O emissions may vary due to practical design limitations and operating costs. For example, the reduction of excess air will result in lower N_2O 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 N_2O emissions for reasonable changes in operating conditions. The operating ranges depicted in the table are subjective and

TABLE 3

Effect of Operating Parameters on N_2O Emissions 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_2O Emissions, mg/MJ	110	104	102	98	60	16
ΔN_2O, mg/MJ	0	-6	-2	-6	-44	-88
ΔParameter	0	20%	0.41 g/MJ	17%	56 K	---
$\Delta N_2O/\Delta$Parameter	---	-0.30	-4.88	-0.24	-0.75	---

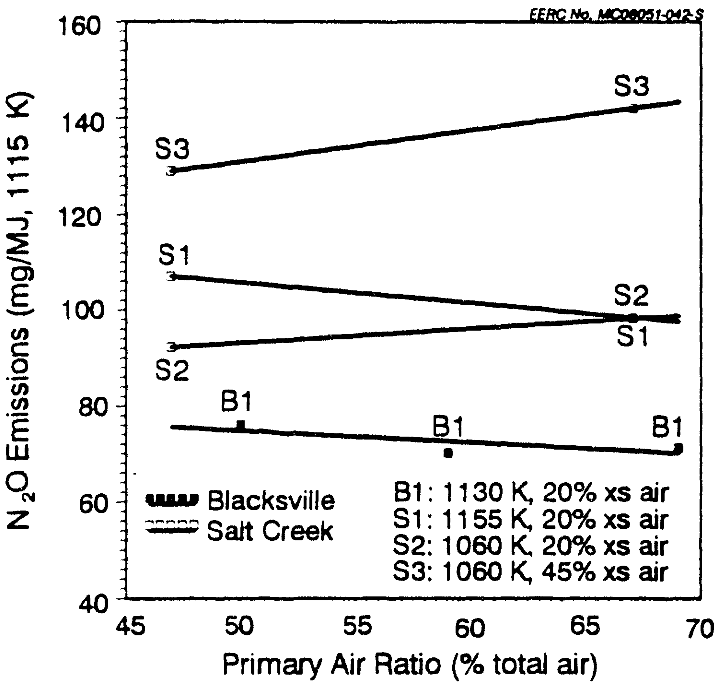


Figure 5. The effect of primary air to total air ratio on N_2O emissions.

must be interpreted from this perspective. Based on the values presented in Table 3, the relative order of importance is given by fuel type > temperature > excess air, primary air split > sorbent feed rate for Salt Creek coal.

3.3 Parameterization of Coal Rank

The previous sections showed the significance of operating parameters and coal rank on N_2O emissions, with the major influence resulting from the particular coal type used in a combustor. In order to predict N_2O emissions through modeling, the effect of coal type needs to be parameterized into a set of readily measurable coal properties. This, in effect, will remove the "coal type" as a discrete variable and replace it with a continuous measure of an interaction with temperature and N_2O emissions. The relation of several parameters including coal nitrogen (N), oxygen (O), volatile matter (VM), fixed carbon (FC), and their ratios were used to correlate with the temperature dependence of N_2O emissions shown in Figure 2. The slopes of the linear best-fit lines in Figure 2 were used instead of absolute N_2O values since the lines do not converge to the same intercept. The absolute values would yield an infinite number of solutions (any vertical line through Figure 2). Additionally, all utility combustors require some degree of temperature excursion from the design specifications to account for load shifts. In this respect, an operating range of temperature/coal-type interactions is required to accurately predict N_2O emissions.

Figures 6 through 11 show the correlations of the coal property parameters with the rate of change of N_2O emissions (dependence) with temperature. The popular approaches indicated in literature include VM, fuel ratio (FC/VM), and O/N ratio. These results are shown in Figures 6 through 8, respectively. The coal properties determined by proximate and ultimate analyses were normalized for heating value (kg of material/MJ of heat input). In effect, this quantity not only normalizes each coal for its heating value, but is also indicative of the actual flux of raw materials entering the combustor. As seen from these figures, only the O/N ratio provides a fair correlation when using a very diverse set of coals. The oxygen level in this ratio does not include oxygen from moisture. Figure 9 shows the temperature dependence of N_2O 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 coals used in this study, when placed on a moist, mineral-matter-free (mmf) heating value basis, should correlate to the approximate rank of the coal. This is only true for the coal rank series of lignite through high-volatile A bituminous due to the rank designations including both fixed carbon and heating value. If the trends are truly rank-dependent, then these rankings should correlate, in a broad sense, with the observed N_2O formation. Figure 10 shows the N_2O/temperature slopes as a function of corrected heating value. The figure shows that the dependence of N_2O emissions on coal rank is more closely preserved with the higher-ranked coals and that additional factors are required to discriminate between subbituminous and lignite coals.

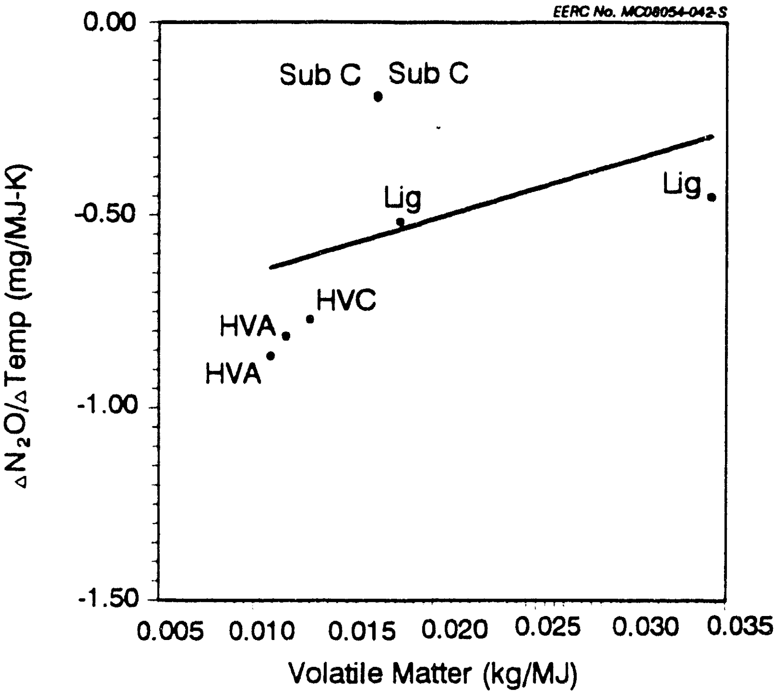


Figure 6. The change in N_2O emissions with temperature versus the volatile-matter-feed rate.

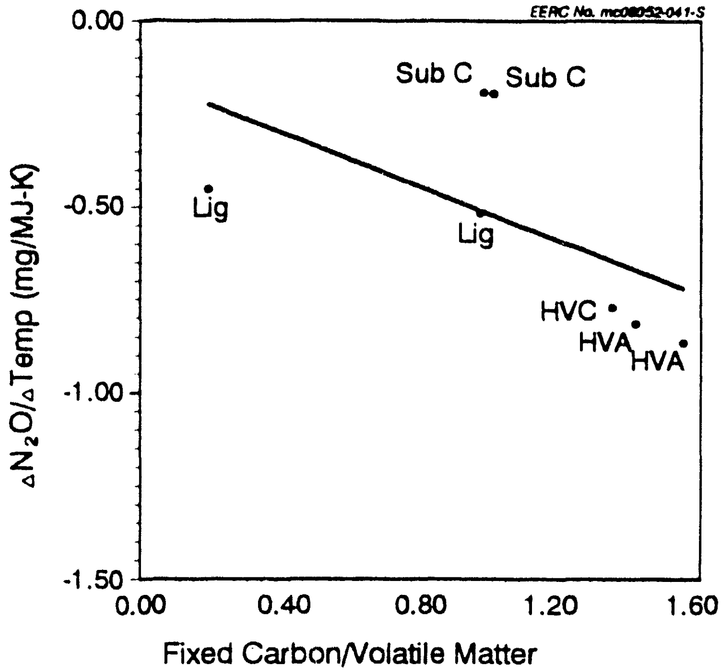


Figure 7. The change in N_2O emissions with temperature versus the fixed-carbon to volatile-matter ratio.

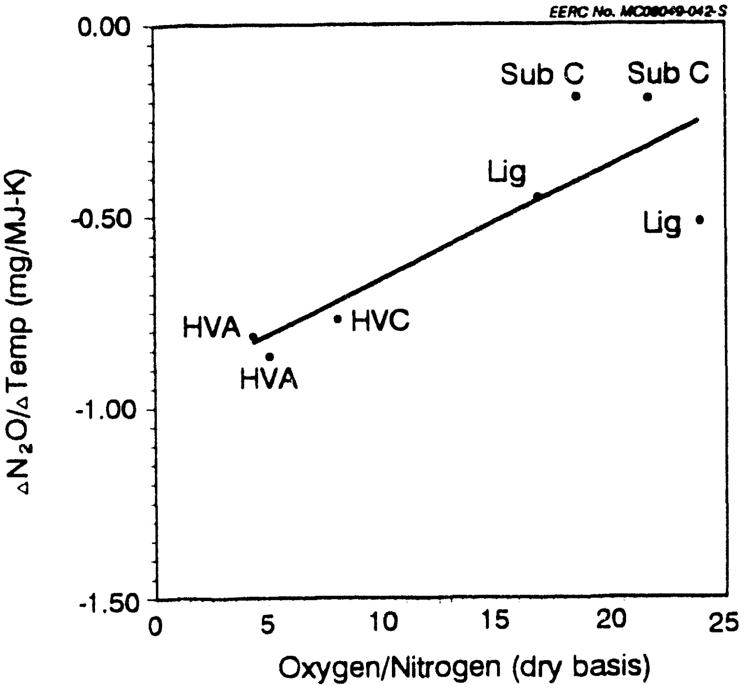


Figure 8. The change in N_2O emissions with temperature versus the dry-basis oxygen to nitrogen ratio.

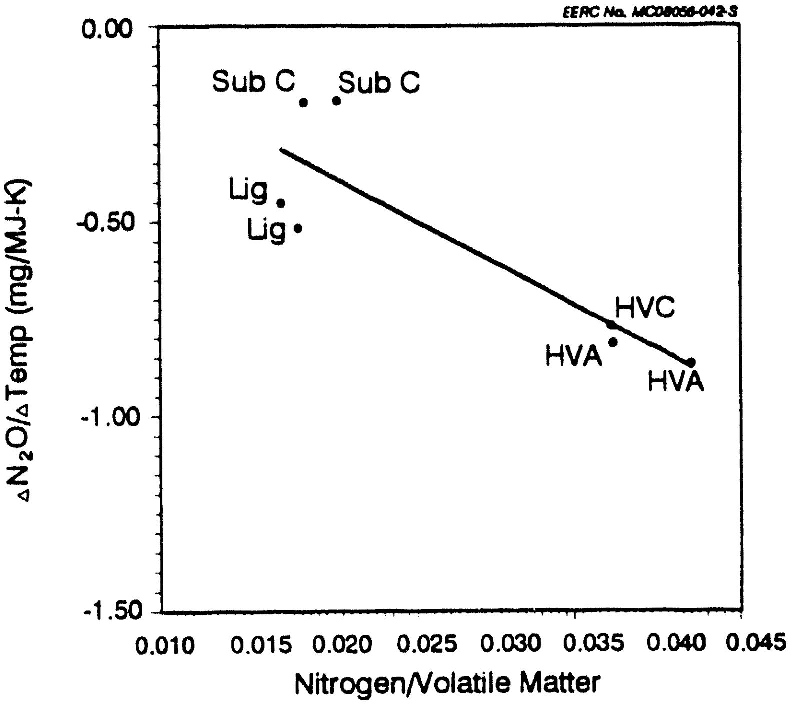


Figure 9. The change in N_2O emissions with temperature versus the nitrogen to volatile-matter ratio.

