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J.G.S. Research Company, Inc.

OXIDATIVE DERIVATIZATION AND SOLUBILIZATION OF COAL

Final Report

Period :

October 1, 1986 - April 30, 1988

By

J. G. Schulz

E. N. Porowski

A. M. Straub

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I SUMMARY

We investigated the solubilization of coal by oxidative means to produce motor fuels. Nitric acid was used in the first of two approaches taken to cleave aliphatic linkages in coal and reduce the size of its macrostructure. Mild conditions, with temperatures up to a maximum of 75°C, and nitric acid concentrations below 20% by weight, characterize this process. The solid product, obtained in high yields, is soluble in polar organic solvents. Lower alcohols, methanol in particular, are of interest as carrier solvents in diesel fuel applications.

Coals investigated during this project were New York State peat, Wyodak subbituminous coal, North Dakota lignite, and Illinois #6 bituminous coal. Of these species the lower rank coals were easily converted and appear well suited to the process, while the bituminous Illinois #6 and Pitt Seam coals were unreactive. We concentrated our efforts on Wyodak coal and North Dakota lignite as the feedstocks of choice.

Reaction conditions with regards to temperature, acid concentration, and time were optimized to obtain high product selectivity at maximum conversion. A continuous process scheme was developed for single pass coal conversions of about 50% to methanol-soluble product. This was accomplished with acid quenching through the addition of fresh coal, and recycling of the product intermediate. Weight yields of product were above 100 % at 50% coal conversion. Between 180 and 200 grams of nitric acid (100% basis) per pound of subbituminous coal or lignite are required under these conditions. This corresponds to a nitric acid cost of 4.5 cents per pound of coal, or 3.5 cents per pound of methanol soluble product.

In addition to carboxyl functionality, nitro groups are contained in the product which impart desired ignition properties. Solutions of 45% of the products from Wyodak coal and North Dakota lignite in methanol were prepared for evaluation in fuel applications. Data obtained by elemental analysis, spectral methods, physical measurements, as well as heating values define these novel products.

Another approach to oxidative coal conversion was the subject of a preliminary study. Molecular oxygen was used as the oxidant at atmospheric pressure and temperatures of 90°C in an attempt to cleave aliphatic linkages. This reaction was run in glacial acetic acid as the solvent and cobalt acetate as the catalyst. While the basic feasibility of this method was established, coal conversion was very low at the low partial pressure of oxygen at atmospheric conditions.

II INTRODUCTION

Coal qualifies as a potential diesel fuel as far as ignition properties and power generation are concerned. Its ash content, however, is a serious detriment to engine life, while its solid nature presents a major inconvenience. Conversion of coal to a liquid or gaseous derivative solves both problems, and is consequently the goal of any coal conversion process. Conventional hydrocracking imparts liquidity by thermal means, requiring large amounts of energy and hydrogen. Further drawbacks include: operation at high pressure, tedious product separation, and handling of toxic products. Furthermore, unless the products are upgraded by costly hydrogenation, their use is limited to boiler fuels.

Oxidative solubilization of coal with nitric acid under uncommonly mild processing conditions offers a simpler, and more economical alternative. It allows production of diesel fuels with good ignition characteristics at costs which may be competitive with petroleum derived fuel. This novel approach to the production of liquid fuels from coal was initially investigated at the former Gulf Research & Development Company.

Dilute nitric acid is used at temperatures around 50°C and atmospheric pressure to convert coal to solid derivatives highly soluble in polar solvents. Oxidative size reduction with formation of carboxy- and nitro-functionalities account for the high solubility of the product in lower alcohols. Methanol and ethanol are of particular interest as carrier solvents for the projected fuels in view of their availability, low cost, and established performance as motor fuels in their own right.

Basic parameters governing coal solubilization with nitric acid had been established during earlier work. The optimization of this process, as well as the solution of peripheral problems, were carried out under this DOE contract. Low temperature interaction of coal with molecular oxygen in the presence of cobalt catalyst was also briefly examined as another possible route to solubilization.

III EXPERIMENTAL DESIGN

Raw Materials

Feedstocks

Bituminous and subbituminous coals as well as lignite and peat were investigated as feedstocks. Samples used were ground to a particle size of 100 mesh and vacuum dried. Their ultimate analysis is shown in Table 1.

Reagents:

Nitric acid, 70% wt. Baker Analyzed Reagent

Methanol, Celanese Company

Cobaltous acetate tetrahydrate, Alfa Products, Thiokol

Acetic acid, glacial, Fisher Scientific Company

Characterization of Coals and Products.

Reaction products and parent coals were defined by the following procedures

1. Elemental Analysis, Galbraith Laboratories
2. C-13 NMR Spectroscopy, Varian XL 200 NMR Spectrometer.
3. Thermoanalysis, Du Pont 1090 Thermal Analysis System.
4. Liquid Chromatography, Waters Associates Liquid Chromatograph.
5. Infrared Spectroscopy, Perkin Elmer Grating Spectrometer.
6. FTIR, Nicolet Instrument Corporation
7. Neutral Equivalent Determination, NE, g of substance required to neutralize 1 mole of NaOH
8. Melting Range Determination, Fisher-Johns Melting Point Apparatus.
9. Solubility in polar solvents, in particular methanol.
10. Viscosity Measurements, Brookfield Viscometer.
11. Heating Value Determination

IV SOLUBILIZATION OF COAL WITH NITRIC ACID

The oxidation of coal with nitric acid to produce derivatives of diverse utility has been the objective of numerous efforts in the past. Products reported were almost exclusively aromatic mono, di, and polyfunctional carboxylic acids of limited use in resin applications. Yields were low under the rather severe conditions of temperature, acid concentration and reaction times employed. The aliphatic constituent of coal was oxidized to carbon dioxide and water under conditions which only aromatic ring structures survived (1-13). Uncommonly mild reaction conditions characterize the approach to coal oxidation addressed in this report. As the result of near ambient reaction temperatures, low nitric acid concentrations, as well as short reaction times, aliphatic structures are preserved, and high yields of products soluble in polar, organic solvents are obtained. Their solutions in methanol or ethanol show promise as motor or boiler fuels.

Apparatus

3 liter pear-shape flask with provision for heating, mixing, and temperature control.

Experimental Procedure

Nitric acid was added to a mixture of coal and water, which was held at selected temperatures for various periods of time. Product slurries were filtered to recover solids that were dried, and extracted with methanol to

obtain methanol-soluble solids after evaporation. Aqueous filtrates were evaporated to recover nitric acid not consumed, water-soluble organics, and ash. This procedure is referred to as the Filtration Mode.

In the Evaporation Mode, another version for recovering methanol-soluble product, product slurries were subjected to gradual evaporation under vacuum. Residual nitric acid, brought up in concentration to a reactive level by the removal of water, reacts with unconverted coal and is eliminated. Resulting solids combine both the water-insoluble, and water-soluble product fractions.

Variables known to affect conversion and product distribution, and reexamined in this study include:

1. Temperature
2. Nitric acid concentration
3. Nitric acid to coal ratio
4. Reaction time (addition time plus hold time)

Fixed Nitric Acid Concentration at Ambient Conditions.

The reactivity of different rank coals in their interaction with nitric acid was examined during preliminary experimentation. Samples of N.D. lignite, Wyodak subbituminous coal, Illinois #6 River King bituminous coal, and Monenco peat were first characterized for ash content, base solubility, neutral equivalent and by elemental analysis. To determine the amount of acid-soluble mineral matter, each coal was assayed by reaction with 25% hydrochloric acid. Samples of each coal were then reacted for a period of two and a half hours at ambient temperature with a large excess of nitric acid, 15% concentration in one series and with 40% acid in another. Excess

nitric acid was used to maintain the chosen concentrations throughout the runs. Products and demineralized coals were characterized in the same way as their parent coals. Illinois #6 River King coal was not analyzed because of the abnormally high mineral content of the particular sample available at that time. It was replaced in later experiments by a sample of Illinois #6 Burning Star. Data from these runs including material balances and elemental analyses are shown in Tables 2 to 4.

Results showed that North Dakota lignite and Wyodak coal are quite similar in reactivity and the amount of soluble product generated. The least reactive species was Illinois #6 River King. On reaction with 40% nitric acid at room temperature products from North Dakota lignite, and Wyodak coal both show a considerable increase in weight over that of the feed, as well as high solubility in base, and dimethylformamide. Peat, unlike the higher rank coals, also formed a considerable amount of water-soluble product in addition to product soluble in base.

As expected, elemental analysis shows that hydrochloric acid treatment does not affect the composition of the feedstock. Its action is limited to the removal of certain metal contaminants. This is seen in Figure 1 which compares the infrared spectra of untreated N.D. lignite (spectrum 1) and lignite washed with hydrochloric acid (spectrum 2). Absorption for carboxyl carbonyl at around 1700 cm^{-1} is not shown as a separate band for the parent coal, but clearly manifests itself in the spectrum of coal washed with hydrochloric acid.

Ineffective at 15% concentration, 40% nitric acid converts coal to products soluble in base. Under these conditions introduction of nitro functionality into coal is the only clearly discernible event, while oxidation is not yet in evidence.

Fixed Nitric Acid Concentration at Different Severity

To elucidate the effect of temperature and nitric acid concentration, on the interaction of coal with nitric acid, experiments were carried out over a wide range of these two variables. Initial experiments were run under comparatively mild conditions, with either temperature or nitric acid concentration at a low level. Results from these experiments are shown in Table 5. The following became apparent at higher temperatures or nitric acid concentrations. At low temperature and low nitric acid concentration metal components are removed with an accompanying weight loss of 7%. Increasing severity promotes nitration with an increase in yield but little evidence of oxidation. At still higher temperature and acid concentration yields of solids decrease due to formation of water-soluble product. Decreasing neutral equivalents signify oxidation and an increasing amount of acid functionality in the product.

Carbon to oxygen and carbon to hydrogen ratios provide additional information. Oxidation will decrease the carbon to oxygen and increase the carbon to hydrogen ratios while decarboxylation should have the opposite effect. A decrease in both the carbon to hydrogen and carbon to oxygen ratios could signify hydrolysis of ether linkages as the other possible event in producing acid functionality. Efforts were also made to establish the molecular size distributions in the reaction product. Solutions of products in dimethylformamide were analyzed by liquid chromatography using a molecular size exclusion linear Ultrastrogel column. Although absolute molecular size ranges could not be established due to lack of comparable standards, a shift in peak elution time in the direction of smaller molecules is evident as oxidation increases. Figure 2 shows peak distributions for

products obtained with 15% nitric acid at 45°C and 80°C, and for products with 25% nitric acid at 25°C. Peak elution times for polyethylene oxide, polystyrene, and two low molecular size acids are marked as references on the chromatogram along with two lignin derived products of known average molecular weights of 1000 and 1800, determined by vapor phase osmometry. These standards indicate that the molecular size range of dimethylformamide soluble product from N.D. lignite is below 5000.

