

LOW-SEVERITY COAL LIQUEFACTION
A CHALLENGE TO COAL STRUCTURE DEPENDENCY

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INTRODUCTION

The purpose of this paper is to summarize recent information from coal liquefaction studies in bench scale as well as in integrated process development units, together with the data from new analytical techniques which have provided substantial amounts of new information on several important aspects of coal structure and coal reactivity. The results of these studies reveal that existing coal models and current empirical tests for coal reactivity no longer reflect adequately the new knowledge of coal structure and coal reactivity.

Earlier approaches to direct coal liquefaction employed high-severity operating conditions of pressure, temperature and coal/solvent slurry contact time, to achieve in one reactor the highest coal conversion and distillate yield possible. High-severity thermal processing did not necessarily lead to reactions that were all desirable, but resulted in undesirable regression reactions, such as polymerization, condensation and an increase in the aromatic nature of the initially-formed coal fragments. Although elevated temperatures may be necessary for the breakdown of the original coal structure, preventive means, such as a kinetically rapid hydrogen transfer from a hydrogen donor solvent to stabilize the overall solvent-coal adduct, have been employed to mitigate the regressive reactions. However, because of lack of sufficient transferable hydrogen to maximize the conversion of the asphaltols and asphaltenes, which contain highly reactive functional groups, polymerization/condensation and dealkylation reactions still occur, as evidenced by high hydrocarbon gas yield.

DISCUSSION

The key role of the functional groups, and in particular of the phenols, in promoting and participating in polymerization/condensation reactions is well established (1). But the seemingly important function of the aliphatic groups attached to the aromatic structure of the coal and of the donor solvent is that of forming free radicals at high thermal severity, competing kinetically and taking away the available hydrogen directed to the condensed aromatic structure, which eventually goes to coke or insoluble organic matter. The fate of the aliphatic groups in coals and those formed by cracking hydrogenated aromatic rings during upgrading of the coal extracts, has not been sufficiently studied, particularly in relation to their key role in coal liquefaction. High thermal severity coal liquefaction processes, which have monopolized bench scale research and scale-up efforts from the early German discoveries to the present time, seem to have a pronounced dependency on coal structure somewhat similar to those of coal gasification and combustion, since all of these are operating above the activation energies of all the major reactions involved and are dominated by an unordered

retrogressive condensation, cracking and transalkylation array of reactions. For these and other reasons the organic structure of coal has appeared to researchers as a highly crosslinked, amorphous and unreactive macro-molecular structure.

A more recent approach uses low-severity coal liquefaction in separated but integrated stages in order to optimize the coal dissolution and coal extract upgrading steps (2). This emerging technology and the development of new analytical techniques have produced results which change substantially our approach to coal liquefaction techniques, have inspired new thoughts in unraveling the complex mechanism of direct coal liquefaction at low-severity and more importantly give us a radically different picture of the structure and reactivity of coals than has been provided by high-severity liquefaction, gasification and combustion processes.

Important new information from this new approach includes:

- o Low-severity processing forms mostly reactive low molecular-weight fragments. If not properly quenched, these reactive fragments, which are formed in the very early stages of liquefaction, can condense to form structures similar to those produced by high-severity liquefaction (3).
- o Thermally produced coal extracts contain high levels of heteroatom compounds and are "refractory" to catalytic hydrogenation. Conversely low-severity produced extracts are low in heteroatoms and more easily hydrogenatable, and consistently yield excellent equilibrium hydrogen donor solvent (4).
- o Perhaps because of the occurrence of low molecular-weight reactive coal fragments, surrounded by a recycle solvent which is low in heteroatoms and rich in hydroaromatics, this approach appears to be successful in processing both high- and low-reactivity coals, and producing similar conversions and similar product qualities from both types of coal, supporting the notion that conversion and product quality is less dependent on coal characteristics and more dependent on process operation than previously believed (4).
- o Proton NMR analysis, modified to provide data on distillate and non-distillate fractions, served to create a working kinetic model for coal extract hydroprocessing, thus enabling us to distinguish catalytic hydrogenation from ring opening and particularly from dealkylation of the highly alkylated condensed hydroaromatic compounds produced by low-severity liquefaction, and to predict solvent donor quality as well as the yield structure of the upgraded products (5).

Other important information has been obtained by various sources working at low-severity process conditions, but this information is mostly related to operability advantages, since processing was the main objective of the projects involved. Nevertheless, the limited information given here appears to disclose a completely different picture of the relationship between the structure and reactivity of coals and low-severity coal liquefaction.

We are discovering more similarities in coal-derived products even though there are large differences in the structure of the coals from which these products are derived. These similarities become more evident as the coal/solvent donor slurry is processed at controlled low-severity in the extraction as well as in the upgrading steps under the conditions where equilibrium is more closely reached and in the presence of an aged catalyst with steady-state activity.

It is extremely difficult to capture in research bench scale units the essence of the results produced in an integrated continuous process because the rapid initial deactivation of fresh catalyst provides continuously changing conditions leading to rather confusing results. Also, most of the key data and benefits, i.e., increased coal conversion, enhanced donor quality, and increased formation of few major condensed hydroaromatic compounds, are obtained only after several cycles of the integrated continuous staged operation. At process equilibrium, benzopyrenes, phenanthrenes and chrysenes and their highly alkylated derivatives constitute more than 60 percent of the total product, whether a bituminous or a subbituminous coal is employed as the starting material (6).

R&D COORDINATION

Current research efforts on coal liquefaction are leading to further improvement in the understanding of the mechanism of reactions occurring at even lower temperatures and overall less severe processing conditions, revealing that coal, asphaltols and asphaltenes are much more reactive species than previously thought. It can be stated that there is a turn of events occurring in direct coal liquefaction, which from a steady evolutionary progress, has recently become a revolutionary processing approach. Preliminary results indicate that this approach will provide a much larger "equalizer" effect on processing any type of coal, making it even more process dependent rather than coal type dependent (7).

On the basis of the above new information, evidently there is an urgent need for in-depth discussion between researchers who are dedicated to unravelling coal characteristics, mechanisms and reactivities and those who are devoted to coal processing and the kinetic aspects of the reactions involved in each phase of the low-severity coal liquefaction process.

Due to changing economics, the introduction of new large-scale coal conversion processes has been postponed and, as a consequence, more time is available for research to gain fundamental insights into coal structure and to obtain a better understanding of its impact on coal liquefaction.

Therefore, the recent exciting results obtained in the development of an emerging technology in direct coal liquefaction should be discussed, possibly in small-scale symposia, as a supplement to the large-scale conferences, i.e., ACS, AIChE, Contractors' and Coal Science Conferences and thus provide the opportunity for in-depth discussions and a maximum profit from exchange of knowledge and ideas, and better utilization of research talents and dollars.

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A Critical Temperature Window for Coal Hydrolysis

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Abstract

Pyrolysis of coals in the presence of hydrogen is known to enhance liquid yields, but this enhancement is often accompanied by increases in methane make. In many instances increased methane yields are detrimental because of the amount of hydrogen consumed to make methane. This paper will discuss the discovery of a critical temperature threshold for coal hydrolysis, below which little methane is formed, and above which significant methane is produced. A simple procedure is described to determine the critical temperature, which is different for each coal and pressure regime used.

INTRODUCTION

Coal has an atomic hydrogen to carbon ratio less than unity. To make desirable liquids, with atomic H/C ratios of 1.5 to 2, hydrogen must be added or carbon removed. The latter approach involves pyrolysis of the coal to produce liquids, gases and a carbonaceous residue called coke or char depending on whether the coal became plastic during the pyrolysis. In the past many researchers have tried to increase the yield of liquids by performing the pyrolysis in the presence of hydrogen under pressure⁽¹⁻⁶⁾. In general, these researchers obtained increased liquid and hydrocarbon gas (C₁ to C₃) yields from such hydrolysis methods relative to pyrolysis under inert atmospheres. These increases came at the expense of significant hydrogen uptake, and the hydrogen reported mainly to the hydrocarbon gases.

In our studies of coal hydrolysis, we confirmed the yield increase trends previously observed. While examining the effect of temperature on the hydrolysis reaction we found that a temperature threshold exists, below which increased liquid yields are obtained without production of large quantities of hydrocarbon gases. Details of this finding are described in this paper.

EXPERIMENTAL

Hydrolysis reactions were carried out in a fixed bed apparatus, a schematic diagram of which is shown in Figure 1. The 620 cc reactor was capable of sustaining pressures of up to 13.3 MPa, and was heated by means of a fluidized sand bath, which could be raised and lowered hydraulically. In a typical experiment, about 400g of coal was charged into the hopper above the reactor and pressurized with either nitrogen or hydrogen. The reactor was placed in the fluidized sand bath and heated at a rate of about 4°C/min, with preheated nitrogen or hydrogen flowing through it at a rate of about 0.4 SCFM at a predetermined reaction pressure. At an appropriate temperature, coal from the hopper was charged to the reactor by opening a butterfly valve, while the heating rate was adjusted to about 2°C/min. Volatile products were carried out of the reactor by the flowing gas into a high pressure knock out vessel. After reducing gas pressure to 1 atm it was passed through a cooled low pressure knockout vessel then into a wet test meter. Gas samples were taken every 10 minutes and analyzed on a Carle GC. At the end of the experiment, the sand bath was lowered, the reactor cooled, and liquid and char products were collected. Figure 2 shows typical temperature profiles for both the sand bath and reactor during constant temperature coal pyrolysis under nitrogen. Reactor

temperature drops as coal is added, but rapidly recovers to the temperature of the sand bath.

Determination of the critical temperature threshold was accomplished by following the above procedure using hydrogen gas at a flow rate of 0.4 SCFM. Coals were added to the reactor at a temperature of 360°C and heating was continued to 525°C. In Figure 3 the temperatures of the sand bath and the reactor are plotted for a typical experiment. We define the critical temperature as the point where the exotherm begins.

RESULTS AND DISCUSSION

Pyrolysis under hydrogen is known to produce higher yields of liquid and hydrocarbon gas products relative to pyrolysis under nitrogen. This was verified using a subbituminous coal following the above procedure, at a pressure of 7MPa and a constant temperature of 525°C. In the hydrogen case, an exotherm was noted after 3 minutes. Figure 4 shows the evolution of gases on a cumulative basis from the coal during pyrolysis under nitrogen at 525°C, and Figure 5 shows cumulative gas evolution and hydrogen consumption rate for the reaction under 7 MPa of hydrogen at 525°C. In the nitrogen case, liquid yield was 10 wt% (dry coal basis), while under hydrogen, liquid yield was 14 wt%. Notably different were the methane yields in nitrogen and hydrogen, 2 wt% for the former and almost 15 wt% for the latter. From Figure 5 it can be seen that hydrogen consumption rate parallels methane evolution, which implies that the increased methane yield is due to the some form of hydrogasification of the coal or char.

To better understand this observation, the hydrolysis was carried out under the programmed temperature conditions described above. Figure 3 shows the temperature profile. Clearly an exotherm occurs at about 45 minutes residence time (temperature of about 465°C). Figure 6 shows the gas evolution for this reaction from which it can be seen that significant methane evolution occurs at about the same time as the exotherm. We define the temperature at which the exotherm appears as a critical temperature threshold.

As indicated in Table 1, the critical temperature threshold appears to be dependent upon hydrogen pressure, decreasing with increasing pressure. Once again the yield of oil is relatively constant, but the methane make is directly related to hydrogen pressure.

Table 1

Onset of Exotherm and Methane Yield Related to Hydrogen Pressure

(370-525°C; 0.4 SCFM)

<u>HYDROGEN PRESSURE, MPa</u>	<u>1.4</u>	<u>7.0</u>	<u>9.2</u>
EXOTHERM, °C	488	465	437
<u>YIELDS, WT% COAL</u>			
METHANE	7.0	11.9	23.0
C ₂ + C ₃	2.2	2.4	2.2
OILS	12.8	14.7	14.8
CHAR	55.3	44.6	38.0
HYDROGEN CONSUMPTION (wt% coal)	2.32	3.76	5.14

The effect of the exotherm on product yields and hydrogen consumption was determined by carrying out the hydropyrolysis in such a way that the reaction temperature never exceeded the critical temperature, which for this coal at these reaction conditions was 465°C. Figure 7 displays the thermal history of this experiment. Several minutes before the critical temperature was reached, the sand bath was lowered, thus assuring that the maximum temperature did not exceed the critical temperature. It is apparent from the figure that the exotherm was completely eliminated in this experiment. Figure 8 shows the gas evolution with time, and it can be seen that methane make is low and in the same range as that for pyrolysis under nitrogen. Table 2 shows a direct comparison of the yield patterns from the hydropyrolysis conducted below and above the critical temperature.

Table 2
Higher Temperature Increases Conversion to Gas Not Oil.
(0.4 SCFM; 7MPa H₂)

<u>YIELDS (WT% COAL)</u>	<u>372-465°C</u> <u>35 MIN</u>	<u>371-525°C</u> <u>85 MIN</u>
METHANE	1.4	11.2
C ₂ + C ₃	1.2	2.4
OILS	14.3	14.7
CHAR	64.5	44.6
HYDROGEN CONSUMPTION (wt% coal)	0.6	3.7

It is obvious from these data that higher pyrolysis temperatures do increase overall conversions, but it is striking that oil yields change very little. Most of the conversion increase is manifested in the methane make. The most significant finding from these data is that hydrogen consumption increases six fold at the higher temperature without adding to the liquid yield. The additional hydrogen appears to be consumed in producing methane.

All of the data discussed to this point was taken on a subbituminous coal. To determine whether the effect is important for coals of different rank, the hydropyrolysis was carried out on a bituminous coal. The data for these experiments are summarized in Table 3 and compared to those from the subbituminous coal. In these experiments the bituminous coal was impregnated with a concentrated potassium hydroxide solution to aid in preventing agglomeration. The treated coal contained 8.44 wt% acid soluble potassium. The critical temperature for this coal was determined in separate experiments to be 474°C and the hydropyrolysis was carried out below the temperature. It can be seen from Table 3 that liquid yield from the bituminous coal increased by about twofold under these hydropyrolysis conditions, while the hydrocarbon gas make is only slightly higher than that produced under nitrogen. Much more work on other coals must be done before a firm conclusion can be made regarding generality, but the data gathered thus far support this as a tentative conclusion.

Virtually nothing is known with certainty regarding the mechanism or mechanisms involved in this phenomenon. One obvious mechanism for methane formation is hydrodealkylation of side chains. If dealkylation is a major pathway, it should be possible to observe differences in the infrared spectra of hydropyrolysis chars made above and below the critical temperature. Figure 9a is a Fourier Transform IR

Table 3

Critical Temperature Threshold May be General

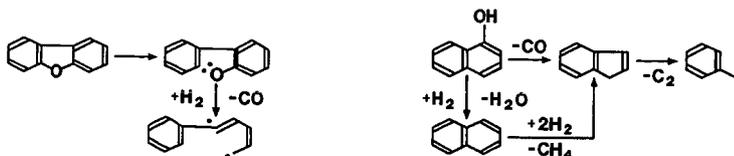
	<u>SUBBITUMINOUS</u>	<u>BITUMINOUS*</u>
CRITICAL TEMP., °C	465	474
LIQUID YIELD (WT% DAF) IN		
H ₂	15.5	18.7
N ₂ (525°C)	11.3	9.7
C ₁ -C ₃ (WT% DAF) IN		
H ₂	2.8	6.4
N ₂ (525°C)	5.6	5.0
CHAR (WT% DAF) IN		
H ₂	61.5	58.4
N ₂ (525°C)	66.4	68.1

* KOH treated

spectrum of the char from the hydropyrolysis reaction which produced 11.2 wt% methane (Table 2), and Figure 9b is the difference spectrum between Figure 9a and that of the spectrum of the char from the hydropyrolysis reaction which made 1.4 wt% methane (Table 2). Figure 9b does not indicate significant differences between the two chars. This appears to be inconsistent with a hydrodealkylation hypothesis.

Elemental analyses of the chars show that oxygen remaining in the chars decrease as more methane is made. These data are displayed in Figure 10, as methane yield plotted against atomic O/C ratio, and may indicate that carbon-oxygen bonds are the sites most readily attacked by hydrogen.

One set of mechanisms which appear to be consistent with the observations discussed above are those proposed by Graber and Hüttinger⁽⁷⁾. They subjected many aromatic, alkylaromatic and heteroatom-containing aromatic model compounds to hydro-pyrolysis at temperatures varying between 600-1000°C. Among their conclusions, they found that oxygen in aromatic rings and hydroxyl groups of phenol and naphthol strongly enhance the methane yield, and that decarbonylation was a key step for both types of oxygen compounds:



Nitrogen containing aromatic systems also showed a propensity to form methane under their conditions. Analyses of the chars described above showed an inverse dependence of methane yield to the atomic N/C ratio.

CONCLUSIONS

A critical temperature threshold exists for coal hydrolysis, above which methane forms rapidly with a concomitant increase in hydrogen consumption. Liquid yields are not increased above the critical temperature. The critical temperature threshold may be a general phenomenon, and depends upon coal, i.e., bituminous or subbituminous coal, hydrogen partial pressure and hydrogen treat rate. The chemistry and mechanisms involved in the effect are not well understood. Preliminary results indicate that dealkylation may not be a major route to methane formation, and that the reactions to produce methane take place at heteroatom sites, particularly oxygen and nitrogen, in the char.

This work suggests that controlling the temperature of the hydrolysis below that of the critical temperature is an important means to improve the utilization of hydrogen, thus improving the efficiency of any hydrolysis process.

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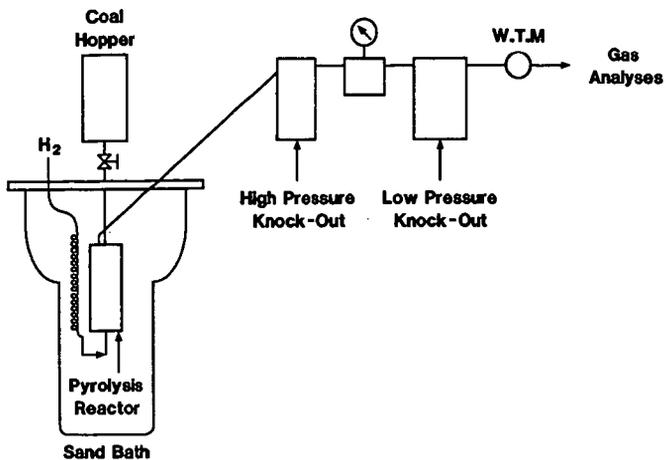


Fig. 1. Fixed Bed Hydrolysis Apparatus

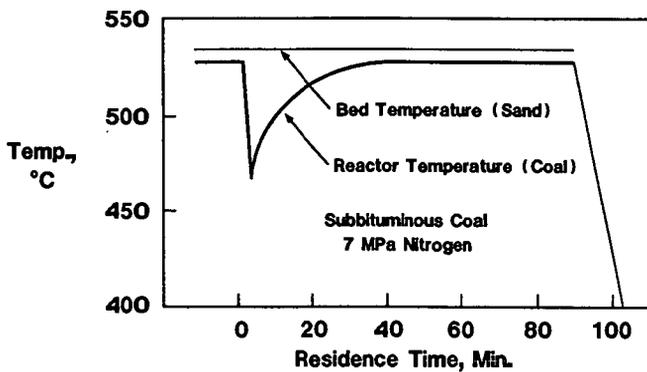


Fig. 2. Typical Thermal History of Coal Under Nitrogen

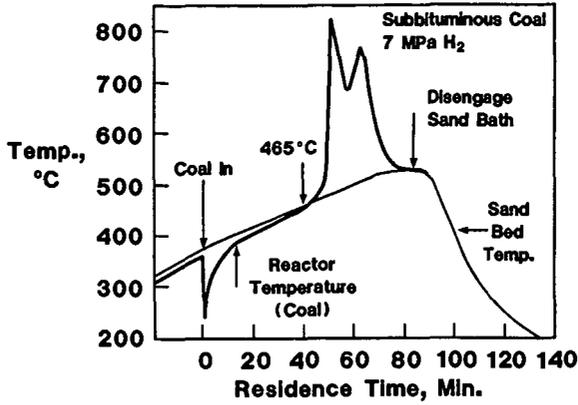


Fig. 3. Programmed Hydropyrolysis Heatup Exhibits Exotherm

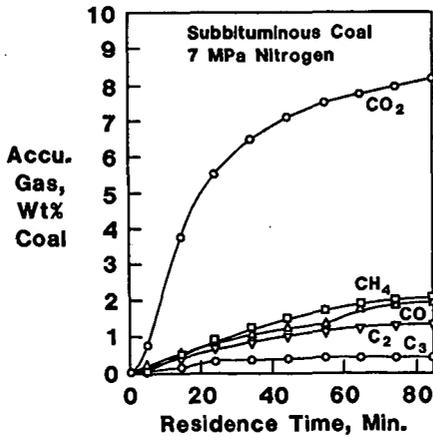


Fig. 4. Low CH₄ Yield From Nitrogen Pyrolysis at 525°C

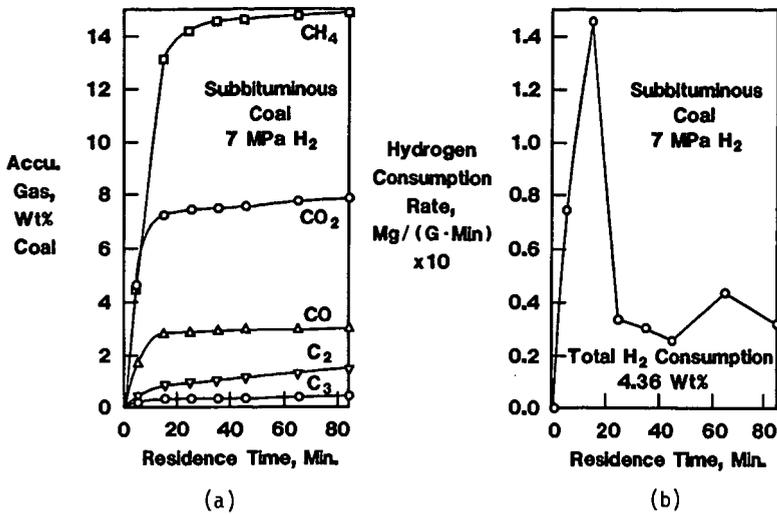


Fig. 5. (a) Gas Make and (b) Hydrogen Consumption Rate for Hydropyrolysis at 525°C

