

THE EFFECT OF THE NATURAL OXIDATION STATE OF
THREE BITUMINOUS COALS ON THE ABILITY OF
THE COALS TO ACCEPT NITROGEN BY AN
OXIDATION-AMMONIATION PROCESS

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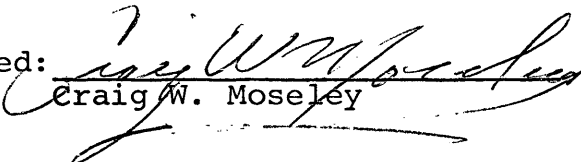
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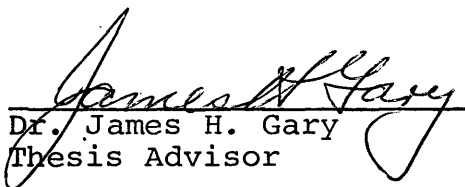
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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Chemical and Petroleum Refining Engineering.

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DEDICATION

Realizing the sacrifices made by my wife, Alice, I
dedicate this effort to her.

ABSTRACT

Nitrogen-enriched coal (N-enriched) can be used as a soil conditioner, providing the nitrogen content is sufficiently high. N-enriched coal has the ability to provide certain humates to the soil, in addition to nitrogen, as it decomposes. The ability of N-enriched coal fertilizers to compete on the market with now available fertilizers depends on the quality of the coal utilized and the efficiency of the nitrogenation process. This study investigates the response of several coals to an oxidation (by air)-ammoniation process utilizing a fixed bed of coal and flowing streams of air and ammonia.

The tests to determine the ability of three bituminous coals to accept nitrogen by repetitive oxidation-ammoniation are presented. The three coals tested are:

1. Sommerset Mine, Sommerset, Colorado.
2. Dutch Creek Mine, Carbondale, Colorado.
3. Redwing Mine, Craig, Colorado.

The oxygen contents of the coals are of interest and are 2.98, 9.85, and 14.78% on a dry basis for the three coals, respectively. The coals were tested at three levels of ammoniation temperature and pressure ranging from 100 to 300°F and 200 to 400 psig, respectively. The upper tempera-

ture was limited by the softening characteristics of the coal. The study was made to determine a relationship between the natural oxidation states of the coals and the coal's ability to accept nitrogen from gaseous ammonia. This investigation shows that at an oxygen level of 2.98% the N-enrichment achieved was 0.24% attached nitrogen while at the 14.70% oxygen level the N-enrichment increased to 2.70% attached nitrogen. These data show a discernible increase in the ability of the coal to accept nitrogen from the process with an increase in the oxidation state of the coal.

The operating parameters temperature and pressure do not show a strong influence on the N-enrichment process. An increase of 200^oF in ammoniation temperature resulted in a decrease of 0.20% attached nitrogen while an increase of 200 psig in ammoniation pressure showed an increase of 0.20% attached nitrogen.

An analysis of variance of the experimental factors shows coal oxygen content to be a significant variable at the 0.001 or 99.9% level by the F-test. Ammoniation temperature is significant at the 0.40 level while pressure is not significant at the 0.50 level.

A linear regression of the experimental data models process response ($y = \% \text{ attached N}$) as a function of coal oxygen content ($x = \% \text{ oxygen}$):

$$y = 1.38 + 0.18 x.$$

A development of this linear model and the above mentioned analysis of variance is found in the statistical analysis section of the text.

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A special word of appreciation is extended to my parents for their continual support and encouragement.

INTRODUCTION

The major constituent of naturally occurring fertilizers and soil conditioners is humus. Humus is the remains of plant and animal matter, an intermediate step in the formation of coal. Coal is not rich in plant nutrients in its natural state but does contain certain organic structures that lend themselves to the formation of humic acids by oxidation (Schwartz, 1965, p. 417). Humic acids are an oxidized constituent of humus. The humic acids formed in the coal may be reacted with ammonia to form nitrohumates, thus increasing the nitrogen content of the coal. Coal has been found to release this excess nitrogen in a manner that makes it available to plants as a nutrient. The ability of coals and humus materials to accept nitrogen in this way has been known since the early twenties. Early studies were concentrated on peat and various forms of low rank coals such as lignite. One such study was done in 1933 by the Bureau of Chemistry and Soils (Scholl, 1933, p. 1074), Washington, D.C., to determine the ability of various peats to accept nitrogen. The process was simple and consisted of reacting the peat with aqueous ammonia at elevated temperatures and pressures.

In recent years a rather extensive study of coal

nitrogenation has been undertaken by the Central Fuel Research Institute, Jealgora, Dhanbad, India. In 1964 the Institute reported having produced nitrogen enriched coals with nitrogen contents of 15 to 20 percent with 55 to 60 percent of the total nitrogen available as a plant nutrient (Mukherjee, 1965, p. 90). The coal fertilizers were prepared by a batch process. The coal and liquid ammonia were slurried in a rocker-type reactor vessel and pressurized with oxygen to approximately 420 psig. Reaction times were 4 to 6 hours at temperatures of about 165 C.

In 1965, the Central Fuel Research Institute again reported the production of nitrogen enriched coal with nitrogen contents of 16 to 20 percent. However, the process had changed to one employing an air-ammonia mixture. A small amount of coal was placed in an aluminum boat in a tubular furnace and subjected to a stream of air and ammonia. The optimum conditions were found to be: 325 ± 10 C reaction temperature, 4 to 5 hours reaction time, -35+150 mesh (Tyler) and an air to ammonia ratio of 4:1 (Mukherjee, 1966, p. 119).

A more recent investigation of coal nitrogenation was conducted by the Coal Research Division, Research Council of Alberta, Canada. In 1968 the Coal Research Division reported work done on humic acids derived directly from coal. The results showed that ammonium nitrohumates with up to 8 percent nitrogen could be formed by reacting the humic acids

with aqueous ammonia. By converting the humic acids to nitrohumic acids with HNO_3 before treatment with aqueous ammonia, ammonium nitrohumates with 12 to 14 percent nitrogen could be formed (Chakrabartty, 1968, p. 165).

The Coal Research Division, at the same time, reported work on a coal nitrogenation process similar to the one described by the above mentioned Indian group in 1965. The process produced coal with total nitrogen content of 16 percent (Chakrabartty, 1968, p. 169) by fluidizing a bed of coal with a mixture of ammonia and air at temperatures between 250 and 350 C. Ammonia input was set at about 15 percent with an ammonia to oxygen ratio of 2:3. A reaction time of about 5 hours was necessary to bring the nitrogen content to the values reported. These results are quite similar to the results reported by the Indian group.

The procedure for coal nitrogenation developed by the Chemical and Petroleum Refining Department, Colorado School of Mines, is modeled after the process described by the Canadian workers. The significant difference is that the process used here consists of an oxidation of the coal by air followed by nitrogenation by ammonia. The air and ammonia streams are not mixed but employed one after the other. A complete run is three oxidation cycles with each followed by a nitrogenation cycle. The work in progress is investigating coal nitrogenation at temperatures between 100 and 300 F and

pressures between 200 and 400 psig. The coals under study are Colorado bituminous with oxygen contents between 2.6 and 14.7 percent, total nitrogen and carbon contents between 89.4 and 78.0 percent (on a dry basis). The intent of the study is to determine if a relationship exists between the coal's ability to accept nitrogen by a gaseous ammonia process and the coal's natural oxidation state.