To more accurately quantify and define small amounts of water soluble product obtained under mild conditions a repeat series was run with acid-washed coal in place of untreated coal used in earlier experiments. This eliminates a large part of inorganic contaminants from the aqueous filtrates. Runs were carried out with North Dakota lignite, Wyodak coal, and New York State peat at various combinations of temperature and nitric acid concentration. Aqueous filtrates obtained were evaporated under vacuum at room temperature. Results of these experiments are shown in Table 6. At all combinations of temperature and acid concentration, neutral equivalents for water insoluble fractions were significantly below those for the parent coal. Water soluble product, formed in minor amounts only with lignite and Wyodak coal under these mild conditions, was significant with peat being by far the most reactive feedstock. Product obtained with 50% nitric acid at 0°C (conditions minimizing oxidation), showed a neutral equivalent of 183 which is higher than values obtained at temperatures up to 60°C. Its solubility in methanol is accordingly much lower than that for higher temperature products.

A plot in Figure 3 shows the percentage of elemental carbon versus that of nitrogen for the water-insoluble product from N.D. lignite. In the temperature region up to 60°C. carbon values obtained are on a slope only

slightly steeper than for theoretical values calculated for different amounts of nitrogen, assuming no oxidation occurred. (curves A and B) Three samples of water insoluble oxidation products from reactions of demineralized N.D.lignite at 0, 25, and 60°C with nitric acid of 50, 35, and 35% concentration respectively, were analyzed by Fourier Transform Infrared Spectroscopy (FTIR). A sample of demineralized lignite treated with 1% aqueous sodium hydroxide was also inspected. Each sample was dried at 70°C in vacuo for 12 hours, then ground with spectroscopic grade KBr, and pressed into a clear pellet at 20,000 lb.

Spectra obtained and shown in Figures 4 to 11 are nearly identical for all water-insoluble products. Absorption in the region of 1900-3600 cm^{-1} is characteristic for lower rank coals. A broad 3300 cm^{-1} band assigned to hydrogen-bonded OH groups appears in all spectra (14) The intensity of bands at about 2950 cm^{-1} and 2850 cm^{-1} (shoulder) in the spectra of coals treated with nitric acid is lower than that for demineralized coal not reacted with nitric acid. These bands are assigned to aliphatic C-H stretching vibration (14). Reduced intensity of aliphatic C-H deformation vibration at 1450 cm^{-1} (15) in spectra of oxidized coal suggests oxidation of aliphatic linkages or groups. A broad band in the region of 2400-2750 cm^{-1} is characteristic for hydroxyl OH stretching vibration of the carboxyl group (16,17). It indicates the presence of carboxylic acids even after treatment with base (Figure 5), and is particularly prominent for product obtained with 35% nitric acid at 60°C (Figure 7) Absorption at 1715-1730 cm^{-1} appears in the spectra of all products, and also in the spectrum of acid washed coal, although its intensity is much stronger in coal treated with nitric acid. It does not appear as a separate band in the spectrum of unwashed coal. (Figure 1) or

in the spectrum of coal treated with sodium hydroxide (Figure 5) The strong intensity of this band in the spectra of oxidized coals can be attributed to an increased amount of carbonyl functionality, (C=O-stretching vibration), from oxidation to carboxylic acids, and possibly other types of carbonyl. A peak at around 1600 cm^{-1} is generally characteristic for coals and is attributed to aromatic ring vibration (18), and/or to absorption arising from other oxygen-containing species in the coal structure.

Absorption considered indicative of the presence of products from interaction with nitric acid is manifest by a peak at $1550\text{-}1560\text{ cm}^{-1}$ (Figures 9-11) This peak does not appear in the spectrum of the parent coal and can be assigned to aromatic nitro (Ar-NO₂) groups. (16,17). Another peak, characteristic for coal reacted with nitric acid at $1340\text{-}1350\text{ cm}^{-1}$ possibly relates to organic nitrates, as most of the metal constituents in coal had been removed by washing with hydrochloric acid. Two samples of N.D. lignite oxidized with 35% nitric acid at 25 and 60°C, along with acid-washed lignite (earlier examined by FTIR analysis) were also analyzed by solid C-13 NMR. Spectra for demineralized N.D. lignite, and oxidation products are given in Figures 12, 13, and 14. All regions of integration are shown in Table 7. A summary of the C-13 NMR shift ranges was taken from a paper by Dereppe et al (19) and is shown in Table 8.

Most prominent differences between spectra for oxidized and parent coal are observed in the aromatic region. Loss of alkyl-substituted aromatic (91-138 ppm) and phenolic carbon (170-149 ppm) is quite evident. This region includes aromatic ethers and anhydrides as well. Narrowing of the aromatic region also indicates the loss of ring substitution. There is also a noticeable increase in the carbonyl/carboxyl region (240-270 ppm) which is likely the result of oxidation. Acid and

ester carbonyl appear in the 190-170 ppm range, aldehyde, ketone, and amide carbonyl is found at 210-190 ppm. The aliphatic region (50-0 ppm) shows little change except for a slight reduction in the 50-35 ppm range, attributed mostly to methylene bridges and bridgehead carbons such as in acenaphthene. A reduction in the region of 60-50 ppm indicates breaking of some aliphatic ether linkages. Nitro substituted aromatic carbons have chemical shifts in the region of 130-148 ppm and thus are overlapped by other aromatic carbon resonances. Their identification by C-13 NMR analysis is very speculative.

The reaction of various coals with nitric acids was investigated in the temperature range of 25 to 80°C. while varying nitric acid concentrations from 15 to 70%. Data obtained show that high nitric acid concentrations and low temperatures favor nitration over oxidation, while oxidation predominates at low acid concentrations. Yields and nature of soluble products depend largely on which of these two events occurs initially.

Initial nitration imparts instability to carboxylic products resulting in subsequent oxidation. Initially oxidized substrates on the other hand, resist nitration due to deactivation by carboxyl functionality.

Fixed Nitric Acid Concentration at Elevated Temperature

Subsequent experimentation was extended to temperatures above 80°C at low nitric acid concentrations, in an attempt to reduce nitration. Several runs were carried out with untreated N.D. lignite in a 1 liter stainless steel autoclave at temperatures ranging from 80 to 175°C. using an excess of nitric acid of 5%, and 10% concentration respectively.

Reaction products were identified by their solubility in water and methanol and characterized by elemental analysis and distribution of ash in each identified fraction. Results of these experiments are shown in Tables 9, 10, and 11. Oxidation clearly manifests itself in this experiments as the major event with formation of water-soluble product and by substantial loss of matter to carbon dioxide and water. Results also show that nitration already occurs at a concentration of 5% nitric acid to about the same extent observed with 70% acid. Nitration is therefore unavoidable when nitric acid is used as the oxidant. With rising temperatures up to 150°C, water-soluble fractions were found to increase. Their amount decreased again beyond this point, and was drastically reduced at 175°C with a large loss in overall yield. Formation of desired water-insoluble but alcohol-soluble product also decreased with rising temperature from a maximum at 100-110°C to negligible amounts at 175°C. Thermal instability of methanol-soluble intermediate likely accounts for its decrease with rising temperature. Water-soluble fractions were highest in ash.

Sequential Solubilization at Constant HNO₃ Concentration

Preliminary experiments discussed so far indicate that in the reaction of coal with nitric acid, formation of methanol-soluble but water-insoluble product proceeds along with its further degradation to water-soluble derivatives and CO₂. Ways to affect respective conversion rates favorably to improve yields of methanol-soluble, water-insoluble product were consequently explored. Two approaches were taken.

- 1) Employing a two-stage sequential mode where the methanol-soluble product is extracted after reaction under an initial set of conditions, followed by further reacting the methanol-insoluble remainder under a different, second set of conditions. (Sequences A, B, and C.)
- 2) Initially reacting under one set of conditions and changing to different conditions after a fixed period of time. (Sequence B, and C)

Run conditions were selected from conditions earlier defined for single stage reactions. Three sequential modes were investigated with demineralized North Dakota lignite in order to establish conditions under which maximum yields of methanol-soluble product could be obtained. Results from these runs are given in Tables 12, 13, and 14, showing yields of products and their elemental composition. Table 12 compares yields of the desired methanol-soluble product obtained by sequential routes "A", "B", and "C".

Starting with 100 g of acid-washed N.D. lignite in sequence "A" under conditions (1) (35% nitric acid, at 45°C) 106g of water-insoluble product was obtained of which 26g were methanol-soluble. The soluble product was separated from the methanol-insoluble portion and further reacted with nitric acid under conditions (1), (2), (35% HNO₃, 60°C) and (4) (70% HNO₃, 25°C). As the result of degradation, amounts of methanol-soluble products recovered from these experiments were reduced by up to 58% of their original amount. When on the other hand the methanol-insoluble fraction from (A) was further reacted under the same conditions, additional methanol-soluble material was obtained in amounts of 9g, 14g, and 21g respectively.

The best yield of methanol soluble product, in an amount of 47g, could therefore be realized by combining steps 1 and 4, which involved separation of the methanol-soluble product after step (1) followed by further reacting the insoluble fraction. Starting with 100g of lignite under conditions (4) in sequence (B), 106g of total water-insoluble product was produced of which 32g were methanol soluble. Further reaction of the total, non-separated product under conditions (3) (10% HNO₃, 60°C), or (4) increased the yield of methanol-soluble product only slightly from 32g to 34g and 35g respectively. When methanol-solubles were extracted after step (4) subjecting only the insoluble portion to further reaction, up to 18g of additional soluble product could be recovered. Two steps under conditions (4) with separation of methanol-solubles after step 1 gave a 50% yield for the desired product.