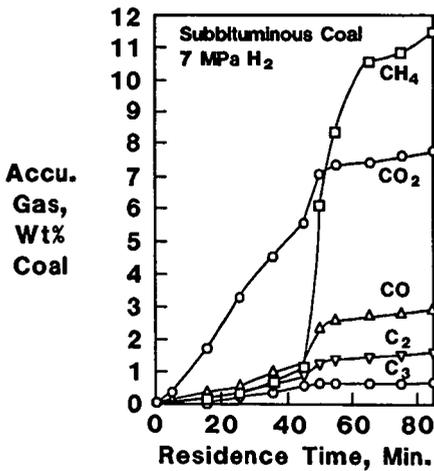


Fig. 6. Increased CH₄ Evolution with Onset of Exotherm

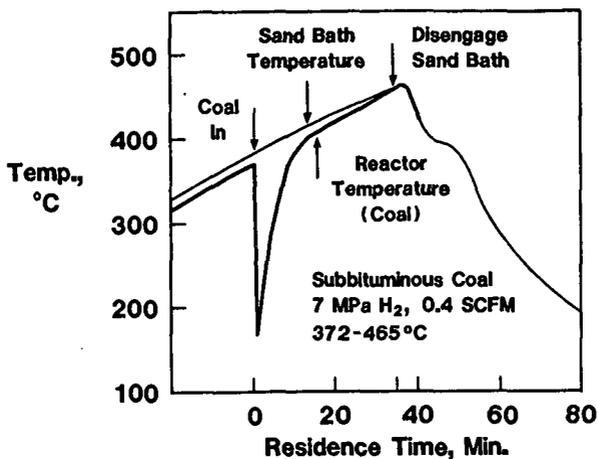


Fig. 7. Controlled Heatup to Below 465°C Eliminates Exotherm

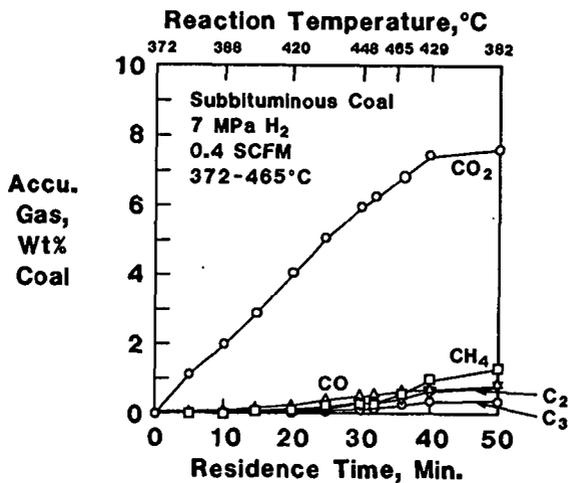


Fig. 8. Rapid Methane Formation is Eliminated

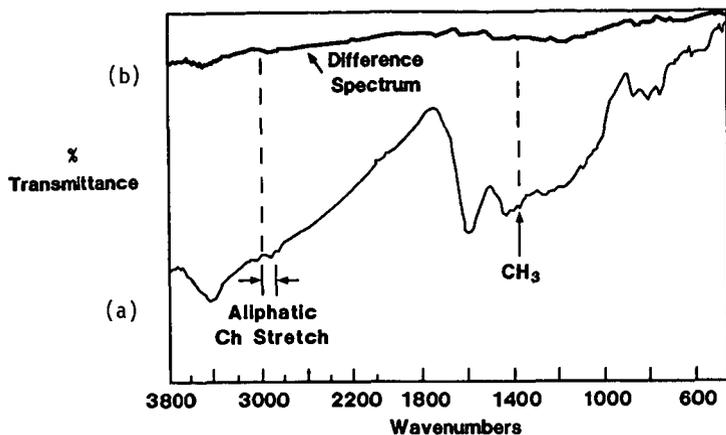


Fig. 9. (a) FTIR Spectrum of Char (11.2 wt.% CH₄); (b) Difference Spectrum of Chars (11.2 wt.% CH₄ and 1.4 wt.% CH₄)

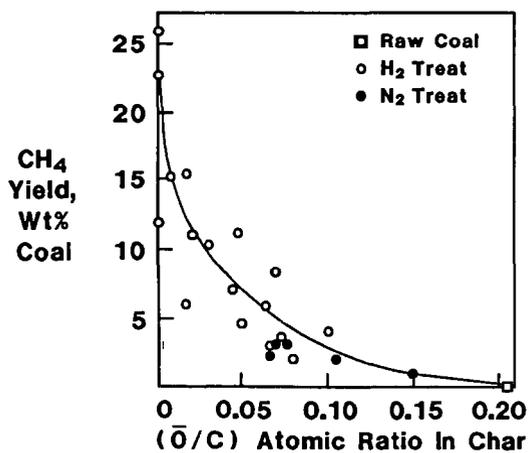


Fig. 10. Methane Yields Inversely Proportional to Oxygen in Char

LOW-TEMPERATURE COAL DEPOLYMERIZATION. 5. CONVERSION OF NEW MEXICO AND UTAH HVB COALS TO HYDROCARBON OILS

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INTRODUCTION

The development of various low-temperature coal solubilization procedures, based on the application of selective chemical-catalytic reactions, has been reviewed in 1981 by Wender et al. (1) Such procedures have recently attracted considerable interest in view of the obvious advantages of coal liquefaction under mild, subsoftening conditions. In the preceding paper of these series, we outlined a new approach to low-temperature coal depolymerization and liquefaction which involves the application of three consecutive reaction steps in which different types of intercluster linkages are subjected to preferential cleavage (2). The procedure, as summarized in Figure 1, consists of the following sequential steps: (1) intercalation of the coal sample with catalytic amounts (3-15%) of FeCl_3 followed by mild hydrotreatment (HT) of the coal- FeCl_3 intercalate; (2) base-catalyzed depolymerization (BCD) of the product from step 1, under super-critical conditions; and (3) hydroprocessing (HPR) of the depolymerized product from the two preceding steps, using a sulfided CoMo catalyst. The high efficiency of the overall procedure was demonstrated by the previously reported conversion of a Wyodak coal sample into a light hydrocarbon oil product, containing 57.2 wt% (or 53.8 wt% calculated on the starting MAF coal) of low-boiling fractions (gasoline, kerosene and light gas oil; b.p. up to 305°C/760 torr). The present paper provides additional examples of the application of the same procedure, using two higher rank coal samples from New Mexico and Utah.

EXPERIMENTAL

Materials. Two HVB coal samples, one from Fruitland, San Juan basin (New Mexico) referred below as F(NM) coal, and another from the vicinity of Helper (Utah) referred below as H(UT) coal, were provided by Amoco Oil Co. The ultimate analysis of the F(NM) coal sample (MAF basis) in wt% was C, 78.69; H, 6.00; N, 1.62; Cl, 0.07; S, 0.96; O (diff.), 12.66; H/C = 0.909; ash content (dry basis), 11.37; BTU/lb (dry basis), 12,691. The ultimate analysis of the H(UT) coal sample in wt% was C, 81.10; H, 5.97; N, 1.09; Cl, 0.03; S, 0.49; O (diff.), 11.32; H/C = 0.877; ash content (dry basis) 9.91%; BTU/lb (dry basis), 13,111.

The coal samples were grinded and sieved through a 200-mesh standard sieve in a nitrogen-purged glove box, and then stored under nitrogen in a refrigerator.

Catalysts. The catalyst used in the mild HT step of the depolymerization procedure (Figure 1) consisted of FeCl_3 , which was intercalated in the powdered coal feed using a newly developed procedure (see below). The catalyst-solvent system, used in the subsequent BCD step consisted of a 10% alcoholic alkali hydroxide solution, preferably a methanolic KOH solution (2). In the final HPR step the catalyst used was sulfided $6\text{Co}8\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ prepared by incipient wetness impregnation of Ketjen $\gamma\text{-Al}_2\text{O}_3$ with an ammoniacal solution of ammonium paramolybdate, followed by impregnation with an aqueous $\text{Co}(\text{NO}_3)_2$ solution. This high Co content catalyst was

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found to be markedly more active for hydrodeoxygenation of depolymerized coal products and other oxygen-rich synguels in comparison with conventional $3\text{Co}8\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts (3).

Apparatus and Experimental Procedure. Mild Hydrotreatment (HT) Step. Each of the powdered coal samples was first pre-extracted with THF in a Soxhlet for 48 hr, yielding small amounts of solubles, including resins (7.6% from the F(NM) coal, and 9.2% from the H(UT) coal). The pre-extracted coal was then intercalated with catalytic amounts (3-15% by wt) of reagent grade FeCl_3 , using the following procedure:

About 20 g of the pre-extracted coal was accurately weighed and placed together with the desired amount of FeCl_3 into a 100 ml glass tube, connected to a previously described impregnation apparatus (4). About 20 ml of acetone was then added to the tube and the coal- FeCl_3 -acetone mixture was stirred in an ultrasonic bath at room temperature for 1 hr. The excess acetone was distilled off under a stream of nitrogen and the resulting FeCl_3 -coal intercalate was transferred to a porcelain dish and dried overnight in a vacuum desiccator oven at $60^\circ\text{C}/0.02$ torr.

3-4 g portions of the dry intercalate were hydrotreated in a specially designed autoclave system described elsewhere (2). Conditions used were: temperature, $250\text{-}270^\circ\text{C}$; hydrogen pressure, 1000-1500 psig; reaction time, 1-2 hr. In all runs the experimental procedure was the same as previously employed in the mild hydrotreatment (HT) of a Wyodak coal sample (2). The hydrotreated product was transferred to a Soxhlet and back-extracted with acetone to remove the FeCl_3 catalyst. Recovery of the latter was essentially quantitative ($>99.5\%$) due to the low hydrotreatment temperature. The extracted product was subsequently extracted also with THF to recover a small amount (usually $<10\%$ by wt) of soluble products from the above HT step.

Base-Catalyzed Depolymerization (BCD) Step. The hydrotreated, FeCl_3 -free coal product from the above HT step, in admixture with the above-mentioned small amount ($<10\%$ by wt) of solvent-free THF-soluble material, was subjected to BCD in a 150 ml autoclave, using a 10% methanolic KOH solution as depolymerizing agent. In all runs the amount of the hydrotreated coal feed was between 3-4 g, and the KOH solution/coal weight ratio was 10:1. The weighed coal sample and KOH solution were charged to the autoclave, and the latter was purged and then pressurized with nitrogen to an initial pressure of 1,000 psig. The autoclave was quickly heated ($15^\circ\text{C}/\text{min}$) to the desired temperature in the range of $250\text{-}290^\circ\text{C}$, at which point stirring at 500 rpm was started and continued for 1 hr. With completion of the run the autoclave was quickly cooled down with water and depressurized. The product was transferred to a beaker and acidified with aqueous 2N HCl solution to $\text{pH} = 2$. The water-insoluble organic material was separated, thoroughly washed with distilled water, and finally dried in a desiccator at $100^\circ\text{C}/0.2$ torr. The dry product was then extracted with THF in a Soxhlet for 24 hr, leaving a solid residue consisting mainly of the original coal ash. In some experiments the solvent-free BCD product was fractionated into cyclohexane-solubles (oils), benzene-solubles, cyclohexane-insolubles (asphaltenes), and residual THF-solubles, benzene-insolubles (asphaltols), using a sequential procedure in which the total THF soluble, solvent-free BCD product was first extracted with benzene, and the resulting benzene-soluble fraction was freed from the solvent and then extracted with cyclohexane to separate it into oil and asphaltene fractions.

Hydroprocessing (HPR) Step. The total product from the sequential HT-BCD depolymerization steps (or in some experiments the oil fraction of the product) was subjected to hydroprocessing with a sulfided $6\text{Co}8\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst (see above), using a 300 ml stirred autoclave and mesitylene as a solvent.

In each run about 5 g of the depolymerized coal product was dissolved in 50 ml of mesitylene and charged together with 1 g of catalyst and several drops of CS₂ to the autoclave. The latter was purged with nitrogen, pressurized with hydrogen to an initial pressure of about 1500-1700 psig, quickly heated (15°C/min) to the selected reaction temperature (350-370°C), and then additionally pressurized with hydrogen to a reaction pressure of 2700 psig. The autoclave was stirred under these conditions for 4 hr, and then cooled down and depressurized. In some experiments the catalyst was exchanged at this point with a fresh catalyst portion (1 g) and the hydroprocessing repeated for another 4 hr. At the end of the run, the HPR product was quantitatively removed from the autoclave, separated by filtration from the catalyst, and analyzed.

Product Analysis. Depolymerized products from the sequential HT-BCD steps and the final hydrocarbon products from the HPR step were subjected to a combination of IR, C₁₃ NMR, PMR and elemental analysis. The boiling point distribution of such products was determined by simulated distillation using a 18" x 0.25" stainless steel gas chromatographic column packed with 3% Dexsil 300 on Anakrom Q. A Hewlett-Packard, Model 5730 gas chromatograph was programmed for operation between -30° to 370°C at a rate of 11°/min (final temperature hold, 4 min; FID temperature, 400°C). Boiling point curves were calibrated with a standard mixture of C₉-C₂₄ 1-phenylalkanes. GC data were fed directly, stored and calculated in a Hewlett-Packard 21MX E-series computer.

RESULTS AND DISCUSSION

Mild Hydrotreatment (HT) Step. Suitable conditions for mild hydrotreatment (HT) of the two FeCl₃-coal intercalates were first determined. This included determination of the optimal concentration of intercalated FeCl₃, the HT temperature, and the reaction time under which there is only partial breakdown of the coal framework by preferential cleavage of alkylene (e.g., methylene), benzyletheric, and some activated aryetheric intercluster linkages, with minimal (usually <10%) attendant solubilization (2,4).

Figure 2 shows the change in the yield of THF-solubles from mild HT (at 250°C) of the FeCl₃-F(NM) and FeCl₃-H(UT) coal intercalates as a function of FeCl₃ concentration. As seen, for the F(NM) coal FeCl₃ concentrations in the range of 8-12.5% by wt are sufficient for an HT step characterized by a desired, low-extent of solubilization (<10%). The slightly higher rank H(UT) coal, however, shows quite different behavior, as expressed in relatively much higher yields (ca 16-20%) at low FeCl₃ concentrations (5-10%) and markedly decreased yields of THF-solubles at higher FeCl₃ concentrations (15-20%). Figure 3 shows, however, that the yield of THF-solubles from HT of the FeCl₃-H(UT) coal intercalate can be brought down to the desired level (<10%) by decreasing the hydrotreatment time to about 1 hr (at 250°C). It is also seen in Figure 3 that increase in HT temperature to 290°C causes an excessive extent of solubilization which is undesirable from the point of view of the efficiency of the overall sequential depolymerization procedure. Specifically, the optimal conditions for the HT step were previously defined as those under which the extent of depolymerization and solubilization in the subsequent BCD step are maximal (see below) (2). Data summarized in Figure 3 show that low concentrations of FeCl₃ (5-10%) in the H(UT) coal intercalate are preferable to a higher concentration of this halide for HT at 250°C and 1-2 hr reaction time. On the basis of these results for the H(UT) coal a FeCl₃ concentration of 5% by wt, a temperature of 250°C, and a reaction time of 1-2 hr were selected as operating conditions for the HT of H(UT) coal. Figures 2 and 4, on the other hand, indicate that for the F(NM) coal a suitable set of HT conditions is a FeCl₃ concentration of 8-12.5%, a temperature of 250°C, and a reaction time of 1-2 hr. After removal of the intercalated FeCl₃ catalyst at the end of the mild HT step (see Experimental), the mildly hydrotreated F(NM) and H(UT) coals were subjected to base-catalyzed

depolymerization (BCD), and the total yields of THF-soluble, depolymerized coal products from the sequential HT-BCD procedure determined (see below, Table 1).

Base-Catalyzed Depolymerization (BCD) Step. Table 1 summarizes the total yields of THF-soluble, depolymerized products from BCD of mildly hydrotreated F(NM) coal as a function of the temperature used in the preceding HT step. As seen, increase in HT temperature from 250° to 290°C results in gradual decrease in the yield of THF-solubles obtained in the BCD step (from 89.6% by wt for an HT temperature of 250°C to 68.0% for a temperature of 290°C). It is further seen that application of BCD alone to the same coal, without HT as preceding step (expt. 60) yields a markedly lower yield of THF-solubles (48.8%) as compared with that obtained by the combined HT-BCD procedure (compare with expt. 66 or 63), under otherwise identical BCD conditions. In experiment 66 the solubilization of the F(NM) coal is complete, as the insoluble residue left after the BCD step consists of the original coal ash only. Fractionation of the total THF-soluble product from the sequential HT-BCD processing shows that it consists mostly (>60% by wt) of cyclohexane-soluble (oil) components. In a series of comparative experiments, the conditions in the HT step were kept constant and identical with those in experiment 66, but the BCD step was performed at three different temperatures, i.e., 275°, 290° and 320°C. Fractionation of the products using solubility differences (see Experimental) showed that the oil fraction increases with increase in BCD temperature and becomes predominant at 290-320°C while the concentration of the combined asphaltene and asphaltol fractions reaches very low levels (<20% by wt). This behavior is consistent with previously reported results on the effect of BCD temperature upon the depolymerization of a Wyodak coal sample (2). It is also consistent with some earlier results which have shown that the product from base-catalyzed depolymerization of a Clear Creek, Utah coal at 320°C with NaOH-ethanol as depolymerizing agent consists predominantly of monocluster components(5).

Table 2 shows the change in the yield of THF-soluble products from BCD of mildly hydrotreated H(UT) coal as a function of BCD temperature in the range of 250-290°C, using otherwise identical conditions in both the HT and BCD steps. As seen, the total yield of THF-solubles increases with increase in BCD temperature from 37.0% (or 41.1% on the MAF coal) at 250°C to 72.6% (or 80.6% on the MAF coal) at 290°C. Complete solubilization of the H(UT) coal at 290°C requires extension of the BCD time to about 2 hr. It is also seen that BCD at 290°C without preliminary mild hydrotreatment (HT) of the coal (expt. 73) results in much lower solubilization yield (45.7%) as compared with that obtained by sequential HT-BCD (72.6%), using an identical temperature in the BCD step (expt. 74). Furthermore, the product from expt. 74 consists primarily (>60%) of cyclohexane-soluble (oil) components whereas the product from expt. 73 (without HT) contains only 21.8% of such components.

Hydroprocessing (HPR) of Depolymerized F(NM) and H(UT) Coals. Table 3 summarizes the elemental compositions of F(NM) and H(UT) depolymerized coal samples, as well as of products obtained from them in the last, i.e., the hydroprocessing (HPR) step of the sequential liquefaction procedure (Figure 1). As seen, the depolymerized coal samples retain the oxygen present in the starting coals, viz., the depolymerizing HT and BCD steps do not cause any appreciable extent of hydrodeoxygenation. However, structural studies based on C¹³ NMR, PMR and FTIR analysis of the products show that there is a major change in the oxygen functionality of the depolymerized coals as compared with the starting coals, i.e., most aryetheric and some dibenzofuranic intercluster linking groups undergo hydrolytic cleavage during the BCD step to yield phenolic groups (6). It is also seen in Table 3 that HPR of the depolymerized coals results in exhaustive hydrodeoxygenation, yielding hydrocarbon products of very low oxygen content. Structural analysis of HPR products and parallel model compound studies have elucidated the nature of some of the main depolymerizing reactions occurring in the HPR step, i.e., hydrogenolytic cleavage of condensed furanic rings (dibenzofuranic groups) and of Ar-Ar bonds (3,6). The reactions of such strong

Table 1

Yield of THF-Soluble Products from BCD of Mildly Hydrotreated F(NM) Coal as a Function of Temperature in the HT Step

Experiment, no.	60	66	63	61	62
<u>HT step^a</u>					
Temperature, °C	--	250	250	275	290
FeCl ₃ concentration	--	8.0	12.5	12.5	12.5
Yield of THF Solubles in HT Step, % by wt	--	6.0	6.7	8.6	14.8
<u>BCD step^b</u>					
Temperature, °C	275	275	275	275	275
Total yield of THF-solubles, % by wt ^c	48.8	89.6	84.5	75.2	68.0
Insoluble residue ^d	51.2	10.4	15.5	24.8	32.0

^aInitial H₂ pressure, 1500 psig; reaction time, 2 hr. ^bInitial N₂ pressure, 1000 psig; reaction time, 1 hr. ^cTotal yield of depolymerized, THF-soluble products from sequential HT-BCD. ^dIncluding ash and non-depolymerized coal.

Table 2

Yield of THF-Soluble Products from BCD of Mildly Hydrotreated H(UT) Coal as a Function of the Temperature in the BCD Step

Experiment no.	71	72	74	73
<u>HT step^a</u>				
Temperature, °C	250	250	250	--
FeCl ₃ concentration, % by wt	5	5	5	--
Yield of THF-Solubles in the HT Step, % by wt	12.9	12.5	12.4	--
<u>BCD step^b</u>				
Temperature, °C	250	275	290	290
Total yield of THF-Solubles, % by wt ^c	37.0	59.4	72.6	45.7
Insoluble residue ^d	63.0	40.6	27.4	54.3

^{a-d}See corresponding footnotes a-d, Table 1.

Table 3

Elemental Composition of Depolymerized F(NM) and H(UT) Coals
and of Hydrocarbon Products Derived from them in the HPR Step

Element, % by wt.	Depolymerized coal ^a		Hydroprocessed (HPR) product ^b	
	F(NM)	H(UT)	F(NM)	H(UT)
Carbon	77.71	77.35	88.38	88.97
Hydrogen	8.34	8.74	10.04	9.83
Nitrogen	0.93	0.50	0.35	0.21
Sulfur	0.14	0.11	<0.01	<0.01
Oxygen (by difference)	12.88	13.29	1.23	0.99

^aThe depolymerized F(NM) coal sample was obtained by HT at 250°C, followed by BCD at 275°C (see expt. 66, Table 1); the depolymerized H(UT) coal sample was obtained by HT at 250°C followed by BCD at 290°C (see expt. 74, Table 2).

^bThe hydroprocessing (HPR) of the depolymerized coals was performed at 370°C and 2700 psig H₂ pressure, using a sulfided 6Co8Mo catalyst and mesitylene as a solvent (for procedure, see Experimental).

Table 4

Boiling Point Distribution of Depolymerized F(NM) and H(UT)
Coals and of Hydrocarbon Products Derived from them
by Hydroprocessing (HPR)^a

Fraction (b.p., °C) wt %	Depolymerized coal ^b		Hydroprocessed (HPR) ^c product	
	F(NM)	H(UT)	F(NM)	H(UT)
Gasoline (<200°)	5.0	1.1	18.0	18.7
Kerosene (200-275°)	3.5	4.2	35.5	27.2
Gas Oil (275-325°)	11.1	5.1	8.1	9.4
Heavy Gas Oil (325-400°)	9.4	6.9	7.2	7.7
Vacuum Gas Oil (400-538°)	12.7	5.7	10.6	13.9
Total Distillable (<538°)	41.8	23.0	79.4	76.9
Atmospheric Residue (>350°)	75.6	87.0	36.3	42.2
Vacuum Residue (>538°C)	58.2	77.0	20.6	23.1

^aBoiling point distributions were determined by simulated distillation (see Experimental). ^bSee footnote a, Table 3. ^cSee footnote b, Table 3.

intercluster linkages involve as a first necessary step ring hydrogenation of at least one aromatic ring adjacent to the linkage, followed by C-O or C-C hydrogenolysis, respectively (3,6).

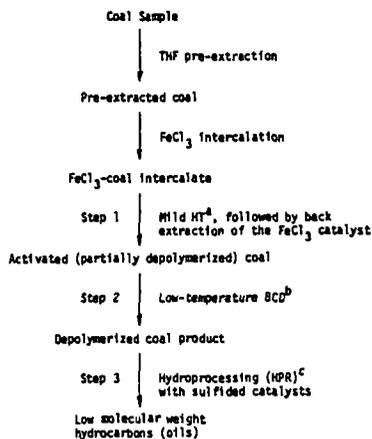
Table 4 summarizes the boiling point distribution of the depolymerized F(NM) and H(UT) coals, and of the hydrocarbon products derived from them in the HPR step. As seen, the oxygen-rich depolymerized coals are characterized by low volatility, as reflected in a total proportion of distillable components (<538°C) of 41.8% for the F(NM) coal and 23.0% for the H(UT) coal. The total proportion of gasoline- plus kerosene- range fractions is only 8.5% for the depolymerized F(NM) coal, and 5.3% for the depolymerized H(UT) coal. Hydroprocessing results in a dramatic change in volatility as reflected in a combined yield of 61.6% of low-boiling fractions (gasoline, kerosene, and gas oil; b.p. up to 325°C/760 torr) for the product from the F(NM) coal, and an yield of 55.3% of such fractions for the product from the H(UT) coal. Those results are similar to those previously reported for a lower rank Wyodak coal, and provide further support for the above outlined processing concept according to which preferential conversion of coals to light hydrocarbon oils requires in-depth, low-temperature coal depolymerization to monocluster products, prior to hydroprocessing.