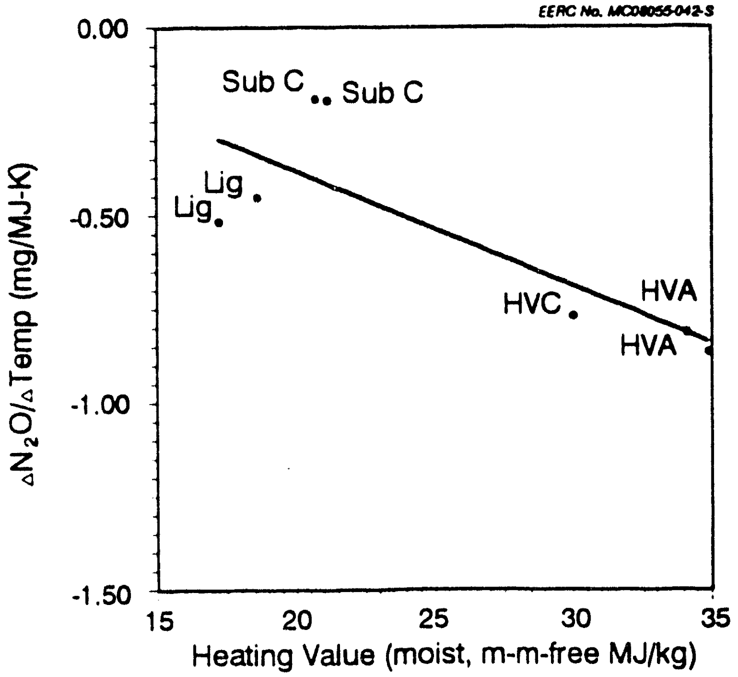


Figure 10. The change in N_2O emissions with temperature versus the moist, mineral-matter-free heating value.

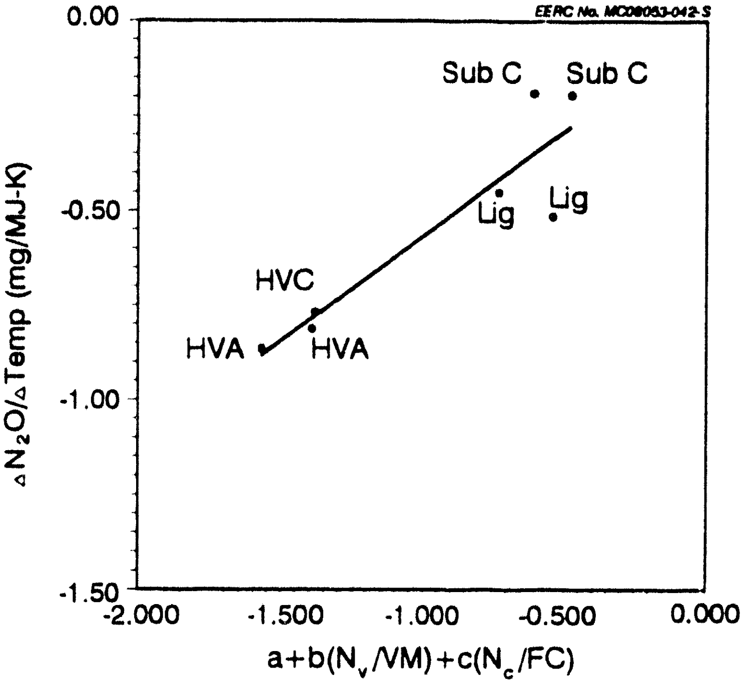


Figure 11. The change in N_2O emissions with temperature versus the distribution of nitrogen in the fixed carbon and volatile matter.

As noted above, there are other important factors that are excluded from the analysis that would further improve the correlation between N_2O emissions and coal rank. These may include char surface characteristics, ash composition, sulfur concentration, and volatile matter composition. An attempt at improving the correlation is shown in Figure 11. The nitrogen in the coal and the coal char were determined, as aforementioned, in order to calculate the partitioning of nitrogen between the volatiles and the produced char. The simple relation of the sum of the ratios of nitrogen leaving in the volatile matter (N_v) to that of the nitrogen remaining in the char (N_c) was used as a possible explanation of the difference between N_2O emissions observed in the coal ranks. As presented in Figure 11, the N_2O formation correlated as well using this relation as with O/N, N/VM, and moist mmf heating value. Again, the higher-ranked coals tend to correlate better to this relation than the lower-ranked coals.

3.4 Preliminary Modeling

Statistical analysis of the experimental data was performed to i) screen the operational parameters for significance, and ii) quantify these parameters for use in an empirically derived model. An 80% confidence level was chosen for this analysis, with two, three, and four variables inputted simultaneously. The results of the modeling showed that, for any given coal, the relationships depicted graphically in Figures 2 through 5 could be adequately predicted. The major obstacle leading to a generalized model for predicting N_2O emissions from a CFBC is the effective parameterization of the coal. In addition, the effect of fuel parameters and their interactions with operational parameters on N_2O emissions are still under investigation and have not been quantified for inclusion into a global model.

The partitioning of the coal nitrogen into the char and volatile matter and the O/N and N/VM ratios were shown as preliminary examples of parameterizing the effect of the fuel with temperature dependence. Using, as an example, the partitioning of fuel nitrogen as a means of describing the coal effects, the predictive equation for N_2O emissions, as derived through linear multiple regression analysis, takes the simplest form:

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

where

N_2O =	mg N_2O/MJ
coal =	effect of coal type
temp =	effect of temperature, K
air =	effect of excess combustion air, %
sorbent =	effect of limestone feed rate, g/MJ heat input
primary =	effect of primary to total air ratio, %

and

$A = a' + b'(\text{fuel variable})$	
$B = c' + d'(N_v/VM) + e'(N_c/FC)$	mg/MJ-K
$C = f' - g'(\text{temp, K})$	ppm/% excess air
$D = h'$	ppm/(g-limestone/MJ)
$E = i'$	ppm/%primary air

where a′ and b′ are constants under development to determine the magnitude of the N_2O emissions with coal selection; c′, d′, and e′ determine the dependence of N_2O emissions with coal and temperature; and f′ through i′ are determined by regression analysis of the database used for modeling coal and operational parameters. The constants a′ and b′ will be used to orient the curves presented in Figure 2, so that absolute N_2O values can be obtained from the slopes. It should be noted that this model and the statistically derived parameter coefficients are representative of the coals used in this experimental database. A generalized form of this empirical relation will require a broad base of fuels, with the accuracy dependent on the success of parameterizing the fuels in the database. Additionally, factors related to the scale and the mode of operation (bubbling versus circulating) of an FBC may be required to further enhance the accuracy of predicting N_2O emissions.

4.0 PUBLICATIONS AND PRESENTATIONS

During the course of the last reporting period, a major effort was made to interpret and disseminate the data that have been acquired to date. The bulk of the data thus far reported has been concerned with the effects of pilot-scale operating parameters and the selection of coals on N_2O emissions. In the future, the implications of coal-property effects will also be addressed due to the significant role the fuel has on establishing the magnitude of N_2O emissions.

The following is a list of publications and presentations that were commenced or finalized during this last reporting period:

1. "Nitrous Oxide Emissions in Fluidized-Bed Combustion: Fundamental Chemistry and Combustion Testing," a review to be published in *Progress in Energy and Combustion Sciences.*
2. "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.
3. "Predicting N_2O Emissions from Circulating Fluidized-Bed Coal Combustion," to be presented at the 1992 Pittsburgh Coal Conference, October 1992.
4. "Pilot-Scale Studies on N_2O Emissions, Coal Properties, and Conditions in a Circulating Fluidized-Bed Combustor," 5th International Workshop on Nitrous Oxide Emissions, Tsukuba, Japan, July 1-3, 1992.
5. "Effect of Coal Rank and Circulating Fluidized-Bed Operating Parameters on Nitrous Oxide Emissions," submitted to *FUEL.*
6. "Nitrous Oxide Emissions from Fluidized-Bed Combustion," Workshop on Nitrous Oxide Emissions, presented at Morgantown Energy Technology Center, April 2, 1992.

This is a list of previous publications and presentations:

7. "Effect of Operating Parameters on N_2O Emissions in a 1-MW CFBC," Eighth Annual International Pittsburgh Coal Conference, October 14-18, 1991.
8. "N_2O 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.
9. "Mini-Workshop on N_2O Emissions from FBCs," presented at Morgantown Energy Technology Center, May 20, 1991.

5.0 REFERENCES

1. Anthony, E.J., Ed. *Proceedings of the 1991 Fluidized-Bed Combustion Conference*, *Nitrous Oxide Forums 1 and 2.*; Montreal, Canada, April 1991, pp 677-730 and 985-1033.
2. Ramanathan, V.; Cicerone, R.J.; Singh, S.B.; Kiehl, J.T. *J. Geophys. Res.*, **1985**, *90* (D3), 5547.
3. Henderson, A.K.; Moe, T.A.; Hajicek, D.R.; Mann, M.D. *In* Proceedings of the Sixteenth Biennial Low-Rank Fuels Symposium; May 1991, pp 407-420.