In sequence (C), conditions (3) were used initially to produce 100g of water-insoluble product of which only 15g were methanol soluble. The total unextracted product was further reacted under conditions (3) or (4) which increased the yield of methanol-soluble product to 25g and 40g respectively. Methanol-insoluble product alone from the first step produced additional amounts of solubles in amounts of 19g and 8g respectively under the same conditions. The yield of methanol-solubles in this case can be maximized to 40g by combining conditions (3) in the initial step with conditions (4) in the second. In a separate study non acid-washed Wyodak subbituminous coal was solubilized with nitric acid in a multi-pass, sequential mode, illustrated in Tables 15 and 16.

After each step, methanol-soluble product was removed from the reaction mixture and the insoluble fraction recycled with additional acid. As with lignite, temperature limits per pass conversion to around 25%.

Operating at this level, conversions to methanol-soluble product of at least 70% were obtainable with weight yields of over 75% based on ash-free coal. Residual unreactive carbonaceous matter in the amount of 27.5% by weight, and 19.3% of water-soluble product add to a yield of 116 wt.% for total product. Consumption of nitric acid per gram of methanol-soluble product was found to be higher with fresh coal than with recycled intermediate as shown in table 16.

Flexible Severity Mode

Data from these studies indicated that operating under conditions, changing in severity throughout the reaction period, higher single pass conversions to soluble product should be obtainable, while degradation of primary, methanol-soluble product could be reduced. In this procedure temperature and acid concentration would be continuously adjusted to the changing requirements of the process.

To elucidate reactivities and stabilities of intermediates and products under different processing condition, runs were carried out analyzing reaction mixtures at various stages of the process. Non acid-washed lignite was used at 60°C and 75°C , with nitric acid added in amounts proportional to the length of the reaction periods investigated (0.5, 1.0, and 1.5 hours; 33, 66, and 99g of acid). Runs with acid addition over a 1.5 hour period were also followed by a 2 h holding time at final temperature. Nitric acid was gradually added to lignite in all runs to control exothermicity and to keep acid concentration in the reactor at a low level.

Results from this work are shown in Tables 17 to 19 . Table 17 follows the reaction of lignite at 60°C, with nitric acid addition over a

period of 1.5h, up to a final acid to lignite ratio of 1.16, This was followed by a two hour holding time at 60°C. Analysis of the reaction mixture after addition of one third of the total acid complement over a half hour period reveals near total consumption of nitric acid, and a 6.6% conversion to methanol-soluble product. A high neutral equivalent of 309 for the methanol-insoluble product fraction indicates the presence of unconverted coal. After another 30 minute interval with addition of the second nitric acid increment, near complete acid consumption is again evident and conversion to soluble product is increased to 14.6%. The methanol-insoluble fraction shows a neutral equivalent of 196 at this point, a value which will not decrease any further, and which identifies this material as the precursor to the desired methanol-soluble product.

Addition of the last portion of acid over another 30 minute interval again increased the conversion to total methanol-soluble product to 22.9%, lowering the amount of the insoluble precursor accordingly. Nitric acid consumption is incomplete with an acid concentration of 20% in the reaction mixture. No further consumption of acid, or conversion of intermediate to soluble product occurred following additional holding for two hours at the reaction temperature. Nitric acid of 20% concentration is therefore ineffective in promoting any further reaction at 60°C. At the final conversion to methanol-soluble product of 22.9%, its efficiency based on lignite (or precursor) consumed is around 100% by weight.

Results also show that methanol-soluble product, once formed, is not destroyed under the chosen reaction conditions. The reaction appears to be very fast, at least during the first hour when essentially all acid was consumed. Water-soluble by-products constitute lower molecular organic

acids, and metal salts. As the result of progressing solubilization, removal of ash gradually increased during the reaction period.

In another sequence at 75°C under otherwise the same conditions, no final holding period was employed. Data shown in Table 18 are essentially identical to those from the 60°C series. Acid consumption ceased at 19% concentration, close to the 20% level in the 60°C experiment. The moderate increase in reaction temperature in this experiment had no effect at the low final acid concentration which is the dominant factor in this run.

In a subsequent experiment the reaction temperature was raised to 75°C for a holding time of 2 hours after acid addition at 60°C, resulting in consumption of additional acid and a conversion of 30% to methanol-soluble product, calculated on a non ash-free basis. Product degradation was not evident under these conditions (Table 19). Studies then continued to establish optima for temperature, nitric acid concentration, and reaction time to obtain highest single pass conversion to methanol-soluble product.

The fact that the methanol-soluble final product is subject to degradation under the very conditions required for its formation is the chief problem in optimizing coal solubilization by this route. As product degradation is concentration dependant, conditions were explored which would afford highest possible conversion to methanol soluble product with minimum degradation. Tables 20 and 21 present results from experiments with North Dakota lignite, varying temperature, amount of acid, and reaction time.

At 60°C, nearly identical conversions to methanol-solubles of 23% to 25% were obtained regardless of the amount of acid used, or the reaction time, as in these runs temperature is clearly the governing factor (Table 20). Methanol-soluble products show neutral equivalents of around 120,

methanol-insoluble precursors values between 180 and 190, a strong indication that within each of these two groups individual species are similar if not identical. Raising the temperature to 75°C after acid addition (Run 37) results in an increase in conversion to 30% , increased nitric acid utilization and no loss in selectivity. At this point 83% of the added nitric acid has been consumed and no further conversion to product can be expected at the final low acid concentration in the reaction mixture.

In subsequent runs at temperatures of 60°C to 75°C additional nitric acid was added to further increase the conversion to methanol-soluble product without loss of selectivity. Results show that nitric acid addition is critical as to what point in time it occurs, as evidenced in Table 21. In Run 47 the full complement of acid, 132g, was gradually added over a period of one hour at 60°C, followed by a holding time of 2 hours at 75°C. In Run 49 on the other hand 99g of acid was added in 18 minutes, and the remaining 33g acid over a period of one hour at 75°C.

The second addition mode results in a nearly 50% higher conversion to methanol-soluble product compared to the first, or 37% versus 26% (calculated on a non ash-free basis). A longer reaction time in Run 50 compared to Run 49, and additional nitric acid in Run 52 gave no further increase in conversion. Raising the temperature under otherwise identical conditions to 85°C for another hour in Run 51, decreased conversion and overall yield. Results so far indicate that single-pass conversions to methanol-soluble product above the present level of 37% could be obtained through a combination of increased amounts of nitric acid with shorter reaction times at temperatures not higher than 70 °C.

Data in Table 22 show three single-pass runs under different conditions, all giving a 41% yield based on ash-free lignite. Run 49

represents an overall optimum with regards to temperature, reaction time, and nitric acid requirement. Single pass yields of 41% were the highest obtained with lignite as the only feed component. Higher yields can be expected from operation with coal plus recycle of the intermediate fraction as projected for continuous operation. Results from additional runs under conditions differing from the established optimum emphasize the criticality of low temperature and reaction time in this process, (Table 23).

Single Pass Conversion

Under conditions experimentally defined as optima for lignite, Wyodak subbituminous coal was converted to methanol-soluble product with single-pass yields of 50% based on ash-free coal. Runs 59, 61, and 64 in Table 24 all show the 50% yield maximum. Conditions in Run 59 are overall most efficient regarding acid consumption and amount of the recycle fraction. Compared to lignite, Wyodak coal is clearly the superior feedstock as far as its convertibility is concerned, but also in other respects to be discussed later. Yield data for methanol-soluble product presented up to this point relate only to the water-insoluble fraction from the batch process. Values for total methanol-soluble product including the water-soluble fraction are significantly higher.

A realistic assessment of the efficiency of the process must consider the following. Product yields have so far been based on ash-free feed. Ash was determined by high temperature ashing which shows less than its actual amount. Based on convertible organic matter in the particular coal reacted, actual yields were therefore higher than those given earlier. They were also based on the amount of coal fed to the process rather than the

amount of coal consumed or its equivalent precursor which is more meaningful.

Table 25 shows calculations for efficiencies based on feed consumed for products from Wyodak coal and lignite respectively. Efficiencies in wt.% are quite high, showing that in the case of Wyodak coal a doubling in weight from coal to total product has occurred due to introduction of nitrogroups and carboxy functionalities into the coal structure. Both lignite and Wyodak coal are easily solubilized under very mild conditions, but Wyodak coal with much higher efficiency. Table 26 shows the distribution of ash in the water-insoluble, and water-soluble product fractions, as well as in the desired methanol-soluble product. Ash present in the first is mineral in nature while the other contains metal salts. Small amounts of ash in the product are the result of marginal filtration which can be readily improved for more complete removal of this residue.

Evaporation Mode

In another process version, the Evaporation Mode (described earlier), Wyodak coal alone or in combination with the intermediate fraction from a preceding run was reacted with nitric to simulate recycle conditions. Table 30, Run 67 shows that production of methanol solubles in the latter case is equivalent to that with coal alone. Conversion of intermediate in the absence of fresh coal (Run 71) again gave comparable or even better results. The problem of removing residual nitric acid from the reaction products was conveniently and effectively solved in these experiments by adding fresh coal after reactions terminated (Runs 68,71, and 73). Acid removal was essentially complete after adding 25% b.wt. based on the

initial coal charge, but smaller amounts of fresh coal would most likely suffice.

Eliminating filtration of the product slurries as well as removing nitric acid from the product through continued reaction of residual acid with coal during the evaporation step are the advantages of the Evaporation Mode. Incomplete acid removal, and additional, less desirable water-soluble components in the final products are its drawbacks, as well as a higher ash content compared to product obtained by filtration. The filtration mode combined with fresh coal addition for nitric acid quenching and recycle of intermediate provides the preferred mode of operation in particular as far as deashing is concerned.

Solubilization of Bituminous Coals

Illinois #6 and Pitt Seam bituminous coals were evaluated under conditions earlier established with Lignite for highest single pass conversions to methanol-soluble product. Results from these experiments are shown in Table 31. Compared to Lignite and Wyodak coal, the higher rank feedstocks were much less reactive, shown by low conversions to methanol-soluble product which increased only marginally when the temperature was raised from 75 to 85 °C. Another drawback is the high amount of the less desirable water-soluble fraction produced which can be expected to further increase under more severe conditions required for higher conversion levels.

Preparation of Samples for Testing in Fuel Applications

Solubilization runs were carried out with North Dakota lignite and Wyodak coal to produce sufficient material to prepare 30% solutions in methanol of each derivative in 1 gal quantities. These products are now available for testing in potential fuel applications. These runs were carried out under conditions established as optima for Wyodak coal. They include a temperature of 75°C, and a reaction time of 1.3 h. Operation was in the preferred Filtration Mode with recycle of product intermediate, and addition of fresh coal for nitric acid quenching. To prevent sludge formation 5% of ethylene glycol monomethyl ether was added to the solutions. No precipitates formed over a period of 3 months.