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^aHT = hydrotreatment (250-275°C; H₂ pressure, 1000-1500 psig)

^bBCD = base-catalyzed depolymerization (250-285°C; initial N₂ pressure, 1000 psig)

^cHPR = hydroprocessing (350-370°C; H₂ pressure, 2700 psig)

Figure 1. Low-Temperature Coal Depolymerization-Liquefaction Procedure.

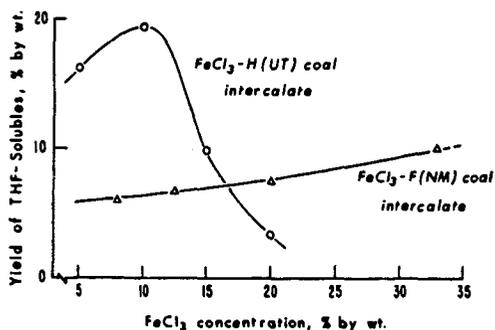


Figure 2. Yield of THF-Soluble Products from Mild HT of FeCl₃-F(NM) Coal and FeCl₃-H(UT) Coal Intercalates as a Function of FeCl₃ Concentration (250°C; 2 hr).

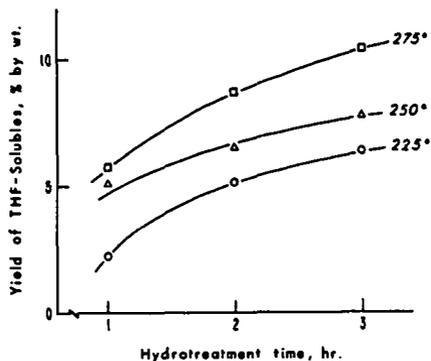


Figure 3. Yield of THF-Soluble Products from Mild HT of FeCl₃-F(NM) Coal Intercalate as a Function of HT Temperature(°C) and Time (FeCl₃ Concentration, 12.5% by wt.)

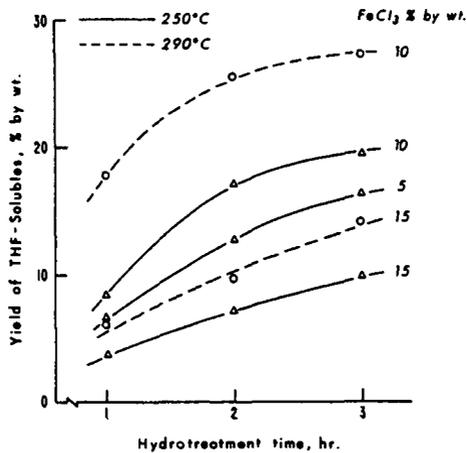


Figure 4. Yield of THF-Soluble Products from Mild HT of FeCl₃-H(UT) Coal Intercalate as a Function of FeCl₃ Concentration and Reaction Time.

Thermal Effects on Liquefaction of Kentucky
#9 Coal with NiMo/AL₂O₃ Catalyst

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Introduction

The main objectives of this research are (1) to investigate effects of heating rates on deactivation of catalysts, (2) to identify interactions between hydrogen donor solvents (HDS) and catalysts, (3) to study effects of initial temperatures on catalytic activities, and (4) to elucidate interactions between physical solvents and catalytic activities in the early stage of coal liquefaction.

A series of liquefaction experiments were conducted for Kentucky #9 coal (Ky #9 coal) without hydrogen donor solvents in the presence of presulfided fresh Shell 324 M catalyst, increasing liquefaction temperatures from 200°C or 300°C up to 380°C and holding liquefaction temperatures at 380°C for 15 min (4,5). Naphthalene (NAP) was hydrogenated with molecular hydrogen in the presence of used catalysts to evaluate catalytic activities of used catalysts. Liquefaction of Ky #9 coal decreases and catalytic activities increase, as heating rates increase, as shown in Figure 1. The initial liquefaction temperatures appear to affect liquefaction of Ky #9 coal in the presence of presulfided fresh Shell 324 M catalyst, whereas catalytic activities appear to be independent of the initial temperatures in the absence of hydrogen donor solvents.

When hexadecane (HEX) was used instead of 1-methylnaphthalene (1-MN) as a physical solvent, both liquefaction of Ky #9 coal and deactivation of Shell 324 M (NiMo) catalyst are less in the presence of Hex than 1-MN.

Another series of liquefaction runs of Ky #9 coal were performed in the presence of both presulfided fresh Shell 324 M catalyst and various hydrogen donor solvents such as anthracene (AN), 9,10-dihydroanthracene (DHA), phenanthrene (PN), 9,10-dihydrophenanthrene (DHP), quinoline (Q), and 1,2,3,4-tetrahydroquinoline (THQ) (1, 2, 6, 7). The liquefaction temperature was increased from 200°C or 300°C up to 380°C in the heating rates of 1-6°C/min.

Liquefaction of Ky #9 coal decreases, as heating rates increase, as shown in Figures 3 through 6. The initial liquefaction temperatures appear to affect both liquefaction of Ky #9 coal and deactivation of Shell 324 M catalyst in the early stage of liquefying Ky #9 coal in the presence of hydrogen donor solvents. Deactivation of Shell 324 M catalyst appears to decrease with increasing heating rates. On the other hand, the initial temperatures appear to affect liquefaction of Ky #9 coal and seem not to affect deactivation of Shell 324 M catalyst in the absence of hydrogen donor solvents.

Experimental

Coal liquefaction runs were conducted, using Ky #9 coal. Either hexadecane or 1-MN was utilized as a physical solvent. A 13 cc, 316 stainless steel microreactor was fed with 1 g coal, 0.1 g hydrogen donor

solvent, 2.9 g physical solvent, 0.1 g presulfided fresh Shell 324 M catalyst and 1200 psig hydrogen at room temperature, as shown in Table 1. Q, THQ, AN, DHA, PN, and DHP were introduced in the reactor as hydrogen donor solvents. Liquefaction temperatures were increased from 200°C or 300°C up to 380°C and held at 380°C for 15 min.

Following coal liquefaction at the desired reaction time and temperature, the reactor was quenched in cold water and the gaseous products were released. The liquid-and-solid liquefaction products as well as the used catalyst were removed completely from the reactor by dissolving these liquefaction products with tetrahydrofuran (THF). The catalyst was separated from the solid-and-liquid liquefaction products and then was washed with 200 cc THF by sonicating the spent catalyst in THF for 12 min.

The liquefaction products were separated into a THF soluble fraction, a toluene-insoluble fraction and a cyclohexane-insoluble fraction to obtain a product distribution in terms of preasphaltene (PRA), asphaltene (ASP) and oil-plus-water-plus-gas (OWG) (8).

Naphthalene was hydrogenated with molecular hydrogen in the presence of the sonicated spent catalyst to examine deactivation of spent catalyst, as shown in Table 2.

Conversions of hydrogen donor solvents were analyzed, using a gas chromatograph, equipped with a flame-ionization detector and an 8 ft. long, 1/8 inch OD, SP 2100 packed column.

Discussions

A series of Ky #9 coal liquefaction runs were carried out without hydrogen donor solvents, in the presence of presulfided fresh Shell 324 (NiMo) catalyst, increasing liquefaction temperatures from 200°C or 300°C up to 380°C and holding liquefaction temperatures at 380°C for 15 min., as shown in Figure 1.

Coal liquefaction decreases with increasing heating rates and levels off at high heating rates. Deactivation of catalyst also decreases with increasing heating rates. The initial temperatures appear to affect liquefaction of Ky #9 coal, whereas the initial temperatures do not appear to affect deactivation of catalyst in the early stage of liquefying Ky #9 coal in the absence of hydrogen donor solvents. Figure 1 shows that liquefaction of Ky #9 coal in the absence of HDS significantly takes place at low heating rates and does not take place at high heating rates between liquefaction temperatures 200°C and 300°C. These data also suggest that deactivation of catalyst in the absence of HDS does not appear to occur significantly between liquefaction temperatures 200°C and 300°C.

When hexadecane as a physical solvent was used instead of 1-MN, both liquefaction of Ky #9 coal and deactivation of catalyst were lower in the presence of hexadecane than 1-MN in liquefying Ky #9 coal in the absence of hydrogen donor solvents, as shown in Figure 1. These facts may indicate that both liquefaction of Ky #9 coal and deactivation of catalyst in the absence of HDS are affected by physical solvents.

Another series of coal liquefaction runs of Ky #9 coal were carried out in the presence of both presulfided fresh Shell 324 M catalyst and various hydrogen donor solvents such as AN, DHA, PN, DHP, Q, and THQ, using 1-MN as a physical solvent. The liquefaction temperature was increased from 200°C or 300°C up to 380°C in the heating rates of 1-6°C/min, as shown in Figures 2 through 6.

Both liquefaction of Ky #9 coal and deactivation of catalyst decrease with increasing heating rates. The initial temperatures affect both liquefaction of Ky #9 coal and deactivation of catalyst in the presence of HDS. These observations may explain that both liquefaction of Ky #9 coal and deactivation of catalyst take place in the presence of HDS between

liquefaction temperatures 200°C and 300°C.

Ky #9 coal was liquefied more in the presence of hydroaromatics such as DHA and DHP than corresponding aromatics such as AN and PN between liquefaction temperatures 200°C and 300°C, as shown in Figures 2, 3 and 6. These facts may elucidate that availability of donative hydrogen from hydrogen donor solvents is quite important in the early stage of liquefying Ky #9 coal in the presence of NiMo catalyst (3).

Deactivation of catalyst significantly takes place in the early stage of liquefying Ky #9 coal in the presence of HDS between liquefaction temperatures 200°C and 300°C, as shown in Figures 2 through 6, whereas deactivation of catalyst does not appear to take place in the early stage of liquefying Ky #9 coal in the absence of HDS between liquefaction temperatures 200°C and 300°C, as shown in Figure 1. These facts may indicate that hydrogen donor solvent itself appears to contribute to deactivation of catalyst in the early stage of liquefying Ky #9 coal.

Liquefaction of Ky #9 coal in the presence of Q decreases less with increasing heating rates than that in the presence of THQ. Deactivation of catalyst in the presence of Q decreases with increasing heating rates, whereas deactivation of catalyst in the presence of THQ decreases and then increases with increasing heating rates, as shown in Figures 4 and 5. This observation may suggest that THQ as a hydrogen donor solvent appears to poison catalyst at high heating rates in the early stage of liquefying Ky #9 coal.

Effects of various hydrogen donor solvents on liquefaction of Ky #9 coal were compared on a THF-solubles-vs-heating rates plot, as shown in Figure 6. The THF solubles-vs-heating rates curves for AN, DHA, Q and THQ are concave upward, whereas THF-soluble-vs-heating rates curves for PN and DHP are concave downward. Effects of heating rates on liquefaction of Ky #9 coal in the presence of quinoline appear to be least among others. These observations may indicate that characteristic plots of THF-solubles-vs-heating rates data are dependent on types of hydrogen donor solvents in the early stage of liquefying Ky #9 coal in the presence of Shell 324 M (NiMo) catalyst.

Conclusions

The following conclusions were made on the basis of the available data in this research.

- Initial temperatures appear to affect liquefaction of Ky #9 coal, whereas initial temperatures do not appear to affect deactivation of Shell 324 M (NiMo) catalyst in the early stage of liquefying Ky #9 coal in the absence of hydrogen donor solvents (See Figure 1)
- Physical solvent itself appears to affect both coal liquefaction and catalytic deactivation in the early stage of liquefying Ky #9 coal in the absence of HDS. (See Figure 1)
- Initial temperatures affect both coal liquefaction and catalytic deactivation in the early stage of liquefying Ky #9 coal in the presence of HDS. (See Figures 2 through 5)
- Hydrogen donor solvent itself appears to contribute to catalytic deactivation in the early stage of liquefying Ky #9 coal. (See Figures 1 vs Figures 2 through 5)
- Characteristic plots of THF-soluble-vs-heating-rate data are depen-

dent on types of hydrogen donor solvents in the early stage of liquefying Ky #9 coal in the presence of Shell 324 M (NiMo) catalyst

- . Quinoline behaves as a hydrogen donor solvent least sensitive to heating rates among others and THQ appears to poison catalyst at high heating rates in the early stage of liquefying Ky #9 coal in the presence of Shell 324 M (NiMo) catalyst and 1-MN as a physical solvent
- . Coal liquefaction as well as catalytic deactivation can be identified, estimated and compared over a desired temperature range of coal liquefaction by liquefying coals at nonisothermal liquefaction temperatures

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Table 1

Liquefaction Conditions of Ky #9 Coal

Initial Temperatures (I.T.) (°C): 200 or 300
 Final Temperature (°C): 380
 Heating Rate (°C/Min) : 1-6
 Liquefaction Duration
 at 380°C (Min) : 0 or 15

Reactor Charge

Hydrogen(H₂) : 1200 psig at room temperature
 Coal : 1 g
 Physical Solvent : 2.9 g or 3 g 1-Methylnaphthalene
 or 3 g Hexadecane
 Hydrogen Donor
 Solvent : 0.1 g
 Presulfided
 Fresh Shell
 324 M Catalyst : 0.1 g

Table 2

Reaction Conditions of Evaluating Deactivation of Catalyst

Reaction Temperature : 380°C
 Reaction Duration : 15 min.

Reactor Charge

Naphthalene : 0.1 g
 Hydrogen : 1200 psig at room temperature
 Used Catalyst : 0.1 g
 Hexadecane : 2.9 g

Figure 1
Effects of Heating Rates on Liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the absence of HDS, increasing liquefaction temperatures from 200°C or 300°C up to 380°C and holding liquefaction temperatures at 380°C for 15 min.

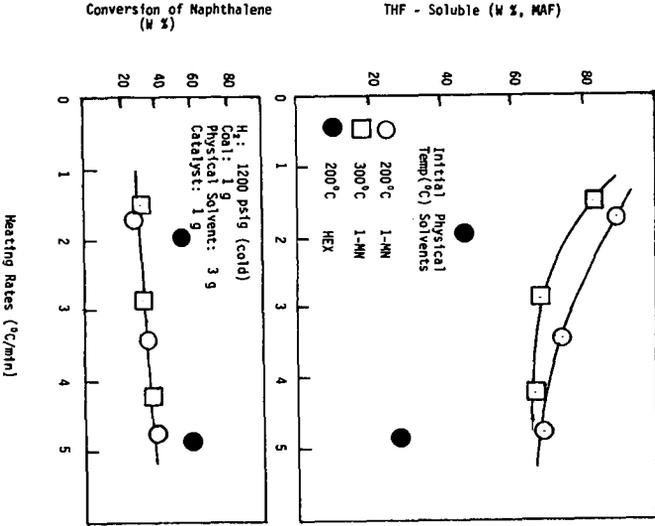


Figure 2
Effects of Heating Rates on both liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the presence of AH, increasing liquefaction temperatures from 200°C or 300°C up to 380°C.

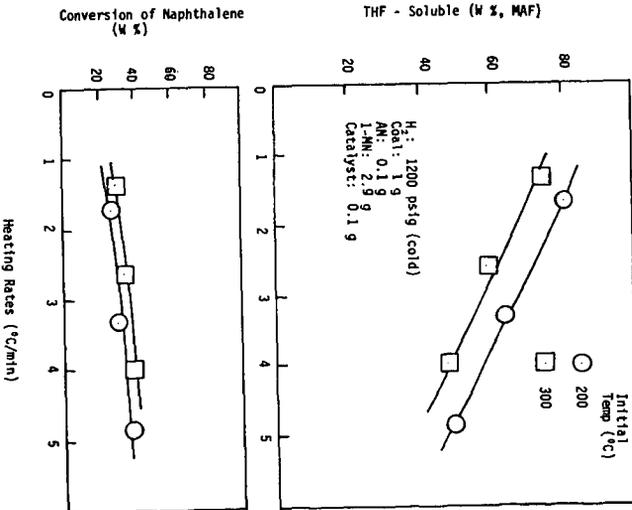


Figure 3
Effects of heating rates on both liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the presence of DHA, increasing liquefaction temperatures from 200°C or 300°C to 380°C.

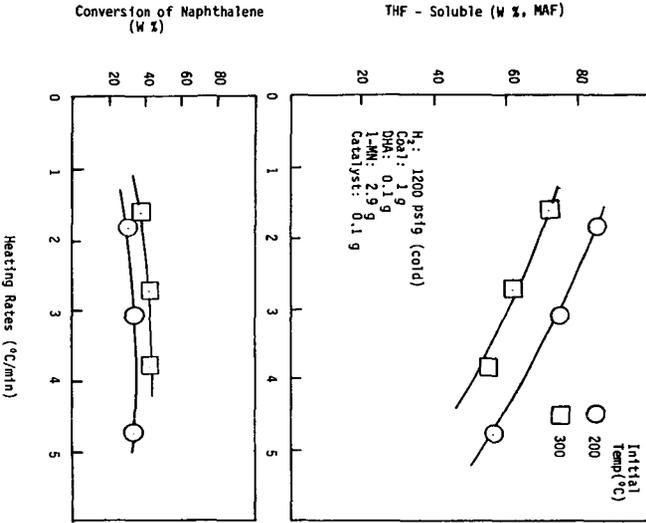


Figure 4
Effects of heating rates on both liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the presence of Q, increasing liquefaction temperatures from 200°C or 300°C up to 380°C.

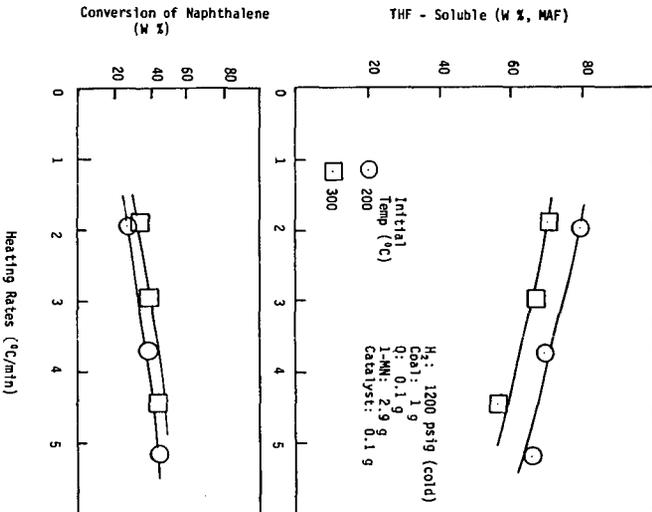


Figure 5
Effects of heating rates on both liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the presence of THQ, increasing liquefaction temperatures from 200°C or 300°C up to 380°C.

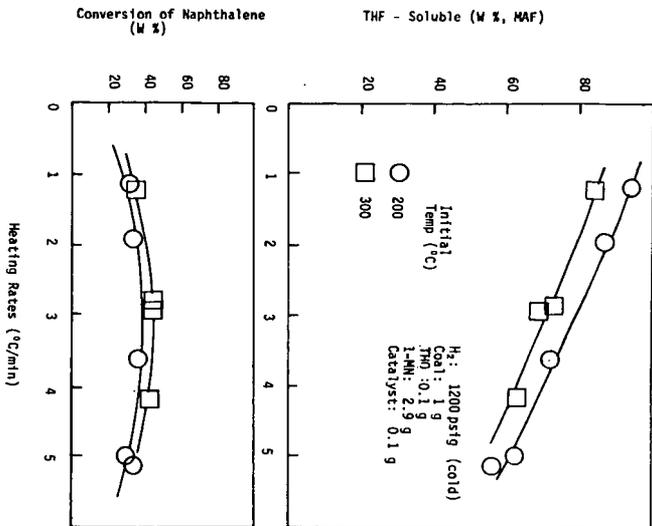
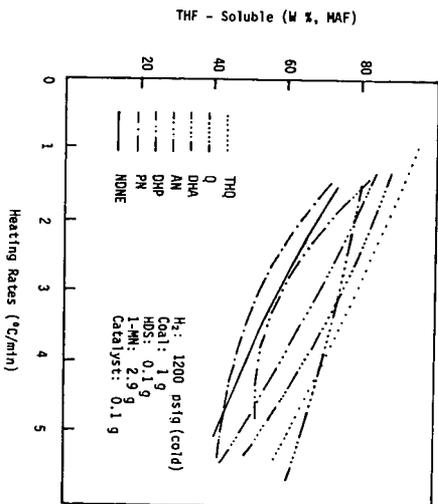


Figure 6
Effects of heating rates on liquefaction of Ky #9 coal in the presence of various HDS and presulfided fresh Shell 324 M catalyst, increasing liquefaction temperatures from 200°C up to 380°C.



MODERATE TEMPERATURE COAL HYDROGENATION

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INTRODUCTION

A well-defined correlation among coal structure, the reaction conditions of liquefaction, and the composition of the products is an important fundamental objective of coal liquefaction research. This objective has been very elusive because of the great complexity of the coal structure and because of the many side reactions that occur at commercial liquefaction temperatures. Such side reactions include thermal fragmentation, and the condensation or polymerization of reactive intermediates, which result in gas and coke formation.

Additional complications are caused by the use of a donor solvent in most coal liquefaction processes. The donor solvent interferes with the investigating of the reaction chemistry and analyzing of the reaction products by forming adducts with the coal-derived intermediates. Furthermore, it is difficult to characterize separately the donor solvent and its derivatives in the complex product mixture. At moderate reaction temperatures, internal hydrogen rearrangement may play a relatively more significant role in radical stabilization. Consequently, hydrogenating coal with gas-phase hydrogen and without a donor solvent offers significant advantages in understanding the mechanisms that occur.

The reaction of coal with H_2 has been investigated in the temperature range of 400 to 500°C (1). At these temperatures, however, cracking and condensation reactions that lead to gas and coke formation are fast and take place indiscriminately. The objective of this research was to explore hydrogenation at lower temperatures where the thermal side reactions are less extensive.

EXPERIMENTAL

The hydrogenation experiments were conducted in a 1-liter stirred autoclave equipped with a liner and a specifically designed anchor-type impeller. It is essential to use a properly designed impeller in this reaction to improve gas-solid contact and mass transfer, particularly during the initial softening of the coal particles, when caking can occur. A liner made of Inconel 600 and an impeller made of 316 SS were used in Experiments 1A through 1E and in Experiment 2. The liner and impeller were coated with glass for Experiments 3 and 4 to eliminate the catalytic effect of the metal surface. In each experiment, 25 g of high volatile bituminous coal was used. The coal was ground to -200 mesh and dried at 115°C in vacuo before use.

Two sets of hydrogenation experiments were conducted using two bituminous coals of slightly different rank. The objective of the first set was to investigate reactions in the 275 to 325°C range using 1-h and 48-h reaction times. The objective of the second set was to explore the effect of coal rank and two catalysts on coal conversion and product oil characteristics. Reaction parameters were selected on the basis of the results of the first set of experiments.

The first set was conducted using a Pittsburgh seam bituminous coal of the following composition (% daf): C:80.1, H:5.1, S:3.6, N:1.6, and O:9.6. The dry coal contained 11.2% ash. The second set was conducted at 325°C using reaction times of 48 h. A Pittsburgh seam bituminous coal of somewhat higher rank was used in these experiments. The elemental composition of this coal (% daf) was as follows: C:82.1, H:5.9, S:3.3, N:1.6, and O:7.1. The ash content of the dry coal was 8.2%.