FORM EIA-459E
(10/80)

U.S. DEPARTMENT OF ENERGY

FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

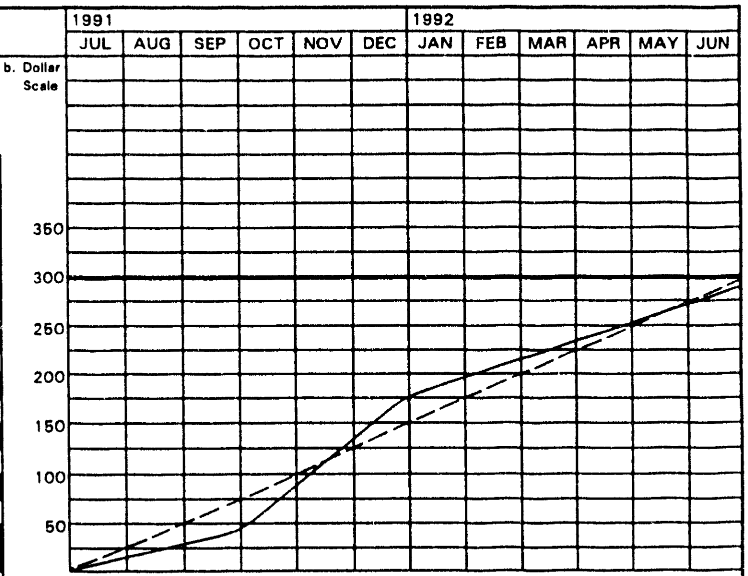
FORM APPROVED
OMB NO. 1900 0127
Page 1 of 2

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Nitrous Oxide Emissions (4.6)	3. Reporting Period 3-1-92 through 6-30-92
4. Name and Address Energy and Environmental Research Center University of North Dakota Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000		5. Program/Project Start Date 4-1-86 6. Completion Date 9-30-92

7. FY 91/92

8. Months or Quarters: Quarters

9. Cost Status a. Dollars Expressed in Thousands b. Dollar Scale



10. Cost Chart

Fund Source		Quarter 1st	2nd	3rd	4th	Cum. to Date	Tot. Plan
DOE	P	75	75	75	74	299	299
	A	46	131	62	56	295	
	P						
	A						
	P						
	A						
	P						
	A						
Total P		75	75	75	74	299	299
Total A		46	131	62	56	295	
Variance		29	(56)	13	18	4	

P = Planned A = Actual

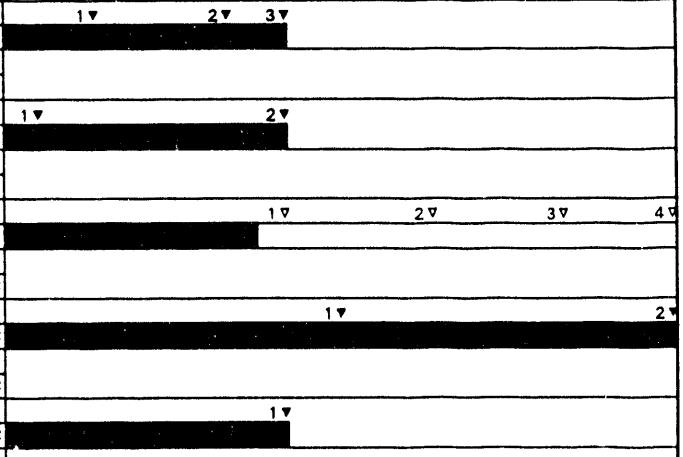
Total Planned Costs for Program/Project

$299

c. Cumulative Accrued Costs

	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN
Planned			75			150			225			299
Actual			46			177			239			295
Variance			29			(27)			(14)			4

11. Major Milestone Status	Units Planned / Units Complete	
A. Literature Survey	P C	No activities in current project year
	P C	
B. Detailed Test Plan	P C	No activities in current project year
	P C	
C. CFBC Testing	P C	
	P C	
D. PFBC Testing	P C	
	P C	
E. Bubbling-Bed Testing	P C	
	P C	
F. Preliminary Engineering Model	P C	
	P C	
G. Second Test Matrix	P C	
	P C	
	P C	
	P C	
	P C	



12. Remarks

Due to EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.

13. Signature of Recipient and Date Michael E. Collings	14. Signature of DOE Reviewing Representative and Date

FORM E1A-459E
(10/80)

U.S. DEPARTMENT OF ENERGY

FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 1900 012
Page 2 of 2

1. Program/Project Identification No.
DE-FC21-86MC10637

2. Program/Project Title
Nitrous Oxide Emissions (4.6)

3. Reporting Period
3-1-92 through 6-30-92

4. Name and Address
Energy and Environmental Research Center
University of North Dakota
Box 8213, University Station
Grand Forks, ND 58202 (701) 777-5000

5. Program/Project Start Date
4-1-86

6. Completion Date
9-30-92

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
Task A	Literature Survey			
	No activities in current project year			
Task B	Detailed Test Plan			
	No activities in current project year			
Task C	CFBC Testing			
c.1	Lignite test	8-15-91	8-15-91	
c.2	Bituminous test	10-30-91	10-18-91	
c.3	Subbituminous test	11-30-91	11-22-91	
Task D	PFBC Testing			
d.1	ANL PFBC testing	7-15-91	7-15-91	
d.2	Report on PFBC test	11-30-91	12-31-91	
Task E	Bubbling-Bed Testing			
e.1	Coal type tests	11-30-91		
e.2	Sorbent tests	2-15-92		
e.3	Dry coal and char tests	4-30-92		
e.4	Mineral additive tests	6-30-92		
Task F	Preliminary Engineering Model			
f.1	Prepare preliminary model	12-31-91	12-31-91	
f.2	Update model	6-30-92	6-30-92	
Task G	Second Test Matrix			
g.1	Establish second matrix	11-30-91	12-31-91	

4.7 Pressurized Fluidized-Bed Combustion

PRESSURIZED FLUIDIZED-BED COMBUSTION

Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992

by

Michael D. Mann, Research Supervisor
John R. Rindt, Research Supervisor
Melanie D. Hetland, Research Engineer
Douglas Hajicek, Senior Research Engineer

Energy and Environmental Research Center
University of North Dakota
Box 8213, University Station
Grand Forks, North Dakota 58202

Technical Monitor: Dr. Donald Bonk

for

U.S. Department of Energy
Morgantown Energy Technology Center
3610 Collins Ferry Road
Morgantown, West Virginia 26507

July 1992

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

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PRESSURIZED FLUIDIZED-BED COMBUSTION

1.0 BACKGROUND

Pressurized fluidized-bed combustion (PFBC) has several advantages that make it attractive as a technology of the future, including:

- Increased efficiency and reduced capital and generating costs compared to pulverized coal-fired (pc-fired) boilers equipped with flue gas desulfurization (FGD).
- Modular units without the usual economy-of-scale penalty.
- Reduced combustor size, permitting shop fabrication and field erection, thereby greatly shortening construction lead time.
- High-sulfur fuels burned in the presence of sorbent in the fluidized-bed combustor (FBC) eliminating the need for FGD.
- Reduced combustion temperature (1400°-1700°F versus 3000°F for a pc-fired boiler), which results in significant reduction of NO_x emissions.
- Increased heat-transfer rate to the working fluid.
- Increased fuel versatility.
- Easily handled by-product material consisting of clinker-free, granular, smooth-flowing ash which may be easily disposed of for landfill uses or potentially sold for industrial or agricultural applications.

Major technical uncertainties identified by the industry as critical areas for PFBC commercialization are:

- Hot-gas cleanup for gas turbine protection, with particular reference to coal alkalies.
- Materials survivability for heat exchanger, gas turbine, and solids-handling equipment.
- Solids-handling improvement in feeding, distribution, and bed removal.
- Combustor configuration, including the heat-transfer bundles, distributor plate, fuels utilization, and operational parameters.

Some of these problems are being addressed by programs such as those at Grimethorpe and New York University. Others may be resolved during operation of three demonstration plants using first-generation technology: the AEP 70-MW_e Tidd Station at Brilliant, Ohio; the 79-MW_e Escatron Power Plant in Spain; and the 135-MW_e Energi Vartan Plant in Stockholm, Sweden. Although these plants show improved efficiency over atmospheric systems, they are still significantly below gas turbine efficiency. In an attempt to increase these efficiencies, several companies are actively involved in the development of second-generation PFBC systems. The goals of the second-generation system are a 45% coal-to-electricity efficiency, a 20% cost-of-electricity advantage over pc-fired systems, modular design for shop fabrication, the capability to meet or exceed New Source Performance Standards (NSPS), and the ability to operate on a wide range of coals.

2.0 GOALS AND OBJECTIVES

The overall goal of the PFBC program at the Energy and Environmental Research Center (EERC) is to generate both fundamental and process information that will foster the development of an economical and environmentally acceptable second-generation PFBC concept. The goal is to focus on generic issues, such as the fate of alkali in PFBC systems, sorbent utilization, and carbonizer performance, while providing input to assist in the development of second-generation systems.

During the two years of this Cooperative Agreement (7/90-6/92), work focused on three main areas: carbonizer performance, fate of alkali, and increased sorbent utilization. Objectives are discussed below.

2.1 Carbonizer Performance Evaluation

In order for a second-generation PFBC to achieve 45% efficiency, it is likely that the coal must be partially gasified and the char residue burned in the PFBC. This will produce gas streams that can be cleaned at an intermediate temperature (e.g., 1600°F) and then afterburned to obtain temperatures higher than those obtainable directly from the PFBC, thereby increasing the efficiency of the gas turbine. Information needs to be generated to determine the extent of gasification desired to obtain the highest efficiency, while maintaining the benefits of the PFBC in terms of meeting environmental standards. The partial gasification step can be referred to by any of several terms, including carbonization, pyrolysis, or mild gasification.

The goal of this task is to use the existing EERC mild gasification reactor, with some modification, to develop a database at temperatures and pressures representative of those for a second-generation system, including:

- Determining gas, tar, and liquid yields for selected coals.
- Investigating the fate of sulfur and alkali.
- Studying the amount of tar generated, its properties, and its elimination, to determine its effect in the hot-gas cleanup device.

2.2 Fate of Alkali in PFBC Systems

Alkali in the coal, especially organically bound alkali, will volatilize even at the low temperatures typical of a fluid-bed gasifier or combustor. This alkali can cause problems in both the filter media and the turbine. The focus of this task is on developing an understanding of how the alkalies are released so that methods of rendering them harmless can be found. Alkalies gettering to keep the alkali in the bed is one potential method of protecting the filter and turbine. Some work will be done on the pilot-scale bubbling and circulating atmospheric fluid beds. Because the vapor pressures of the alkali species are low and not greatly influenced by pressure, it is felt that data from the atmospheric units will be applicable to pressurized systems. Work will also be done on the bench-scale pressurized reactor. PHOEBE, a thermo-dynamic code for predicting gas-solid-liquid equilibrium stages, will be used as a tool to help predict trends with changing operating conditions and coal types.

2.3 Bench-Scale Reactor Testing

A bench-scale reactor to study PFBC reaction kinetics and conversions was designed around an already-existing piece of equipment to minimize costs. Design efforts attempted to minimize the impacts of the small size on the usefulness of the data, while providing for a wide range of conditions applicable to combustion and gasification in bubbling and entrained/circulating fluidized beds. A 3-inch ID reactor is envisioned. This reactor will be used to study sorbent utilization and alkali gettering. It is important to improve sorbent utilization to minimize the amount of sorbent feed and waste disposal. Extending the operating conditions where conventional sorbents are effective may help improve the overall efficiency of the PFBC. If properly designed, it is envisioned that this reactor could also be used for studying N_2O emissions, if time and budget allow.

2.4 Objectives of Current Year (7/91-6/92) Research

2.4.1 Task 1. Carbonizer Performance Evaluation

Baseline testing will be attempted using a Pittsburgh #8 coal and Plum Run dolomite. If successful operation can be maintained on the Pittsburgh #8, an experimental test matrix will be designed in collaboration with Foster Wheeler Development Corporation (FWDC) and the Morgantown Energy Technology Center (METC) so that a common database can be generated between the EERC system and that being built by Foster Wheeler. The establishment of a common point to allow scalability of data will allow other test data generated on the system to be used by Foster Wheeler when evaluating the impact of coal properties on the performance of the second-generation system.