EXPERIMENTAL EQUIPMENT

The experimental equipment consists principally of a tubular reactor, furnace, furnace control, temperature recorder, flow meter, and the necessary tubing and pump to pass ammonia, air and nitrogen through the reactor. A flow diagram of the equipment is shown in figure 1.

REACTOR

The reactor is constructed of 316 stainless steel pipe, 32.5 in. long with 1.25 in. O.D. and 1.0 in. I.D. It is fitted with a tee of 316 stainless steel at the top to allow entry of gas and the necessary thermocouples to monitor the temperature profile within the sample bed. The position of the thermocouples is shown in figure 2. The reactor and tee are flanged and gasketed with Teflon. The sample is held in the middle portion of the reactor by two spacers. The sample is supported on the spacers by a 30-mesh (Tyler) 316 stainless steel screen. At the reactor inlet and outlet are 0.25 in. 316 stainless steel Swagelok couplings.

FURNACE

Purpose: Provide heat to reactor.
Type: Lindberg Hevi-Duty 3-zone tube furnace,
Model No. 54356-A.
Volts: 230 v.
Watts: 3000 w.

FURNACE TEMPERATURE CONTROL

Purpose: Maintain reactor temperature.
Type: Lindberg Hevi-Duty 3-zone tube furnace control console, Model No. 59744.

TEMPERATURE RECORDER

Purpose: To record temperature profile within sample bed during run.
Type: Brown 8-point potentiometer, Model No. 153X60p8X-61f1.

AMMONIA PUMP

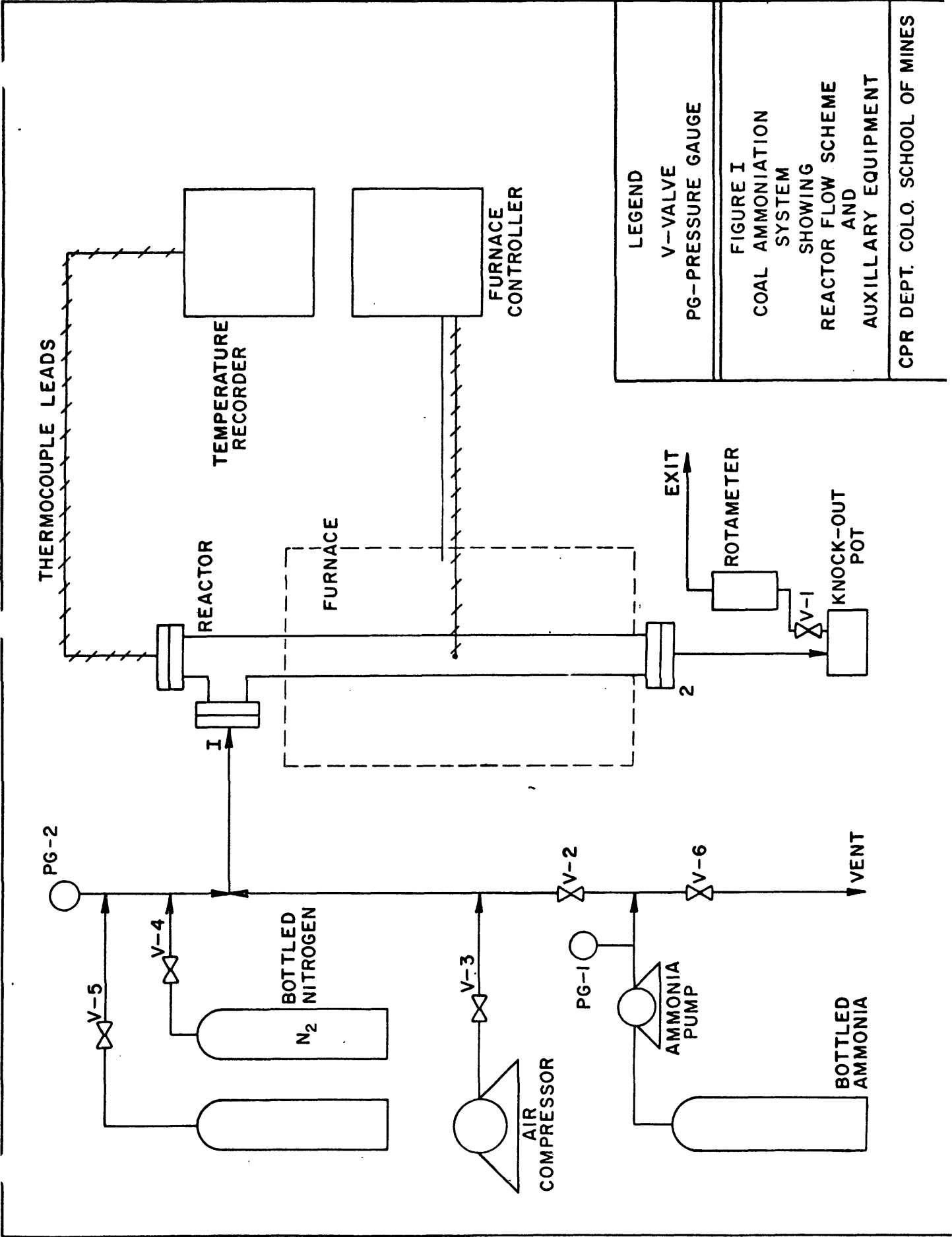
Purpose: To maintain ammoniation pressures greater than the vapor pressure of ammonia at room temperature.
Type: Lapp Micro Pulsafeeder, Model No. LS-20.

ROTAMETER

Purpose: To provide a means of maintaining a constant flow of air, ammonia and nitrogen through the reactor during a run.

TUBING, VALVES AND FITTINGS

Type: 316 stainless steel throughout.