Each experiment was conducted at a hydrogen pressure of approximately 20.7 MPa. After the product gases had been measured and analyzed, the hydrogenated product was Soxhlet-extracted with benzene. The benzene solution was concentrated by distillation and then poured into excess hexane to precipitate the asphaltenes. After filtration, the hexane solution was distilled and the hexane evaporated to recover the oil fraction. The benzene-insoluble residue was Soxhlet-extracted with THF and separated into a THF-soluble fraction and an insoluble residue. This procedure was based on a separation method recommended by Mima et al (2). The solvent-separated fractions were analyzed for elemental composition. A detailed characterization of the product oils was made using simulated distillation, vapor phase osmometry, field ionization mass spectrometry (FIMS), and proton nuclear magnetic resonance (NMR) spectrometry.

RESULTS AND DISCUSSION

The test conditions and product yields of the first set of experiments are presented in Table 1. Very little reaction was observed by visual inspection or chemical analysis in a 1-h reaction period at the lowest test temperature (275°C). The appearance of the dry powder product very closely resembled that of the starting coal. Most of the gas products consisted of carbon oxides; the gaseous hydrocarbon (CH₄) yield was only 0.04%. Compared with the starting coal, the amount of the THF-soluble extract increased from 5% to 8%. Some of these results have been presented elsewhere (3).

An experiment made using D₂ under the same conditions (1B), however, showed that a significant H-exchange had taken place at 275°C. About 15% of the protium (¹H) in the coal was replaced by deuterium (²H or D). In this experiment, a sizable increase in the THF solubility also was observed. At 310 to 325°C, the product was a shiny black solid, and there were significant increases in the THF solubility. Finally, when the reaction time was increased to 48 h at 325°C, the THF solubility of the product increased to 77%. Of this amount, 72% was hexane-soluble oil (daf coal basis). The fraction of gaseous products increased only slightly as the temperature was increased from 275 to 325°C, and the reaction time increased from 1 h to 48 h. This indicates that the product liquids were stable under these experimental conditions. The structural characterization of the product oil from this last experiment at 325°C for 48 h is discussed below.

The product yields from the second set of experiments (2 through 4) are listed in Table 2. These experiments were designed to test the effect of coal rank and two selected catalytic conditions on coal conversion and product oil characteristics. Table 2 also includes the product yields from the lower rank coal (Experiment 1E) for comparison. The product yields from Experiments 1E and 2 show that the lower rank coal used in Experiment 1E was much more reactive, particularly with regard to the conversion of the asphaltenes to oil.

The evaluation of Experiments 2 and 3 shows that the autoclave's metal surfaces have a strong catalytic effect on oil production. The results of Experiment 4 indicate that nickel very effectively catalyzes the conversion of coal to soluble products but is somewhat less effective than the autoclave surfaces in catalyzing oil production. Gas formation was remarkably low in every experiment. It appears that gas formation is proportional to oil production; the gas yield was approximately 10% of the oil yield in each experiment.

The elemental composition of the oil products is given in Table 3. The H/C atomic ratios varied from 1.13 to 1.24, and the oil from the nickel-catalyzed reaction had the highest value. The oil produced from lower rank coal (Experiment 1E) had the same H/C ratio as the oil product from the higher ranking coal (Experiment 2), even though the oil yield in Experiment 1E was 50% higher. The oil from Experiment 1E had a significantly lower oxygen content than the oil from Experiment 2. This difference may indicate that the cleavage of certain C-O bonds has an important role in oil formation.

The hydrogen-type distributions of the oil products were determined by proton NMR spectroscopy. Figure 1 shows the spectrum of the oil from Experiment 1E as an example. The integration results are presented in Table 4. In agreement with the elemental analysis data, the NMR integration values show that the oil made by nickel catalysis (Experiment 4) had significantly more saturated structures than the oil formed via catalytic effect of the autoclave surfaces (Experiment 2). These results plus the fact that the oil yield was greater in Experiment 2 than in Experiment 4 indicate that the catalytic effect of the autoclave surfaces preferentially catalyzed hydrocracking reactions leading to oil formation, while nickel catalysis resulted in more hydrogen uptake leading to the formation of saturated structures.

The oil products from Experiments 2 through 4 were further characterized by simulated distillation and by FIMS. The data indicate that there is close similarity between the structural features of the oils from Experiments 2 and 3. The presence of several homologous series (such as alkyl derivatives of phenol, diphenyl/acenaphthene, and pyrene) has been indicated in these oil products. The product oil from the nickel-catalyzed hydrogenation is quite different in that the data indicated the presence of more hydrogenated ring structures in it.

The hydrogen type distributions of an oil fraction obtained by moderate temperature hydrogenation and of distilled oil fractions of extract and process solvent samples from an integrated two-stage liquefaction pilot plant, are compared in Table 5. The oil from moderate temperature hydrogenation is much less aromatic and contains more saturated structures than the pilot plant products, which were produced at significantly higher temperatures.

SUMMARY AND CONCLUSIONS

Hydroliquefaction of two bituminous coals was explored to obtain information on the chemistry of liquefaction. Tests were conducted in the temperature range of 275 to 325°C and at 20.7 MPa hydrogen pressure. No donor solvent was added to the reactant to simplify product analysis and the evaluation of the results. The results and conclusions are summarized below:

1. Exploratory tests showed that at a liquefaction temperature of 325°C, high conversion to oil can be obtained with few side reactions resulting in gas or coke formation. Therefore, this temperature was selected to explore further the effect of coal rank and catalysis on coal conversion.

2. Of the two bituminous coals tested, the lower rank coal (C = 80%) was much more reactive and gave 50% higher oil yield than the higher rank coal (C = 82%). The oil yields were 72% and 48%, respectively.
3. It was shown in experiments made with the higher rank coal (C = 82%) that the metal components of the autoclave (liner and impeller) had a strong catalytic effect on the liquefaction reaction. When the metal parts of the autoclave were replaced with a glass-coated liner and impeller, the oil yield was reduced from 48% to 19%.
4. Catalysis by nickel, applied as nickel acetate impregnated into the coal, gave significantly different results from those obtained in the metal-lined reactor. Overall conversion to soluble products was higher using the nickel catalyst (94% versus 87%). However, nickel catalysis gave lower conversion to oil (40% versus 48%).
5. The oil produced in the nickel-catalyzed hydrogenation was significantly more aliphatic in character than the product from the metal-surface catalyzed reactions. The aliphatic to aromatic proton ratios were 83/17 and 74/26, respectively. Also, the nickel-catalyzed product had a much higher $(\beta + \gamma)/\alpha$ aliphatic proton ratio than the metal-catalyzed product (55/28 versus 43/32). These data indicate that nickel catalysis strongly promoted hydrogenation of aromatic rings while the metal components more effectively catalyzed hydrocracking reactions, which resulted in oil formation.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Kwang E. Chung of the Rockwell International Science Center for his assistance with the autoclave experiments and Dr. Kwang E. Chung and Mr. Joseph J. Ratto for recording the proton NMR spectra. In addition, the field ionization mass spectrometry work done by Dr. Ripudaman Malhotra of SRI International is gratefully acknowledged. This research was supported by the Electric Power Research Institute, the U.S. Department of Energy, and Rockwell International Corporation.

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TABLE 1
TEST CONDITIONS AND PRODUCT YIELDS

Experiment	Temperature (°C)	Pressure (MPa)	Time (h)	Conversion (% daf Coal)		Product Appearance
				Gas	THF Soluble	
Untreated coal	-	-	-	-	5	Dry powder
1A	272	20.0	1.0	0.4	8	Dry powder
1B (D ₂)	271	20.3	1.0	0.3	15	Dry powder
1C	310	20.7	1.0	1.0	22	Black solid
1D	325	19.3	1.0	1.7	29	Shiny black solid
1E	325	19.3	48.0	5.8	77 ^a	Thick dark oil

^aMost of this THF-soluble product was hexane-soluble oil (72% based on daf coal).

TABLE 2
PRODUCT DISTRIBUTIONS FROM MODERATE TEMPERATURE
LIQUEFACTION EXPERIMENTS^{a,b}

Experiment	1E	2	3	4
Coal rank	80	82	82	82
% C, daf	9.6	7.1	7.1	7.1
% O, daf				
Catalyst	Yes (Liner/ impeller)	Yes (Liner/ impeller)	No	Yes (Nickel- acetate)
Conversion	84	87	80	94
Product yields:				
Gas	6	4	3	4
Oil	72	48	19	40
Asphaltene	6	18	33	28
Preasphaltene	1	17	25	22
Residue	16	13	20	6

^aAll hydrogenation experiments made at 325°C, ~20 MPa, and using 48-h reaction time.

^bPercent on loss-free, daf-basis.

TABLE 3
ELEMENTAL COMPOSITIONS OF PRODUCT LIQUIDS

Sample	Composition (wt. %)						H/C
	C	H	N	O	S	Total	
Experiment 1E, oil	88.2	8.4	1.1	1.8	0.6	100.1	1.14
Experiment 2, distilled liquid	86.3	8.1	1.2	3.6	0.4	99.6	1.13
Experiment 2, oil	86.1	8.2	0.9	4.2	0.4	99.8	1.14
Experiment 3, oil	87.2	8.6	0.8	2.7	0.7	100.0	1.18
Experiment 4, oil	86.5	8.9	0.9	2.7	0.6	99.6	1.24

TABLE 4
PROTON NMR INTEGRATION VALUES

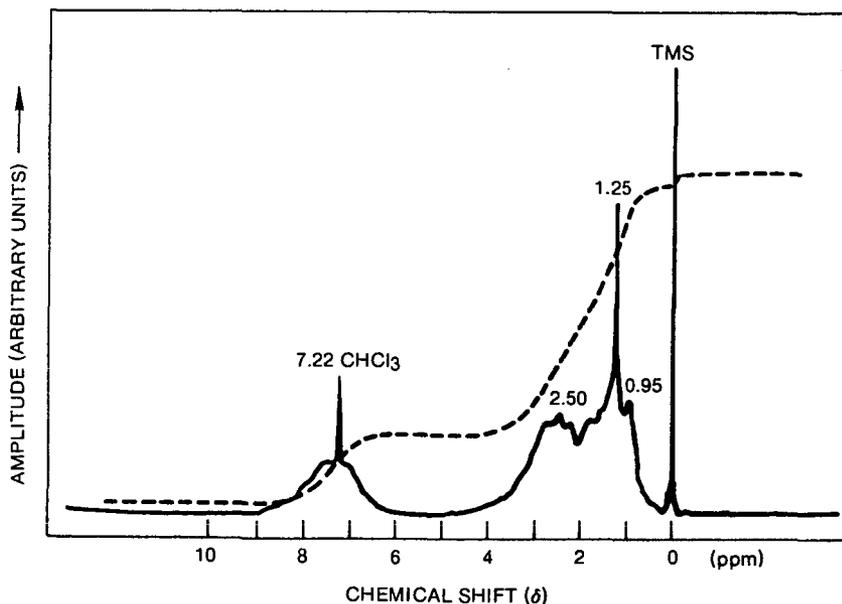
Hydrogen Type	Chemical Shift (ppm)	Experiment Number				
		Hydrogen-Type Distribution (%)				
		1E (Oil)	2 (Liquid)	2 (Oil)	3 (Oil)	4 (Oil)
Condensed aromatic, 4+ rings	7.85	4.0	2.5	3.1	1.5	1.4
Condensed aromatic, 2-3 rings	7.2-7.85	10.1	10.4	10.5	7.7	6.4
Aromatic single ring	6.8-7.2	4.7	6.7	6.6	6.8	5.4
Phenolic OH	6.3-6.8	1.4	5.2	7.2 ^a	2.8	3.1
α^2 -aliphatic	3.7-4.2	1.8	2.1	0.9	1.1	0.6
α -aliphatic	2.0-3.7	33.9	30.7	29.7	32.3	28.5
β -aliphatic	1.0-2.0	35.4	34.4	33.2	36.9	39.3
γ -aliphatic	0.5-1.0	8.7	8.0	8.8	10.9	15.3

^aIncludes 2.3% contribution from 4.2 to 5.2-ppm region.

TABLE 5
 MODERATE TEMPERATURE VS TWO-STAGE LIQUEFACTION-COMPARISON
 OF HYDROGEN TYPES

Oil Product From	Yield (%)	Hydrogen Distribution (%)				
		Condensed Aromatic	Single Ring Aromatic	Aliphatics		
				α	β	γ
Moderate temperature liquefaction ^a	72	14	6	36	35	9
Two-stage liquefaction ^b Extract ^c	41	27	14	28	29	4
Process solvent ^c	48	26	10	24	35	3

^aPittsburgh seam coal, C = 80.1%
^bIllinois No. 6 coal, C = 79.2% (from Ref. 4)
^c-454°C distillate



COAL PROCESSING IN NON-DISSOLVING MEDIA

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Introduction

If coal is contacted with an organic reagent in a medium in which the reagent is marginally soluble, there may be a tendency for the reagent to transfer to the pores and surfaces of the coal, where it has maximum utility for reactions which cleave the coal macromolecular network. Thus, in such media it may be possible to employ lower concentrations of reagents than would be required in totally soluble systems. If, in addition, coal fragments are insoluble in the processing medium, the coal particles will be recovered intact after processing. The reagent can then be washed from the coal, and coal conversion assessed as solubility in a standard solvent. Since the reagent is not present when solubility is measured, conversion should be independent of the solvent properties of the reagent, and only dependent on its ability to break bonds during processing. In our work, we have focused on the reagent 1,2,3,4-tetrahydroquinoline (THQ), which has the unusual ability to disrupt coal macromolecules under mild conditions (200-250°C). A number of previous workers have commented on the efficacy of THQ as a coal solvent and have attributed it to either the basicity or the hydrogen-donating property of this molecule (1-3). Two types of non-dissolving media, perfluorocarbon liquids and water, have been employed in our studies.

Experimental

The perfluorocarbon liquids used in our experiments are typified by FC-70 (3M Corp.), a mixture of perfluorinated tertiary aliphatic amines, with a boiling point of 215°C. FC-70 has high solubility for gases such as H₂ and CO, but very low room temperature solubility for both polar and nonpolar organic molecules. Recently, we have performed some experiments in water, which is an interesting medium, since its solubility properties can be varied by adjusting pH.

Three very different coals, with the properties given in Table 1, are used in our experiments. Typically, 0.5g of coal, 0.1g of THQ and 7 ml of FC-70 or water are heated in a stainless tubing bomb under 8 MPa of H₂. Detailed procedures for carrying out the reactions and for removal of THQ before measuring the pyridine solubility of the coal have been given (4,5). Model compound studies were carried out in FC-70 with roughly equal weights of the model compound and THQ (or other reagent). The occurrence and nature of reaction was assessed by thin layer chromatography and 90 MHz proton NMR.

Table 1. Coal Properties

PSOC Designation	1104	247	1098
Moisture (%)	1.95	30.36	4.19
Ash (% on dry basis)	3.43	11.29	15.86
Volatile Matter (% MAF)	43.83	46.22	41.78
C (% MAF)	84.47	74.44	80.20
H (% MAF)	5.66	4.93	5.73
N (% MAF)	1.46	1.49	5.73
S (% MAF)	1.86	0.53	4.73
O (by difference)	6.48	18.61	7.89

1104 - HVA bituminous coal from Elkhorn #3 Seam

247 - North Dakota lignite A from Noonan Seam

1098 - Illinois #6 coal

Results

As previously reported, the pyridine solubilities of three very different coals were increased to 33-35% by long-term (18 hour) heating at 250°C with THQ in FC-70. For each coal, the kinetics were first-order with rate constant of ca. 0.6 hr⁻¹, and not mass-transport limited, as indicated by lack of dependence on particle size. A number of other reagents were evaluated concerning their ability to increase coal conversion under the mild conditions employed in these experiments. Quinoline, diethylamine, triethylamine, ethylenediamine and tetralin all produced less than 6% increase in the pyridine solubility of a bituminous coal heated at 250°C for 4 hours, while THQ produced almost a 20% increase under these conditions.

In order to determine the nature of the bonds in coal that were being cleaved by THQ under our mild conditions, a number of model compounds were heated with THQ in FC-70 under conditions identical to our coal experiments. These model compounds consisted of phenyl groups connected by various linkages that have been discussed as being of some importance in the coal macromolecular structure. The results of these studies are given in Table 2. For the two model compounds for which reaction was noted (diphenyldisulfide and phenyl benzoate), the reactions with tetralin and diethylamine were also investigated.

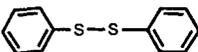
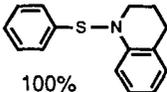
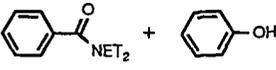
Two other media were employed to help understand the effectiveness with which small additions of THQ increase coal conversion in perfluorocarbon liquids. Dodecane has a similar boiling point to FC-70, but considerably greater solubility for THQ. It is probably only an effective extraction medium for free saturated hydrocarbons in coal. Water, on the other hand, while it has very low solubility for THQ, can dissolve strongly polar and highly acidic or basic components of coal. When bituminous coal was treated with THQ at 250°C for 4 hours in dodecane only 2% increase in coal pyridine solubility was obtained. With neutral pH water the results were very similar to what was obtained with FC-70. Very little of the coal dissolved in the water, as indicated by its light color. However, after washing out the THQ and water, the pyridine solubility of the coal was found to have increased by ca. 20%, a value very close to that achieved with THQ under similar conditions. Somewhat different results were obtained when a strongly basic (ca. 1M NaOH) solution was employed. In this case, the aqueous phase was very dark, but the remaining coal had only the pyridine solubility of unprocessed coal.

Discussion

Comparison of the results in FC-70, water and dodecane indicate that it is the marginal solubility of THQ in the first two of these media that permits low concentrations of this reagent to produce substantial increases in coal solubility. We envision that in FC-70 and water, THQ selectively transfers into the pores and onto the surfaces of the coal, while in dodecane it maintains a more uniform and low concentration throughout the system.

Although the model compound studies have not probed all possible bonds in coal macromolecules, our results suggest that only ester and disulfide bonds are susceptible to attack by THQ under the mild conditions of our experiments. In both cases the initial mode of reaction appears to be nucleophilic attack by the nitrogen lone pair, followed by bond scission and hydrogen donation in either a concerted or successive manner. Since tetralin is not a nucleophile, it cannot initiate similar reactions. The thiol produced with tetralin and diphenyldisulfide probably results from thermal scission of the disulfide, followed by hydrogen abstraction by the thio radical. Small amounts of thiol are formed when the tetralin is omitted in this experiment. In this case, with only H₂ available as a hydrogen donor, many of the thio radicals probably recombine. Since ester bonds are considerably stronger than disulfide bonds, it is not surprising that there is little reaction between tetralin and phenyl benzoate at 250°C. Diethylamine should be a more potent nucleophile than

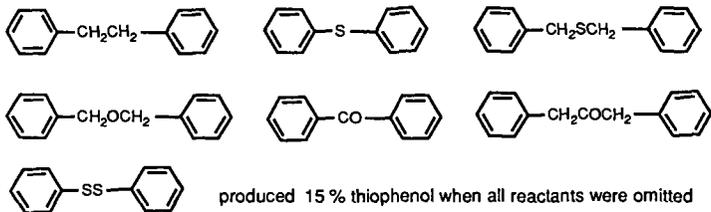
TABLE 2 MODEL COMPOUND STUDIES

Substrates	
Reactants	
THQ	 100%
Tetralin	 100%
Diethylamine	50 % substrate recovered *  100%

Conditions: 4 hrs at 250 C in FC-70 with 7 MPa H₂.

* Black, insoluble material was formed

The following substrates did not react with THQ under these conditions:



THQ, and indeed it does react with both diphenyldisulfide and phenyl benzoate at rates comparable to THQ. (The product of the disulfide reaction is a black, insoluble material that we have not yet been able to identify.)

In attempting to choose between esters and disulfides as the predominant bonds broken by THQ in our experiments, we must rationalize the observed attack of diphenyldisulfide by tetralin and both diphenyldisulfide and phenyl benzoate by diethylamine, while neither of these reagents are substantially effective in increasing coal solubility. Since tetralin has a similar boiling point and aromaticity to THQ, it is very difficult to explain the tetralin results if disulfide bonds are predominant. Diethylamine, however, with its lack of aromatic character, might find the coal environment much less favorable for selective partitioning. In addition, the high volatility of diethylamine would result in a substantial partitioning into the gas phase. Thus, the ineffectiveness of diethylamine with coal can be rationalized, and we prefer ester bonds as the primary linkages being attacked in our coal experiments. The surprising result that three very different coals all achieved very similar ultimate solubility upon long-term reaction with THQ in FC-70 at 250°C could most easily be explained by the postulate that these coals in their early stages of development all had similar concentrations of ester bonds in their macromolecular networks. At the so-called first coalification step, which occurs at ca. 78% carbon, coals lose CO₂, much of which comes from ester bonds, and the destruction of these bonds could account for the higher initial solubilities of PSOC 1098 and 1104. Van Bodegom *et al.* have reported that while low-rank coals contained ester bonds that could be broken in reactions with primary amines at temperatures of 120-180°C, no such bonds were found in medium and high-rank coals (6). Our work suggests that there are additional ester bonds in medium-rank coals that can be attacked by THQ at 250°C.

In both FC-70 and water, the amides generated by reaction of THQ with ester bonds in coal would show very little solubility, and thus it is not surprising that the coal does not dissolve in these media. With strongly basic water, however, further saponification of the amide occurs, with ionization of the resulting acids. The aqueous phase in this experiment therefore dissolves large concentrations of the coal fragments.

Acknowledgment

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EXTRACTION OF LOW-RANK COALS WITH SUPERCRITICAL WATER

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Abstract

Supercritical water extractions were performed on low-rank coals utilizing a semicontinuous supercritical solvent extraction system. Percent conversions ranged from 40% to 50% while extract yields ranged from 10% to 30% at 380°C. The conversions and extract yields increased with increasing operating temperature and pressure. The conversions also decreased with increasing coal rank and correlated well with the percent volatile matter in the coals.

Organic analyses of the resulting extracts have included separations into pentane, methylene chloride and methanol soluble fractions by short column chromatography, 200 MHz proton NMR, IR spectroscopy and capillary gas chromatography. Proximate and ultimate analyses indicated that supercritical water extracts the volatile, hydrogen-rich fraction of the coal. Organic analyses show that the extract is highly polar in nature with significant quantities of phenols and long-chain aliphatic fatty acids.

Introduction

Interest in the extraction of solutes with supercritical solvents has been increasing rapidly over the past fifteen years. This interest is primarily due to the enhanced solubility of substrates in the fluid phase that occurs at or above the critical point. It has only been in the last few years that considerable research has addressed the use of supercritical water as a solvent suitable for obtaining high yields of environmentally acceptable fuels and chemical feedstocks from coal (1, 2, 3). Under ambient conditions, organics and water are generally immiscible. However, as water approaches its critical point, the solubility of organics in water increases drastically (4, 5) while the solubility of inorganics in water substantially decreases (6). These solubility changes contribute to the potential of supercritical water to obtain high yields of relatively ash-free hydrocarbons from coal. In addition, other investigations have shown the potential for increasing supercritical water yields even further through the addition of a reducing agent such as CO or H₂S to the supercritical water system (7, 8, 9).

The objective of this research was to investigate the use of water as a cheap supercritical extraction solvent for obtaining environmentally acceptable liquid fuels and chemical feedstocks from coal and attempt to use supercritical solvent extraction as a means for determining the composition of various molecular fractions present in low-rank coals.