If the baseline testing is sucessful, and if funds are available, parametric tests will be performed with other coals. Variables for these tests may include temperature, pressure, velocity, coal and sorbent type and size, and sorbent calcium-to-sulfur ratio. The goal is to collect process data on the formation of agglomerates and clinkers; tar-vapor condensation; the stickiness of the char-sorbent-elutriated effluent; levels and forms of sulfur and nitrogen; levels, forms, and phases of alkalies; yields, composition, and heating value of effluent; effects of tar cracking on sorbent-sulfur-capture effectiveness; and char physical characteristics. The coal and sorbent types tested and the test matrix will be reviewed with FWDC and METC before testing.

2.4.2 Task 2. Fate of Alkali in PFBC Systems

Several good thermochemical models are available to help predict the equilibrium concentrations of the solid, liquid, and gaseous species as a function of temperature and pressure. Two of these models, PHEOBE and SolGas

Mix, are used as tools to predict how changes in coal types and operating conditions will affect the amount and type of alkali released. This information is used in conjunction with results of bench- and pilot-scale work.

Some bench-scale work will be done using thermogravimetric analysis (TGA) and the pressurized drop-tube furnace. The purpose of this work is to look at the impact of coal type on the release of alkalies. The form of the alkali in the raw coal can significantly affect the quality of alkali released in the vapor and that retained within the original minerals of the coal.

Since techniques such as thermogravimetric analysis and drop-tube furnace tests cannot simulate the turbulent mixing of burning coal, and sorbent particles cannot provide the fluid dynamics of an FBC, alkali studies will also be performed on the bench-scale PFBC and on the pilot-scale atmospheric bubbling and circulating FBCs. The main purpose of this testing is to investigate the use of ash matrix modifiers to capture alkali in the bed. Conditions such as pressure, temperature, oxygen level, and ash modifier type will be investigated. An end goal of this phase is to find a material that can reduce both alkali and sulfur levels.

2.4.3 Task 3. Bench-Scale Reactor Testing

The bench-scale reactor designed during the previous program year will be constructed. The design calls for a 3-inch ID reactor vessel capable of operating up to 150 psi and 1800°F. Provisions will be made to sample at several locations in the bed and freeboard, with the hope of freezing reactions so that reaction pathways and kinetics can be determined. The design goals of this reactor are to study alkali release, ash modification, and sorbent utilization. Nitrous oxide emissions could also be studied.

As a part of this task, the bench-scale testing will focus on sorbent utilization for PFBC applications. A fundamental understanding and prediction of sulfur-capture efficiency for alkaline ash and limestone/dolomite sorbents over a wide range of conditions will be developed. Performance in both the carbonizer and combustor are important. During carbonizer testing, a sulfur balance will be performed to determine the form and product stream in which the sulfur will be present. Bench-scale tests will attempt to improve the overall sulfur capture. Potential advancements to the industry include improving the utilization of the sorbent material and extending the range of operating conditions in which sorbents are effective.

3.0 RESULTS AND DISCUSSION

3.1 Carbonizer Performance Evaluation

3.1.1 PFBC PDU Operation Summary During P022

The modified 100-lb/hr mild gasification process development unit (PDU) was run as a PFBC carbonizer to evaluate the use of Pittsburgh No. 8 bituminous coal under second-generation PFBC operating conditions. The experimental matrix for this test was discussed in the July through December 1991 semiannual technical report for this project. The test, P022, was conducted on December 2-3, 1991, and consisted of three run periods. Run conditions are presented in Table 1, and a description of the run is contained in the following paragraphs.

The carbonizer was pressure-tested and then heated at atmospheric pressure to the reaction temperature (1600°F) using methane. (Additional heat was supposed to have been supplied using propane, but condensation in the feed line from the propane tank to the system prompted the change to methane.)

TABLE 1

Carbonizer Test P022 Run Conditions

	Run Period		
	1	2	3
Coal	Wyodak	Wyodak	Pittsburgh No. 8
Wt. Dolomite/Wt. Coal	0.3	0.3	0.3
Dolomite/Coal Feed Rate, lb/hr	94	94	54.1[a]
Temperature, °F	1625	1625	1625
Pressure, psig	7	56	56
Gas Flow Rates, scfh			
Air	2187	3934	2919
Tempering N_2	0	2506	340
Transport N_2	387	1817	440
Purge	7	111	500
O_2	310	294	204
CH_4	177	312	255
Total	3068	8974	4658
Superficial Velocity[b]	6.1	5.6	2.8
Air/Coal, scfh/lb per hr	30.2	54.4	70.2

[a] Average value, feed rate increased during the run period.
[b] At reaction conditions.

Agglomeration had been noted during earlier tests using Pittsburgh No. 8 bituminous coal. Therefore, to ensure a successful system start-up, the run was initiated using Wyodak subbituminous coal, and the first run period consisted of operation using Wyodak coal at 7 psig (1.5 atm) and 1625°F. Char, condensate, and product gas samples were quantitatively taken during this run period.

Once steady-state conditions were achieved during the first run period, the pressure was increased and the unit allowed to come to steady state again. The second run period consisted of operation of the unit on Wyodak coal at 1625°F and 56 psig (4.8 atm). Product gas samples were taken during this run period, but condensate and char samples were not.

The changeover to Pittsburgh No. 8 coal was scheduled to take place gradually to minimize the possibility of agglomeration. The system was to be fed a mixture of Wyodak and Pittsburgh No. 8 coals and allowed to reach steady-state conditions. At that point, Pittsburgh No. 8 coal was to be introduced at a slow feed rate, increasing in 20-lb/hr increments and allowing the system to reach steady state.

The changeover to Pittsburgh No. 8 coal was not as gradual as had been planned. When the pressure was maintained at 56 psig (4.8 atm) and the temperature at 1625°F, the feed was abruptly changed from Wyodak to Pittsburgh No. 8 coal. The coal/dolomite feed rate was increased over the course of the entire third run period, from 20 lb/hr to 80 lb/hr. A hot spot developed on the side of the vessel where an unused nozzle had been insufficiently insulated, and the run was terminated. Following shutdown, no evidence existed of the extensive agglomeration of the Pittsburgh No. 8 coal that had occurred during the earlier attempts to carbonize it. A product gas sample was taken during the run period, and the char present in the cyclones and the char hopper at the end of the run was collected. A sample of the condensate was not taken during this run period.

3.1.2 Analytical Protocol of Samples Taken During P022

The product gas samples that were collected during P022 were analyzed by gas chromatography. Char samples were analyzed for moisture, fixed carbon, volatile matter, and ash contents (proximate analysis); for C, H, N, S, and O (by difference) contents (ultimate analysis); and via x-ray fluorescence analysis to determine the inorganic constituents of the ash. The condensate was filtered and the solids subjected to determination of moisture, volatile matter, fixed carbon, ash, and sulfur contents; heating value; and solubility in tetrahydrofuran (THF). The condensate liquids were analyzed for total organic carbon and total phenolic contents. The density of the liquid fraction of the condensate was also determined.

3.1.3 Data Reduction and Model Modification

A good mass balance could only be performed for the first run period due to the lack of quantitative samples. Mass and material balances were performed for this run period and yielded the data presented in Table 2. An elemental balance over this run period is shown in Table 3. The elemental balance presents the values for H and O on a dry basis; therefore, a water balance is also included.

Because the data necessary to perform the mass balances were unavailable, the yield structure for the third run period (performed with Pittsburgh No. 8 coal) was determined in an alternate manner. The computer model of the mild gasification unit, that had been developed for use in determining the various gas flows necessary to meet the experimental matrix conditions, was modified to predict the product slate of carbonization. The model was originally developed using three steps:

1. Input of the flow rates and analyses of the feedstocks.

2. Description of the chemical reactions occurring within the vessel with respect to the production of heat (i.e., burning methane and/or coal).

TABLE 2

Material Balance for P022 Run Period 1 with Wyodak Coal[a]

<u>In</u>	
Coal Feed	
Wyodak (maf[b] basis)	450
Dolomite + Ash	200
Water	118
Gas Feed	
Air	1436
N_2	251
CH_4	53
O_2	226
Scrubber Water	269
<u>Out</u>	
Solids	
Char (maf basis)	62
Ash	91
Water	5
Condensate	294
Product Gas	
O_2	21
H_2	30
CO_2	577
N_2	1430
CO	402
CH_4	22
H_2O	5.6
Char Yield	11.2%
Closure	98.14%

[a] All weights in lb.

[b] Moisture- and ash-free.

3. Performance of a heat balance over the system to obtain an estimate of the reactor heat loss.

Additional information was added to the model so that it could be used to predict the yield structure of the carbonizer tests. The following information was incorporated during modification of the model:

4. Description of the chemical reactions taking place within the carbonizer.

TABLE 3

Elemental Balance for P022 Run Period 1
with Wyodak Coal[a]

	In	Out
C	408	399
H[b]	38	38
N	1357	1431
S	1	1
O[b]	713	688
Ash	99	93
Water	387	299

[a] All weights in lb.
[b] Moisture-free basis.

Several reactions take place within the vessel proper, including the combustion of methane ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$); the reaction of the methane combustion-produced water with carbon in the coal ($H_2O + C \rightarrow CO + H_2$); the combustion of carbon in the coal ($\frac{1}{2}O_2 + C \rightarrow CO$; $O_2 + C \rightarrow CO_2$); the reaction of coal moisture with carbon in the coal ($H_2O + C \rightarrow CO + H_2$); pyrolysis of the coal, resulting in approximately equal molar ratios of H_2O and CO_2 (in which the reaction is essentially $CH_2O_3 \rightarrow H_2O + CO_2$); the reaction of the pyrolysis water with carbon in the coal ($H_2O + C \rightarrow CO + H_2$); and, finally, the production of CO_2 during heating of the dolomite.

5. Development of chemical boundary machine constants based upon the behavior of the system during operation using Wyodak coal.

   Approximately 41.5 mol% of the methane and 23.5 mol% of the oxygen channeled during the first run period with Wyodak coal. About 20 mol% of the water available for reaction did not react and left the system with the product gas. Three assumptions were made with respect to the chemical reactions taking place in the reaction vessel: 1) the ratio of CO to CO_2 produced during carbon combustion was 0.35 to 0.65, 2) approximately 35 mol% of the elemental hydrogen present in the dry coal went to the production of pyrolysis water, and 3) the dolomite weight loss was assigned entirely to the production of CO_2.

6. Determination of the quantity of char produced.

7. Determination of the quantity and speciation of product gases.

8. Performance of mass and material balances on the system and the inclusion of this information in the model.

9. Performance of an elemental balance over the vessel proper.

10. Definition of the fourth reaction zone (in the water scrubber) and the reactions occurring there.

    The hot product gas, rich in CO, was contacted with water in the scrubbers. The gas temperature at this point was high enough for the water/gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) to take place.

11. Verification of mass, material, elemental, and heat balances for the entire system.

Figure 1 is a diagram of the reaction zones that occur in the system.