Nitric Acid Balance in Wyodak Coal Solubilization in the Filtration Mode.

To establish a nitric acid balance for the process, the amount of nitric acid consumed in the two principal reactive events, nitration and oxidation, was calculated. Analysis for nitrogen in the product fractions provides a ready answer for the first. The amount of nitric acid consumed during oxidation is the difference between total acid consumed and the amount used in introducing nitro functionality. Table 32 shows that only 20% of nitric acid consumed is used in nitration with oxidation accounting for the remainder.

During oxidation nitric acid is reduced to nitrogen oxide (NO), dinitrogen oxide (N₂O), and nitrogen. Of these only nitrogen oxide can be regenerated to nitric acid. For economic reasons it is therefore important to avoid formation of N₂O and nitrogen. To assess the composition of the exit

gas, samples of it were taken at half hour intervals throughout the reaction and analyzed by mass spectrometry.

Table 33 shows the presence of nitrogen oxide, dinitrogen oxide, and nitrogen, along with carbon dioxide. The composition of the gas stream changes with time, showing a gradual increase in the concentration of dinitrogen oxide and nitrogen while that of the regenerable nitrogen oxide decreases. This trend is explained by the fact that with decreasing concentration of nitric acid over the run period residual acid is more fully reduced to the lower valency states. Maintaining relatively high nitric acid concentrations during the process should therefore favor reduction to nitrogen oxide resulting in increased regeneration of nitric acid.

This process consumes nitric acid to introduce nitrogroups into coal structure which impart desirable ignition characteristics, solubility, and an increase in weight yield. Additional acid is consumed by oxidation with reduction to nitrogen oxide which can be regenerated. About 15% of the nitric acid is lost to N_2O and nitrogen. This translates into a requirement of 186 g of nitric acid per pound of Wyodak coal without recycling of product intermediate or 140 g of nitric acid per pound of coal with recycling, as projected for an industrial application of the process.

Elemental Analysis and Heating Values.

Elemental analysis for N.D. lignite, Wyodak coal, and products derived, along with other data are presented in Tables 27 and 28. Table 29 shows heating values for Wyodak coal, de-ashed products derived, and their methanol solutions.

Evaluation of Methanol-Soluble Products from Coal Thermal Properties.

The methanol-soluble product is a dark brown solid which does not undergo transition into the liquid state on heating on the hot surface of a Fisher-Johns melting point apparatus. Thermal stability of the methanol soluble product from Wyodak coal, the preferred feedstock for this process, was determined by dynamic thermogravimetric analysis. The test was run in air at a flow rate of 40 cm/min and a heating rate of 20 degrees/min. Weight loss began around 80°C and reached 2% at 120°C. Rapid degradation occurred in two stages around 200°C and 250°C and was close to 50% at 480°C. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves are shown in Figure 15.

Corrosivity of Methanol Solutions of Coal Derivatives

A piston of a pump element used in Bosch Diesel injection pumps was immersed in a 30% methanol solution of the Wyodak coal derivative having a pH of 3.5. No trace of corrosion was detected after a period of one month of exposure as well as any change in weight of the piston. It should be emphasized that the pump element is one of the critical and vulnerable parts of the injection system.

Stability of Methanol Solutions

Methanol solutions of 30% to 45 % concentration of products from New York State peat, Wyodak subbituminous coal, and North Dakota lignite were examined for stability with regard to sludge formation. Following preparation of the methanol solutions slight precipitation of solids was observed with each solution after standing at room temperature for 3 days. Addition of 5% by weight of ethylene glycol monomethyl ether (Methyl Cellusolve) re-dissolved these precipitates and the solutions have remained stable for over 3 months (time of last inspection) Experimentation with various other potential co-solvents showed that other ethers, including tetrahydrofuran, and dioxane, as well as acetone are also effective in preventing sediment formation if added during the dissolving step. Higher boiling species however, are preferable.

Viscosity of Methanol Solutions

Conventional injection systems for diesel engines are designed for fuels in the viscosity range of 3 to 5 cp. Higher viscosities up to 15 cp can be accommodated. Viscosities of methanol solutions of solubilized Wyodak coal were determined using the digital Brookfield viscosimeter, model LVTD with UL adapter. The effect of concentration and temperature on the viscosity of these solutions is shown in Table 34.

Liquid Phase Oxidation of Coal with Molecular Oxygen

Another approach to size reduction of coal and resulting solubilization or liquefaction involves electron transfer reactions with molecular oxygen, catalyzed by transition metal salts such as cobaltic acetate in acetic acid solution. This system involves two basic steps.

At temperatures generally below 100 °C a peroxide forming additive generates oxygen radicals which convert divalent cobalt to its trivalent oxidation state. Trivalent cobaltic ion in turn oxidatively cleaves aliphatic linkages, with formation of carboxylic derivatives, in particular when attached to aromatic structures. Cobaltic ion, continually reduced and reoxidized is not consumed in this process. Systems of this nature have been described in the literature (20-31) and successfully implemented commercially with single component substrates such as the alkylbenzenes to produce aromatic carboxylic acids. Critical for success with this scheme is the absence of inhibitors, among which hydroxyl compounds such as phenols, alcohols, and water, as well as amines are prominent radical scavengers.

The experimental set-up during the initial stage of this study consisted of a round bottom flask equipped with a fritted glass sparger, thermometer, condenser, and magnetic stirrer. During later experiments a tubular glass reactor with fritted glass bottom was used. The latter reactor version allowed for more effective contact of the liquid phase with oxygen to assure efficient reoxidation of cobalteous acetate. Plugging of the fritted plate was initially encountered when only sparingly soluble cobalteous acetate was used in the start-up. This problem was overcome by

preoxidizing the divalent form to the much more soluble cobaltic state prior to reaction with coal.

A continuous flow of oxygen at about 3.3 cbf/h provided vigorous agitation of the reaction mixture. Cobaltic acetate solutions used in these experiments were prepared by gradual heating and reacting a mixture of glacial acetic acid, cobaltheous acetate tetrahydrate and methyl ethyl ketone promoter. After a clear pink solution was obtained, oxygen was introduced at 40°C. The temperature was then raised to 90-95°C continuing the oxygen flow at this temperature until a dark green solution of cobaltic acetate was obtained. To prevent possible inhibition of the free radical promoted reaction by metal contaminants samples of lignite and peat were demineralized by treatment with 25% hydrochloric acid. This treatment gave a substantial decrease in the ash content, for lignite from 9.2% to 2.5% and for peat from 11.9 to 2.3%.

A series of reactions was run with acid-washed as well as untreated feeds using fixed amounts of coal, glacial acetic acid solvent, cobaltheous acetate, and methyl ethyl ketone promoter. Reactions were carried out at 90-95°C for 2 hours unless terminated earlier if regeneration of cobaltic ion ceased, as manifest by a persistent pink color of the liquid phase. Reaction products were filtered to recover a solid fraction which was washed with dilute hydrochloric acid for the removal of cobalt, then with water and dried at 50-60°C in a vacuum oven.

Reagents, reaction conditions, and results from these studies are shown in Table 33 and 34. Products were characterized by their solubility in base and polar solvents, as well as their neutral equivalents. Results were also compared to those separately obtained without oxygen, in the

absence of cobaltic acetate, as well as in the presence of added water under otherwise identical conditions.

Using oxygen and acetic acid solvent in the absence of cobalt no oxidation was observed, in contrast to claims in the literature (31). When cobaltic acetate and dilute acetic acid were used along with oxygen no reoxidation of divalent cobalt to the trivalent stage occurred as water in the solvent inhibited regeneration. Oxidation of the coal was limited in this case to the amount of cobaltic ion initially introduced. Continuous regeneration of Cobalt(II) to cobalt(III) ion was observed with glacial acetic acid even with untreated coal.

Resulting neutral equivalents show that both, lignite and peat can be converted oxidatively in this system. The extent of their conversion to oxygenated products is however low at atmospheric conditions. Runs in an autoclave at 120°C with North Dakota lignite and peat respectively did not provide increased conversion. Higher conversion levels, it is believed, should result not from operation at higher temperatures but rather higher partial pressures of oxygen. This approach while promising, was not pursued further due to constraints in time.

IV CONCLUSION

Oxidative solubilization with nitric acid is a realistic, alternative for the production of liquid fuels from coal. Operation at near ambient temperatures, use of nitric acid as the regenerable oxidant and simple equipment are among its advantages. Conversion of coal to a soluble product is realized with only a 10% loss in heating value when compared with the parent coal. On an equal energy basis both methanol and the coal derivative appear to be cost competitive with normal diesel fuel. We estimate a price of 5 cents per pound for the coal product, below a quoted cost of 6.1 cents per pound for methanol (40 cents per gallon) (32), which is the other component in the projected liquid fuel composite. The United States Environmental Protection Agency has promulgated strict new emission limits for diesel engines scheduled to be put into effect in 1991 through 1994. These regulations can be met fairly easily using methanol, but not with petroleum-derived fuel. Methanol alone will not readily ignite in a diesel engine. Therefore it must be used in conjunction with an ignition promoter. The product from our process is well suited towards this end. Mixtures of solubilized coal and methanol, in varying proportions should perform well in many different types of diesel engines with low particulate emissions. Our work has provided data to prepare larger quantities of coal solubilized in methanol for meaningful performance testing over extended periods of time. Continuing efforts should also address fine tuning of the novel fuel with regards to viscosity and lubricity through the development of additives to accommodate present engine requirements.

Catalytic conversion with oxygen at moderate temperatures is another possible route to coal solubilization. Results obtained from a

preliminary study at atmospheric conditions recommend the use of higher oxygen pressures to increase conversion rates to practical levels.

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Figure 1. Infrared Spectra of Untreated (I) and Acid-Washed (II) N.D. Lignite

Linear Ultrastrogel Column

A : major peak, 25.2 min

B : major peak, 25.2 min
major peak, 27.4 min

C : major peak, 27.4 min
minor peak, 25.2 min

Peaks of standards

A : 15% HNO₃, 45° C

B : 70% HNO₃, 25° C

C : 15% HNO₃, 80° C

dimethylbenzo-
phene diacid

MW 208

mesitylenic acid

MW 150

polystyrene

50 K

17 K

9 K

4 K

2 K

oxidized lignin
1000 MW by VPO

oxidized lignin
1800 MW by VPO

Figure 2. Molecular Size Distribution of Water-Insoluble Products
Derived From the Reaction of N.D. Lignite with Nitric Acid.