LEGEND
 V-VALVE
 PG-PRESSURE GAUGE

FIGURE I
 COAL AMMONIATION SYSTEM SHOWING REACTOR FLOW SCHEME AND AUXILLARY EQUIPMENT

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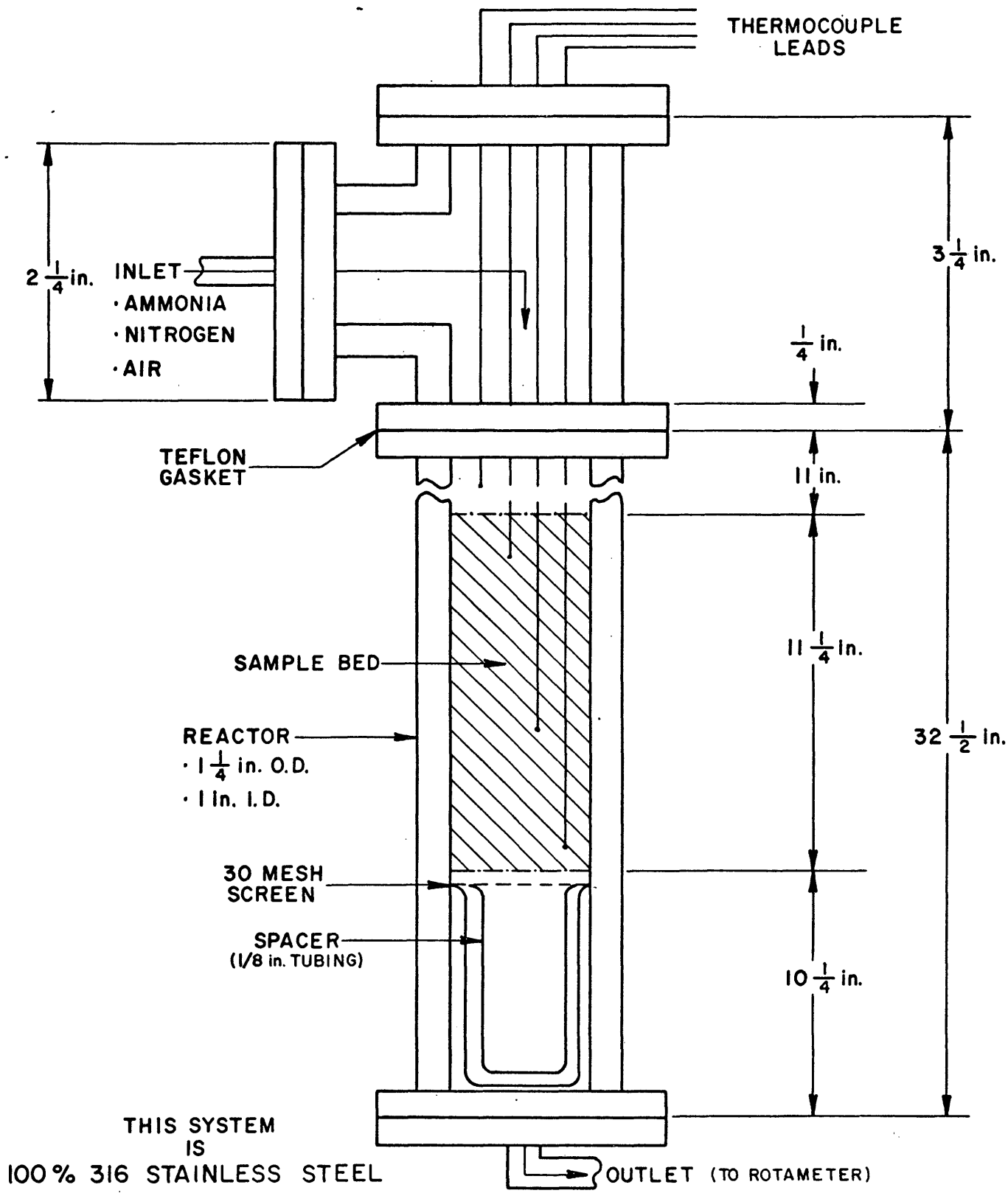


FIGURE 2
DETAIL OF COAL AMMONIATION
REACTOR

EXPERIMENTAL DESIGN

The experimental runs to test the coal samples were selected and fitted into an experimental design to facilitate the statistical analysis of the results. This statistical design of the experiment was critical to a valid statistical analysis and was established prior to experimentation to allow the results to be as unbiased as possible.

Construction of Experimental Design

The design selected was a full factorial of the 3^3 design (Johnson, 1964, v. 2, p. 219). This indicates there are three factors to be tested, each at three levels or values. The first factor, designated as factor "A", is the oxygen content of the coal. This factor appears at three levels:

$$A_0 = 2.98\%$$

$$A_1 = 9.85\%$$

$$A_2 = 14.78\%$$

An ultimate and approximate analysis of these three coals appear in Appendix III. Also in Appendix III is a description of the origin of these coal samples. The second factor, factor "B", is ammoniation pressure and appears at the three levels:

$$B_0 = 200 \text{ psig}$$

$$B_1 = 300$$

$$B_2 = 400$$

The third factor, factor "C", is ammoniation temperature and appears at the three levels:

$$C_0 = 100 \text{ F}$$

$$C_1 = 200$$

$$C_2 = 300$$

This experimental design is shown in figure 3.

To achieve the full effect of the statistical analysis of results, the order of experimental runs must be completely randomized. This order was obtained through the use of a table of random numbers and appears in Table I.

Table I. Randomized Order of Experimental Runs as Shown in Figure 3.

<u>Run No.</u>	<u>Exp. Run</u>	<u>Run No.</u>	<u>Exp. Run</u>	<u>Run No.</u>	<u>Exp. Run</u>
1	010	10	122	19	212
2	200	11	110	20	101
3	021	12	102	21	002
4	210	13	011	22	120
5	000	14	012	23	202
6	201	15	100	24	022
7	111	16	112	25	221
8	222	17	121	26	211
9	001	18	020	27	220

		B ₀	B ₁	B ₂
A ₀	C ₀	(000)	010	020
	C ₁	001	011	021
	C ₂	002	012	022
A ₁	C ₀	100	110	120
	C ₁	101	111	121
	C ₂	102	112	122
A ₂	C ₀	200	210	220
	C ₁	201	211	221
	C ₂	202	212	222

Note: The values (ijk) above indicate the factor levels for each of the 27 experimental runs. The levels of A, B, and C are shown by ijk, respectively.

Figure 3. 3³ Experimental Design.

Each experimental run (figure 3) was conducted in three stages. Each stage consisted of an oxidation of the coal by air, followed by a nitrogenation by ammonia. After each oxidation and ammoniation the system was purged with nitrogen.

The operating parameters which were varied from run to run for a particular coal (factor A) are:

1. Ammoniation temperature
2. Ammoniation pressure.

The operating parameters which were held constant from run to run for a particular coal are

1. Oxidation temperature
2. Oxidation pressure
3. Oxidation flow rate
4. Air flow rate
5. Duration of ammoniation
6. Duration of oxidation
7. Volume of sample tested.

Selection of Operating Parameters

The Chemical and Petroleum Refining Department, Colorado School of Mines, conducted in 1971, a study of the significance of the various operating parameters on the nitrogenation of coal by the previously described oxidation-ammoniation process. The parameters investigated were ammoniation temperature and pressure and oxidation pressure. That study showed

ammoniation temperature and pressure to be more significant variables in the nitrogenation of coal than oxidation pressure. The levels of ammoniation temperature ($^{\circ}\text{F}$) and pressure (psig) investigated at that time were 100, 300, 500, and 100, 200, 300, respectively. The levels of oxidation pressure (psig) were 50, 75, and 100. For the purposes of this study, the oxidation pressure was held constant at 100 psig and the levels of ammoniation temperature and pressure were shifted slightly. The duration of oxidation and ammoniation was 15 minutes. This reaction time was also chosen on the basis of these studies. Reaction times of 15, 30, and 45 minutes were investigated, resulting in no appreciable nitrogen enrichment beyond 15 minutes.

The oxidation temperature is a function of the oxidation state of the coal. The ignition temperature of the coal, and hence the maximum allowable oxidation temperature, decreases with an increase in the oxidation state, whether that increase is due to natural causes or induced during an experimental run is not known. Table II lists the oxidation temperatures at three levels of factor A for each stage in an experimental run. The data of Table II reflect an attempt to establish oxidation temperatures at 25°F below the ignition temperature of the coal in each case.