3.1.4 Discussion of Results

Once completed, the model was used to predict the product slate of the first run period. This predicted product slate is compared to the actual product slate in Table 4. As the table shows, the model accurately predicts the product slate for the run period using Wyodak subbituminous coal. There is little reason to expect that it could not also be successfully used to predict the product slate of the carbonization of Pittsburgh No. 8 bituminous coal.

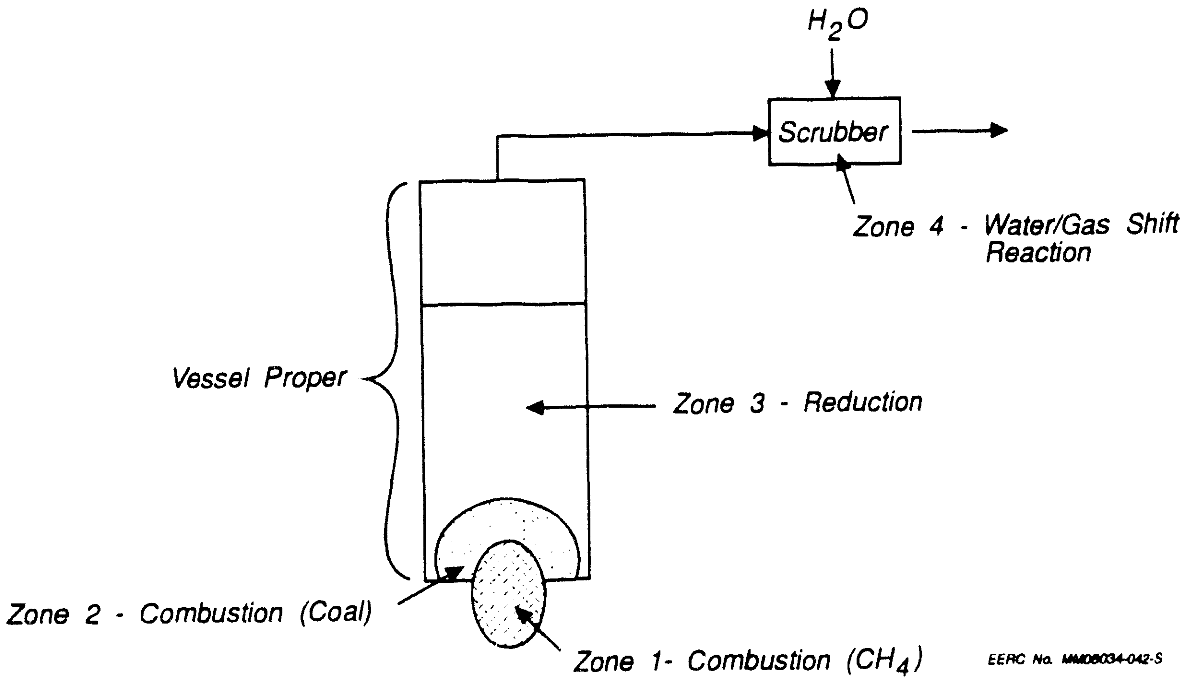

Figure 1. Reaction zones included in the predictive model.

Due to differences between the Wyodak and Pittsburgh No. 8 coals, it was assumed that slightly less elemental hydrogen would go to the production of pyrolysis water (33% rather than 35%). It was also assumed that the amount of water that did not react increased from 19.9 mol% to 30 mol% and that the ratio of CO to CO_2 produced during combustion of the carbon decreased from 0.35:0.65 to 0.10:0.90.

Table 5 compares the predicted product slate for run period 3 with the actual product slate (such as could be calculated) from the Pittsburgh No. 8 run period. Not all values could be compared due to the lack of samples, but the predicted and actual gas product slates agree fairly well. The char samples collected during this run period were taken from the char hopper and the cyclones. The ultimate analysis of the char in the char hopper was quite different from that of the cyclone fines, as can be seen in Table 6. Based upon the quantities collected from each location during the Wyodak run period, these values were weighted to arrive at an average char analysis, which is shown in Table 5. The predicted and average values agree fairly well when it is taken into account that small real differences at this scale can result in

TABLE 4

Comparison of Predicted P022 Run Period 1 Product Slate with Actual Product Slate[a]

Coal:	Predicted Wyodak	Actual Wyodak
Product Gas, lb		
O_2	66	21
H_2	30	30
CO_2	617	577
N_2	1355	1430
CO	410	402
CH_4	27	22
H_2O	5.5	5.6
Total	2510.5	2487.6
Condensate, lb	322	294
Char (maf[b]), lb	62	62
Dolomite + Ash, lb	110	91
Water in Char, lb	4.9	4.7
Closure	100%	98.14%
Char Yield	13.8%	11.2%

[a] Total quantities produced during run period with Wyodak coal.

[b] Moisture- and ash-free.

TABLE 5

Comparison of Predicted P022 Run Period 3 Product Slate with Actual Product Slate[a]

Coal:	Predicted Pittsburgh #8	Actual Pittsburgh #8	
Product Gas, lb			
O_2	21	5	
H_2	6	3	
CO_2	175	119	
N_2	686	750	
CO	45	37	
CH_4	12	8	
H_2O	6.6	--[b]	
Total	951.6	--	
Condensate, lb	26.4	--	
Char (maf[c]), lb	22.5	--	
Dolomite + Ash, lb	25.5	--	
Water in Char, lb	0.2	--	
Char Analysis, wt% maf coal			
H	3.14	0.67	Weighted average of all analyses[e]
C	72.31	72.04	
N	2.17	0.98	
S	10.48	3.34	
O[d]	11.91	22.96	
Closure	99%	--	
Char Yield	25.6%	--	

[a] Total quantities produced during run period with Pittsburgh No. 8 coal.
[b] Information not available.
[c] Moisture- and ash-free.
[d] By difference.
[e] Ranges of analyses are given in Table 6.

dramatically different percentages. It should also be noted that most of the predicted values fall within the range defined by the two char analyses.

Based upon the product slate predicted using the computer model, it appears that operation at 1625°F, 4.8 atm, and the gas flow rates noted in Table 1, results in a char yield of approximately 25 wt% of the Pittsburgh No. 8 coal fed to the system.

3.2 Bench-Scale Reactor Testing

A pressurized fluidized-bed (PFB) reactor has been designed and is being constructed to allow extensive alkali and hot-gas cleanup testing on a cost-effective manner over a wide range of operational conditions. A side view of

TABLE 6

Elemental Analysis of Char and Cyclone Fines
From P022 Run Period 3[a]

	Char Hopper	Cyclone Fines
H	0.91	0.54
C	90.10	62.99
N	1.37	0.76
S	9.29	0.05
O[b]	-1.69	35.64

[a] All values in wt% on a moisture- and ash-free basis.
[b] By difference.

the reactor and cyclone are shown in Figure 2. Preheated fluidizing gas at temperatures up to 1000°F and pressures up to 150 psig will be supplied at the bottom of the reactor through a 1-in schedule 40 pipe at sufficiently high velocities to prevent the sized bed material from dropping out during operation. Bed material can be sampled or collected using a lock hopper system located at the bottom of the reactor. The fluidizing gas enters into the 3-in schedule 80 main section of the reactor through a conical transition. The operating velocities in the 3-in section will allow some internal recirculation of the fluidized-bed material. External heaters will be used for heating and maintaining the reactor and hot cyclone at temperatures up to 2000°F for atmospheric operation and up to 1700°F for operation at 150 psig.

Limestone, inert bed material, or ash generated from a combustor or by an ashing procedure can be added at the start of a test using a lock hopper system. Selected additives and coal can be fed separately at controlled rates during testing. Coal feed, when utilized, will be maintained at a low rate to eliminate any heat removal requirements from the reactor. Fluidizing gas can be supplied as air or as various mixtures of nitrogen, oxygen, carbon dioxide, carbon monoxide, sulfur dioxide, and nitrogen oxides to result in a flue gas similar to that generated in a full-scale fluidized-bed boiler. Different oxidizing and reducing condition tests can also be conducted. An alkali sampling probe can be inserted through the top of the reactor or through the top of the hot cyclone for when hot-gas cleanup testing is being conducted.

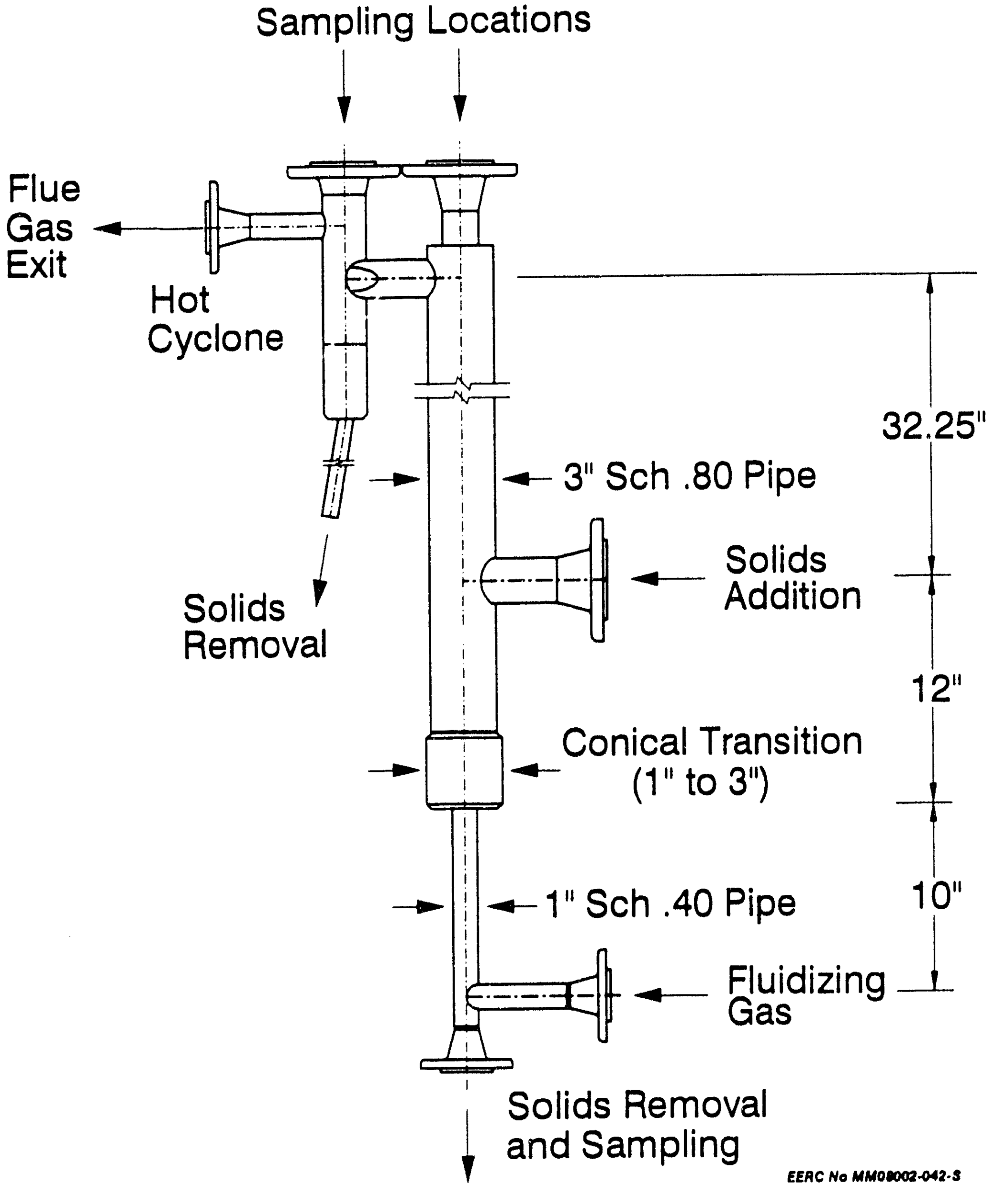

Figure 2. Side view of pressurized fluidized-bed reactor.