Experimental Procedure

Supercritical water extractions were performed using a semicontinuous extraction system in which deionized water under supercritical conditions was passed through a fixed bed of coal. The coals used in this experiments included the Indian Head, Center, and Martin Lake lignites along with Sarpy Creek and Wyodak subbituminous coals. Proximate and ultimate analyses for these coals are shown in Table I. As shown in Table I, there was a difference between the beginning and ending samples of the Indian Head lignite used in these experiments. Figure 1 is a flowsheet of the supercritical solvent extraction system as it was used for most of the supercritical water experiments. In this system, a fixed bed of coal was detained by sintered metal frits in a horizontal section of high pressure tubing. A rehabilitated GC

TABLE I. Proximate and Ultimate Analyses of Coals Used in Supercritical Water Experiments

	Sample Name and Location					
	Indian Head 1 Mercer Co., ND	Indian Head 2 Mercer Co., ND	Center Oliver Co., ND	Martin Lake Panola Co., TX	Wyodak Campbell Co., WY	Samy Creek Big Horn Co., MT
<u>Proximate Analysis (wt%)</u>						
Volatile Matter	43.8	49.8	43.0	42.2	43.5	34.8
Fixed Carbon	48.0	41.9	48.6	42.8	50.0	45.4
Ash	8.2	8.3	8.4	15.0	6.5	19.8
<u>Ultimate Analysis (wt%)</u>						
Hydrogen	4.74	4.45	4.13	0.32	4.26	3.64
Carbon	66.20	64.96	64.07	61.88	64.62	59.43
Nitrogen	0.96	1.00	1.13	1.23	1.01	0.83
Sulfur	0.72	0.33	1.16	1.17	0.58	4.22
Oxygen (1nd)	19.19	20.96	21.08	20.40	23.04	12.11
Ash	8.2	8.3	8.42	15.0	6.5	19.8

oven was used to heat the solvent and extraction vessel to temperature at 20°C/min., after which a pulseless flow of solvent was started through the system. The extracted organics and solvent then passed through a back pressure regulator where the precipitated extract was collected in a heated sample cylinder while the vaporous solvent and light gases were collected in chilled sample vessels. The volume of noncondensable product gas was measured and collected for analysis.

Analytical Procedure

After each experiment, any water remaining in the extract sample cylinder was filtered from the solid extract and selected samples of the recovered water solvent were analyzed by gas chromatography for their concentrations of water soluble organics. The solid extract was washed from the sample cylinder with acetone and the extracted coal residue and solvent-extract mixture were then rotary vacuum distilled to remove the solvent. This procedure allowed a relatively moisture-free product to be obtained for material balance purposes. Residues were analyzed by thermogravimetric analysis (TGA) and proximate and ultimate analyses were performed on selected samples.

Discussion and Results

The operating conditions and the corresponding results of these supercritical water extractions are shown in Tables II and III. The effect of extraction time on percent conversions is shown in Figure 2. This figure indicates that the percent conversions increase linearly with an increase in coal residence time up to approximately 45 minutes after which the conversions leveled off at 42% to 43%. A vacuum dried sample (0.65 wt% moisture) was also extracted for 60 minutes with supercritical water at similar operating conditions and resulted in a 33.5% conversion. This lower conversion was due to a sample size effect since drying the coal resulted in a 60% larger sample of maf coal being extracted. A conversion of 44.2% was obtained for a separate run using a vacuum dried coal at longer residence times which indicated that no advantage resulted in extracting "as received" coals with their inherent moisture already present in the sample's porous structure. Also, considering that a 33% larger sample of maf coal was being extracted, the slightly higher conversions obtained for the supercritical water experiment performed at a flow rate of 240 cc/hr suggests that an increase in the solvent flow rate increased the rate of extraction.

The effects of operating temperature and pressure on the resulting conversions was investigated using operating temperatures of 380°C or 440°C ($T_r = 1.01$ or 1.10) while the operating pressures used were 3265, 4013, or 4815 psia ($P_r = 1.02, 1.25, 1.50$). Results of these experiments are summarized in Table II. Figure 3 is a plot of the reduced pressure versus the percent conversion at both operating temperatures. This figure indicates that a small increase in the conversions was obtained with an increase in the operating temperature. The conversion also displayed a larger increase with increasing pressure up to 4000 psia. Above 4000 psia, there appeared to be no effect on the resulting conversions. This increase in conversions is the result of a large increase in solvent density caused by the increased pressure. The increase in conversion with higher temperature was the result increasing thermal decomposition or reactions of the lignite in this temperature region. The product gas compositions and yields appeared to be only temperature and coal dependent and were not affected to any large degree by operating pressure or solvent flow rate.

Table III shows the effect coal rank had on the percent conversion obtained using supercritical water at 380°C and pressures of either 3265 or 4013 psia. For comparison purposes, supercritical water experiments were also performed on a Red Lake Peat and a biomass sample and the results are also displayed in Table III. These results suggest that there is a high degree of correlation between the percent conversions obtained using supercritical water and the amount of volatile matter present in the starting coal. This finding is consistent with results reported by Great Britain's National Coal Board in which percent conversions using supercritical

TABLE II. Operating Conditions and Results from Supercritical Water Extractions of Indian Head Lignite

Coal	Temp (°C)	Tr**	Pressure (psia)	Pr**	Solvent Density (g/cc)	Solvent Flowrate (g/cc)	Residence Time (min)	Percent Conversion (MAF)*	Extract Yield* (MAF)	Volatile Yield* (MAF)	Product Gas Yield*
Indian Head (as received)	380	1.009	3265	1.017	.193	120	15	25.2	8.0	0.2	5.5
Indian Head (as received)	380	1.009	3265	1.017	.193	120	30	34.3	10.4	1.4	10.4
Indian Head (as received)	380	1.009	3265	1.017	.193	120	45	43.1	10.1	2.2	9.6
Indian Head (as received)	380	1.009	3265	1.017	.193	120	60	42.7	22.6	ND	12.5
Indian Head (vacuum dried)	380	1.009	3265	1.017	.193	120	60	33.5	8.5	1.8	11.4
Indian Head (as received)	380	1.009	3265	1.017	.193	120	80	42.6	12.0	2.9	11.6
Indian Head (as received)	380	1.009	3265	1.017	.193	240	30	36.0	9.9	2.1	8.0
+ Indian Head (as received)	380	1.009	3265	1.017	.193	120	240	43.3	18.8	2.5	10.8
+ Indian Head (as received)	380	1.009	4013	1.250	.504	120	240	50.6	22.4	2.3	12.6
+ Indian Head (as received)	380	1.009	4815	1.500	.558	120	240	50.3	23.8	2.9	12.1
Indian Head (as received)	440	1.102	3265	1.017	.097	120	240	43.3	13.3	ND	19.3
+ Indian Head (as received)	440	1.102	4013	1.250	.137	120	240	53.2	21.1	ND	17.0
Indian Head (as received)	440	1.102	4815	1.500	.199	120	240	54.4	21.8	ND	16.3
Indian Head (vacuum dried)	380	1.009	3265	1.017	.193	120	150	44.2	12.2	2.3	16.7

* % conversion = $\frac{\text{wt maf coal} - \text{wt maf residue}}{\text{wt maf coal}}$; % yield = $\frac{\text{wt maf product}}{\text{wt maf coal}}$

+ - average value
ND - not determined

** Tr = operating temperature of solvent (°K); Pr = operating pressure of solvent (psia)
critical temperature of solvent (°K); Pr = critical pressure of solvent (psia)

TABLE III. Operating Conditions and Results from Supercritical Water Extractions of Low-Rank Coals

Coal	Temp (°C)	Tr**	Pressure (psia)	Pr**	Solvent Density (g/cc)	Solvent Flowrate (g/cc)	Residence Time (min)	Percent Conversion (MAF)	Extract Yield* (MAF)	Volatile Yield* (MAF)	Product Gas Yield*
Coal Type Experiments											
Center	380	1.009	3265	1.017	.193	120	60	43.4	24.6	ND	ND
Martin Lake	380	1.009	4013	1.250	.504	120	150	45.2	20.2	1.7	12.1
Wyodak	380	1.009	3265	1.017	.193	120	150	33.7	14.0	ND	14.5
Wyodak	380	1.009	4013	1.250	.504	120	150	39.5	15.0	1.6	22.4
Sarpy Creek	380	1.009	4013	1.250	.504	120	150	33.5	21.2	1.3	3.6
Red Lake Peat	380	1.009	3265	1.017	.193	120	60	75.8	25.6	3.6	20.5
Biomass (Douglas Fir Sawdust)	380	1.009	3265	1.017	.193	120	60	83.8	33.7	3.6	33.6
Lithotype Experiments											
Indian Head Vitrain (50% of original)	380	1.009	3265	1.017	.193	120	60	42.3	22.2	6.9	6.7
Indian Head Durain (45% of original)	380	1.009	3265	1.017	.193	120	60	39.8	18.0	1.8	7.6
Indian Head Fusain (5% of original)	380	1.009	3265	1.017	.193	120	60	32.3	28.1	0.4	4.7
Special Run											
Indian Head (w 90% H ₂ O-10% CO)	383	1.003	3300	ND	ND	120+CO	60	41.2	12.3	2.1	NA

* % conversion = $\frac{\text{wt maf coal} - \text{wt maf residue}}{\text{wt maf coal}}$; % yield = $\frac{\text{wt maf product}}{\text{wt maf coal}}$

+ - average value
ND - not determined

** Tr = operating temperature of solvent (°C); Pr = operating pressure of solvent (psia);
Critical temperature of solvent (°K); Critical pressure of solvent (psia)

toluene also correlated well with volatile matter of the original coal (10). As a result, the conversions decreased with an increase in coal rank. This increase in conversions which occurred is the result of the increased concentration of thermally labile carbohydrate, lignin or lignin-derived components which exist in the lignite, peat, and biomass.

Supercritical water extractions of the Indian Head lithotypes; vitrain, durain, and fusain were performed. Approximately 12 to 15 grams of each lithotype were microscopically separated. The conversions obtained for the vitrain and durain fractions (which make up approximately 50 and 45 wt% of the original Indian Head) were found to be similar to those obtained using the original Indian Head lignite as shown in Table III. Table III also shows that the conversion of the fusain portion (5% of the original Indian Head) was significantly less than that for the original lignite. These results agree with other reported results in which vitrains and durains have been found to be highly susceptible to liquefaction, (i.e., susceptible to thermal cleavage and reaction with hydrogen) while fusain has been found to behave as more of an inert material (11). The yields of water-soluble organics from these lithotypes and the original lignite are shown in Table IV. As shown, the vitrain fraction contains considerably more of the oxygenated water-soluble volatile compounds (i.e., acetone, methanol, and phenol) than the original Indian Head, while the durain fraction contains slightly less of these compounds than the original lignite. The concentrations of these compounds in the fusain fraction were very small compared to that of the original lignite.

TABLE IV. Percent Yields of Volatile Components Found in Recovered Supercritical Water Solvent

Component	Supercritical Water Extraction				
	Indian Head 2	Sarpy Creek	Indian Head Vitrain	Indian Head Durain	Indian Head Fusain
Phenol	0.63	0.21	1.14	0.48	0.14
o-Cresol	0.17	0.06	0.20	0.10	0.05
m,p-Cresol	0.17	0.13	0.22	0.18	0.05
Total Phenolics	0.97	0.40	1.56	0.76	0.24
Methanol	0.80	0.04	1.32	0.22	--
Acetone	0.91	0.42	3.93	0.70	0.15
MEK	0.25	0.10	0.12	0.14	0.05
Total	2.93	0.96	6.93	1.82	0.44

As shown in Table III, a special experiment was performed using a 90-10 mole% mixture of water-carbon monoxide to extract Indian Head lignite at 383°C and 3300 psia. The purpose of this experiment was to determine what effects the addition of a reducing gas such as CO has on the molecular composition of the extract. The conversion and yields obtained were similar to those obtained for an experiment using pure water under similar conditions.

Results From Analysis of Supercritical Water Residues and Extracts

Proximate and ultimate analyses of selected residues and extracts from supercritical water and the original Indian Head are shown in Table V. The proximate analysis indicates that the supercritical water extract contains a significantly higher fraction of volatile matter while the residue contains a significantly lower fraction of volatile matter than the original Indian Head. The

TABLE V. Comparison of Proximate and Ultimate Analyses of Supercritical Water Residues and Extracts to the Original Sample

	Sample Description - All Samples run at 380°C, 3265 psia, 120 cc/hr											
	Indian Head		Indian Head		Indian Head		Red Lake		Red Lake		Original	
	Water - 30 ml n	Water - 60 ml n	Water - 30 ml n	Water - 60 ml n	Water - 30 ml n	Water - 60 ml n	Water - 30 ml n	Water - 60 ml n	Water - 30 ml n	Water - 60 ml n	Water - 30 ml n	Water - 60 ml n
	Residue	Extract	Residue	Extract	Residue	Extract	Residue	Extract	Residue	Extract	Residue	Extract
Percent Conversion (MAF)	34.3	42.7	41.2	41.2	74.7	74.7	NA	NA	83.8	83.8	NA	NA
Percent Extract Yield (MAF)	10.4	22.6	12.3	12.3	26.1	26.1	NA	NA	33.7	33.7	NA	NA
<u>Proximate Analysis (ME)</u>												
Volatle Matter	27.8	71.3	30.4	79.8	27.6	99.6	67.4	23.6	97.9	85.4	35.2	97.5
Fixed Carbon	63.8	26.7	61.0	19.8	60.7	0.4	12.9	32.8	1.9	13.2	62.0	2.5
Ash	8.4	2.0	8.6	0.4	11.7	0.0	19.7	43.6	0.2	1.4	2.8	0.0
<u>Ultimate Analysis (MF)</u>												
Hydrogen	3.67	7.67	3.53	7.63	3.41	9.01	2.62	2.52	8.51	6.55	3.62	6.28
Carbon	73.81	78.10	75.10	78.73	72.55	66.44	54.99	44.98	74.66	52.48	77.92	72.09
Nitrogen	1.34	0.69	1.38	0.84	1.40	0.72	2.89	2.22	2.80	0.40	0.75	0.71
Sulfur	0.42	1.42	0.38	0.42	0.39	0.30	0.31	0.25	0.15	0.09	0.13	0.08
Oxygen (Ind.)	12.36	10.11	11.01	11.97	10.54	23.53	19.49	6.43	13.67	39.09	14.78	20.84
Ash	8.4	2.0	8.6	0.4	11.7	0.0	19.7	43.6	0.2	1.4	2.8	0.0

ultimate analysis shows that the extract had a lower C/H ratio than the original Indian Head whereas the residue had a higher C/H ratio than the original Indian Head. These analyses indicate that the hydrogen-rich, lower molecular weight portion of the lignite is being extracted while leaving a highly carbonaceous residue.

The analyses also indicate that the mineral matter is concentrated in the residue while a relatively ash-free extract is obtained. Table V compares the proximate and ultimate analyses of the residues and extracts for runs using supercritical water and the supercritical water-CO mixture. The C/H ratio is substantially lower for the run using the H₂O-CO mixture which suggests the possible addition of H₂, which was generated by the water-gas shift reaction, to the extract.

Thermogravimetric analyses were performed in argon on samples of the original coal and supercritical water residues using a heating rate of 20°C/min. and a final temperature of 900°C. The weight-temperature profiles indicated that ~20 wt% of the supercritical residues were volatilized while approximately 41% of the original coal would volatilize under the same conditions. The differential weight loss curves for two supercritical water residues and the original Indian Head lignite are shown in Figure 4. This figure indicates that supercritical water has extracted most of the compounds which would devolatilize below ~550°C, thus, concentrating the higher molecular weight material in the residue which results in the higher differential weight loss curve at temperatures above 550°C.

Analysis of a supercritical water extract was carried out using chromatographic separations, infrared (IR), and nuclear magnetic resonance (NMR) spectroscopy. The extract was separated into three fractions by short column chromatography on silica gel. The first fraction was separated by successive elution with pentane and then isooctane. This fraction was found to make up approximately 5% of the extract and the NMR spectra showed that this fraction consisted only of aliphatic materials. This fraction was analyzed by capillary column gas chromatography and was found to contain a series of alkanes and alkenes in the range of C-18 to C-34. The presence of the alkenes indicates that thermal cracking is occurring but the relative amounts of the alkanes alternate as the carbon chain increases in the series, which suggest that the cracking was minimal, perhaps confined to reactions near the acid or ester function. Also, the predominance of the odd-number chains and the high concentration of CO₂ in the product gas indicate that a significant amount of decarboxylation was occurring.

The second fraction was separated by elution with methylene chloride and was found to make approximately 26% of the extract. Some identified individual hydrocarbons include phenanthrene, fluorene, anthracene, pyrene, benzofluorenes, and fluoranthene. The NMR spectrum shown in Figure 5 also suggests the possible presence of ester groups between 3.8 and 4.0 ppm. The last fraction was obtained by elution with methanol and was found to make up the majority (~69-70%) of the extract. The NMR and IR spectra on this fraction indicate the presence of phenolics and long chain aliphatic acids.

Table VI shows some of the individual coal-derived compounds which have been identified and their approximate yields. These yields indicate that the identified phenolics constituted a small fraction (from ~2.9% to 0.8%) of the supercritical water extracts. The dependence of phenol yields in the extract on coal type is noticeable with the Wyodak subbituminous coal generally yielding higher concentrations of phenols in the extract. The distribution of the individual phenols is essentially identical for the three coals, indicating that they originate from the same type of substructure in the coal and that the reactions which release them during supercritical water extraction must be identical. Thus, the ratio of the phenol yields in the three coals must result from different amounts of the substructure in the coals (probably in the same ratio).

TABLE VI. Identification and Determination of Yields for Individual Compounds in Supercritical Water Extracts Obtained at 380°C and 4013 psia

Compound	Indian Head		Wyodak		Martin Lake	
	% Yields (mcf)		% Yields (mcf)		% Yield (mcf)	
	In Extract	In Water	In Extract	In Water	In Extract	In Water
Methanol	ND	0.649	ND	0.113	ND	0.421
Acetone	ND	0.607	ND	0.538	ND	0.568
Acetonitrile	ND	0.001	ND	0.001	ND	0.005
Methyl Ethyl Ketone	ND	0.160	ND	0.170	ND	0.176
Propionitrile	ND	0.034	ND	0.005	ND	0.020
Catechol	ND	0.202	ND	0.151	ND	0.157
Phenol	0.028	0.362	0.075	0.340	0.026	0.167
o-cresol	0.022	0.101	0.062	0.104	0.020	0.049
m-cresol	0.030	0.110	0.067	0.094	0.024	0.049
p-cresol	0.030	0.118	0.007	0.122	0.022	0.059
2,6-diMePhe	0.002	ND	0.034	ND	+	ND
2-EtPhe	0.002	ND	0.045	ND	0.010	ND
2,4-diMePhe	0.013	ND	0.045	ND	0.017	ND
2,5-diMePhe	0.019	ND	0.018	ND	0.006	ND
2,3-diMePhe	0.009	ND	0.018	ND	0.006	ND
4-McGuaigcol	0.010	ND	0.003	ND	0	ND
2,4,6-triMePhe	0.007	ND	0 +	ND	+	ND
2,3,6-triMePhe	0.001	ND	0.003	ND	0	ND
2,4,5-triMePhe	0.004	ND	0.006	ND	0.020	ND
4-Indanol	+	ND	0.007	ND	0	ND
5-Indanol	0.009	ND	0.012	ND	0.012	ND
2,3,5,6-tetraMePhe	0.001	ND	0.003	ND	+	ND
1-Napthol	0.002	ND	0.006	ND	+	ND
2-Napthol	0.009	ND	0.018	ND	0.012	ND
Total	0.198	2.343	0.426	1.638	0.155	1.670

+ - trace

ND - not detected

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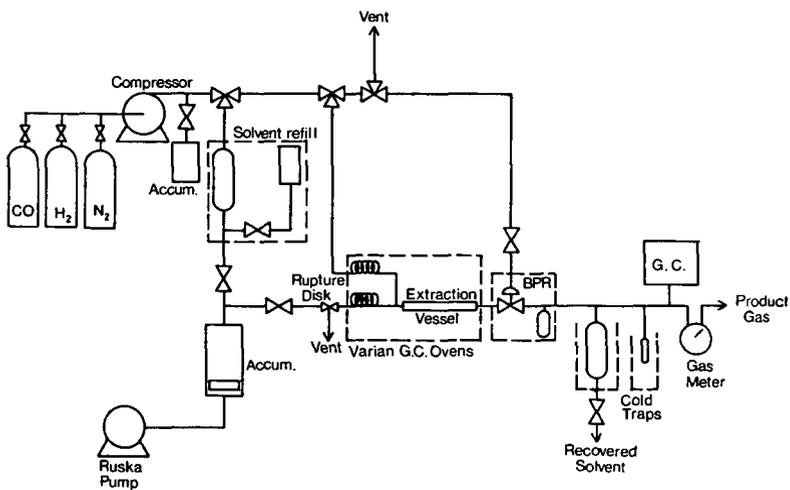


Figure 1. Flowsheet for the semicontinuous supercritical solvent extraction.

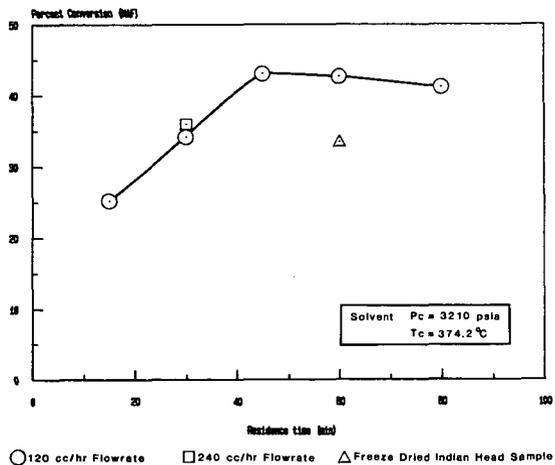


Figure 2. Extraction time and flow rate effects on supercritical water extraction.

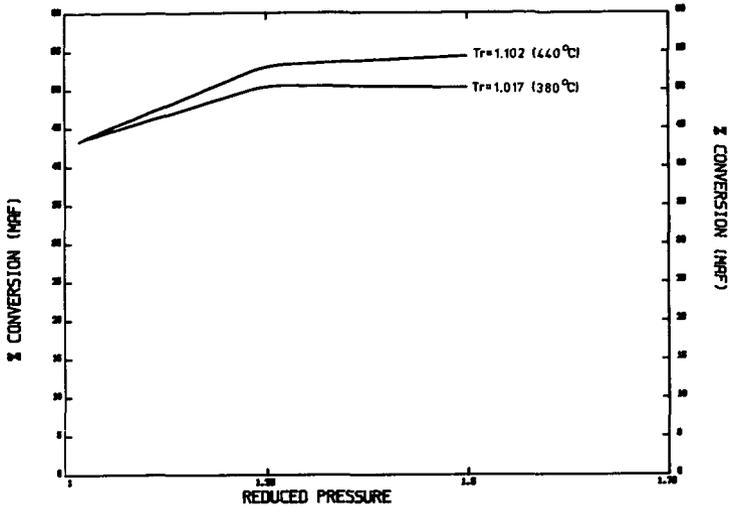


Figure 3. Effect of operating pressure and temperature on conversion of Indian Head lignite with supercritical water.

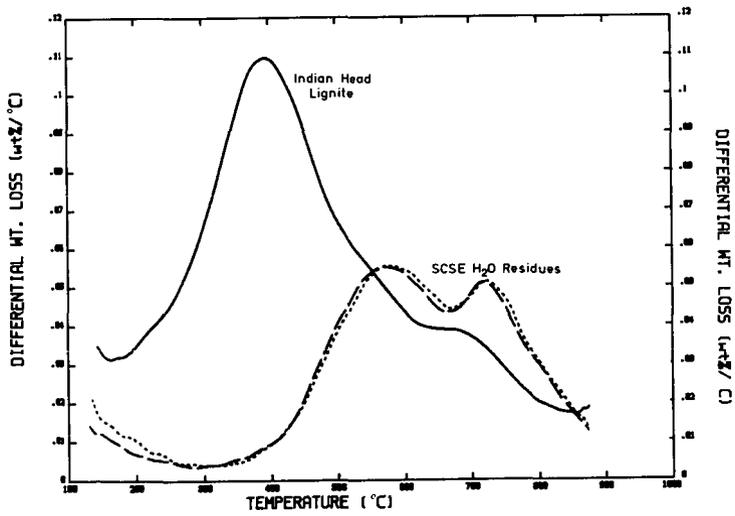


Figure 4. Differential weight loss curves for two supercritical water residues and the original coal.