The flow rate of ammonia was held constant for all runs at approximately 40 standard cubic centimeters per minute

Table II. Oxidation Temperatures ($^{\circ}\text{F}$) at Three Levels of Factor A (Coal).

Factor A Levels	Experimental Run Stages		
	1	2	3
A ₀	300 $^{\circ}\text{F}$	275	250
A ₁	275	240	215
A ₂	200	185	175

Note: Natural oxidation of coals increases from A₀ to A₂; induced oxidation increases from Stage 1 to Stage 3.

per gram of coal. The flow rate of air was held constant at approximately 35 scc per minute per gram of coal. These values of flow rate were established on the basis of a study done by P. N. Mukherjee for the Central Fuel Research Institute, Jealgora, India, in 1965. His work indicated that ammonia flow rates greater than 0.01 cc per minute per gram of coal (Mukherjee, 1966, p. 121) had no additional effect in terms of nitrogen fixation. The value of 40 scc ammonia per minute per gram of coal, established for this present study, supplied the process with excess ammonia on the basis of the work done by P. N. Mukherjee. The value of air flow rate, mentioned above, was based on the same study by P. N. Mukherjee.

The volume of sample tested was dictated by the experimental apparatus and remained fixed at 146 cc. The coal was

screened to select the +30-16 mesh (Tyler) fraction for convenience of handling and to obtain a sufficient quantity of coal for experimentation from the samples acquired from the mines.

EXPERIMENTAL PROCEDURE

The experimental procedure established for coal nitro-
genation studies performed in 1971 by the Chemical and
Petroleum Refining Department was used in this program. For
convenience the procedure is broken into three basic parts:

1. Sample preparations, 2. oxidation and ammoniation, and
3. chemical analyses of samples for nitrogen content.

Sample Preparation

The coal sample to be tested is screened to select the
fraction between 16 and 30 U.S. Standard Mesh. The fraction
is dried for two hours at 100°C and then thoroughly mixed.
The volume needed to fill the reactor is measured and weighed.
The weighed sample is then charged to the reactor (figure 1).

Oxidation and Ammoniation of Sample

The dried coal is weighed and charged to the reactor.
In the reactor it is oxidized with air three times and nitro-
genated with ammonia three times. The sample is then dis-
charged from the reactor and immediately weighed and placed
in a sealed jar. A detailed explanation of the oxidation and
ammoniation cycles follows. All reference to pieces of
apparatus is from figure 1.

1. A 146 cc portion of the sample is weighed. The volume of sample is dictated by the region of uniform heating within the furnace.

2. The furnace is opened and the reactor is disconnected at points 1 and 2. The reactor is opened at the bottom and the spacer in the bottom section of the reactor is removed. The sample is poured into the reactor. The reactor is reassembled and placed on stream with the furnace closed.

3. The system is purged with nitrogen for 5 minutes at 50 psig at a rate of approximately 40 scc per minute per gram of sample. All valves are closed except V-1 and V-4. Adjustment of V-1 and V-4 is necessary to maintain flow rate and pressure. At end of purge V-4 is closed.

4. The desired oxidation temperature is set on the furnace temperature controller and the system is allowed to come to temperature.

5. All valves are closed and V-3 is opened until PG-2 reads desired oxidation pressure. V-1 is opened to maintain an air flow rate of approximately 35 scc per minute per gram of sample. V-3 is regulated to maintain the desired pressure. At the end of the 15-minute run time, V-3 is closed and the pressure is allowed to drop to zero.

6. The desired ammoniation temperature is set on the furnace temperature controller and the system is allowed to come to temperature.

7. While the system is regaining the proper temperature, Step 3 is repeated with a purge time of 15 minutes.

8. With reactor at desired ammoniation temperature, all valves are closed and V-2 is opened. If the desired pressure is greater than the vapor pressure of ammonia then the ammonia pump must be turned on. If the pump is used then both PG-2 and PG-1 must be closely watched, in the event that V-2 becomes plugged. When the system reaches desired pressure V-1 is opened to maintain an ammonia flow rate of approximately 40 scc per minute per gram of sample. At the end of the 15-minute run time, the pump is turned off and V-2 is closed (in that order). The system pressure is allowed to come to atmospheric. V-6 is momentarily opened to allow PG-1 to come back to the pressure of the NH_3 bottle.

9. The system is purged with nitrogen as described in Step 7.

10. For additional oxidation and ammoniation cycles, Steps 4 through 9 are repeated. The procedure employed during these tests called for two more oxidations and ammoniations, that is, a repetition of Steps 4 through 9 twice.

11. After the sample has been oxidized and ammoniated three times, with each oxidation and ammoniation followed by a nitrogen purge, the sample is discharged from the reactor by the following steps.

12. When the system has reached zero pressure after the last nitrogen purge, the reactor is disconnected at points 1

and 2, the reactor is opened at the bottom (point 2), and the reactor spacer is removed. The coal is emptied into a tared container for weighing.

13. The sample is placed in a vacuum flask and subjected to vacuum (approximately 23 in. of Hg) for 24 hours.

14. The sample is weighed.

Nitrogen Analysis of Coal Product

The coal product from the reactor is analyzed for weight percent of total nitrogen by the Kjeldahl method. The nitrogen determination used is described in the official Methods of Analysis of the Association of Official Agricultural Chemists (Horwitz, 1965, p. 15).

RESULTS

The results of the 3³ experimental design, described previously, are presented below in tabular form. The response of the three coals tested to the process is then discussed from a non-statistical viewpoint. A detailed description of the coals tested is available in Appendix III.

Comparison of the Coal Sample Responses

The response of the three coal samples to the oxidation-ammoniation process is presented in two ways to give perspective to the analysis of the data. Both sets of results are reported to show the relative abilities of the coals to accept nitrogen from ammonia. The first set of data present response as % total nitrogen by wt (% Tot N) in the product coal:

$$\% \text{ Tot N} = \frac{(\text{gram N in product}) \times 100}{(\text{gram product analyzed})} .$$

These values are of practical importance in that for commercial application of the coal product as a soil conditioner, the absolute value of nitrogen content is of prime importance. The second set of data present response as % attached (added) nitrogen by wt (% Att N) in the product coal.

$$\% \text{ Att N} = \frac{(\text{gm N in product} - \text{gm original N}) \times 100}{(\text{gm product analyzed})} .$$

These data show the relative nitrogen enrichment obtained for the three coals tested. The response reported as % Att N gives a normalized basis for comparison by the elimination of the effect of the nitrogen present in the untreated coal, on the nitrogen content of the product. The response to the process is reported as % Tot N and %Att N in Tables III, IV, and V as a function of the two operating parameters, ammonia- tion temperature and pressure. A detailed description of the coals as a factor in the experiments is found in the previous discussion of the experimental design. Table VI summarizes Tables III, IV, and V.