Effect of Increasing Reaction Temperature at Various Nitric Acid Concentrations

Effect of Increasing Nitric Acid Concentration at Various Reaction Temperatures

Figure 3. Changes in Elemental Carbon and Nitrogen of Water-Insoluble Product from the Reaction of North Dakota Lignite with Nitric Acid under Mild Conditions

FFA=2.00K
NSCAN=100
FCI=30

SCHULTZ / NOL-HCL (RT) / DRIFT

RES=6 DP

7/17/87 12:49:34

Figure 4. Acid-Washed North Dakota Lignite

PTA-SMK
N2CAND-400
FCT-3C

AL3-6 DF

NOL-HCL + NaOH / DRIFT

6/4/67 18:3:48

Figure 5. Acid-Washed N.D. Lignite Treated with 18 Aqueous NaOH

PTA-SUM
 NSCAN=100
 FCT=30

RES=8 DP

7/17/87 13:9:39

Figure 6. Water-Insoluble Product from Reaction of N.D. Lignite with 35% HNO₃ at 25°C

Figure 7. Water-Insoluble Product from Reaction of N.D. Lignite
with 35% HNO₃ at 60°C

Figure 8. Water-Insoluble Product from Reaction of N.D. Lignite
with 50% HNO₃ at 0°C

Figure 9. Differential : Spectrum 6 minus Spectrum 4

Figure 10. Differential : Spectrum 7 minus Spectrum 4

Figure 11. Differential : Spectrum 8 minus Spectrum 4

Figure 12. Solid State ^{13}C -NMR Spectrum of Acid-Washed N.D. Lignite

Figure 13. Solid State ^{13}C -NMR Spectrum of Water-Insoluble Product from Reaction of N.D. Lignite with 35% HNO_3 at 25°C .

Figure 15. Thermogravimetric Analysis of the Methanol-Soluble Product of Wyodak Coal

Table 1
Ultimate Analysis of Candidate Coals

(Moisture-free Basis)

	N.Y.Peat	N.D.Lignite	Wyodak	Illinois # 6 (Burning Star)
Wt. % -----				
Carbon	55.16	63.88	66.26	68.46
Hydrogen	5.98	4.25	4.51	4.91
Oxygen(diff.)	30.80	19.08	17.30	11.6
Nitrogen	2.0	0.78	0.95	1.48
Sulfur-Total	0.15	1.17	0.78	2.8
" Pyritic		0.56	0.15	0.7
" Sulfatic		0.05	0.04	0.1
" Organic		0.56	0.59	2.0
Ash	12.3	10.84	10.20	10.5

Table 2

Interaction of Coals of Different Rank with Hydrochloric Acid
and Nitric Acid Respectively at Ambient Conditions. Rx.time: 2.5h.

Yield of Water-Insoluble Product, wt.%. -----				
Coal ----- reacted with	Lignite -----	Wyodak -----	Ill.#6 * -----	Peat -----
: 25% HCl	94	96	97	88
15% HNO ₃	92	100	95	89
40% HNO ₃	104	108	100	71
Ash Content of Product, wt.%. -----				
Coal	10.5	10.2	33	12.3
: 25% HCl	2.2	2.7	30	1.6
15% HNO ₃	3.8	4.8	31	3.5
40% HNO ₃	2.7	3.7	26	2.5
Neutral Equivalents -----				
Coal	524	467	1646	634
: 25% HCl	314	330	1126	220
15% HNO ₃	319	378	1494	255
40% HNO ₃	176	143	408	182
Solubility in Dilute Aqueous NaOH, wt.%. -----				
Coal	20	11	1	14
: 25% HCl	25	15	1	16
15% HNO ₃	32	24	1	55
40% HNO ₃	82	89	57	68
Solubility in Dimethylformamide, wt.%. -----				
Coal	0	0	0	0
: 25% HCl	0	0	3	6
15% HNO ₃	2	7	8	3
40% HNO ₃	23	22	14	10

* River King Mine

Table 3

Interaction of Coals of Different Rank with Hydrochloric Acid
and Nitric Acid Respectively at Ambient Conditions. Rx.time: 2.5 h

Material balances

Coal feed (10g)	H ₂ O-ins.prod. yield,g	H ₂ O-ins.prod,g		Organics,g		Base sol.product,g		Base insol.product,g	
		organ.	ash	base-sol.	base-ins.	organ.	ash	organ.	ash
N.D.Lignite	10.0	8.94	1.05	2.0	7.8				
+ 25% HCl	9.4	9.2	0.21	1.5	7.6				
+ 15% HNO ₃	9.2	8.9	0.35	3.0	6.4	2.9	0.05	6.14	0.26
+ 40% HNO ₃	10.4	10.1	0.28	8.5	1.7	8.4	0.15	1.5	0.18
Wyodak	10	8.96	1.02	1.1	8.7				
+ 25% HCl	9.6	9.3	0.26	1.5	8.2				
+ 15% HNO ₃	10	9.5	0.48	2.4	7.8	2.3	0.12	7.4	0.39
+ 40% HNO ₃	10.8	10.4	0.40	9.6	1.2	9.3	0.30	1.0	0.22
Illinois #6	10	6.7	3.3	0.1	9.4				
+25% HCl	9.7	6.8	2.9	0.1	9.2				
+15% HNO ₃	9.5	6.5	3.0	0.1	9.3			5.8	3.5
+40% HNO ₃	10	7.4	2.6	5.7	4.6	5.2	0.53	2.5	2.1
N.Y.Peat	10	8.8	1.2	1.4	7.5				
+25% HCl	8.8	8.7	0.14	1.4	7.1				
+15% HNO ₃	8.9	8.6	0.31	4.9	3.6	4.9	0.04	3.4	0.22
+40% HNO ₃	7.1	6.9	0.25	4.8	1.4	4.7	0.09	1.2	0.18

Table 4

Interaction of Coals of Different Rank with Hydrochloric Acid and Nitric Acid Respectively at Ambient Conditions. Rx. time: 2.5 h

Elemental Analysis of Water-Insoluble Products, wt. %.

	<u>C</u>	<u>H</u>	<u>N</u>	<u>O</u>	<u>NO₂</u>	<u>C/O</u>	<u>C/H</u>
<u>N.D. Lignite</u>	68.16	5.04	0.68	26.12	-	3.48	1.13
+ HCl, 25%	67.90	4.54	1.01	26.55	-	3.41	1.25
+ HNO ₃ , 15%	68.77	4.84	1.11	25.28	-	3.63	1.18
+ HNO ₃ , 40% *	59.36	3.97	4.37	24.72	10.9	3.20	1.25
 <u>Monenco Peat</u>	 56.62	 5.51	 1.75	 36.32	 -	 2.08	 0.89
+ HCl, 25%	55.82	5.19	2.09	36.90	-	2.02	0.90
+ HNO ₃ , 15%	57.28	5.34	2.06	35.32	-	2.16	0.89
+ HNO ₃ , 40% *	52.38	4.78	4.38	33.16	7.6	2.11	0.91
 <u>Wyodak coal</u>	 70.31	 5.38	 0.90	 23.41	 -	 4.01	 1.09
+ HCl, 25%	67.23	5.10	0.89	26.78	-	3.35	1.10
+ HNO ₃ , 15%	69.09	5.30	0.84	24.77	-	3.72	1.09
+ HNO ₃ , 40% *	59.52	4.37	4.52	23.34	12.0	3.40	1.14

* Base-soluble

Table 5

Characteristics of Water-Insoluble Products from Reactions of
North Dakota Lignite with Nitric Acid at Different Severity.

Effect of nitric acid concentration at 25 C.

HNO ₃ %	Yield Wt. %	N.E.	Elemental Analysis, wt. % *				Atom. ratio		soluble, %, in			
			C	H	N	O	C/O	C/H	EtOH	MeOH	DMF	Base
15	93	335	67.4	4.8	1.2	26.2	3.43	1.17	<3		10	<3
25	103	183	59.0	4.0	3.9	26.6	2.96	1.23	20		33	>70
35	101	166							20			>70
45	99	155	57.2	3.4	5.0	25.2	3.02	1.40	38		74	>70
70	89	138	53.8	3.5	5.0	28.6	2.50	1.30	58	43	82	>70

Effect of temperature at 15% HNO₃ concentration

Temp. C												
25	93	335	67.4	4.8	1.2	26.2	3.5	1.2	<3		10	<3
45	101	176	60.3	3.7	4.3	25.4	3.1		28		62	>70
55	94	165	59.0	3.7	4.3	25.5	3.1	1.3	50	25	61	>70
80	97	153	59.9	3.1	4.3	25.2	3.2	1.6	60	32	76	>70

Effect of temperature at 25% HNO₃ concentration.

Temp. C												
25	103	183	59.0	4.0	3.9	26.6	3.0	1.2	20	-	33	>70
60	82	154	57.0	3.5	4.5	27.1	2.8	1.4	59	32	67	>70

* Ash-free basis

Table 6

Effect of Various Combinations of Nitric Acid Concentration and Temperature on Product Solubility with Coals of Different Rank.

		<u>Lignite</u>	<u>Wyodak</u>	<u>Peat</u>
	ash :	3.2	4.3	3.9
	N.E.:	325	342	236
<hr/>				
Products :				
15% HNO3 45C	Wt.% water-sol.	4	3	22
	: Wt.% water-ins.	104	105	73
	a) Neutr.Eq.	153	161	141
	b) DMF-sol.	59	53	48
	c) MeOH-sol.	15	-	-
15% HNO3 60C	Wt.% water-sol.	8	8	48
	: Wt.% water-ins.	102	104	47
	a) Neutr.Eq.	153	144	161
	b) DMF-sol.	77	89	67
	c) MeOH-sol.	25	-	-
35% HNO3 25 C	Wt.% water-sol.	2	2	15
	: Wt.% water-ins.	106	109	83
	a) Neutr.Eq.	145	164	125
	b) DMF-sol.	31	25	55
35% HNO3 45 C	Wt.% water-sol.	5	8	45
	: Wt.% water-ins.	103	107	52
	a) Neutr.Eq.	137	137	142
	b) DMF-sol.	72	89	72
	c) MeOH-sol.	30	-	-
35% HNO3 60 C	Wt.% water-sol.	24	20	65
	: Wt.% water-ins.	89	98	29
	a) Neutr.Eq.	143	137	159
	b) DMF-sol.	79	90	72
	c) MeOH-sol.	32	-	-
50% HNO3 0 C	: Wt.% water-sol.	-	-	-
	Wt.% water-ins.	110	-	-
	a) Neutr.Eq.	183	-	-
	c) MeOH-sol.	8	-	-

Percentages for water-soluble, and water-insoluble fractions are based on the feed coal. Fractions b and c relate to water-insolubles.