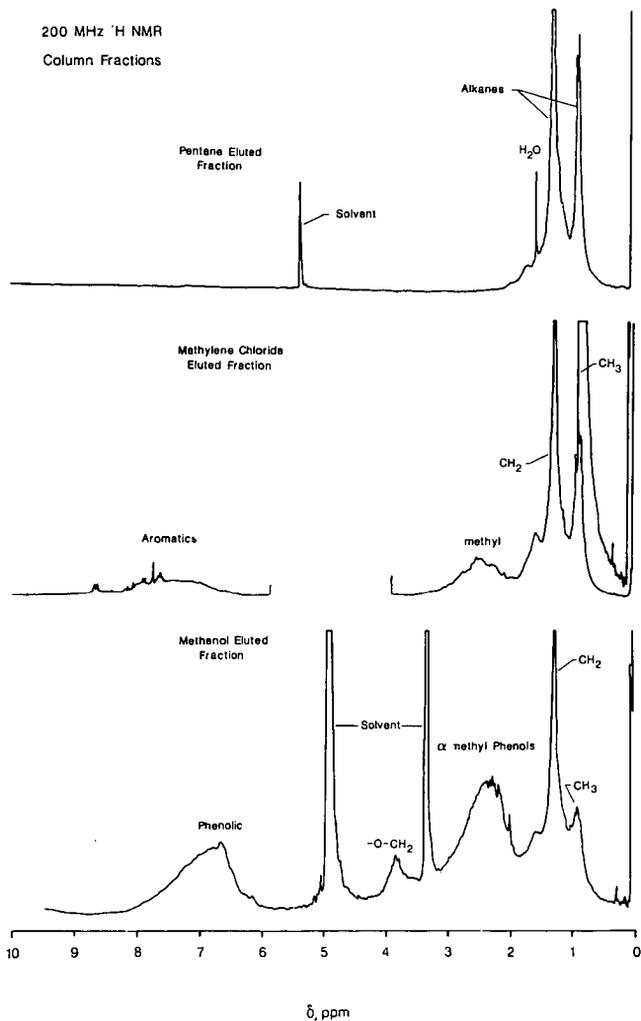


Figure 5. 200 MHz proton NMR of three fractions of a supercritical water extract obtained at 380°C and 3265 psia.

REACTIONS OF COAL AND COAL MODEL COMPOUNDS WITH SUPERCRITICAL WATER

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INTRODUCTION

We recently reported on the successful replacement of recycle solvent by water in conventional coal liquefaction, with and without added hydrogenation catalyst precursors (1). High coal conversions (as measured by THF solubilities) were obtained at modest temperatures (370°-385°) with the use of little or no organic recycle solvent and short reaction times (5-30 minutes).

Water has been used in the past in the liquefaction or the extraction of coal for a variety of reasons. When used in combination with carbon monoxide and a suitable catalyst, water was a source of hydrogen for the reduction of coal (2,3). Appell and co-workers frequently used an organic solvent in combination with water in these studies.

Liquefaction under carbon monoxide has also been carried out by Ross and colleagues (4,5) with slurries composed of coal and either water or aqueous base without an organic solvent. In some cases, Ross has used water to carry dissolved metal salts as homogeneous catalysts as well as a liquefaction medium (6), but still in the presence of carbon monoxide as the reducing gas.

In comparison with conventional organic liquefaction solvents, Stenberg et al. have shown water to be quite effective when used in combination with H₂S, in particular under synthesis gas rather than hydrogen (7).

Aqueous liquefaction using impregnated catalysts has also been combined in a single operation with supercritical water distillation to separate the oil and asphaltene from the coal char residue (8). Barton's results clearly show that the liquids produced by hydrogenation can be extracted by supercritical water and transported away from insoluble coal residues.

Wender and co-workers have also shown that the simple treatment of coal with supercritical water in the absence of hydrogen or catalyst renders a substantial portion of the treated coal extractable by THF after the product was cooled and recovered from the autoclave (9). The amount of extract obtained depended on the density of the supercritical water. Higher yields were obtained when coal was injected into supercritical water, thus providing a rapid heat-up of the coal, than when a coal-water slurry was heated to operating temperature.

In addition to the physical role of water reported by Wender, it has also been reported that water may directly participate as a reactant in the thermolytic chemistry of certain model compounds. In the presence of water, dibenzyl ether decomposed at 400° C by both pyrolytic and hydrolytic pathways, the latter leading to the formation of benzyl alcohol (10).

The removal of nitrogen from heterocyclic compounds, such as isoquinoline, was also reported to be accelerated in the presence of supercritical water (11).

Taken together, these previous studies by other researchers indicate that under various conditions, supercritical water may act as a good liquefaction medium, dissolve or extract coal-derived liquid products, promote the cleavage of certain bonds likely to be found in coal, provide hydrogen through the water-gas shift reaction, and possibly assist the contracting of coal with catalysts or hydrogen.

Though these reports suggest a rich and varied chemistry in liquefaction with water, fundamental studies with models has received inadequate attention. The objective of this study was to initiate an investigation into the organic reaction mechanisms of coal and coal model compounds with supercritical water.

EXPERIMENTAL

A multireactor consisting of five individual microautoclaves, each of approximately 45-ml capacity and attached to a single yoke, was used to study these reactions (12). The entire assembly was immersed rapidly into a preheated, fluidized sand bath, allowing heat-up to reaction temperature in 4-6 minutes. Immersion in a second fluidized sand bath held at room temperature provided rapid quenching. The autoclaves were agitated by a rapid horizontal-shaking motion, assuring good mixing of heterogeneous, multiphase mixtures. Individual thermocouples allowed continuous temperature monitoring of each microautoclave. For all experiments reported here, the reactors, once pressurized, were isolated from the gas-handling manifold by a valve and a short length of tubing of negligible volume. This prevented loss of water from the reaction zone due to condensation in the unheated portion of the system. Separate experiments using different reactors, in which it was possible for water to migrate to unheated regions of the system, indicated that such water loss had a profound but erratic effect on measured values for pressure and coal conversion, and generally led to misleading data.

The pressure at reaction temperature was not measured directly in these experiments. The partial pressure of water was estimated using van der Waal's equation.

Table 1 gives the analyses of the Illinois No. 6 (River King Mine) bituminous coal and process derived solvent (SRC II). The conversion values were obtained by the centrifugation method described earlier (1).

Model compound experiments were performed in the identical reaction apparatus. Any product gases were uncollected. The reactors were washed out with dichloromethane (Fisher; ACS certified) and the aqueous layer removed. The organic layer was filtered through a sintered glass funnel, with subsequent analysis by capillary gc/ms (Hewlett Packard model 5790A gas chromatograph equipped with a Hewlett Packard model 5970A mass selective detector). Mass spectral ionization currents and gc parameters were identical in the analysis of standards and reaction products.

All model compound experiments were reacted at 385° C for 30 minutes. A 1200 psig cold charge of H₂ was employed in each experiment utilizing molecular hydrogen. The bibenzyl reactions used 2.5g (0.014mol) bibenzyl (Aldrich) and 1.8g (0.09 mol) deuterium oxide (Aldrich, gold label). The biphenyl experiments also employed 2.5g (0.016 mol) biphenyl (Aldrich) and 1.8g D₂O. The reactions with 4-benzylphenol (Chemical Sales Co.), dibenzyl ether (Aldrich) and benzyl ethyl ether (Pfaltz & Bauer), used 0.92 (0.005 mol), 0.99g (0.005 mol), and 0.68g (0.005 mol) respectively, and 4.0g D₂O in each reactor.

RESULTS AND DISCUSSION

I. Bituminous Coal Studies

Inverse isotope effects has been observed by Appell (13) and Ross (14) when water was replaced with D_2O in coal liquefaction. Appell observed an enhanced conversion of nearly 6% when D_2O was utilized in place of water with hexahydropyrene (HHP) as a solvent. A significant enhancement was similarly observed by Ross through substitution of water by D_2O in his use of CO/water systems without a solvent. Ross has attributed this phenomenon to a phenol-keto equilibrium followed by hydride transfer from formate to coal moieties in a Michael sense. The inverse isotope effect, in Ross' argument, results from the fact that the formate reaction with water experiences a normal isotope effect and is therefore slowed in D_2O , consequently enhancing the stability of active formate by precluding the termination reaction to CO_2 and H_2 , which he suggests rapidly prevails under these conditions.

Ross further contends that all coal liquefaction reactions can be viewed along similar lines. Donor solvent liquefaction, in his concept, results via hydride transfer from hydroaromatic compounds to effect reductions of quinones and/or semiquinones with subsequent elimination of substituent groups.

If the mechanism of liquefaction is indeed ionic, water may be envisioned as a polar solvent, resulting in a lowering of the transition state energy via solvation and correspondingly increased conversions. With this discussion in mind, we undertook two sets of experiments, each comparing H_2O with D_2O . The first was essentially a repeat of Appell's experiment with minor variations. Tetralin was employed as the solvent and a higher hydrogen charge was utilized. In an attempt to enhance the ionic character of these reactions, 2mmol of Cs_2CO_3 was added to the water. Ross had utilized the observed catalytic effect of bases in his reactions as a major argument for his proposal of an ionic mechanism. Cs_2CO_3 was chosen since Cs has been reported as the most mobile of the Group IA metals in the gasification of coals (15) and we wished to circumvent, as far as possible, any anomalies from selected ion exchange.

The conversions obtained were identical, within experimental error, as illustrated in Table 2 (68-70 wt. %). Clearly, under these conditions, no isotope effect is evident. It is significant that Appell's work, at much lower hydrogen pressure and 5 fewer minutes residence time, resulted in dramatically higher conversions (84-90 wt. %). The greater ease of hydrogen abstraction from HHP than tetralin is dramatically evidenced by these results. These results do little, however, to support the role of water as reactant in our systems, or an ionic mechanism for liquefaction in general.

If one accepts the arguments of Ross, molecular hydrogen should play no kinetic role in coal conversion. Elimination of hydrogen in favor of the polar solvent water should therefore enhance overall conversions. In this regard, we undertook four experiments, in the absence of molecular hydrogen, as illustrated in Table 3. Comparison of H_2O and D_2O with added KOH as a catalyst and tetralin as a solvent resulted in slightly lower conversions for the D_2O than H_2O experiments. More significantly, the conversions were considerably lower than those observed in Table 3 where less water, but molecular hydrogen was present. Clearly, molecular hydrogen plays a dominant role even when experimental conditions favor an ionic pathway. Since it is difficult to envision an ionic mechanism for the role of molecular hydrogen in liquefaction, such observations are inconsistent with a general ionic mechanism for

liquefaction and support the free radical hydrogenolysis mechanism proposed by Vernon (16).

Further evidence refuting not only an ionic mechanism, but the role of water as a reactant as well, can be found in comparison of Experiments 5B and 5C. Removal of the KOH catalyst and reduction of water by a factor of two resulted in no appreciable change in conversion.

A change in solvent from tetralin to SRC II, however, gave a dramatic decrease in conversion. Such an effect may be easily attributed to a lower number of hydrogen atom donors in SRC II when compared to tetralin. The significant role of such donors in water assisted liquefaction, regardless of the liquefaction mechanism, is clearly evident from these experiments.

2. MODEL COMPOUND STUDIES

In Appell's experiments with coal (13), the incorporation of deuterium into coal derived hydrocarbons, pyrene, and HHP was noted. Ross noted a lack of correlation between exchange and conversion in his study (14). Though his results suggested to Appell that water was a reactant under his conditions, these results could also be explained by an initial low temperature exchange of phenolic hydroxyls with D_2O , followed by higher temperature deuterium atom transfers between these now deuterated phenols and hydrocarbon radicals.

If our proposed explanation is operative, the use of O-alkylated coals could circumvent the low temperature exchange. Observation of deuterium exchange in coal products derived from such a coal may then indicate true reaction chemistry. Hydrolysis of the methyl ether of guaiacol by supercritical water was observed by Paulaitis, however. If the hydrolysis of methyl ethers is general and ionic in supercritical water, as their work with guaiacol would indicate, the formation of phenols from these hydrolysis reactions may also lead to exchange. Such an occurrence would invalidate our arguments for the experiments with O-alkylated coal.

Further, the hydrogenolysis of anisole, as reported by Friedman (17), may also indicate a reaction pathway by which phenols, protected as methyl ethers, could react in what is essentially an exchange reaction. If the phenoxyl radical initially formed from anisole is reduced to the phenoxide ion, such exchange may occur. The observation of cresols in Friedman's work, however, would tend to indicate that such is not the case.

We attempted to address both concerns via the reaction of several model compounds with D_2O in the presence and absence of molecular hydrogen.

Significant exchange between bibenzyl and D_2O was observed only upon the introduction of molecular hydrogen to the system. Exchange was not observed with biphenyl either in the absence or presence of molecular hydrogen. These results suggest that H-atoms produced from the hydrogenolysis of bibenzyl reacted with the large molar excess of D_2O to produce HD and hydroxyl radicals. Once HD was formed, incorporation of deuterium into a variety of products would be expected. The hydroxyl radical could then be capped by a variety of species, including molecular hydrogen in what would amount to a chain reaction.

There was no evidence for the observation of hydroxylated products in the total-ion-chromatograph (TIC) of the dichloromethane soluble fraction. The aqueous fraction was unanalyzed.

The TIC of the dichloromethane soluble products from the reaction of benzyl ethyl ether indicated only alcohol-d exchanged benzyl alcohol. There was no evidence in the mass spectra for incorporation of deuterium into any C-H bond. The hydrolysis appeared complete. It is important to note that molecular hydrogen was unempoyed in this experiment.

Analysis of the TIC from the organic fraction of the similar reaction with dibenzyl ether indicated only unexchanged reactant. Benzyl alcohol was not observed.

Analysis of the dichloromethane soluble products from the reaction of 4-benzyl phenol with deuterium oxide in the absence of molecular hydrogen is most intriguing. Only 4-benzyl phenol was observed in the TIC, however, massspectral analysis indicated the major product to be doubly labeled. Fragment ions clearly illustrate the incorporation of deuterium into C-H bonds.

Taken together, these results suggest electrophilic aromatic substitution between the activated phenol and a hydronium ion-d₃. Activation of the aromatic ring was insufficient with the other models to effect such exchange.

Additional experiments are currently underway in our laboratory to further substantiate this hypothesis. The possibility of similar reaction between coal and water would be easy to support. Coal would be expected to possess structural units with relatively low energy as carbocation leaving groups through substitution by a proton in water. Such moieties would include carbocations with the possibility of resonance stabilization by an aromatic system (e.g., benzyl carbocation), alpha to an ether oxygen (similar to those discussed by Larsen (18)) or carbonyls (e.g., decarboxylation).

Should additional model compound studies support the feasibility of similar reactions between water and coal, the observed enhanced yields from liquefaction with water may, at least partially, be attributed to the ipso substitution of a proton for a substituent on an aromatic moiety in coal.

This suggestion in no way presupposes that electrophilic aromatic substitution is the only mechanism operating in liquefaction. It may, however, indicate a dormant reaction pathway under the traditional donor solvent liquefaction conditions, which now contributes to the overall production of liquid products, thus the apparent increase in yield. The solvation effect of supercritical water in promoting these possibly new ionic pathways in aqueous liquefaction is currently under investigation in our laboratory.

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TABLE 1. ELEMENTAL ANALYSES OF COAL AND VEHICLES.^a

<u>Material</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>O</u>	<u>S</u>
Illinois No. 6 Coal, River King Mine ^b	73.7	5.6	1.5	14.8	4.5
SRC-II Distillate	87.1	8.0	1.4	3.0	0.4

^a wt.%, daf basis, Huffman Labs, Wheatridge, Colo.

^b Moisture-free ash content was determined to be 13.6 wt.% for the River King Coal. As used, the coal contained 3 wt.% water.

Table 2. Comparison of H₂O and D₂O as Vehicles Under Water Assisted Liquefaction Conditions¹

<u>Ex. #</u>	<u>Vehicle</u>	<u>Conversion²</u>
4A	H ₂ O	68
4B	D ₂ O	70

¹ Reaction Conditions: 4.00 g River King Coal; 1.70 g H₂O or D₂O; 1.50 g tetralin; 1200 psig H₂ (cold); 385°C; 20 mins. at temp.; 2 mmol Cs₂CO₃ added via the water.

² DAF basis; average of duplicate runs; reproducibility ± 1 wt. %.

Table 3. Aqueous Liquefaction Without Molecular Hydrogen¹

Ex.#	Vehicle	Solvent ²	Catalyst ³	Est. Reaction ⁴ Pressure	Water ⁵ Density	THF Conversion ⁶
5A	D ₂ O (22 mmol)	Tetralin	KOH (8 mmol)	4350	0.110	42
5B	H ₂ O (22 mmol)	Tetralin	KOH (8 mmol)	4350	0.097	45
5C	H ₂ O (9 mmol)	Tetralin	-----	1790	0.043	46
5D	H ₂ O (9 mmol)	SRC II	-----	1790	0.043	26

¹ Reaction Conditions: 4.00 g River King Coal; 385° C; 40 minutes at temperature

² 1.50 g per reactor

³ as an aqueous solution

⁴ as calculated by van der Waal's Equation does not include solvent contributions

⁵ g/cc

⁶ DAF basis; average of duplicate runs; reproducibility ± 1 wt. %

REACTIONS OF LOW-RANK COALS IN SUPERCRITICAL METHANOL

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Supercritical fluid extraction of coals has been investigated as a promising method for the production of liquid fuel products from coal under mild conditions. Studies with alcohols as the supercritical fluid have recently been reported (1, 2, 3, 4). Alcohols would be expected to exhibit greater solubility for polar organic molecules, because of hydrogen bonding or dipole attractive forces; they also provide the opportunity for chemical reactions during the extraction, because of the nucleophilicity of the alcohol oxygen and the tendency to act as a hydrogen donor. Alkylation reactions can also occur. Chen and coworkers have shown that sulfur compounds were removed selectively in supercritical methanol and ethanol extractions (4). This potentially useful application may involve reaction of the alcohol with some of the organosulfur moieties and possibly pyrite in the coal. The exact mechanism of the sulfur removal reaction is unknown. Earlier workers used alcohols at very high temperatures (460-600°C) (5) or in combination with sodium hydroxide (6).

As a part of our study of the interaction of supercritical solvents with low-rank coals, a series of extractions of lignites and subbituminous coals were performed with supercritical methanol in a semicontinuous extraction apparatus. These studies were concerned with establishing yield and conversion data for several coals at various supercritical conditions. Not only can the solvation power of the solvent (which depends on the fluid density) be conveniently controlled over a large range with changes in solvent pressure or temperature, but the rates of chemical reactions occurring in and with the solvent may also be controlled by the wide variation in viscosity and density which are obtained with supercritical fluids.

Experimental

Supercritical methanol extractions were performed using the semicontinuous processing unit described earlier (7). Methanol solvent was pumped through the fixed coal bed (50 g of dried coal) at 120 ml/hr for 2 hr. The pressure of the supercritical solvent was reduced to atmospheric pressure after passing a back pressure regulator. The extract and solvent were collected in a chilled sample vessel. The noncondensable product gas was measured and collected for subsequent GC analysis. Both the solvent-extract mixture and the extracted coal residue were rotary vacuum distilled to give a moisture and methanol free product. Extracts were analyzed by a number of methods including extraction into base, HPLC and ¹H-NMR of methylated (diazomethane) samples and GC for quantitative determination of individual phenols and carboxylic acids. The phenol analysis involved addition of 2-fluorophenol as an internal standard, extraction into base to remove hydrocarbons and amides, addition of acid and extraction into chloroform, Kuderna-Danish evaporation of the chloroform and GC analysis on a calibrated 60 m DB5 capillary column (FID). Photoacoustic spectra of the coal residues were obtained using a cell obtained from MTEch Photoacoustics with a Nicolet 205XB spectrometer. Thermogravimetric analyses of the coal residues were obtained using a Cahn 2000 thermobalance with an argon atmosphere and a 20°C/min temperature ramp.

Results and Discussion

Effects of Temperature and Pressure on Yields

Table 1 summarizes the operating conditions and the experimental results obtained for the supercritical methanol extractions. A series of runs at 250 C using Indian Head lignite was performed at pressures ranging from 1233 psia to 2935 psia ($P_r = 1.05$ to 2.5). The conversions (weight loss on a maf basis) were found to increase with increasing pressure (i.e. from 4.3 to 6.1 %), while the extract yields (weight of extracted material recovered on an maf basis) increased from 1.8 to 4.4% respectively. This increase in extract yields with pressure can be attributed to change in solvent density. Figure 1 is a plot of the effect of calculated solvent density on the extract yields from Indian Head lignite.

A series of isobaric experiments were performed at 2348 psia ($P_r = 2.0$) with temperatures at 250, 275, 300 and 350°C using several coals. The conversion and extract yields all increased significantly with temperature, however, at the higher temperatures the extract and gas yields become significantly higher than the actual weight loss of the original coal. This net yield of products suggests that the methanol is being incorporated into the products by reacting with various groups in the coal and extract components and also being converted to gas, which contains large amounts of methane.

Table 1. Operating Conditions and Results from the Extraction of Various Coals with Supercritical Methanol. See Table 3 for coal analyses. Reduced temperature (T_r) and reduced pressure (P_r) are the ratios of temperature and pressure to supercritical temperature and pressure.

Coal	Temp. (°C)	T_r	Pressure (psia)	P_r	Calc. Solvent Density (g/ml)	Pct. Conv. (maf)	Pct Yield, maf	
							Extract	Gas
Indian Head	250	1.021	1233	1.050	0.134	4.27	1.76	2.25
Indian Head	250	1.021	1468	1.250	0.295	4.98	2.86	2.05
Indian Head	250	1.021	1761	1.500	0.368	4.17	3.05	1.36
Indian Head	250	1.021	2348	2.000	0.412	5.49	3.80	1.66
Indian Head	250	1.021	2935	2.500	0.434	6.13	4.43	2.23
Indian Head	275	1.069	2348	2.000	0.320	8.20	3.88	3.67
Indian Head	300	1.118	2348	2.000	0.224	9.55	4.74	6.91
Indian Head	350	1.216	2348	2.000	0.144	23.30	12.43	22.04
Wyodak	250	1.021	1233	1.050	0.134	1.56	3.08	0.70
Wyodak	250	1.021	2348	2.000	0.412	4.16	6.33	0.65
Wyodak	300	1.118	1233	1.050	0.079	2.73	11.28	3.49
Wyodak	300	1.118	2348	2.000	0.224	6.17	6.59	3.10
Wyodak	350	1.216	1233	1.050	0.063	14.74	12.39	21.60
Wyodak	350	1.216	2348	2.000	0.144	17.55	23.29	22.61
Deer Creek	250	1.021	1233	1.050	0.134	0.20	4.02	0.37
Deer Creek	250	1.021	2348	2.000	0.412	10.11	10.50	0.16
Deer Creek	300	1.118	2348	2.000	0.224	7.99	8.69	0.75
Deer Creek	350	1.216	2348	2.000	0.144	11.79	13.69	5.17
Martin Lake	250	1.021	2348	2.000	0.412	3.95	5.57	0.69
Martin Lake	300	1.118	2348	2.000	0.224	5.60	6.64	1.93
Martin Lake	350	1.216	2348	2.000	0.144	18.24	17.54	19.88

Composition of the Extracted Material

The composition of the extract obtained from each of the coals varied substantially with the increase in temperature of the extraction with supercritical methanol. The extracts contained the waxy material (alkanes and long chain fatty acids) which were also present in the hydrocarbon extracts of these coals (7). In addition, the methanol extractions contained phenolics, anisoles and methyl esters of mono and dicarboxylic acids. The phenolics and anisoles predominate in the extractions of Indian Head lignite which were carried out at the higher temperatures (Table 2). The methyl esters of dicarboxylic acids, such as dimethyl succinate, predominate at the lower temperature. The anisoles and methyl esters have not been found in any supercritical hydrocarbon solvent or water extraction products from coal nor in any pyrolysis products. The anisoles resulted from methylation of the corresponding phenol hydroxyl groups. The esters have resulted from esterification of carboxylic acids in the supercritical methanol; however, the dicarboxylic acids required for these reactions are produced from the coal by oxidation rather than pyrolysis. Thus the reactions for formation of esters have not been sufficiently elucidated.