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(10/80)

U.S. DEPARTMENT OF ENERGY

FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 1900-0127
Page 1 of 2

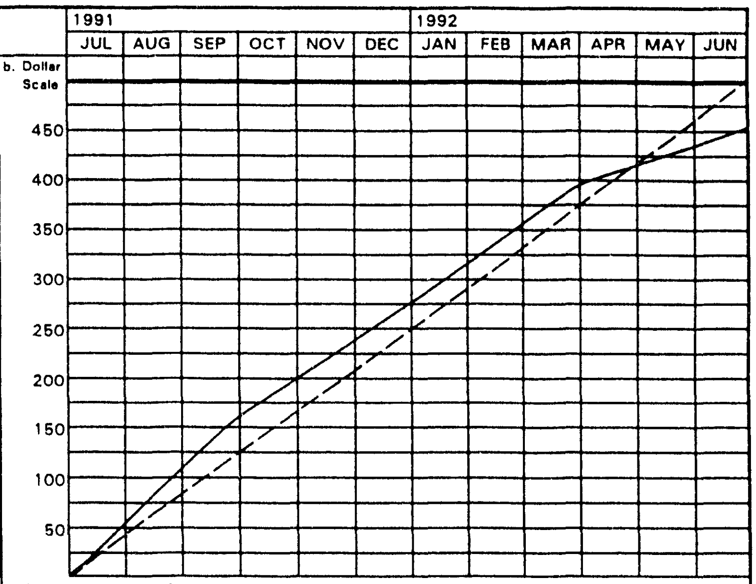
1. Program/Project Identification No. DE-FC21-86MC10637
2. Program/Project Title Pressurized Fluidized-Bed Combustion (4.7)
3. Reporting Period 3-1-92 through 6-30-92
4. Name and Address Energy and Environmental Research Center
University of North Dakota
Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000
5. Program/Project Start Date 4-1-86
6. Completion Date 6-30-92
7. FY 91/92
8. Months or Quarters Quarters
9. Cost Status a. Dollars Expressed in Thousands b. Dollar Scale

10. Cost Chart

Fund Source		Quarter 1st	2nd	3rd	4th	Cum. to Date	Tot. Plan
DOE	P	125	125	125	126	501	501
	A	161	118	114	58	451	
	P						
	A						
	P						
	A						
	P						
	A						
Total P		125	125	125	126	501	501
Total A		161	118	114	58	451	
Variance		(36)	7	11	68	50	

P = Planned A = Actual

Total Planned Costs for Program/Project $501

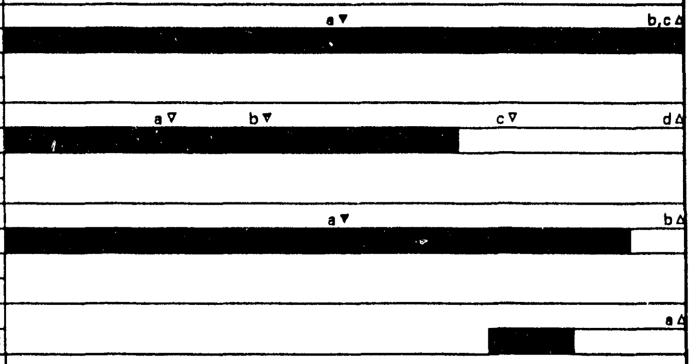


c. Cumulative Accrued Costs

	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN
Planned			125			250			375			501
Actual			161			279			393			451
Variance			(36)			(29)			(18)			50

11. Major Milestone Status — Units Planned / Units Complete

1. Carbonizer Performance Evaluation P C
2. Fate of Alkali in PFBC Systems P C
3. Bench-Scale Reactor Testing P C
4. Sulfation of FWDC Bed Material P C



12. Remarks

Due to EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.

13. Signature of Recipient and Date

14. Signature of DOE Reviewing Representative and Date

FORM E1A-459E
(10/80)

U.S. DEPARTMENT OF ENERGY

FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 1900 0127

Page 2 of 2

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Pressurized Fluidized-Bed Combustion (4.7)	3. Reporting Period 3-1-92 through 6-30-92
4. Name and Address	Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000	5. Program/Project Start Date 4-1-86 6. Completion Date 9-30-92

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
Task 1	Carbonizer Performance Evaluation:			
1.a	Perform baseline tests	12-31-91	3-31-92	
1.b	Develop process data on other coals	6-30-92		
1.c	Identify operability constraints	6-30-92		
Task 2	Fate of Alkali in PFBC Systems:			
2.a	Recommendation of modifiers to FWDC	10-1-91		
2.b	Modeling studies	11-15-91	3-31-92	
2.c	Bench-scale studies	3-31-92	*	
2.d	Ash modification/pilot scale	6-30-92	*	
Task 3	Bench-Scale Reactor Testing			
3.a	Sulfur balance on carbonizer	12-31-91	5-31-92	
3.b	Bench-scale studies	6-30-92		
Task 4	Sulfation of FWDC Bed Material	6-30-92		
	* Tasks replaced by Task 4			

5.0 LIQUEFACTION RESEARCH

5.1 Low-Rank Coal Direct Liquefaction

LOW-RANK COAL DIRECT LIQUEFACTION

Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992

by

John R. Rindt, Research Supervisor
Melanie D. Hetland, Research Engineer

Energy and Environmental Research Center
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Grand Forks, North Dakota 58202-8213

Technical Monitor: Mr. Michael J. Baird

for

U. S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, Pennsylvania 15236-0940

July 1992

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

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LIST OF TABLES

LOW-RANK COAL DIRECT LIQUEFACTION

EXECUTIVE SUMMARY

The Energy and Environmental Research Center has developed a multistep direct liquefaction process designed specifically to take advantage of the positive characteristics of low-rank coals (LRCs). The steps consist of 1) a pretreatment soak at very low-severity conditions in a hydrogen-donating solvent, 2) a solubilization step in which most of the coal dissolves in a process-derived solvent under relatively low-severity conditions, 3) a polishing step in which hydrogen gas and a process-derived solvent are added to the system to solubilize the remaining coal, and 4) hydrotreatment using hydrogen gas and a catalyst.

The entire multistep sequence was preliminarily investigated during the period from January through June 1992. Four complete run sequences were performed, including 1) pretreatment of an Indian Head lignite/hydrogenated, coal-derived anthracene oil (HA061) slurry at 175°C and 2100 psi with Ar and H_2S; 2) solubilization at either 350° or 375°C and 3500 psi with CO; 3) polishing using cresylic acid at either 435° or 460°C and 3200 psi with H_2; and 4) hydrotreatment in HA061 vehicle solvent at 425°C and 3500 psi with H_2 and Shell 424 catalyst. The hydrotreatment was performed until no significant hydrogen uptake was noted in order to define the upper range of hydrotreatability of the slurry. Testing was performed in the EERC's hot-charge, batch autoclave system. Products were analyzed for tetrahydrofuran (THF) solubility and ash and water content.

Mass and material balances were performed for the series, and the analytical results were incorporated. The resulting yield structures define the hydrotreated products of the entire four-step system based upon moisture- and ash-free (maf) coal fed to the pretreatment step. The most successful series (N562) resulted in a conversion of 96.64 wt% of the maf coal fed to the system. Of that total, 17.27 wt% consisted of gaseous products, 66.04 wt% consisted of premium distillate, 4.12 wt% consisted of soluble residuum, and 9.13 wt% consisted of light oxygenate material.

1.0 INTRODUCTION

To expand the scientific and engineering database of low-rank coal (LRC) liquefaction, investigations of direct liquefaction processes that produce the most competitive feedstocks or liquid fuels must be investigated. Coal can be converted to very high yields of oils with increasing levels of efficiency using a two-stage processing approach. Current two-stage direct liquefaction processes are usually performed with high-rank coals at temperatures greater than 400°C and pressures of approximately 2500 psi. Catalysts, which are very expensive, are generally used in both stages. While the economics of direct liquefaction have improved during the last five years, it is not yet a commercially viable method of producing liquid fuels due to its use of catalysts in both stages and the severity of the conditions employed.

Work performed early in the 1980s showed that LRCs are very reactive. It seems logical that they could be cost-effectively substituted into the direct liquefaction process since they would most likely require less severe reaction conditions. However, most attempts to use LRCs during direct liquefaction have not been successful because the coal reacts too rapidly for the available hydrogen source(s), resulting in the production of retrograded material. Any successful use of LRCs in direct liquefaction will require that advantage be taken of their positive characteristics.

This is the view taken by the EERC, which sees the initial solubilization of coal in the solvent as reverse coalification and the subsequent upgrading as reforming or refining. Under this scenario, it is assumed that the structure of coal is composed of physically and chemically tangled, highly cross-linked molecules. The molecular structures of premium distillate fuels (the desired product), by comparison, are discrete molecules of similar size and chemical nature, having virtually no chemical or physical attachments. The goal, therefore, is to go from a chemical knot to an orderly structure. The first phase in liquefaction should be to "untangle" the coal structure (at low-severity conditions to prevent coalification [retrograde] reactions), while the second phase should be to "organize" the untangled pieces so that those of similar size and chemical nature are first separated from the remaining material and then stabilized to prevent back reactions.

Through funding provided under the Cooperative Agreement, the EERC has been working on this concept for a number of years and has developed a process specifically designed for LRCs that consists of four steps, only the last of which is catalytic. The first step is a pretreatment soak at very low-severity conditions (175°C) in a hydrogen-donating solvent. (This is analogous to the coal-drying step currently performed prior to liquefaction processing. Drying is usually performed at approximately 115°C.) The purpose of this step is to place hydrogen or radical-capping agents in a location so that they are available to the coal when needed during the "untangling" portion of the reaction. The second step is a solubilization ("untangling") step, in which most of the coal dissolves in a process-derived solvent under relatively low-severity conditions. The third is a polishing step, in which hydrogen gas and a process-derived solvent are added to the system to solubilize the remaining coal. (Low-rank coals tend to produce phenolic material as they undergo liquefaction; the highest probability of dissolving them would be in a solvent similar to such a coal-derived solvent.) The final, or "organizing" step, consists of hydrotreating the solubilized coal using a catalyst and hydrogen gas under moderately severe conditions. It may be possible to increase the conversion to upgraded liquids, and/or improve the product slate, and/or lower the reaction severity required during the fourth step (hydrotreatment) if appropriately solubilized material is produced during the first three steps (pretreatment, solubilization, and polishing).