Discussion of the Results

Referring to Table VI, it can be seen that as the natural oxidation state of the coals tested increased, the resulting nitrogen content of the product coal increased also. An increase in oxygen content of 6.87% (2.98% to 9.85%) allowed an increase in percent attached nitrogen of 1.45% (0.24% to 1.69%). An increase in oxygen content of 4.93% (9.85% to 14.78%) allowed an increase in percent attached nitrogen of 1.01% (1.69% to 2.70%). The values of total nitrogen content of the product also show this same increase in the ability of the coals to accept nitrogen from the oxidation-ammoniation process with an increase in the coal's natural oxidation state. The development of a linear regression model of

Table III. Experimental Response at Coal Factor Level A_0
as % Tot N and % Att N.

		Coal A_0		
		Ammoniation Pressure (psig)		
		B_0	B_1	B_2
		(1.85)*	1.83	2.15
Ammoniation Temp. ($^{\circ}$ F)	C_0	000	010	020
		(0.10)**	0.65	0.41
		1.82	1.81	2.10
	C_1	001	011	021
		0.07	0.06	0.36
		2.00	1.85	1.92
	C_2	002	012	022
		0.25	0.10	0.18

Note: The values ()* are response as % Tot N.
The values ()** are response as % Att N.

Table IV. Experimental Response at Coal Factor Level A_1
as % Tot N and % Att N.

		<u>Coal A_1</u>		
		Ammoniation Pressure (psig)		
		B_0	B_1	B_2
		(3.30)*	3.01	3.39
Ammoniation Temp. (°F)	C_0	100	110	120
		(1.86)**	1.56	1.95
		2.92	3.38	3.27
	C_1	101	111	121
		1.47	1.94	1.85
		2.86	2.90	3.22
C_2	102	112	122	
	1.40	1.40	1.77	

Note: The values ()* are response as % Tot N.
The values ()** are response as % Att N.

Table V. Experimental Response at Coal Factor Level A₂ as % Tot N and % Att N.

		<u>Coal A₂</u>		
		Ammoniation Pressure (psig)		
		B ₀	B ₁	B ₂
Ammoniation Temperature (°F)	C ₀	(4.35)*	4.18	3.76
		200	210	220
	C ₁	(3.03)**	2.86	2.43
		201	211	221
	C ₂	4.18	4.10	4.14
		202	212	222
		2.86	2.77	2.83
		3.26	4.39	3.86
		1.93	3.07	2.54

Note: The values ()* are response as % Tot N.
 The values ()** are response as % Att N.

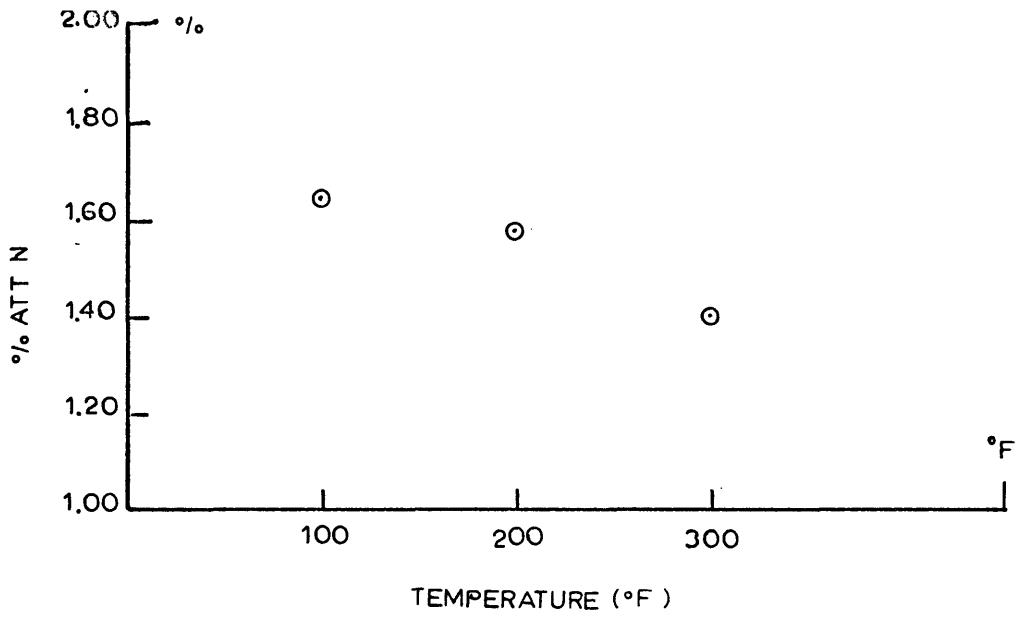
Table VI. Summary of Data Appearing in Tables III, IV, and V as Average % Tot N and %Att N for Each Coal Tested.

	Coals Tested		
	<u>A₀</u>	<u>A₁</u>	<u>A₂</u>
% Tot N	1.92	3.14	4.02
% Att N	0.24	1.69	2.70

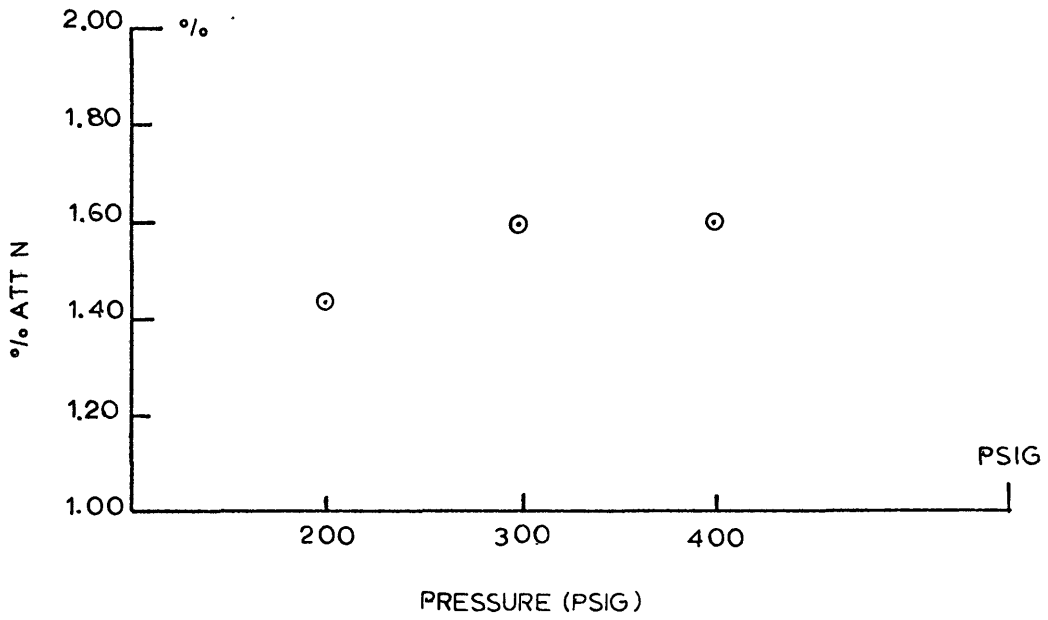
Note: Natural oxidation state of the coals tested increases from A₀ to A₂ with respective oxygen contents of 2.98%, 9.85%, and 14.78%.

response as a function of coal oxygen content is presented in the next section and plotted in figure 6.