All products are base soluble to at least 80 wt.%

Table 7

Carbon Distribution by Solid C-13 NMR Analysis

(% of total carbon)

	NMR Region ppm	ND-L HCl	ND-L: 35-25	ND-L: 35-60
Aliphatic Carbonyl	240-190	1.2	6.9	5.9
Aromatic Carbonyl	190-170	6.8	13.5	17.6
Phenolic Ar.Ether	170-149	10.4	11.5	6.0
Arom. Alkyl Subst. Conj. Double Bonds	149-138	15.2	11.5	7.1
Aromatic (=C-)	138-95	46.6	36.2	45.2
Methoxy	95-60	0.9	2.9	4.0
Alkyl Ether	60-50	1.6	0.7	0.2
Aliphatic				
-CH-, -C-	50-35	4.5	3.6	1.6
-CH2-	35-24	6.2	6.3	5.4
Alpha C	24-17	3.3	3.4	3.2
-CH3	17-0	3.3	3.5	3.7
Total		100.0 9.989	100.0 9.983	100.0 9.978
Summary				
Carbonyl/ Carboxyl	240-170	8.0	20.4	23.5
Aromatic	170-95	72.2	59.2	58.3
Methoxy	95-50	2.4	3.6	4.3
Aliphatic	50-0	17.3	16.8	14.0

Table 8

C-13 NMR Shift Ranges (19)

220-188 ppm	C=O in carbonyls, ketones, amides, and esters
188-164 ppm	C=O in COOH and COOR groups
164-148 ppm	O-substituted aromatic carbons in phenols
148-137 ppm	Alkyl substituted aromatic carbons
137-130 ppm	Bridgehead aromatic carbons
130-104 ppm	Unsubstituted aromatic carbons
104-53 ppm	O-substituted aliphatic carbons in ethers, alcohols, and methoxy groups
53-37 ppm	Methylene bridge and bridgehead carbons of naphthalenes
37-23 ppm	Methylene group carbons in saturated chains
23-0 ppm	Methyl group carbons

Table 9

Reaction of North Dakota Lignite with 5% Nitric Acid at Elevated Temperatures

Temperature, °C	80		100		110		120		130		150		175	
Products	% sel.	NE.	% sel.	NE.	% sel.	NE.	% sel.	NE.	% sel.	NE.	% sel.	NE.	% sel.	NE.
Insoluble	82.2	-	66.0	171	36.0	183	32.8	188	27.9	181	20.6	197	14.2	-
Methanol-sol.	13.1		20.2		22.0		15.9		10.5		5.3		0.8	
Water-sol.	14.0	-	14.0	141	30.0	122	45.4	128	41.4	-	46.6	122	24.0	-
Total :	109.3		100.2		88.0		92.2		78.5		71.2		39.0	
Ash content, % *														
Insol.fr.	2.4		-		-		2.9		2.3		2.4		2.0	
H ₂ O-sol.fr.	7.1		-		-		7.9		7.0		7.9		7.6	
Acetone-sol.fr.	0.0		-		-		0.0		0.0		0.0		0.0	
HNO ₃ cons.	12.0		19.0		27.0		34.0		37.0		60.0		49.0	

Ratio of HNO₃/lignite = 5:1 ; Rx.time : 1 h

* based on feed coal

Table 10

Reaction of North Dakota Lignite with 10 % Nitric Acid
at Elevated Temperatures

	120 °C		150 °C	
Products	% sel.	NE.	% sel.	NE.
-----	-----	---	-----	---
Insoluble	27.9		17.8	
Methanol-sol.	14.8		4.6	
Water-sol.	41.3	131	48.0	111
Total :	83.3		69.0	
Ash content, % *				

Insoluble	2.2		2.1	
Water-sol.	7.7		8.0	
Methanol-sol.	0.0		0.0	

* based on feed coal

Ratio of HNO₃/lignite = 5:1

Table 11

Elemental Analysis of Products from Interaction of
North Dakota Lignite with Nitric Acid at Elevated Temperature.

N.D.Lignite % C 62.75, % H 4.21, % N 0.84, C / N : 87

<u>Conditions</u>		<u>Methanol sol. fraction</u>				<u>Water sol. fraction</u>				<u>Water ins.fraction</u>			
C	% HNO ₃ .	% C	% H	% N	C/N	% C	% H	% N	C/N	% C	% H	% N	C/N
120	5	56.95	4.38	4.60	14	32.37	3.40	4.00	9	-	-	-	-
120	10	56.65	4.28	4.83	14	30.94	3.58	4.00	9	-	-	-	-
130	5	57.76	5.03	4.33	16	34.57	3.48	3.93	10	-	-	-	-
150	5	59.48	6.14	3.94	18	35.30	2.75	3.45	12	56.76	1.94	2.74	24
150	10	57.96	4.00	4.37	15	31.48	2.87	4.52	8	56.08	1.86	2.57	25
175	5	-	-	-	-	37.16	1.97	3.47	12	53.61	1.76	2.30	27

Table 12

Oxidation of North Dakota Lignite with Nitric Acid
in Sequential Modes at Varying Severity

Sequence "A"

Sequence "B"

Sequence "C"

Reaction Conditions

-
- (1)--35% HNO₃, 45 C, 2.5 h
 (2)--35% HNO₃, 60 C, 2.5 h
 (3)--10% HNO₃, 60 C, 2.5 h
 (4)--70% HNO₃, 25 C, 2.5 h

Table 13

Yields in Wt.% of Methanol-Soluble, Water-insoluble and Methanol-Insoluble Products from Sequential Oxidation of North Dakota Lignite, Sequence "A"

Table 14
Sequential Oxidation of North Dakota Lignite under Three Different Sets of Conditions

N.D Lignite (acid-washed)					
% C : 66.90, % H : 4.41, % N : 0.79					
35% HNO ₃			45 C		
MeOH-sol			MeOH-ins		
% C : 53.55			% C : 57.59		
% H : 3.89			% H : 3.40		
% N : 5.43			% N : 3.85		
calc. % O : 37.13			calc. % O : 35.16		
C/N : 11.5			C/N : 17.45		
70% HNO ₃ 25 C	35% HNO ₃ 45 C	35% HNO ₃ 60 C	70% HNO ₃ 25 C	35% HNO ₃ 45 C	35% HNO ₃ 60 C
Methanol-Soluble Products			Methanol-Soluble Products		
% C : 52.30	% C : 54.44	% C : 54.89	% C : 52.51	% C : 53.46	% C : 53.53
% H : 3.65	% H : 3.92	% H : 3.98	% H : 3.78	% H : 3.77	% H : 3.87
% N : 5.50	% N : 4.92	% N : 5.20	% N : 5.40	% N : 4.97	% N : 4.93
C/N : 11.34	C/N : 12.90	C/N : 12.3	C/N : 11.34	C/N : 12.54	C/N : 12.87
+ Methanol-Insoluble Products +			+ Methanol-Insoluble Products +		
% C : 57.56			% C : 57.53		
% H : 3.24			% H : 3.29		
% N : 3.78			% N : 4.05		
C/N : 17.76			C/N : 16.30		
			C/N : 18.61		

Table 15

Sequential Oxidation of Wyodak Coal with Nitric Acid at 60 - 65°C.

Reaction time: 1 h.

Stage	HNO ₃ /coal	HNO ₃ cons. %		Products		
				MeOH insol.	MeOH sol.	H ₂ O-sol.
1	0.87:1	90	-----	↓	Dry Coal (9.5% ash)	↓
Wt. % converted to Product						
2	0.54:1	80	-----	↓ 81.3*	↓ 23.7	↓ 13.1
3	0.51:1	50	-----	↓ 51.8*	↓ 25.7	↓ 4.0
4	1.1 :1	50	-----	↓ 39.5*	↓ 10.6	↓ 0.9
				↓ 27.5	↓ 9.3	↓ 1.3
Total Yield :				27.5	69.3	19.3
					74.1 **	

* Recycled to next stage

** ash-free

Table 16

Sequential Oxidation of Wyodak Coal with Nitric Acid at 60 - 65°C.

Reaction time: 1 h.

Stage	HNO ₃ add.g.	HNO ₃ cons.g.	g HNO ₃ cons./ g MeOH sol.		Products		
					MeOH insol.	MeOH sol.	H ₂ O-sol.
1	39	34.2	3.1	-----	↓	↓	↓
						Feed: 45 g dry Coal (9.5% ash)	
						Yield of Product in Grams	
2	19.6	15.4	1.4	-----	↓ 36.6*	↓ 10.7	↓ 5.9
3	11.8	6.1	1.4	-----	↓ 23.3*	↓ 11.3	↓ 1.8
4	19.6	9.7	2.3	-----	↓ 17.8*	↓ 4.8	↓ 0.4
					↓ 12.4	↓ 4.2	↓ 0.6
Total:	90.0	65.4			↓ 12.4	↓ 31.0	↓ 8.7

* MeOH ins. recycled to next stage

Table 17

Progress of Lignite Solubilization with Time and Increasing Amount of Nitric acid at 60 C

Reagents: Dry North Dakota lignite, 70% nitric Acid in amounts specified on a 100% basis
Ratio of nitric acid to coal : 0.39, 0.78, and 1.16 respectively.

HNO3 added, g.	33	66	99	99
HNO3 add. time, h.	0.5	1.0	1.5	1.5
Hold time, h.	0	0	0	2.0
HNO3 consumption, %	93	86	74	74
Final acid conc. %	3.8	8	20	20
<u>Wt.% yields*</u>				
Total Prod. :	113	116	116	120
		NE		NE
		---		---
<u>1) Water-ins.solids</u>	100	-	101	-
		NE		NE
		---		---
A) MeOH-sol.(Product)	6.6 (102)	14.6 (125)	22.9 (120)	23 (121)
B) MeOH-ins.(Intermed)	93.4 (309)	86.4 (196)	76.1 (190)	78 (190)
<u>2) Water-sol.Solids</u>	13	15	17	19
A) Ash	2.6	4.8	5.8	8.8
B) Combustible Matter	10.4	9.2	11.2	10.2

* based on lignite

Table 18

Progress of Lignite Solubilization with Time and Increasing Amount of Nitric Acid at 75 C

Reagents: North Dakota lignite, dry.