2.0 GOALS AND OBJECTIVES

2.1 Three-Year Program Beginning FY'89-90

The primary objective of the three-year Low-Rank Coal Direct Liquefaction program has been to develop an LRC liquefaction process that will result in increased levels of conversion to distillable liquids. The work effort associated with meeting this objective has included an investigation of low-severity preconversion treatment of LRCs and a mechanistic study of the retrograde reactions which occur during processing as a function of conversion. Through mechanistic inference, the results of this work may be applicable to higher-rank coals.

The potential role of preconversion treatment of LRCs has been evaluated empirically by determining which systems can successfully prepare LRCs for thermal first-stage conversion during two-stage processing. The initial work screened various proposed systems for their effect on first-stage conversion. Second-year work focused on promising systems identified during the initial screening, evaluating them more fully with respect to their impact on thermal first-stage processing.

Preliminary evaluation of the use of hydrogen-donating solvents during preconversion treatment was performed on the batch scale. The products from the batch-scale pretreatment tests were subjected to two-step, thermal first-stage processing to determine the effects of pretreatment on the first-stage yield structure. The results were compared to those of previous tests performed with a nonhydrogen-donating solvent.

A preliminary mechanistic study of the retrograde reactions that occur as a function of typical liquefaction processing was scheduled for the first year. For this study, samples were produced at low-severity processing conditions with conversions of 10%, 50%, and 95%. An additional test was performed at more severe conditions to produce a coked product. Analysis of the products of the tests indicated which changes occur in the products with respect to increasing conversions to soluble material. A relatively detailed examination of the fate of the chemical functional groups present in the coal was provided by ^{13}C NMR analysis. This technique made it possible to observe and follow specific retrograde trends, expanding on the knowledge necessary to devise a more efficient processing scenario for LRCs.

2.2 Third-Year (FY'91-92) Work Plans

Specific work scheduled for FY'91-92 has undergone several changes in scope. The following paragraphs describe the tasks as they were, or will be, performed.

Task 1 consisted of the integration of pretreatment (Step 1) with low-severity first-stage processing developed during earlier EERC work (Step 2 plus Step 3), followed by hydrotreatment (Step 4) of the solubilized product.

The best of the pretreatment schemes studied was added to first-stage processing at conditions that, during the transition quarter of FY'88-89, provided the most favorable yield structure for LRCs. Hydrotreatment was performed at conditions that would result in the maximum possible upgrading.

Task 2 was eliminated when Task 1 was amended to include the hydrotreatment step.

Task 3 consists of the preparation of the final project report covering the period July 1, 1989, through the end of the project (including the proposed work mentioned in Section 3.2). The final report will summarize all of the information gathered during the integration of the EERC multistep, two-stage liquefaction process.

3.0 ACCOMPLISHMENTS

3.1 FY'91-92 Task 1--Further Investigation of Pretreatment and Lower-Severity Processing

As mentioned in Section 1.0, the EERC has developed a four-step liquefaction process consisting of:

- Step 1 - Pretreatment, which was investigated during FY'89-90 and FY'90-91.
- Step 2 - Solubilization.
- Step 3 - Polishing, which was investigated during FY'88-89, Task K.
- Step 4 - Hydrotreatment.

The first three steps comprise the thermal first stage of liquefaction, but have never been performed as part of an integrated run scheme. The objective of the FY'91-92 Task 1 test matrix was to add the polishing step (Step 3, a 20-minute, or less, reaction with H_2 at 425°C) to the best pretreatment-solubilization combination tested during FY'90-91 (i.e., pretreatment under Ar and H_2S at 175°C and 2000 psi for 60 minutes, followed by solubilization under CO at 375°C and 3500 psi for 60 minutes). Due to the promising results obtained during the FY'90-91 studies, it was decided that the annual project plan would be amended to include hydrotreatment of the products of the integrated three-step sequence.

3.1.1 Methods and Materials

The test matrix for Task 1 is presented in Figure 1. As the figure shows, the testing was performed according to a tree diagram-type of matrix. Performing the tests in this manner, i.e., using the same feed slurry whenever possible, enabled direct comparisons to be made between the run sequences. Two Step 1 runs were performed at identical conditions to obtain sufficient pretreated slurry for the remaining processing. The pretreated slurries from these two runs, N553 and N554, were combined into a bulk sample. (All analyses were performed on the bulk sample rather than on the individual pretreated slurries.) Pretreated slurry was then solubilized in two batches, one at ~375°C (N555) and one at ~350°C (N556). The solubilized products of each of these Step 2 runs were polished (Step 3) at either 460°C (N558 or N557) or 435°C (N559 and N560) with a small amount of added cresylic acid. Each polished product was combined with a heavier vehicle solvent (hydrogenated anthracene oil) and distilled to remove a quantity of water and light, highly oxygenated solvent/coal-derived liquid equal to that added during the polishing step. Finally, each of the polished product slurries from Step 3 was hydrotreated in Step 4 (N562, N564, N563, and N566, respectively). The multistep run sequences are referred to in this report by the run numbers of their hydrotreatment steps. The specific run solvents, additives, and conditions for each step of the four run sequences are given in Table 1.

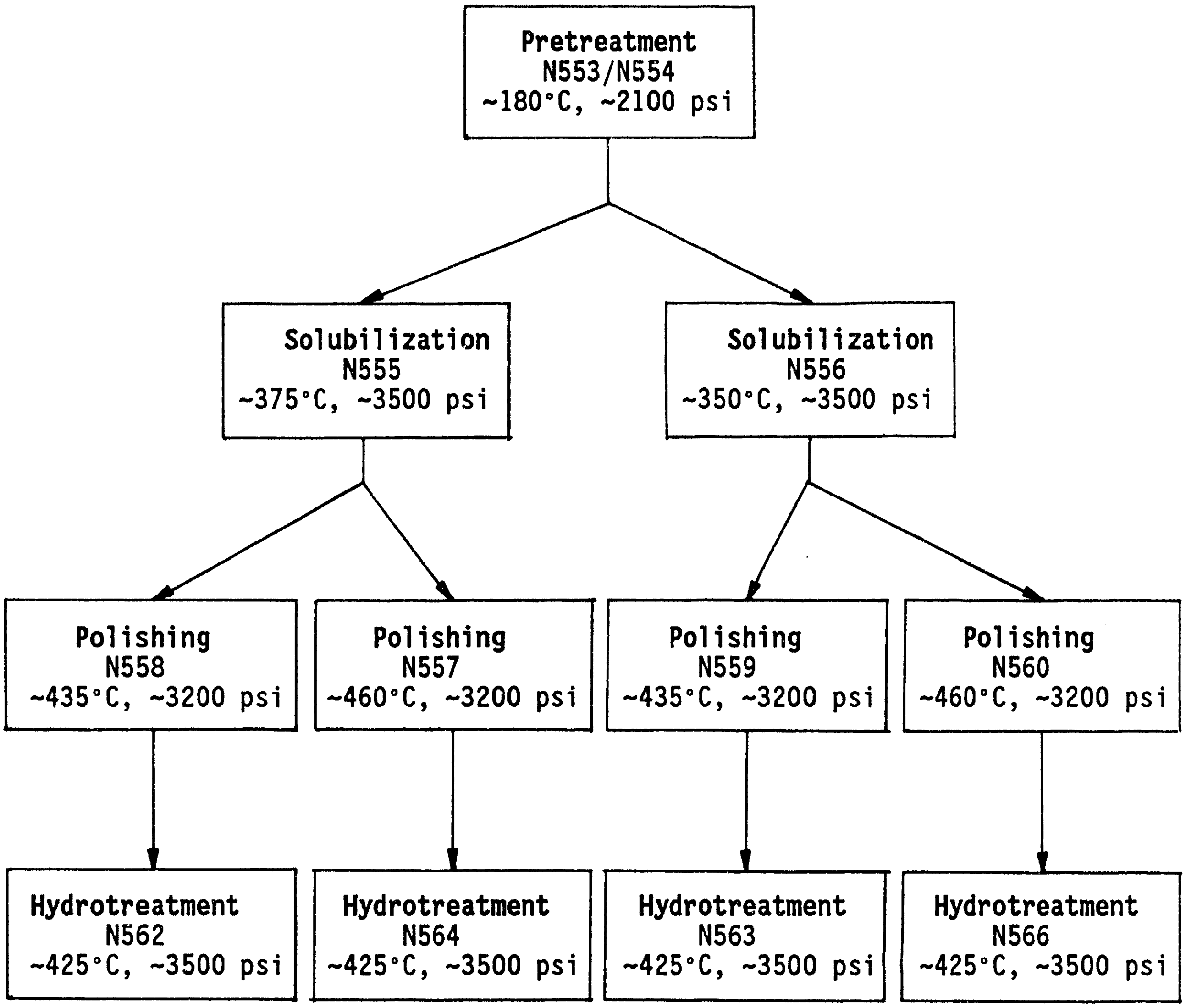

Figure 1. Run sequences tested during FY'91-'92 Task 1.

TABLE 1

Conditions of Task 1 Run Series

	N562	N563	N564	N565
<u>Step 1 - Pretreatment</u>				
Run No.	N553+N554	N553+N554	N553+N554	N553+N554
Solvent	HA061[a]	HA061	HA061	HA061
Additive	H_2S	H_2S	H_2S	H_2S
Gas	Ar	Ar	Ar	Ar
Avg. Temp., °C	179	179	179	179
Max. Temp., °C	184	184	184	184
Avg. Pressure, psi	2064	2064	2064	2064
Max. Pressure, psi	2100	2100	2100	2100
Residence Time, min	60	60	60	60
<u>Step 2 - Solubilization</u>				
Run No.	N555	N556	N555	N556
Feed	N553+N554	N553+N554	N553+N554	N553+N554
Additive	None	None	None	None
Gas	CO	CO	CO	CO
Avg. Temp., °C	375	353	375	353
Max. Temp., °C	385	354	385	354
Avg. Pressure, psi	3488	3460	3488	3460
Max. Pressure, psi	3600	3515	3600	3515
Residence Time, min	60	60	60	60
<u>Step 3 - Polishing</u>				
Run No.	N558	N559	N557	N560
Feed	N555	N556	N555	N556
Additive	CA1[b]	CA1	CA1	CA1
Gas	H_2	H_2	H_2	H_2
Avg. Temp., °C	435	433	458	461
Max. Temp., °C	437	435	461	465
Avg. Pressure, psi	3190	3363	3200	3439
Max. Pressure, psi	3226	3435	3275	3540
Residence Time, min	20	20	20	20
<u>Step 4 - Hydrotreatment</u>				
Run No.	N562	N563	N564	N566
Feed	N558	N559	N557	N560
Additive	Shell424	Shell424	Shell424	Shell424
Gas	H_2	H_2	H_2	H_2
Avg. Temp., °C	423	424	422	420
Max. Temp., °C	426	425	426	421
Avg. Pressure, psi	3459	3461	3525	3554
Max. Pressure, psi	3655	3635	3675	3675
Residence Time, min	180	180	180	180

[a] Hydrogenated coal-derived anthracene oil.