The effect of factors B and C (ammoniation pressure and temperature, respectively) are not as easily deduced from the responses reported in Tables III, IV, and V. There does not appear to be a strong discernible trend in the degree of nitrogenation with changes in temperature and pressure levels. Figures 4 and 5 represent graphically the effects that temperature and pressure do have on the response as %Att N. Figure 4 shows response averaged over factors A and B (coal and pressure) for each level of factor C (temperature). Figure 5 shows response averaged over factors A and C (coal



PROCESS RESPONSE (% ATT N) VS. AMMONIATION TEMPERATURE
FIGURE - 4



PROCESS RESPONSE (% ATT N) VS. AMMONIATION PRESSURE
FIGURE - 5

and temperature) for each level of factor B. Figure 4 shows a decrease of 0.20% attached nitrogen for an increase of 200°F in ammoniation temperature. An increase of 200 psig in ammoniation pressure is shown to increase percent attached nitrogen by 0.20%. Realizing that changes in N-enrichment with changes in temperature and pressure are quite small, optimum response is seen to occur at lower values of temperature and higher values of pressure.

The response to the oxidation-ammoniation process studied is shown to be more sensitive to the state of oxidation of the coal than to the nitrogenation parameters, temperature and pressure. This indicates that the achievement of N-enrichment is more dependent on the absolute number of oxidized reaction sites than the operating or reaction conditions. This conclusion holds at the factor levels studied.

The analysis of variance of the factors A, B, and C in the next section allows the same deductions to be made as those above.

STATISTICAL ANALYSIS OF EXPERIMENTAL RESPONSE

The three factors (coal oxygen content, ammoniation pressure, and temperature) A, B, and C were investigated, each at the three levels 0, 1, and 2, as described in the discussion of experimental design. These factors are arranged in a 3^3 experimental design for purposes of statistical analysis. The statistical analysis of the results establishes the relative significance of the effects of the factors on the measurable response of the process. The F-test is employed to establish this significance at the 95% confidence level.

The prediction of response, for a given coal, from available data is important for commercial applications. For this reason, the data of Tables III, IV, and V, of the preceding section, are linearly modeled by a regression technique (Johnson, 1964, v. 1, p. 377). The models presented are:

$$\% \text{ Tot N} = f(\text{coal oxygen content})$$

$$\% \text{ Att N} = f(\text{coal oxygen content}).$$

Analysis of Variance

The sum of squares, used ultimately to apply the F-test to the factors A, B, and C, are arrived at by the Yate's Technique. The Yate's Technique applied to factors at three levels (Davies, 1966, p. 363) allows the separation of both

linear and quadratic effects of the factors and factor interactions. Response as % Att N is used exclusively for the analysis of variance. The normalized value of response gives an unbiased basis of comparison for the three levels of factor A. The sum of squares for the separated effects of the factors are calculated directly from the process response and presented in Table VII. The combined effects of the factors and factor interactions are the summations of the separate linear and quadratic effects. That is, the sum of squares of A_L and A_Q equal the sum of squares for the factor A (coal). The combined effects with their sum of squares also appear in Table VII.

The analysis of variance table, Table VIII, summarizes the sum of squares for the combined effects of A, B, C, and the interactions AB, AC, BC, and ABC. The degrees of freedom (DF) in each case are the number of separate effects inherent in each combined effect. The three-way interaction, ABC, is assumed to be less important than the single effects or two-way interactions and hence is defined as the residual error of the process. The mean square value (mean sq) of Table VIII is the quotient SS/DF in each case. The mean square ratio is the mean square over the mean square of the residual in each case. The statistic mean square applied to the F-test at a significance level of 0.001 indicates that, with 99.9% confidence, the factor A (coal oxygen content) is a

Table VII. Sum of Squares for Combined and Separate Effects of Factors A, B, and C.

<u>Effect</u>	<u>Separate</u>	<u>S.S.</u>	<u>Effect</u>	<u>Combined</u>	<u>S.S.</u>
A_L		27.23			
A_Q		.28	A		27.51
B_L		.10			
B_Q		.04	B		.14
C_L		.27			
C_Q		.02	C		.29
$A_L B_L$.03			
$A_Q B_Q$.04			
$A_L B_Q$.07			
$A_Q B_L$.09	AB		.23
$A_L C_L$.00			
$A_Q C_L$.00			
$A_L C_Q$.09			
$A_Q C_Q$.01	AC		.10
$B_L C_L$.10			
$B_Q C_L$.01			
$B_L C_Q$.01			
$B_Q C_Q$.01	BC		.13

Table VII. (Continued)

<u>Effect</u>	<u>Separate</u>	<u>S.S.</u>	<u>Effect</u>	<u>Combined</u>	<u>S.S.</u>
$A_L B_L C_L$.32			
$A_Q B_L C_L$.00			
$A_L B_Q C_L$.25			
$A_Q B_Q C_L$.00			
$A_L B_L C_Q$.01			
$A_Q B_L C_Q$.00			
$A_L B_Q C_Q$.02			
$A_Q B_Q C_Q$.28	ABC		.88

Table VIII. Analysis of Variance of the Factors A, B, and C.

<u>Source</u>	<u>S.S.</u>	<u>DF</u>	<u>Mean Sq.</u>	<u>Mean Sq. Ratio</u>	<u>Sig. Level</u>
A Coal	27.51	2	13.76	125.09	0.001
B Press.	.14	2	.07	.64	<0.50
C Temp.	.29	2	.15	1.36	0.40
AB	.23	4	.06	.55	<0.50
AC	.10	4	.03	.27	<0.50
BC	.13	4	.03	.27	<0.50
ABC	.88	8	.11	(Residual)	

significant process variable for the system under study. The factors B and C show a much lower level of significance (Fryer, 1966, p. 570) by the F-test than does factor A. Factor C (ammoniation temperature) is a significant process variable at the 0.40 or 60% level while factor B (ammoniation pressure) is not even significant at the 0.50 or 50% level. An explanation for the relative non-significance of factors B and C by the F-test is that the levels studied are grouped closely to optimum values for the process. The effect of a level change, for these two factors, on the process response is undetectable and therefore gives a non-significant result to the F-test for the factor. That is, if the levels of factors B and C were shifted, the F-test would show significance. It is possible that a shift in factor levels would indicate a two-way interaction of some significance. At the levels studied the two-way interactions are not shown to be significant at the 0.50 level.

Linear Regression Model

A mathematical model of the process, in terms of the factors investigated through the 3^3 experimental design, gives response (y) as a function of the three factors A, B, and C:

$$y = a + bx_i + cx_j + dx_k \quad (1)$$

where: y = process response as % Tot N or % Att N

x_i = level of factor A

x_j = level of factor B

x_k = level of factor C

a, b, c and d = constants.