Table 2. Yields of Phenols in Supercritical Methanol Extractions as Wt% of Extract Weight.

Phenol	Indian Head Lignite (1)			Wyodak Subbituminous			
	250	300	350	250 (1)	300 (1)	350 (1)	350 (2)
Phenol	.18	.44	.77	.059	.056	.066	.038
o-Cresol	.01	.36	2.02	.007	.065	.149	.132
m-Cresol	.03	.33	1.25	.024	.080	.056	.060
p-Cresol	t	.47	.45	.032	.037	.045	.030
Guaiacol	.42	1.17	1.30	t	t	.003	t
2,6-DiMePhe	t	.19	3.86	.003	.041	.435	.388
2-EtPhe	0	.05	0.43	.003	.014	.019	.022
2,4-DiMePhe	t	.41	5.57	.005	.123	.178	.199
2,5-DiMePhe	t	.04	.97	.002	.020	.041	.055
2,3-DiMePhe	.02	.32	2.37	.006	.045	.117	.116
4-MeGuaiacol	.10	.82	1.98	t	t	.035	.030
2,4,6-TriMePhe	t	.29	13.22	.001	.070	.549	.571
2,3,6-TriMePhe	t	.08	3.61	t	.024	.211	.311
4-MeOPhe	0	.01	.43	t	t	.004	.012
2,4,5-TriMePhe	t	.04	4.42	.007	.040	.092	.114
4,6-DiMeGua	t	.41	1.86	t	t	.045	.004
4-Indanol	t	.24	1.77	.003	.081	.099	.127
3,4,5-TriMePhe	t	t	.84	0	0	.004	.003
5-Indanol	t	.03	.57	.001	.014	.024	.032
2,3,5,6-TMePhe	t	.07	5.59	.003	.016	.147	.252
4-nPrGuaiacol	.02	.22	.58	0	0	.002	.009
1-Naphthol	t	.02	.28	.006	.002	.001	.003
2-Naphthol	t	.05	1.40	t	t	.019	.001

Pressures: (1) = 2348 psia; (2) = 1233 psia

Abbreviations: Phe = phenol; Me = methyl; Et = ethyl; Pr = propyl; Gua = guaiacol; MeO = methoxy; T = tetra; t = trace

Other phenols identified by GC/MS and retention time but not quantitatively determined: 6-MeGuaiacol, 3,4-DiMePhe, 3,5-DiMePhe, 4-EtPhe, 4-EtGuaiacol, 2,3,5-TriMePhe, 2,3,4,6-TMePhe, EtMePhe (5).

The distribution of phenol types found in the extracts of Indian Head lignite carried out at 250° (Table 2) was similar to that found in pyrolysis products (8); that is, large amounts of phenol and cresols, smaller amounts of virtually every type of alkyl phenol isomer, a limited series of mainly 4-substituted guaiacols and catechols (these were not quantitatively analyzed). Since the Wyodak subbituminous coal has a very small methoxy group content, corresponding to a low concentration of guaiacol groups in the coal, only traces of guaiacols were found in the low-temperature extracts. The yields of phenols from the Indian Head extractions were much higher than those from the Wyodak coal at all temperatures.

With both coals the higher temperature extractions yielded a distribution of phenols distinctly different from that obtained in the low-temperature extractions. Large increases in the yields of 2,6-dimethylphenol and 2,4,6-trimethyl phenol were especially noticeable. This is evidence for methylation of the ring carbons of the phenols which occurs mainly at the positions ortho to the hydroxyl group of the phenol. In addition to the quantities reported in Table 2 for the phenols which were included in our calibration, numerous other C₄-, C₅- and C₆-substituted phenols were identified in the 350° extracts by GC/MS. Methylation of the aromatic rings of the guaiacols and catechols was also observed to have occurred during the extraction at high temperatures; large amounts of 4,6-dimethylguaiacol, 3,4-dimethylguaiacol, 3,6-dimethylguaiacol, C₃-guaiacols, C₄-guaiacols and C₅-guaiacols were found by GC/MS. Most of the components of the product from extraction of Indian Head lignite at 250°C and most of the low molecular weight products from extraction at higher temperatures have been identified; however, many of the Wyodak extraction products are still under investigation.

The effects of pressure on the yields of phenols was investigated at two pressures, 2348 psia and 1233 psia. The data for extraction of Wyodak subbituminous coal at 350°C at these two pressures are presented in Table 2. Similar yields for each of the individual phenols are observed. The phenol yield structure is therefore dominated by temperature rather than pressure effects, consistent with the hypothesis that release of phenols from the coal matrix is controlled by activation energies for bond cleavage rather than diffusion. Density and viscosity effects on the phenol reaction products are negligible.

Comparison of residue surface groups

The residues from the supercritical methanol extraction of Indian Head lignite at three temperatures were examined using photoacoustic spectroscopy to determine the changes in functional groups on the surface which result from extraction and reactions of the lignite with the solvent. The spectra for the original dried lignite and three residues are shown in Figure 2. The broad carboxyl OH stretching band extending from 3500 to 2000 cm⁻¹ progressively decreases with samples of increasing extraction temperatures, corresponding to conversion of the carboxylic acids to methyl esters or to decarboxylation. The carbonyl stretching band in the original lignite at 1695 cm⁻¹ is changed to 1717 cm⁻¹ (with shoulder at higher wave number) in the 250° and 300°C extracts, also indicating the conversion to the ester. The carbonyl band decreases somewhat and exhibits a peak at 1730 cm⁻¹ in the 350°C extract, which indicates further conversions. The intensities of the methyl absorptions at 2960 and 1455 cm⁻¹ increase significantly with the extraction temperature. These changes in vibrational bands of the surface groups are consistent with the alkylation which has occurred during the extraction with supercritical methanol.

Thermogravimetric data obtained with the extracted coal residues indicate that the supercritical methanol extracts a significant portion of the compounds which would have normally volatilized in the 200° to 400°C range. These curves also exhibit the effect of methylation of oxygen groups which thermally decompose at temperatures above 400° resulting in release of additional products.

Table 3. Proximate and Ultimate Analyses of Coal Samples Used in Experiments.

	<u>Wyodak</u>	<u>Deer Creek</u>	<u>Gascoyne</u>	<u>Indian Head</u>	<u>Martin Lake</u>
<u>Proximate Analysis</u>					
Volatile Matter	43.5	42.0	40.1	43.8	42.2
Fixed Carbon (by diff)	50.0	47.2	41.2	48.0	42.8
Ash	6.5	10.8	18.6	8.5	15.0
<u>Ultimate Analysis</u>					
Hydrogen	4.26	5.66	3.93	4.74	0.32
Carbon	64.62	71.21	57.56	66.20	61.88
Nitrogen	1.01	1.27	.87	.96	1.23
Sulfur	.58	.36	1.76	.72	1.17
Oxygen (by diff)	23.04	10.70	17.28	19.19	20.40
Ash	6.5	10.8	18.6	8.2	15.0

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Acknowledgment

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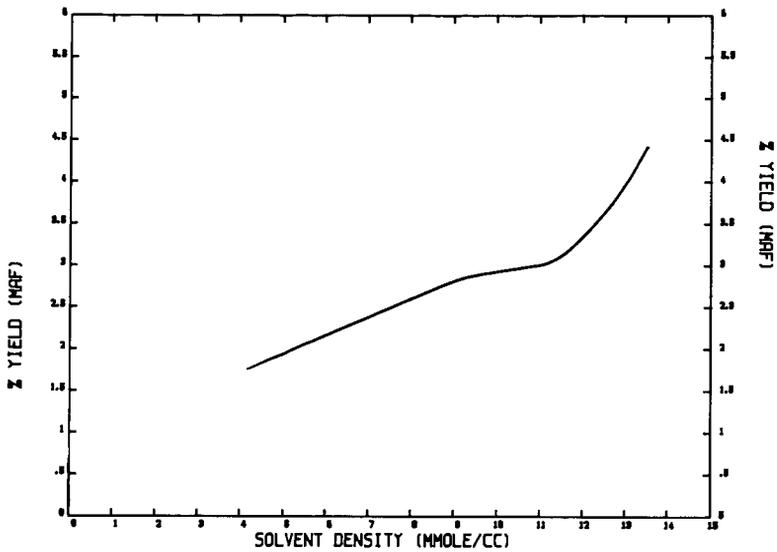


Figure 1. Plot of extraction yields from Indian Head lignite versus solvent density of methanol at 250°C.

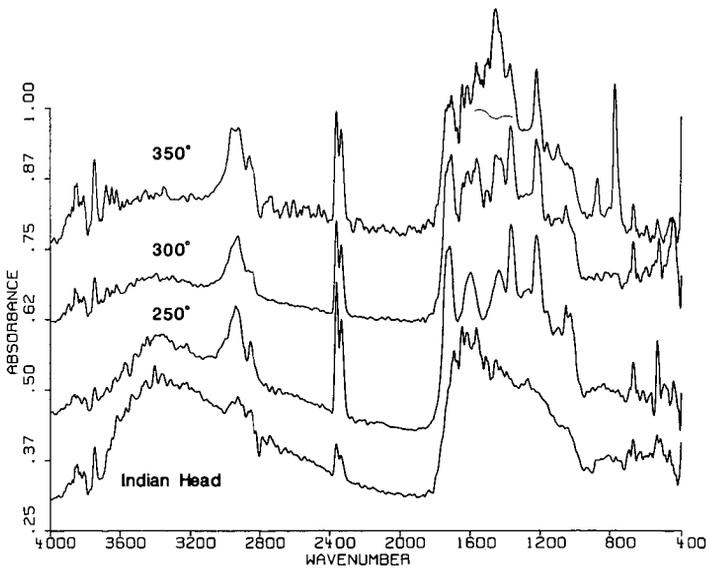


Figure 2. Photoacoustic spectra of dried Indian Head coal and residues from supercritical methanol extraction.

THE CHEMCOAL PROCESS
FOR
LOW TEMPERATURE CONVERSION

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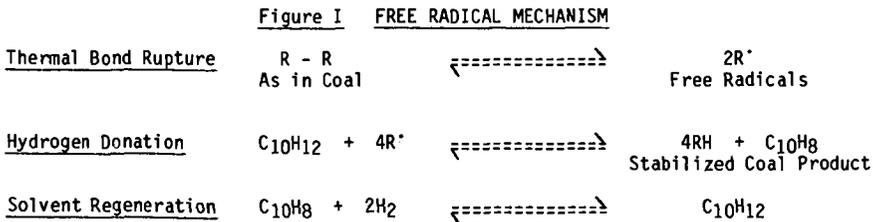
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INTRODUCTION

The ChemCoal Process utilizes chemical means to transform coal and other carbonaceous materials to solid, liquid, and slurry products. The process uses coal-derived solvents and aqueous alkali to dissolve and breakdown carbonaceous materials. Carbon monoxide is used to generate hydrogen via the water gas shift reaction to cap organic species. Insoluble sulfur and ash impurities are separated from the soluble organic fraction. Recycle solvent, light oils, alkali, and water are extracted from the soluble fraction and preasphaltenes (PA) and asphaltenes (A) are precipitated by the addition of methanol. The precipitated PA and A, the ChemCoal solid products, have been slurried and used in a diesel engine. The methanol fraction is processed to recovery recycle solvent, alkali, water, light oils, and methanol. The process has been evaluated under continuous process operation at the University of North Dakota Energy Research Center (UNDERC). A 10 TPD demonstration plant is proposed and will be sited near Powhatan Point, Ohio.

CLASSICAL THERMAL PROCESSES

Classical direct coal liquefaction processes involve high temperature thermal treatment of coal to rupture chemical bonds producing free radical coal fragments. The free radical fragments are stabilized by capping with hydrogen of a coal-derived solvent usually represented as Tetrahydrodecalin (THD), C₁₀H₁₂. This is represented as Figure I.



The classical process requires temperatures and pressures of approximately 425°C and 2500 psig. In the SRC process thermal bond rupture, hydrogen donation and solvent regeneration are carried out simultaneously in the liquefaction reactor. The hydrogen gas treatment rate may be 20,000 SCF/ton of coal feed with a consumption of 4,000 SCF/ton of coal.

Competing free radical reactions, not shown in Figure I, can occur resulting in recondensation of the free radical coal fragments and degradation of the hydrogen shuttle species. Hydrogen shuttle species are converted to degradation spe-

cies which do not lend themselves to regeneration. Conditions which favor the hydrogen donation reaction do not necessarily favor solvent regeneration. The EDS process attempts to overcome the solvent degradation and regeneration limitations by use of a separate catalytic regeneration reactor.

IONICALLY-AIDED CONVERSION

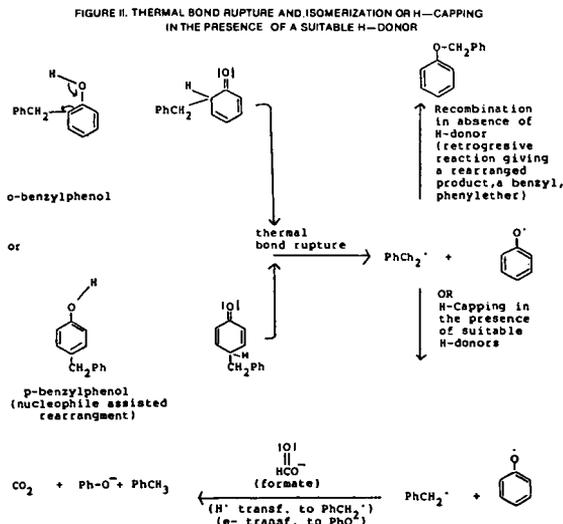
The chemical transformation of coal, by the ChemCoal Process, may make use of ionic chemistry while benefiting from low temperature thermal bond rupture mechanisms. Ionic reactions are represented in Figure II.

ChemCoal Process mechanisms may benefit from both ionic and thermal processes. The keto form of the *o*-(hydroxyphenyl)phenylmethane, OPPM, shown in Figure II is more easily formed into toluene and phenol than the enol form. The C-C bond shown by 'x' in II decreases in strength from 86 to 46 kcal/mol. This decrease in bond strength, due to a shift from sp^2-sp^3 to sp^3-sp^3 bondings as well as its allylic position with respect to the oxygen atom, is correlated to a decrease in activation energy over unassisted bond cleavage. The major effect of a nucleophile such as PhO^- is to facilitate proton transfer in keto/enol tautomerisms. The bond may then be broken homolytically at a lower temperature. Keto-enol tautomerisms may be ionically aided leading to the low temperature thermal bond rupture.

The role of the PhO^- and formate mechanism in the ChemCoal Process has been reported by Porter and co-workers.⁽¹⁾ The role of oxygenates on hydrocarbon bond dissociation has been reported by McMillen and co-workers.⁽²⁾⁽³⁾⁽⁴⁾

In the ChemCoal Process the transformation of coal is achieved at about 325°C and 1250 psig in the presence of phenolics, added alkali and water, and carbon monoxide. The requirement for tetralin or other hydrogen shuttles does not exist. Hydrogen plays a part in the conversion but an external source of hydrogen is not required, as the hydrogen is supplied from the water and CO.

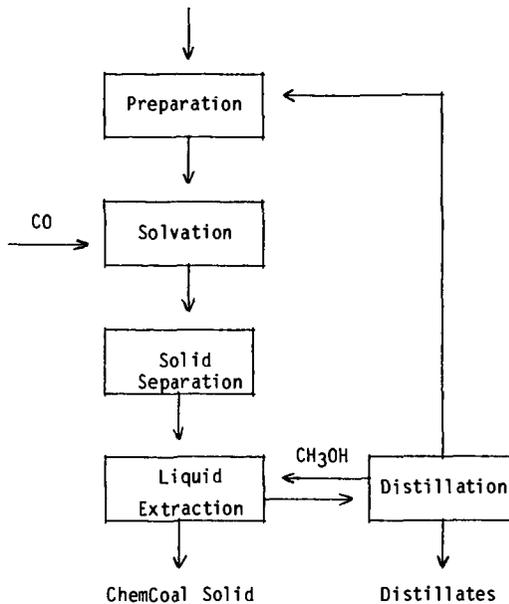
Under the ChemCoal processing conditions, the water gas shift reaction (WGSR) is promoted. It has been observed in the laboratory that those conditions which promote the WGSR do not necessarily promote transformation of coal. Therefore, it is assumed that there is a competing reaction but the presence of hydrogen and the formate ion are beneficial.



PROCESS DESCRIPTION

The ChemCoal Process involves the following five steps shown in Figure III:

Figure III ChemCoal Process Schematic



Preparation:

The coal is crushed and mixed with recycle solvent.

Solvation:

The coal slurry is heated to about 325°C in the presence of syngas at approximately 1250 psig. The preheater and reactor design incorporates a slow heating rate and a means to maintain S/C ratios in the reactor.

Solid Separation:

The slurry is centrifuged to remove the solids.

Liquid Separation:

The filtrate is treated with methanol to extract phenol, water, and alkali. The ChemCoal solid precipitates and is separated from the liquid phase.

Distillation:

The liquid phase is distilled to recover methanol, distillates, and recycle solvents.

PROCESS RESULTS

Table I summarizes the ultimate analysis of three ChemCoal Process coal-derived solid products. It is important to note that the coal-derived products are similar to No. 2 and No. 6 fuel oil in terms of sulfur, nitrogen, and ash content.

Table I ChemCoal Product Analyses Compared to Fuel Oils

Coal Rank: Source:	Lignite No. Dak.	Bituminous Ohio No. 6	Fuel Oil No. 6	Fuel Oil No. 2
Ash	0.19	0.12	0.01- 0.5	Nil
Carbon	83.5	86.06	86.5 -90.2	86.1-88.2
Hydrogen	6.41	6.11	9.5-12.0	11.8-13.9
Nitrogen	0.92	1.23	2.0	0.2
Sulfur	0.25	0.41	0.7- 3.5	.05- 1.0
Oxygen (diff)	8.73	6.07	2.0	Nil
HHV (Btu/lb)	15,400	15,700	17,400-19,000	19,000-19,750
1b Ash/MMBtu	0.115	0.076	0.005-0.30	Nil
1b SO ₂ /MMBtu	0.32	0.52	0.75-4.0	05.1.0

Other ChemCoal Product Properties (typical):

Autoignition Temperature 1100, \pm 30°F

Equilibrium Moisture 0.9%

Specific Gravity 1.03

Also of concern in the processing of coal is the sulfur and ash content of the products. Results obtained from a series of coals are summarized in Table II which shows that the products are very low in ash and sulfur content. In the case of an Eastern coal from the Sunnyhill Mine in Ohio (Ohio No. 6 seam), it is seen that the sulfur and ash content are reduced from 2.11 weight % to 0.41 weight % and 10.5 weight % to 0.12 weight %, respectively. In the case of the Western low-rank coal from the Indian Head Mine (Zap seam) of North Dakota, the sulfur and ash are reduced from 1.18 weight % to 0.25 weight % and 12.93 weight % to 0.19%, respectively.

Table II ChemCoal Process Results

Feedstock: Identification:	Coal Feed ^a		ChemCoal Product ^a		Percent Reduction	
	Sulfur	Ash	Sulfur	Ash	Sulfur	Ash
Ohio No. 6 (Sunnyhill)	2.11	10.5	0.41	0.12	80.6	98.9
North Dakota Lignite (Indian Head Mine)	1.18	12.93	0.25	0.19	78.8	98.1
Colorado Wadge (Energy Fuels II)	0.51	8.56	0.23	0.03	54.9	99.6
Texas Lignite (Big Brown)	0.85	14.10	0.07	0.07	91.8	99.5

^a Weight percent, on a moisture-free basis.

CONTINUOUS PROCESS UNIT (CPU) OPERATION

A continuous process unit was operated at UNDERC under the ChemCoal processing mode. The unit is depicted schematically in Figure IV(5). Table III summarizes the operating conditions for the CPU test on an Indian Head Lignite. The CPU operated for 40 recycle passes. During passes 30-39, GC/MS data indicated the recycle solvent was approximately 95% coal-derived from the process.

Table IV summarizes the results from the recycle test. The results confirmed earlier batch conversion data, established operability of the process, and solvent balances.

FIGURE IV
The ChemCoal CPU Scheme

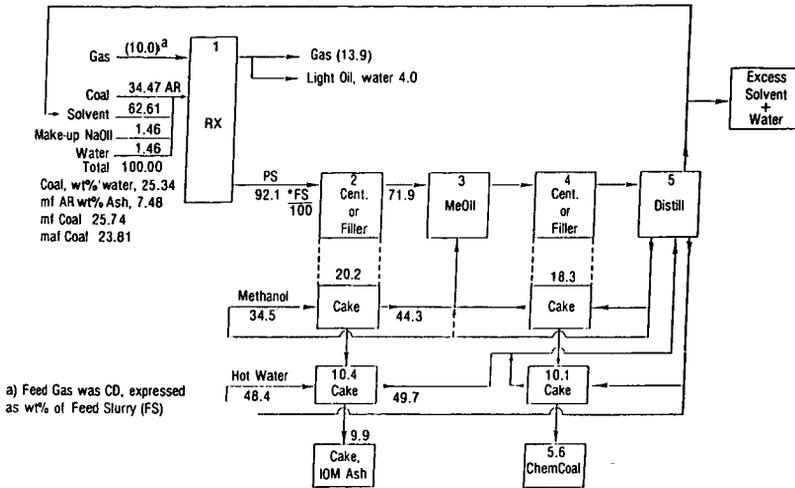


FIGURE 2.4. Developing Stream Data as wt% of Feed Slurry

Table III ChemCoal Recycle Test - Operating Conditions
Indian Head Lignite

- 1.8 solvent-to-coal ratio (2.5 lbs/hr)
- Alkali at 6% of MAF coal
- Preheater/reflux -- 250°C/1800 psi
- Reactor/reflux -- 340°/1800 psi
- Syngas feed before reactors (7 SCFH)
- MEOH addition to PPT ChemCoal solids
- Centrifuge -- solids removal
- Distillation -- 19" VAC/100°C

Table IV ChemCoal Recycle Test - Results
Indian Head Lignite

- System operable for 40 recycle passes
- Solvent balance achieved
- Conversions -- ≈ 85% MAF coal
- Reductant consumption (CO) in H₂ equivalents ≈ 1.5% MAF coal
- Gas make -- ≈ 2.0% MAF coal
- PA and A yield -- 50% MAF coal
- Distillate yield -- 30% MAF coal

DEMONSTRATION PLANT

An overall block flow diagram of a conceptual 10 TPD ChemCoal demonstration plant is shown in Figure V. A brief description of the processing steps is given in the following paragraphs.

The coal is received from storage, crushed and ground to 80% minus 200 mesh. The coal is then mixed with two parts of process-derived recycle solvent to one part coal and an amount of aqueous alkali.