[b] Cresylic acid solvent.

Testing was performed in the EERC hot-charge, batch autoclave system. The 1-gal autoclave was used when larger quantities were processed (i.e., during Steps 1 and 2 [pretreatment and solubilization]). The 1-L autoclave was used for the polishing and catalytic upgrading (Steps 3 and 4). Karl Fischer water, ash, and THF solubility analyses were performed on the feed and product slurries. Due to a lack of funding, elemental analyses were performed for only a few runs.

3.1.2 Discussion of Results

Mass and material balances were performed for the run sequences based upon maf coal fed to the pretreatment step. Allowances were made for the removal of sample aliquots for analysis. Combining the analytical results and the material balances resulted in the calculation of product slates for the integrated run series. In other words, product slates were calculated for the entire four-step system based upon maf coal fed to the pretreatment step. These product slates are presented in Table 2.

Tables 3 and 4 summarize this information and organize it in a simplified manner to permit easier comparisons between run series. As seen in Table 3, comparison of solubilization (Step 2) at 350° and 375°C shows that higher-temperature solubilization ultimately resulted in less gas + water production (about 17 wt% compared to 34 wt%) and more total liquid product (about 70-80 wt% compared to 59 wt%) than solubilization at the lower temperature. More of the hydrotreated liquid product was in the form of premium distillate (66 wt% compared to 31-56 wt%) when the slurry had been solubilized at 375°C.

When the polishing (Step 3) temperatures are compared, it can be seen that the higher-temperature polishing (~460°C) resulted in yields that were similar to those of the lower-temperature polishing (~435°C), but that the liquid product slates were very different. This is especially noticeable for N563 and N566, the run series with 353°C solubilization. The lower-temperature polishing step resulted in substantial differences in yields of distillate, soluble resid, and oxygenates. In this case, the higher polishing temperature seems to have cracked more of the coal-derived material, resulting in the production of far more oxygenates at the expense of distillate production. The higher polishing temperature also resulted in an increased production of soluble resid. The same differences were present, but not as obvious for the N562 and N564 run series with 375°C solubilization. Slightly more distillate and soluble resid were produced when the higher polishing temperature was used, but far fewer oxygenates were produced. The highest overall conversions were produced when polishing was performed at the lower temperature. The higher polishing temperature seems to have retrograded some of the coal-derived material (probably the phenolic material), resulting in a conversion loss at the expense of the production of the oxygenates.

A comparison of the gas + water yields is presented in Table 4. As the table shows, 2.0 wt% of the maf coal fed to the system was removed during the pretreatment (Step 1) as gaseous products. Twice as much of the maf coal left the system as gas during both the solubilization and polishing steps (Steps 2 and 3, respectively) when the solubilization was performed at ~350°C. The gaseous product slates of the polishing step were very different for the run series performed at higher solubilization temperatures compared to those performed at lower solubilization temperatures. It appears that more CO_2 is

TABLE 2

Product Slates of Task 1 Run Series[a]

Hydrotreatment Run No.	N562	N563	N564	N566
Solubilization Temp., °C	375	353	375	353
Polishing Temp., °C	435	433	458	461
Gas Out				
CO	-65.92	-36.92	-63.20	-36.44
H_2	-1.50	-0.93	-5.46	-2.64
CO_2	114.26	93.05	116.00	93.65
C1-C3	11.53	13.50	11.70	14.38
H_2S	1.48	0.58	0.92	0.42
H_2O	-42.57	-34.12	-42.27	-35.32
Total Gas + Water	17.27	35.16	17.68	34.04
Liquid Out				
Oxygenated Liquids	9.13	-0.13	2.49	17.77
Premium Distillate	66.04	56.35	67.08	31.46
Soluble Residuum	4.12	3.33	3.26	9.00
Total Liquids	79.29	59.55	72.83	58.23
Unconverted IOM	3.36	7.60	9.12	6.43
Total, All Products	99.93	102.31	99.64	98.70

[a] Product slates given include all steps (pretreatment, solubilization, polishing, and hydrotreatment) and are based upon percentage of maf coal fed to the pretreatment step. Positive values indicate production of a component; negative values indicate a consumption.

TABLE 3

Comparison of Effect of Solubilization and Polishing Temperatures on Final Hydrotreated Product Slate[a]

Hydrotreatment Run No.	N563	N566	N562	N564
Solubilization Step Temp., °C	353	353	375	375
Polishing Step Temp., °C	433	461	435	458
Gas + Water Yield	35.16	34.04	17.27	17.68
Liquid Yield				
Distillate	56.35	31.46	66.04	67.08
Soluble Resid	3.33	9.00	4.12	3.26
Oxygenates	-0.13	17.77	9.13	2.49
Total	59.55	58.23	79.29	72.83
Conversion, % maf coal fed to system	92.40	93.57	96.64	90.88

[a] Yields are given as percentage of maf coal fed to the pretreatment step. Positive values indicate production of a component; negative values indicate a consumption.

TABLE 4

Comparison of Gas Plus Water Production for Task 1 Run Series[a]

Hydrotreatment Run No.	N563	N566	N562	N564
Solubilization Step Temp., °C	353	353	375	375
Polishing Step Temp., °C	433	461	435	458
Pretreatment	2.00	2.00	2.00	2.00
Solubilization	17.95	17.95	8.29	8.29
Polishing				
CO_2	4.77	5.42	2.55	4.50
C1-C3	6.77	7.62	2.91	2.75
Other	3.01	2.61	-0.21	0.15
Total Polishing	14.55	15.65	5.25	7.40
Hydrotreatment	0.66	-1.56	1.73	0.00

[a] Gas + water yields are given as the percentage of maf coal fed to the pretreatment step. Positive values indicate production of a component; negative values indicate a consumption.

produced at higher polishing temperatures, but that the hydrocarbon gas (C1-C3) yield is about the same.

3.1.3 Conclusions

- As part of the integrated run sequence, solubilization (Step 2) performed at 375°C produces higher yields of better-quality hydrotreated liquid products than solubilization performed at ~353°C.
- As part of the integrated run sequence, polishing (Step 3) performed at ~435°C results in desirable liquid product slates and high conversion levels without the retrograding that was noticed at the higher polishing temperature.
- Of the run sequences tested, it would appear that a run sequence incorporating a solubilization step at 375°C and a polishing step at 435°C (i.e., a run series similar to that of N562) would produce the greatest yield of high-quality, desirable products.

3.2 FY'91-92 Task 3--Final Project Report

The final project report, covering all activities relevant to the development of the EERC multistep liquefaction process, will be prepared after all remaining studies have been completed. Funding is currently being pursued to evaluate the effect of changes in severity of the hydrotreatment step (Step 4). If the funding is approved, the task will consist of 12 autoclave tests, supporting analytical effort, and the reduction and reporting of data. It is expected that this task will require 12 months to complete following receipt of funding. The final project report will incorporate the information gathered during this task.

4.0 FUTURE OBJECTIVES

- If approved, lower-severity hydrotreatment conditions (lower temperatures and pressures, shorter residence times) will be investigated to determine their effect on the EERC's integrated liquefaction process.
- The final project report will be prepared.

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(10/80)

U.S. DEPARTMENT OF ENERGY

FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 1900 0127
Page 1 of 4

1. Program/Project Identification No. DE-FC21-86MC10637
2. Program/Project Title Low-Rank Coal Direct Liquefaction (5.1)
3. Reporting Period 3-1-92 through 6-30-92
4. Name and Address Energy and Environmental Research Center
University of North Dakota
Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000
5. Program/Project Start Date 4-1-86
6. Completion Date 9-30-92

7. FY 91/92
8. Months or Quarters Quarters

1991: JUL AUG SEP OCT NOV DEC — 1992: JAN FEB MAR APR MAY JUN

9. Cost Status a. Dollars Expressed In Thousands b. Dollar Scale

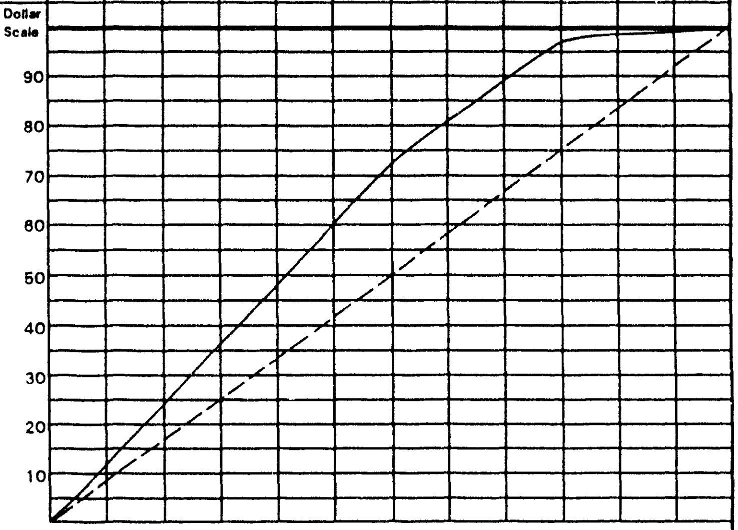
10. Cost Chart

Fund Source		Quarter 1st	2nd	3rd	4th	Cum. to Date	Tot. Plan
DOE	P	25	25	25	25	100	100
	A	37	36	25	2	100	
	P						
	A						
	P						
	A						
	P						
	A						
Total P		25	25	25	25	100	100
Total A		37	36	25	2	100	
Variance		(12)	(11)	0	23	0	

P = Planned A = Actual

Total Planned Costs for Program/Project

$100 K

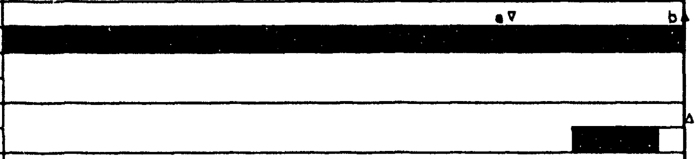


c. Cumulative Accrued Costs

	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN
Planned			25			50			75			100
Actual			37			73			98			100
Variance			(12)			(23)			(23)			0

11. Major Milestone Status

	Units Planned / Units Complete
1. Further Investigation of Pretreatment and Lower-Severity Processing	P C
(Including Hydrotreatment)	P C
3. Final Project Report	P C
	P C
	P C
	P C
	P C
	P C
	P C
	P C
	P C
	P C
	P C
	P C
	P C
	P C



12. Remarks

Due to EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.

13. Signature of Recipient and Date 7/25/92

14. Signature of DOE Reviewing Representative and Date

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Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
Task 1	Further Investigation of Pretreatment and Lower-Severity Processing:			
1.a	Batch testing	3-31-92	5-92	Changed during re-APP
1.b	Analytical	6-30-92	6-92	
Task 2	Investigation of Cationic Pretreatment:			Task 2 deleted during re-APP
2.a	Batch testing			
2.b	Analytical			
Task 3	Final Project Report	8-31-92		