For purposes of the development of a linear model, factors B and C do not appear to affect the response significantly, on the basis of the analysis of variance, and therefore, will be eliminated from equation (1) to give:

$$y = a + bx_i \quad (2)$$

where: $a = \bar{y} - b\bar{x}$

$$b = s_{xy}/s_{xx}$$

$$\bar{y} = \Sigma y/n$$

$$\bar{x} = \Sigma x/n.$$

The values s_{xx} , s_{yy} , and s_{xy} are obtained from response (y) and factor level input (x) data (Lee, 1968, p. 104):

$$s_{xx} = n(\Sigma x^2) - (\Sigma x)^2 \quad (3)$$

$$s_{yy} = n(\Sigma y^2) - (\Sigma y)^2 \quad (4)$$

$$s_{xy} = n(\Sigma xy) - (\Sigma x)(\Sigma y) \quad (5)$$

Referring to Tables III, IV, and V (Results section), the response y as % Tot N are paired with their respective levels of factor A. The 27 (n) pairs of x and y values allow the calculation of s_{xx} , s_{yy} , and s_{xy} in accordance with equations (3) through (5). Substituting these values, along with the values of \bar{x} and \bar{y} , into equation (2) gives:

$$y(\% \text{ Tot N}) = 1.38 + 0.18 x \quad (6)$$

where: $\bar{y} = 3.03 \% \text{ Tot N}$

$$\bar{x} = 9.02 \% \text{ Tot O}$$

$$s_{xx} = 17067.8$$

$$s_{xy} = 3034.5$$

Equation (6) is plotted in figure 6.

It is convenient to establish confidence bands (Johnson, 1964, v. 1, p. 389) above and below the line plotted in figure 6. This band would simply imply that with a certain degree of confidence any additional points plotted within the band are, in fact, included in the linear model (Eq. 6).

The confidence band alters equation (6) to read:

$$y(\% \text{ Tot N}) = 1.38 + 0.18 x \pm e \quad (7)$$

where: $e = 1/2$ the width of the confidence band for any value of x .

The value of e is given in terms of the students $-t$ statistic ($t_{\alpha/2, n-2}$) as:

$$e = t_{\alpha/2, n-2} \text{ Se} \left[\frac{1}{n} + n \left(\frac{x - \bar{x}}{s_{xx}} \right)^2 \right]^{1/2} \quad (8)$$

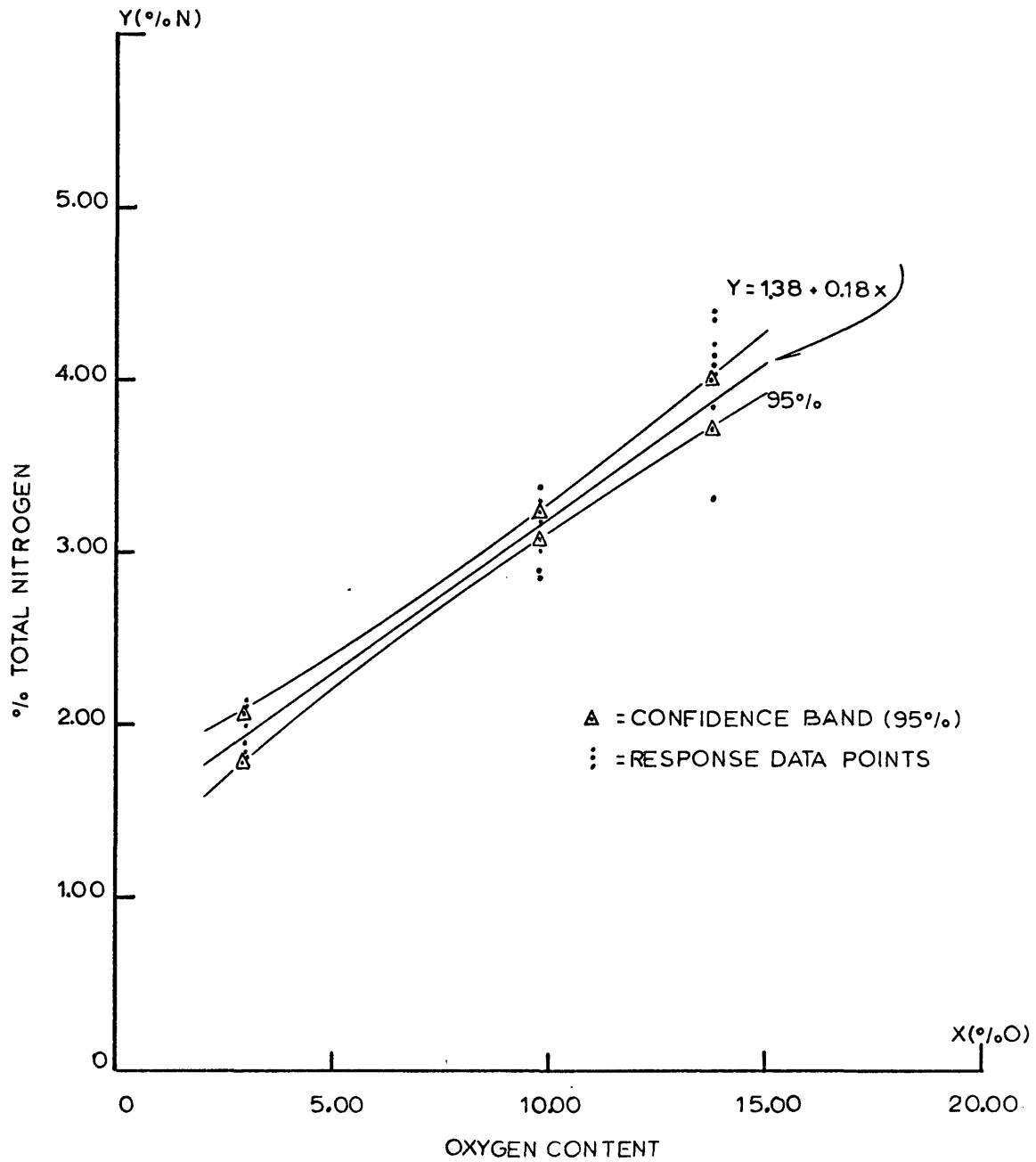
where: $\alpha = 100\%$ confidence desired = 0.05

$n-2 =$ degrees of freedom = 25

$$t_{(0.025)(25)} = 2.060$$

Se = estimate of variance

$$= \left[\frac{(s_{xx})(s_{yy}) - (s_{xy})^2}{n(n-2)(s_{xx})} \right]^{1/2} = 0.24$$



PROCESS RESPONSE (%TOT N) VS.
COAL OXYGEN CONTENT (LINEAR REGRESSION MODEL of %O)

FIGURE-6

at $x = 2.98\%$

$e = 0.15$

$x = 9.85\%$

$e = 0.10$

$x = 14.78\%$

$e = 0.14$

The above values of e are plotted above and below the line,

$$y(\% \text{ Tot N}) = 1.38 + 0.18 x.$$

in figure 6. With 95% confidence, the expected value of $y(\% \text{ Tot N})$ will fall within the band. The confidence band opens as the linear model is extrapolated, indicating that the model is most reliable in the region of observed data.

A similar regression of the process response as $\% \text{ Att N}$ gives:

$$y(\% \text{ Att N}) = -0.39 + 0.21 x$$

with the 95% confidence band at

$x = 2.98$

$e = 0.17$

$x = 9.85$

$e = 0.11$

$x = 14.78$

$e = 0.15$

CONCLUSIONS

The principle conclusion to be drawn from these tests is that as the natural oxidation state of the coals tested increased, the ability of the coals to accept nitrogen from the oxidation-ammoniation process, increased also.