70% nitric acid in amounts specified on a 100% basis.

Ratio of nitric acid to coal : 0.39, 0.78, and 1.16 respectively.

HNO ₃ added, g.	33	66	99
HNO ₃ add. time, h.	0.5	1.0	1.5
Hold time, h.	0	0	0
HNO ₃ consumption, %	93	91	77
Final acid conc. %	3.8	6.5	19
<u>Wt.% yields*</u>			
Total Prod. :	108.5	111.6	116
	NE	NE	NE
	---	---	---
<u>1) Water-ins.solids</u>	99 -	98 -	97 -
A) MeOH-sol.(Product)	6 (114)	15.8 (122)	23 (120)
B) MeOH-ins.(Intermed)	93 (239)	82.2 (182)	78 (174)
<u>2) Water-sol.solids</u>	9.5	13.6	19

Table 19

Lignite Solubilization with Nitric Acid as Function of Reaction Time and Temperature

Ratio of nitric acid to coal : 1.16

Reagents: Dry North Dakota Lignite, 70% nitric acid in amounts specified on a 100% basis.

Temperature, C	60	60, 75	75	60
Reaction time, h.*	1.5	3.5	1.5	3.5
HNO ₃ added, g.	99	99	99	99
HNO ₃ add. time, h.	1.5	1.5 (60 C)	1.5	1.5
Hold time, h.	0	2.0 (75 C)	0	2
HNO ₃ consumption, %	74	84	77	74
Final acid conc. %	20	11	20	20
<u>Wt.% yields**</u>				
Total Prod. :	116	118	116	120
	NE	NE	NE	NE
	—	—	—	—
<u>1) Water-ins.solids</u>	99	102	97	101
	-	-	-	-
A) MeOH-sol.(Product)	22.9 (120)	30 (120)	22 (120)	23 (121)
B) MeOH-ins.(Intermed.)	76.1 (190)	72 (180)	72 (174)	78 (190)
<u>2) Water-sol. Solids</u>	17	16	19	19
A) Ash	5.8	6.8	-	8.8
B) Combustible Matter	11.2	9.2	-	10.2

* Addition time plus holding time

** based on lignite

Table 20

Lignite Solubilization with Nitric Acid in Different Reaction Modes.

Reagents: Dry North Dakota Lignite, 70% Nitric Acid in Amounts Specified on a 100% Basis.

	# 44	# 33	# 35	# 43	# 45	# 37
Temperature, C	60	60	60	60	60	60/75
Reaction time, h.*	0.25	1.5	3.5	3.5	0.5	3.5
HNO ₃ added, g.	99	99	99	99	132	99
HNO ₃ add. time, h.	0.25	1.5	1.5	1.5	0.5	1.5 (60C)
Hold time, h.	0	0	2.0	2	0.1	2 (75C)
HNO ₃ consumption, g.	67.0	73.1	72.1	85.8	77.1	83.2
HNO ₃ consumption, %	68	74	74	87	58	84
Wt. % yields**						
Total Prod. :	113	116	120	111	110	118
	NE	NE	NE	NE	NE	NE
	—	—	—	—	—	—
1) Water-ins. solids	98	99	101	92	94	102
	-	-	-	-	-	-
A) MeOH-sol. (Product)	24 (116)	22.9 (120)	23 (121)	25 (114)	23 (121)	30 (120)
B) MeOH-ins. (Interm.)	74 (176)	76.1 (190)	78 (190)	67 (185)	71 (202)	72 (180)
2) Water-sol. Solids	15	17	19	19	16	16
A) Ash	-	5.8	8.8	6.8	-	6.8
B) Combustible Matter	-	11.2	10.2	9.2	-	9.2

* Addition time plus holding time

** Based on lignite

Table 21

Lignite Solubilization with Nitric Acid in Different Acid Addition / Temperature Modes.

Reagents: Dry North Dakota Lignite, 70% Nitric Acid in Amounts Specified on a 100% Basis.
Ratio of Nitric Acid to Coal : 1.16 to 1.9

	# 47	# 49	# 50	# 52	# 51
HNO ₃ addition :	132g, 1.0 h, 60 C. 2.0 h, 75 C.	99g, 0.3 h, 60 C 33g, 1.0 h, 75 C	99g, 0.3 h, 60 C 33g, 2.0 h, 75 C	99g, 0.3 h, 60 C 66g, 2.0 h, 75 C	99g, 0.3 h, 60 C 33g, 2.0 h, 75 C 1.0 h, 85 C
Temperature, C	60/75	60/75	60/75	60/75	60/75/85
Reaction time, h	3	1.3	2.3	2.3	3.3
HNO ₃ added, g.	132	132	132	165	132
HNO ₃ consumption, g.	104.0	107.6	107	132	124
HNO ₃ consumption, %	78	82	81	80	94
Wt.% yields*					
Total Prod. :	106	110	109	105	107
	NE —	NE —	NE —	NE —	NE —
1) Water-ins. solids	85 -	90 -	86 -	81 -	78
A) MeOH-sol. (Product)	26 (116)	37 (119)	35 (117)	37 (114)	33 (118)
B) MeOH-ins. (Intern.)	59 (207)	53 (208)	51 (180)	44 (169)	45 (172)
2) Water-sol. Solids	21	20	23	24	29

* Based on lignite

Table 22

Lignite Solubilization with Nitric Acid in Different Acid Addition Modes.

Reagents: Dry N.D. lignite (10.8% ash), 70% nitric acid specified as 100%

	# 49		# 56		# 52
HNO ₃ -Time-Temp.	99g, 0.3 h, 60°C		99g, 0.3 h, 60°C		99g, 0.3 h, 60°C
Parameter	33g, 1.0 h, 75°C		66g, 1.0 h, 75°C		66g, 2.0 h, 75°C
Ratio HNO ₃ /Lignite	1.55		1.94		1.94
HNO ₃ added, g.	132		165		165
HNO ₃ consumption, g.	108		121		132
HNO ₃ consumption, %	82		74		80
Wt.% yields					

Total Prod. :	120		134		114
		NE		NE	
		--		--	
1) Water-ins.solids	100	-	114	-	90

A) MeOH-sol.(Product)*	41	(119)	41	(112)	41
B) MeOH-ins.(Interm.)*	59	(208)	73	(181)	49
					(205)
2) Water-sol. Solids **	20		20		24

* Based on ash-free lignite

** Contain metal ash

Table 23

Lignite Solubilization with Nitric Acid in different Acid Addition Modes.

Reagents: Dry N.D. lignite (10.8% ash), 70% nitric acid specified as 100%

	# 50	# 51	# 58	# 53
HNO ₃ -Time-Temp. Parameter	99g, 0.3 h, 60 C 33g, 2.0 h, 75 C	99g, 0.3 h, 60 C 66g, 2.0 h, 75 C	99g, 0.3 h, 60 C 66g, 1.0 h, 60 C	99g, 0.3 h, 60 C 66g, 2.0 h, 60 C 1.0 h, 85 C
Ratio HNO ₃ /Lignite	1.55	1.55	1.94	1.94
HNO ₃ added, g.	132	132	165	165
HNO ₃ consumption, g.	107	124	106.4	122
HNO ₃ consumption, %	81	94	64	74
Wt. % yields				
Total Prod. :	119	116	124	121
	NE —	NE —	NE —	NE —
1) Water-ins. solids	96 —	87 —	104	103
A) MeOH-sol. (Product)*	39 (117)	37 (118)	36 (115)	39 (114)
B) MeOH-ins. (Interm.)*	57 (180)	50 (172)	68 (183)	64 (180)
2) Water-sol. Solids **	23	29	20	18

* Based on ash-free lignite

** Contain metal ash

Table 24

Single-Pass Solubilization of Wyodak Coal with Nitric Acid in Different Acid Addition Modes.

Reagents: dry coal (10.5% ash), 70% nitric acid in amounts specified on a 100% basis.

	# 59	# 60	# 61	# 64
HNO ₃ -Time-Temp.	99g, 0.3 h, 60°C.	99g, 0.3 h, 60°C	99g, 0.3 h, 60°C	99g, 0.3 h, 60°C
Parameter :	33g, 1.0 h, 75°C	33g, 1.0 h, 60°C	66g, 1.0 h, 75°C	66g, 2.0 h, 75°C
Ratio HNO ₃ /Coal	1.55	1.55	1.94	1.94
HNO ₃ added, g	132	132	165	165
HNO ₃ consumption, g	111.2	87	114	123
HNO ₃ consumption, %	84	66	70	75
Yield, wt. %				
Total Prod. :	134.5	125.6	121	121
	NE	NE	NE	NE
	---	---	---	---
1) Water-ins. solids	118.5 -	111.6 -	100 -	100
A) MeOH-sol. Prod. *	50 (123)	37.6 (121)	50 (124)	50 (122)
B) MeOH-ins. Interm. *	68.5 (179)	74 (172)	50 (172)	50 (172)
2) Water-sol. Solids **	16 (133)	14	21 (119)	21 (119)

* Based on ash-free coal

** Contain metal ash.

Table 25

Single-Pass Solubilization of Wyodak Coal with Nitric Acid.

Selectivity to products at a 50% conversion optimum.

Charge	:	100 g of Wyodak coal (ash-free basis)
<u>Products</u>		
1. Water-insol. fraction.	:	"A" 50.0 g MeOH-soluble product.
	:	"B" 68.5 g of product precursor.
2. Water-sol. fraction	:	"X" 11.2 g MeOH-soluble product.
3. Tot.organics.	:	129.7 g
Feed converted	:	31.5 g (coal minus precursor)
Efficiency to "A"	:	159 Wt.%
Efficiency to "A"+"B"	:	194 Wt.%

Single-Pass Solubilization of N.D. Lignite with Nitric Acid.

Selectivity to products at a 41% conversion optimum.

Charge	:	100 g of Lignite (ash-free basis)
<u>Products</u>		
1. Water-insol. fraction.	:	"A" 41.0 g MeOH-soluble product.
	:	"B" 59.0 g of product precursor.
2. Water-sol. fraction	:	"X" 12.8 g MeOH-soluble product.
3. Tot.organics.	:	112.8 g
Feed converted	:	41.0 g (coal minus precursor)
Efficiency to "A"	:	100 Wt.%
Efficiency to "A"+"B"	:	131 Wt.%

* Tentative values for recycle operation

Table 26

Content and Distribution of Ash in Products from N.D. Lignite and Wyodak Coal.

	Ash Content, Wt.%										
	N.D. Lignite : 10.7 % Ash								Wyodak : 9.5 % Ash		
Run :	# 37		# 39		# 42		# 56		# 59		# 63
<u>Water-insoluble fraction</u>											
a) based on wt.of prod.	3.3		3.7		3.7		4.4		4.3		6.3
b) based on wt.of coal	3.5		3.5		3.3		4.5		5.3		4.5
<u>MeOH-sol. prod.</u>											
a) based on wt.of prod.	0.7		0.7		0.6		1.0		0.4		0.3
b) based on wt.of coal.	0.2		0.15		0.2		0.4		0.2		0.15
<u>Water-soluble fraction</u>											
a) based on wt.of prod.	36.0		43.0		36.0		37.0		30.0		29.0
b) based on wt.of coal	6.8		6.6		6.7		7.5		4.7		4.9

Table 27

North Dakota Lignite and Products Derived through Solubilization with Nitric Acid

Elemental Analysis (Wt. %)

	N.D. Lignite	MeOH-soluble Product	MeOH-insoluble Product	H2O-soluble Product
<hr/>				
C	: 63.49	: 53.56	: 57.65	: 22.16
H	: 3.95	: 3.99	: 3.15	: 1.63
N	: 0.95	: 5.21	: 3.97	: 3.16
O (calc.)	: 19.74	: 30.55	: 32.5	: 36.95
S	: 1.17	: 0.05	: 0.08	: 0.1
ASH	: 10.70	: 0.6	: 3.1	: 36.0
<hr/>				
Neut.Equiv.	: 516	: ~ 120	: ~ 180	:
Average M.Wt.	: —	: ~ 1500	: ~ —	: 950
BTU's/lb	: 10144	: 9100	: —	: 4500

Table 28

Elemental Analysis of Wyodak Coal and Derived Products.

(Wt. %)

	Wyodak Coal	MeOH-soluble Product	MeOH-insoluble Intermediate	H2O-soluble Product
<hr/>				
C	: 63.33	: 53.98	: 53.66	: 22.94
H	: 4.43	: 4.01	: 3.54	: 1.94
N	: 0.81	: 5.15	: 4.28	: 2.36
O (calc.)	: 20.47	: 36.32	: 31.5	: 37.1
S	: 0.91	: 0.08	: 0.4	: 2.73
ASH	: 10.04	: 0.46	: 6.62	: 32.93
Ratio C/H	: 1.19	: 1.12	: 1.26	: 0.99
Ratio C/N	: 91.2	: 12.2	: 14.62	: 11.3
Neut.Equiv.	: 396	: 120	: 175	: 133

Table 29

Heating Values for Wyodak Coal and Deashed Products

		BTU/lb
Wyodak Coal, 10% ash	:	10672

MeOH-sol.product, deashed		

A) from filtration mode	:	8825
B) from evaporation mode	:	7640
MeOH-ins.intermediate,	:	10570

Methanol-based "Solution Fuels"

Methanol	:	9600	BTU/lb

30% "A" in methanol	:	9368	"
50% "A" in methanol	:	9213	"
" "	:	78310	BTU/gal
" " spec.grav.	:	1.04	g/cm3

Table 30

Solubilization of Wyodak Coal in the Evaporation Mode

Reagents: dry Wyodak coal, 70% nitric acid

	# 66	# 68	# 73	# 67	# 71
Feed :	Coal	Coal	Coal	Coal+Interm.	Intermed.# 68
Recycle :	-	plus 50% coal at end of run	plus 25% coal at end of run	plus interm.#66	plus 50% coal at end of run
HNO ₃ -Time-Temp. Parameter :	99g, 0.3 h, 60°C 56g, 1.0 h, 75°C	99g, 0.3 h, 60°C 56g, 1.0 h, 75°C	99g, 0.3 h, 60°C 56g, 1.0 h, 75°C	99g, 0.3 h, 60°C 56g, 2.0 h, 75°C	99g, 0.3 h, 60°C 56g, 1.0 h, 75°C
Ratio HNO ₃ /coal :	1.55	1.55	1.55	1.55	1.55
HNO ₃ added, g :	155	155	155	155	155
HNO ₃ consumption, g	148	154	153	132	147
HNO ₃ consumption, %	95	99	99	85	95
Wt.% yields*					
Total prod. :	128	144	144	114	127
	NE —	NE —	NE —	NE —	NE —
A) MeOH-sol.(product) **	71 @ (118)	70 # (127)	60 (119)	70 (136)	78 (103)
B) MeOH-ins.(interm.)	57 (184)	74 (172)	84 (180)	44 (186)	49 (169)

* Ash-free basis

@ ash content : 4.6 %

** Includes water-solubles

" " : 4.8 %

Table 31

Solubilization of Bituminous Coals with Nitric Acid.

Reagents: dry coal, 70% nitric acid in amounts specified on a 100% basis.

Coal :	Illinois #6 "Burning Star"	Illinois #6 "Burning Star"	Pitt Seam
NE :	838	838	1229
HNO3 addition :	99g, 0.3 h, 60°C. 33g, 1.0 h, 75°C	99g, 0.3 h, 60°C 33g, 1.0 h, 85°C	99g,0.3 h,60°C 66g,1.0 h,85°C
HNO3 added, g	132	132	132
HNO3 consumption, g	90	101	104
HNO3 consumption, %	68	77	79
Wt.% yields*			

Total Prod. :	137	121	111
	NE	NE	NE
	--	--	--
1) Water-ins.solids	127	127	125

A) MeOH-sol.(product)	14 (120)	17 (125)	10 (130)
B) MeOH-ins.(interm.)	113 (212)	110 (217)	115 (260)
2) Water-sol. solids	10	12	17

* Based on ash-free coal

Table 32

Nitric Acid Balance

Solubilization of Wyodak Coal with Nitric Acid (# 59)

Reagents : 100 g of Coal, 155g of HNO₃ (100% basis)

Products -----	MeOH-soluble -----	MeOH-insoluble -----	H ₂ O-soluble -----	Total -----
g	: 50.0	: 68.0	: 16.0	: 134.0
N, %	: 5.15	: 4.28	: 2.36	
N, g	: 2.58	: 2.91	: 0.32	
Nitric acid consumed by event, g -----				
A. Nitration -----	: 11.6 -----	: 13.11 -----	: 1.44 -----	26.2 -----
B. Oxidation -----		155 minus 54.2 (26.2+28)		100.8 -----
C. Unreacted HNO ₃ -----				28 --

Table 33

Mass Spectrometric Off-Gas Analysis from Conversion of Wyodak Coal
with Nitric Acid at 75 C

	<u>Air-free basis</u>					
	<u>0.5 hour</u>		<u>1.0 hour</u>		<u>1.5 hours</u>	
	Mole %	Weight %	Mole %	Weight %	Mole %	Weight %
Nitrogen	11.21	6.18	12.43	6.63	16.69	9.20
Nitric Oxide	38.24	31.61	29.40	23.50	25.96	21.46
Nitrous Oxide	7.03	8.53	8.05	9.44	8.48	10.29
Carbon Dioxide	41.21	49.96	43.40	50.87	47.91	58.08

Table 34

Viscosities of Methanol Solutions of Solubilized Wyodak Coal

	<u>Viscosity in centipoise</u>					
Temp., °C	<u>-10</u>	<u>0</u>	<u>20</u>	<u>30</u>	<u>40</u>	<u>50</u>
No.2 Diesel (reference)	8.9	6.5	3.8	2.5	2.3	2.1
Wyodak solution, %						
30	47	21	7	4	3	2
35	-	-	8	6	5	5
40	-	-	19	15	10	9
45	-	-	45	28	21	16
50			210	91	50	35
Peat solution, %						
50%	315	150	16	7	5.4	4.3

Viscosities were determined using the Brookfield Digital Viscometer Model LVTD with UL Adapter.

Table 35

Oxidation of Demineralized North Dakota Lignite
with Oxygen at Atmospheric Pressure

Reaction Conditions : Temp. 80°- 90°C, Oxygen flow : 3.3 ft³ /hr, Rx.time : 2hr

Lignite, NE:390, ash : 2.5% (9.6)@

Coal, g	10	10	10 .	10	10 #	10 !	10 #**
Co(II)acet.g	20	20	-	40	20	20	20
MEK,g	20	20	-	40	20	20	20
Gl.Acetic Acid, g	300	150	150	300	300	300	300
Water, g	-	150	150	-	-	-	-

Reaction Products

Yield, %	107	100	90	104	100	94	100
Base solub. % *	16	9	13	15	13	14	10
MeOH solub.%	2	-	2	-	2	3	2
Acetone solub.%	1	-	0.1	-	1	1	1
Neutral Equivalent	299	283	340	295	326	286	332
Ash content, %	2.7		2.6		2.4	3.2	-

@ Original ash content of acid washed coal

* Solubility in 1% aqueous NaOH

Oxygen replaced by nitrogen

! Untreated lignite used.

** Temp. 120 C, 100 psig.

Table 36

Oxidation of Demineralized New York State Peat
with Oxygen at Atmospheric Pressure

3

Reaction Conditions : Temp. 80 - 90 C, Oxygen flow : 3.3 ft³/h
Rx.time : 2 h

Peat, NE:267, ash:2.2% (11.6%)@

Coal, g	10	10	10	10	10#
Co(II)acet.,g	20	20	-	20	20
MEK,g	20	20	-	20	20
Gl.Acetic Acid, g	300	150	150	300	300
Water, g	-	150	150	-	-

Reaction Products

Yield, %	91	103	93	95	95
Base solub. % *	12	6	5	7	8
MeOH solub.%	-	-	4	5	6
Acetone solub.%	-	-	0.2	1	1
Neutral Equivalen	201	238	260	228	239
Ash content, %	-	4.7	2.2	2.0	-

@ Original ash content of acid washed coal

* Solubility in 1% aqueous NaOH

Temperature 120 C, 100 psig. oxygen replaced by nitrogen.