The effect of changes in ammoniation temperature and pressure on the process were small at the levels of these two factors studied; but showed increased N-enrichment at the low temperature levels and high pressure levels.

The statistical analysis of the process response to the 3^3 experimental design shows that the operating parameters varied had the following significance, by the F-test, relative to the change in nitrogen content of the sample:

1. Oxygen content of the coals tested was found to be a statistically significant variable at the significance level = 0.001.
2. Ammoniation temperature was found to be a statistically significant variable at the significance level = 0.40.
3. Ammoniation pressure was not found to be a statistically significant variable at the significance level = 0.50.
4. The two-way interactions of ammoniation temperature and pressure were not found to be statistically significant at the significance level = 0.50.

RECOMMENDATIONS FOR FURTHER STUDY

The principle recommendation made for further study of the oxidation-ammoniation process for nitrogen enrichment of coal is that a more efficient means of oxidizing the coal, prior to ammoniation, be investigated; such as strong chemical oxidizers. It appears from this study that the oxidation state of the coal is critical to the feasibility of the process. The establishment of a means to obtain a desirable oxidation state in the coal specimen under study would assuredly lead to favorable results in the nitrogen-enrichment of coal gasification char product.

APPENDIX I

RANDOM EXPERIMENTAL ERROR

<u>Apparatus</u>	<u>Error</u>
Lindberg Hevi-Duty Temperature Controller	$\pm 1.0^{\circ}\text{F}$
Brown Temperature Recorder	$\pm 2.5^{\circ}\text{F}$
Rotameter	± 250 scc per min
Pressure Gauge 1	± 5 psig
Pressure Gauge 2	± 2.5 psig

APPENDIX II

EQUIPMENT CALIBRATION

Brown Temperature Controller

The temperature recorder was calibrated with a Leeds and Northrup Potentiometer (serial no. 307969).

Rotameter

The rotameter was calibrated with air, nitrogen, and ammonia by the use of a wet test meter.

Pressure Gauges

The two pressure gauges used were calibrated with a water dead head tester.

APPENDIX III

ANALYTICAL DESCRIPTION OF COAL SAMPLES TESTED

The three bituminous coals tested were obtained in Colorado and were selected on the basis of their varying oxygen contents. A description of the three coals is presented below, followed by an approximate and ultimate analysis of each one.

1. This coal is designated as A₀ in the experimental design and CB on the ultimate analysis. The origin of this coal is:
Mine: Dutch Creek
Company: Mid-Continent Coal and Coke Co.
County: Pitkin
Town: Carbondale, Colorado
2. This coal is designated as A₁ in the experimental design and SS on the ultimate analysis. The origin of this coal is:
Mine: Somerset
Company: United States Steel, Western Div.
County: Gunnison
Town: Somerset, Colorado
3. This coal is designated as A₂ in the experimental design and RW on the ultimate analysis. The origin of this coal is:
Mine: Red Wing
Company: Colowyo Coal Co.
County: Moffat
Town: Craig, Colorado

October 19, 1972



COLORADO SCHOOL OF MINES
CPR Department
Golden, Colorado 80401

MAIL ADDRESS
2180 EAST 40TH AVENUE
DENVER, COLORADO 80205
PHONE 303 255-3371

Sample identification
by Colorado School of Mines

Kind of sample
reported to us Coal

CB Coal
N-Head

Sample taken at XXXXX

P. O. No. ORS 11533

Sample taken by Colorado School of Mines

Date sampled Received 10-9-72

Analysis report no. 72-13158

PROXIMATE ANALYSIS

	<u>As received</u>	<u>Dry basis</u>
% Moisture	0.58	XXXXX
% Ash	6.74	6.78
% Volatile	22.88	23.01
% Fixed Carbon	69.80	70.21
	<u>100.00</u>	<u>100.00</u>
BTU	14631	14716
% Sulfur	0.57	0.57

ULTIMATE ANALYSIS

	<u>As received</u>	<u>Dry basis</u>
% Moisture	0.58	XXXXX
% Carbon	82.53	83.01
% Hydrogen	4.87	4.90
% Nitrogen	1.74	1.75
% Chlorine	0.01	0.01
% Sulfur	0.57	0.57
% Ash	6.74	6.78
% Oxygen (diff)	2.96	2.98
	<u>100.00</u>	<u>100.00</u>



LWT/pg

Member

Respectfully submitted,

CT & E Co.

L. W. Taylor

L.W. TAYLOR, District Manager

October 19, 1972



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CPR Department
Golden, Colorado 80401

MAIL ADDRESS
2180 EAST 40TH AVENUE
DENVER, COLORADO 80205
PHONE 303 255-3371

Sample identification
by Colorado School of Mines

Kind of sample
reported to us Coal

SS Coal
N-Head

Sample taken at XXXXX

P. O. No. ORS 11533

Sample taken by Colorado School of Mines

Date sampled Received 10-9-72

Analysis report no. 72-13157

PROXIMATE ANALYSIS

	<u>As received</u>	<u>Dry basis</u>
% Moisture	2.80	XXXXX
% Ash	5.65	5.81
% Volatile	37.78	38.87
% Fixed Carbon	53.77	55.32
	<u>100.00</u>	<u>100.00</u>
BTU	13295	13678
% Sulfur	0.50	0.51

ULTIMATE ANALYSIS

	<u>As received</u>	<u>Dry basis</u>
% Moisture	2.80	XXXXX
% Carbon	74.73	76.88
% Hydrogen	5.32	5.47
% Nitrogen	1.43	1.47
% Chlorine	0.01	0.01
% Sulfur	0.50	0.51
% Ash	5.65	5.81
% Oxygen (diff.)	9.56	9.85
	<u>100.00</u>	<u>100.00</u>



LWT/pg

Member

Respectfully submitted,

CT & E Co.

L.W. TAYLOR, District Manager

October 19, 1972



COLORADO SCHOOL OF MINES
CPR Department
Golden, Colorado 80401

MAIL ADDRESS
2180 EAST 40TH AVENUE
DENVER, COLORADO 80205
PHONE 303 255-3371

Sample identification
by

Colorado School of Mines

Kind of sample
reported to us

Coal

RW Coal

N-Head

Sample taken at

XXXXX

P. O. No. ORS 11533

Sample taken by

Colorado School of Mines

Date sampled

Received 10-9-72

Analysis report no.

72-13161

PROXIMATE ANALYSIS

ULTIMATE ANALYSIS

	<u>As received</u>	<u>Dry basis</u>
% Moisture	5.80	XXXXX
% Ash	3.55	3.77
% Volatile	39.69	42.13
% Fixed Carbon	50.96	54.10
	<u>100.00</u>	<u>100.00</u>
BTU	12189	12940
% Sulfur	0.26	0.28

	<u>As received</u>	<u>Dry basis</u>
% Moisture	5.80	XXXXX
% Carbon	70.35	74.68
% Hydrogen	4.83	5.13
% Nitrogen	1.27	1.35
% Chlorine	0.01	0.01
% Sulfur	0.26	0.28
% Ash	3.55	3.77
% Oxygen(diff)	13.93	14.78
	<u>100.00</u>	<u>100.00</u>



LWT/pg

Charter Member

Respectfully submitted,

CT & E Co.

L.W. TAYLOR, District Manager

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