The slurry mix is pumped to about 1500 psig through a heater/preheater/reactor system. In the presence of carbon monoxide, coal solvation occurs at about 340°C.

The reactor effluent mixture (gas, liquid, and solids) is separated in a phase separator. Residual liquids are condensed from the gas stream and returned to the liquid slurry streams. The gases are flared and scrubbed to remove noxious species.

The slurry stream is processed through a centrifuge to remove solids. The filter cake (centrifuge solids) is washed to recover process solvent constituents, which are returned to the process. The cleaned cake is rendered inert by heat treatment (pyrolyzed), all liquids returned to the process, and all gases (not shown) flared and scrubbed.

The filtrate (centrifuge liquids) are contacted with a recycle methanol stream. The ChemCoal solid product (coal-derived preasphaltenes and asphaltenes) precipitates when contacted with methanol. The precipitate is removed by centrifugation, washed, and stored for subsequent product testing. The liquid stream is distilled to recover recycle solvent, coal-derived distillate, and methanol.

ChemCoal Associates, a joint teaming arrangement between Carbon Resources, Inc., CRI Associates, Limited, and The North American Coal Corporation is planning to design, construct, and operate a demonstration plant at a facility near Powhatan Point, Ohio. The University of North Dakota Energy Research Center and the MK-Ferguson Company of Cleveland, Ohio are assisting ChemCoal Associates in this effort.

ACKNOWLEDGEMENTS

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THE DIRECT USE OF NATURAL GAS IN COAL LIQUEFACTION

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The main objective in coal liquefaction is to convert coal into a better fuel that is easier to transport and cleaner to burn. During the liquefaction process, the macromolecular network of coal substance is broken into smaller units and rearranged into lighter products of reduced molecular weight. More specifically, the chemical conversion of coal involves an upgrading in its hydrogen content or in other words, increasing the H/C ratio.

In liquefaction, this is achieved by rapidly heating coal, slurried in a hydrogen donor vehicle, to temperatures of 350-500°C for considerably long residence times. The slurry vehicle serves both as a dispersant as well as the reactant. The commonly employed slurry vehicles contain partly saturated structures such as tetralin. The importance of the vehicle was recognized by Fischer in 1937⁽¹⁾ and the role of hydrogen transfer from vehicles to coal was discussed by Curran et al.⁽²⁾ Recently Neavel studied the hydrogen transfer process in much more detail.^(3,4) In these interesting studies, he found that during initial stages of liquefaction, very little hydrogen is required to stabilize the free radicals generated from coal; however, during the later stages - when more benzene-soluble products are formed - each successive increment of benzene-soluble material required more hydrogen than the previous increment. For example, the incremental conversion from 40 to 50% consumed 0.23 parts by weight of hydrogen, whereas the same 10% conversion increment from 80 to 90% consumed 0.8 parts by weight of hydrogen. Thus, the hydrogen transfer and hence hydrogen requirement is found to increase exponentially with coal conversion.

The hydrogen required has to come either from the coal itself or it must be supplied from an external source, e.g. the slurry vehicle or gaseous hydrogen, or both. A large number of solvents have been used as slurry vehicles. The hydrogen donor capacity of a solvent depends on its molecular structure. Wise found that the hydro-aromatic compounds were more effective hydrogen donors than the aromatic analog; for example, piperidine/pyridine, pyrrolidine/pyrrole, indoline/indole, tetrahydroquinoline/quinoline, tetrahydronaphthalene (tetralin)/naphthalene, perhydroprylene/pyrene, etc.⁽⁵⁾ Tetralin has been used as a hydrogen donor solvent for a long time.⁽⁶⁾ The use of synthetic recycle solvents has increased recently for economic process purposes. However, for laboratory research studies, tetralin is still used extensively where a hydro-aromatic solvent is required.

The hydro-aromatic solvents, rich in donor hydrogen, can meet the hydrogen demand even in the absence of gaseous hydrogen. However, in most of the processes currently under development, solvents with high hydro-aromatic contents are not always practical. For example, in the Exxon donor solvent (EDS) process, in which an externally hydrogenated recycle donor solvent is used, about 50% of the hydrogen requirement is directly

met by the gaseous hydrogen.(7,8) Thus, if the concentration of hydroaromatics is less in the recycle solvent, then the gaseous hydrogen would be anticipated to make up the deficiency. This was the case in which an Illinois No. 6 (Monterey) coal was reacted for 90 minutes under 1000 psi hydrogen pressure in the presence of synthetic recycle solvents of varying tetralin contents.(9)

Vernon(10) studied the role of molecular hydrogen on the pyrolysis of model compounds present in coal. From this study, he concluded that, "...high pressure hydrogen can promote the hydrocracking of some carbon-carbon bonds in the coal structure that are too strong to break thermally, and lead to higher distillable liquid yields." This is also supported by the SRC-I Pilot Plant data.(11) An increase in the partial pressure of hydrogen in the dissolver increased the coal conversion with an attendant increase in the hydrogen consumption. In short-contact-time-liquefaction of several coals of different ranks, the low rank coals consumed greater amounts of hydrogen than the high rank coals and in those cases where the hydrogen consumption was high, substantial quantity of hydrogen was derived from the hydrogen gas.(12) Under long residence times, the hydrogen consumption increased monotonically, both with temperature and pressure.(13)

The deuterium tracer method developed by Heredy and coworkers has revealed that the hydrogen contact opportunity is very important for the production of soluble products. The soluble products increased from 3 to 11 to 23%, as a result of increasing the hydrogen contact opportunity. They concluded that apparently there was a direct route for incorporation of deuterium (presumably hydrogen, too) into the coal matrix without the aid of tetralin.(14,15)

Recent studies by Morita, et al(16) show that the effect of hydrogen pressure on coal hydrogenation was influenced by the type of coal used. The liquefaction conversion of a low volatile, oxygen rich Morwell coal (Australia) was not affected by hydrogen pressure. On the other hand, high oil yields were obtained from a high volatile Taiheiyo coal (Japan) at high hydrogen pressures.

Wilson, et al(17) have concluded that the large consumption of hydrogen at 400-425°C and 1000 psi hydrogen pressure, in tetralin donor solvent liquefaction of Australian Liddell coal, is not due to the hydrogenation of the aromatic ring, but due to the alkyl bond fission and hydrogenolysis reactions. Thus, high hydrogen pressures can lead to enhanced yield of by-product hydrocarbon gases, C₁-C₄, which result in the unprofitable consumption of expensive hydrogen.

It appears that certain constituents of coal mineral matter may have catalytic effect on the hydrogen transfer. The general agreement is that iron containing minerals, Fe₂O₃ and iron sulfides in particular, are exceptionally good in enhancing the distillable product yield.(18,19)

All existing processes for direct liquefaction of coal by solvent extraction, SRC-I, SRC-II and SRC-SCTL processes, the EDS process and the H-coal process, utilize molecular hydrogen at high pressures (over 1000 psig). The total hydrogen consumption is in the range of 3-5% of the amount of the coal feed of which a significant portion comes from molecular hydrogen depending on the rank of the coal and the quality of the recycle oil. The cost analysis of a typical coal liquefaction process shows that as much as one-third of the overall cost goes towards hydrogen production.(20)

This, naturally, has increased interest in finding cheaper substitutes for expensive hydrogen. The use of CO, CO-H₂O and CO-H₂ in direct coal liquefaction has been explored.(21-24) The beneficial effects of direct addition of H₂S on coal liquefaction has also been reported by several workers.(25,26) More recently, addition of H₂S to the synthesis gas in the liquefaction of a lignite has been found to increase the hydrogen donor capacity of the recycle solvent.(27) The catalytic activity of sulfide minerals in coal liquefaction largely seems to be related to the capacity to generate H₂S via free radical chain reactions.(28,29) However, H₂S might be advantageously recycled only in a process where a high degree of sulfur removal is not required. This is due to the decreased sulfur removal from the product despite the improved conversion of coal. For example, increasing the partial pressure of H₂S, from 6 psi to 40 psi in 1600 psi hydrogen, caused a decrease in the THF insolubles from 10.4 to 5.6%, but at the same time the sulfur in the product liquid rose from 0.45 to 0.61%.(30) This can impose a severe economic penalty.

One of the reasons for the use of CO + H₂, CO + H₂O, CO + H₂ + H₂S, and H₂S in coal hydrogenation is that these gases are produced during the coal liquefaction, and in a real process they could be recycled. It is noted, however, that among the gaseous reaction products, the yield of light hydrocarbon gases (C₁ to C₄), in general, is greater than the combined yield of gases containing hetero-atoms. Roughly, about half of the C₁-C₄ light hydrocarbons is made up of methane alone and the low rank coals produce far greater amounts of methane and C₂-C₄ gases than the higher rank coals.(31)

This leads to an interesting possibility of using methane as a substitute for hydrogen in the direct liquefaction of coal. Though methane gas is homogeneously stable at liquefaction temperatures (methane is thermodynamically stable to temperatures of 750°C), thermally produced free radicals from coal and, the free radicals from the solvent can abstract hydrogen atom from methane, thereby setting the stage for an array of free radical reactions. It should be noted that methane and hydrogen both have the same bond dissociation energy (CH₄ → CH₃ + H, and → H₂ + H.) equal to 104 Kcal/mole.(32) It is possible that during the course of the free radical reactions, the methyl radicals generated from the dissociation of methane could react with radicals from coal thereby causing alkylation of coal. Alkylated coal has been found to produce greater yield of benzene and pyridine soluble products than the untreated coal.(33)

There is, yet, another possible factor to be considered in the interactions of methane with coal in a solvent vehicle. The free radicals produced from the methane will either react with the solvent, the coal, or even the methane itself. This would tend to increase the total liquid and gaseous yield in the system. Thus, it may be expected that not only will the coal be converted to liquid hydrocarbon products, but the makeup feed material also would be converted to valuable higher hydrocarbon products. The economic attractiveness of the entire process should, therefore, improve.

No experimental data on the use of methane in direct liquefaction of coal exist in the literature. In an effort to define the possible role of methane in the conversion of coal to liquid products, experiments were conducted with an Illinois No. 6 coal, designated as PSOC-1098 in Penn State/DOE coal data base. An analysis of the coal employed in this investigation is given in Table 1.

Detailed description of the construction and operation of the tubing bomb reactor is available.⁽³⁴⁾ The liquefaction conditions were as follows: 2.5gm coal + 7ml tetraline as donor vehicle, 400-425°C, gas pressure (at temperature) 1400 psi, 30 minutes reaction time and agitation at 400 min⁻¹. At the end of the reaction, the contents were cooled by quenching the reactor in cold water and the gases were vented to the atmosphere. The remaining products were rinsed out of the reactor into a soxhlet thimble with ethyl acetate (EtoAc). This was then followed by exhaustive extraction of the products with EtoAc in a soxhlet apparatus for 24 hours. After removal of EtoAc in a vacuum oven, the residue was weighed to determine the total conversion. From a knowledge of the coal mineral matter content of coal, liquefaction conversion on a dry, mineral matter free basis can be calculated.

Table 1

Analysis of PSOC-1098, Illinois No. 6 hvAb Coal

Proximate Analysis:		Ultimate Analysis:		
	daf	dmmf (Parr)		mm: 19.32%
% Volatile matter:	35.15	C	80.20	83.64
% Fixed carbon :	48.99	H	5.73	5.97
% Dry ash :	15.86	N	1.45	1.51
		S	4.73	
		Cl	0.06	0.06
		O (diff)	7.84	8.03

The liquefaction experiments in methane atmosphere were conducted with bottled methane gas at 400, 425, and 450°C. The coal liquefaction conversions to ethyl acetate solubles (oils + asphaltenes) plus gases were 71.3, 73.4 and 75.4% (dmmf) at 400, 425 and 450°C, respectively. These data are plotted as a function of temperature in Figure 1. In comparison, the liquefaction of the same coal at 425°C yielded 74.8% (dmmf) of gases

and liquids in the presence of hydrogen which is only slightly higher than in methane (73.4%) and 68.2% (dmmf) in nitrogen, which is considerably lower than in methane. Thus, the indication is that methane could be a potentially useful hydrogenation agent in direct coal liquefaction. A simplified process block-diagram of the various processing steps are shown in Figure 2.

A comparative assessment of the performance of the coal-methane system with the coal-hydrogen system under nominal liquefaction conditions, in various solvents, will be an important contribution to the emerging coal liquefaction science and technology. This study could lead to the development of alternate, new and economically attractive coal liquefaction processes.

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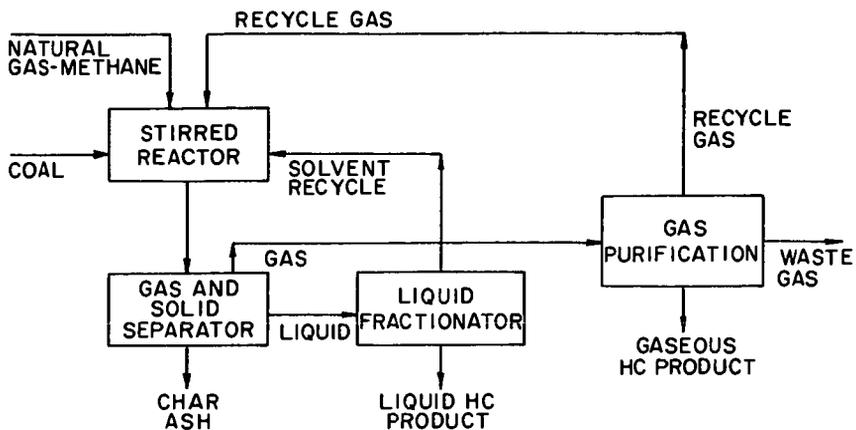


FIGURE 2.

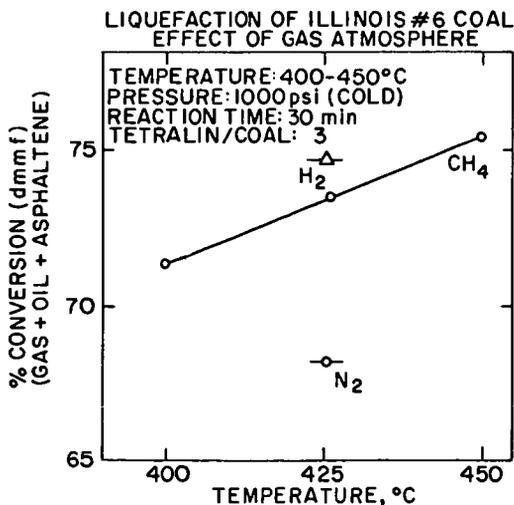


FIGURE 1.

Reaction of a Bituminous Coal with the Potassium-Crown Ether Reagent

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Introduction

It is generally accepted that a bituminous coal is best represented as a macromolecular, highly cross-linked, three-dimensional structure with aromatic clusters cross-linked by ether and alkane bridges and hydrogen bonds (1,2). Therefore, most coal conversion reactions involve reacting coal under severe conditions of temperature and pressure. As a result of the severe conditions, bond cleavage was nonselective and often accompanied by retrogressive (bond-forming) reactions. In this paper, we report on the reaction of a bituminous coal with a powerful yet selective site-specific reagent, namely, potassium-crown ether operating at *room temperature* and *atmospheric pressure*. The potassium-crown ether reagent can generate a stable solution of electrons at room temperature and atmospheric pressure (3,4). The small size of the electron and its high reactivity permits it to diffuse into the macromolecular coal network and transfer onto the aromatic substrates in the coal. This results in the formation of aromatic radical anions or dianions which undergo cleavage reactions at ether (5,6) and diaryl alkane linkages (7,8). Furthermore, crown ethers act as phase transfer catalysts in promoting the electron transfer to the solid coal. The reduction of the aromatic rings to dihydro or tetrahydro products occurs along with the cleavage reactions (9).

Experimental

A 250 ml round bottom flask was flame dried and flushed with nitrogen. Potassium metal (2.96 g, 75 mmole) was cleaned and cut under hexane and transferred into the round bottom flask in a nitrogen atmosphere glove box. The flask was again flame dried and flushed with nitrogen to remove traces of hexane. 100 ml THF solution of crown ether (4.0 g, 15 mmole) was added to the potassium metal via a double-ended needle. A dark blue solution was obtained which was cooled to 0°C in an ice bath for 30 minutes. One gram of Illinois No. 6 coal (C=74.69%; H=5.44%; N=1.88%; O=18.06%; 100 mesh) was added to the K-CE/THF solution using a transferring tube which was originally attached to the round bottom flask. The reaction mixture was stirred for 48 hours under nitrogen at room temperature. It was then cooled to 0°C and quenched with water. The THF was removed by rotaevaporation. The aqueous slurry of the coal was freeze-dried to remove the water. The work-up of the reacted coal is shown in Figure 1.

Results and Discussion

The Illinois No. 6 bituminous coal was reacted with the potassium-crown ether reagent at room temperature and atmospheric pressure. The reaction mixture was quenched with water and fractionated into THF extracts and alkali-solubles as shown in Figure 1. For each K-CE reaction, 15-20% of the coal was solubilized into THF and aqueous alkali fractions. After the third and fourth K-CE reactions, about 50% and 75% of the original coal was

solubilized, respectively. The formation of the alkali-soluble coal fragments indicated that ether linkages are being cleaved to form phenolic coal fragments.

Table 1. Total Solubility of Illinois No. 6 Coal
inr Each Fraction After Three and Four K-CE Reactions

Notebook #	THF-1	ALK	THF-2	Total Solubility	
	(%)	(%)	(%)	Solubles	Residue
H2-52A (A-C) Three K-CE Reactions	9.9	26.9	14.7	51.5	51.2
H3-6 Four K-CE Reactions	13.7	51.6	12.8	78.0	22.8

The reason for successive K-CE reactions is due to certain limiting steps in the electron transfer process: (1) concentration of the solvated electrons in solution—more concentration of electrons, greater would be the transfer to the aromatic substrates in coal which in turn would mean greater cleavage and reduction reactions being initiated; (2) intrinsic repulsive barrier of the negatively charged aromatic substrates generally by the initial electron transfer; and (3) mass transport limitations. Obviously, one can increase the solubility of the coal into the various fractions by optimizing the potassium-crown ether to coal ratio, reaction time, temperature, and etc. However, successive potassium-crown ether reaction allows us to selectively snip at the macromolecular network at room temperature and atmospheric pressure conditions to prepare solubilized coal fragments with are amenable to detailed chemical, spectroscopic, chromatographic, and mass spectrometry analysis.

The elemental composition of each soluble fraction (THF-1, alkali, THF-2) and insoluble coal residue was determined by microanalysis. (Table 2). The hydrogen to carbon ratios are also included in Table 2. The results showed that after each K-CE reaction of coal there is an increase in the number of hydrogen atoms. The overall hydrogen uptakes are 7, 18, and 22 per 100 C-atoms for first, second, and third K-CE treatment, respectively. The hydrogen uptake is due to reactions such as Birch-Huckel-type reduction, cleavage of aliphatic bridges and ether linkages occurring during the K-CE reaction with coal.

Both THF extracts (THF-1 and THF-2) have higher H/C ratio as compared to the alkali soluble fraction and the insoluble residue during each K-CE reaction. A gradual increase in H/C ratio for each fraction after second and third consecutive K-CE treatment was also observed. This result corresponds well with the overall increase in hydrogen content and suggests further that reduction and cleavage of coal molecules upon additional K-CE treatment were occurring.

Figure 2 shows the infrared spectra of the various extracts obtained from the K-CE reaction with the coal. The IR spectrum of THF-1 extract was dominated by sharp aliphatic CH stretching bands just below 3000 cm^{-1} suggesting that this extract contains predominantly aliphatic material. This finding is in agreement with the high H/C ratio obtained for this extract. The spectrum of THF-2 extract also showed the dominating C-H stretching vibrations just below 3000 cm^{-1} ; however, a broad OH stretching vibration in the

Table 2. Elemental Analysis of K-CE Treated Coal

	Analysis (wt%) (daf)				H/C
	C	H	N	O	
Illinois No. 6 untreated coal	74.69	5.44	1.88	18.06	0.87
(1st K-CE Reaction)					
2-52A-THF-1	79.00	8.74	2.35	9.90	1.33
2-52A-Alk	71.76	5.90	1.55	20.77	0.99
2-52A-THF-2	74.02	7.04	0.81	18.14	1.14
2-52A-Res	73.23	5.95	1.28	19.50	0.90
(2nd K-CE Reaction)					
2-52A-THF-1	75.01	7.96	0.44	16.59	1.28
2-52A-Alk	68.34	5.97	0.90	24.80	1.05
2-52A-THF-2	67.93	7.22	0.56	24.20	1.28
2-52A-Res	74.12	6.27	0.71	19.70	1.02
(3rd K-CE Reaction)					
2-52A-THF-1	-	-	-	-	-
2-52A-Alk	71.00	6.67	0.99	21.34	1.13
2-52A-THF-2	70.67	7.51	0.77	21.05	1.28
2-52A-Res	73.00	6.54	1.02	1.94	1.08

Note: THF-1: THF extract of alkali residue

Alk: Aqueous alkali soluble fraction after THF-1 extraction

THF-2: THF extract of acidified residue after THF-1 and Alkali extraction

3400-3200 cm^{-1} was also present. Thus, the THF-2 extract also contains aliphatic material which may be attached to a hydroxy aromatic ring system. Again, the increased H/C ratio nicely corroborates the presence of aliphatics. Both THF extracts showed carbonyl absorptions around 1710 cm^{-1} . The alkali-soluble fraction showed a strong carbonyl stretching vibration at 1700 cm^{-1} coupled with a broad O-H stretching vibration extending down from 3500 cm^{-1} . The infrared spectrum of the residue was similar to the untreated coal but showed weak carbonyl absorption bands.

The carbonyl absorption bands present in the IR spectra of all the extracts suggests that reduction of phenolic units to cyclohexanone (i.e., OH to C=O) units was a major reaction pathway in the reaction of coal with the K-CE reagent. The reduction of phenols and naphthols to the corresponding dihydro or tetrahydro aromatic carbonyl compounds by the K-CE reagent has been confirmed by us using model compounds. More work needs to be done to clarify the reaction mechanism; however, the increased hydrogen content of the alkali soluble and residue fractions on consecutive K-CE treatments of coal supports this reduction chemistry. The reasons for the carbonyl components to be fractionated into an alkali soluble fraction, an insoluble residue fraction, and in the THF extracts are: (1) carbonyl units that can undergo a keto-enol-tautomerism would be rendered alkali soluble; (2) the cyclohexanone type units which are hooked to coal phenolic units would also be alkali soluble; and (3) the carbonyl components in the THF extracts would be the relatively nonpolar components.

Figure 3 shows the proton NMR spectrum of the THF-1 extract. The spectrum confirmed the presence of predominantly aliphatic material in this extract. Thus, the dominant sharp signal at 1.2 ppm is characteristic for methylene protons of long-chain polymethylenes. The group of signals in the 2-3 ppm region can be assigned to dihydro aromatic protons. Based on the mechanism of the K-CE reaction reduction of the aromatic ring to dihydro and even tetrahydro aromatics was expected and the NMR evidence nicely corroborates it. Thus, one of the major constituents of this extract is long-chain polymethylenes which may or may not be attached to a hydroaromatic ring system. The ^{13}C NMR spectrum (Figure 4) also strongly supported the presence of long-chain polymethylene groups in the extract. The most intense signal is at 30.2 ppm which is generally assigned to the internal methylene carbons of straight-chain alkanes (an average carbon chain length of approximately 8). The presence of a broad spectral envelope in the 15-50 ppm region in addition to the sharp alkane lines is indicative of the extract's complexity arising out of the presence of only small amounts of these polymethylene-type compounds. The broad complex band of carbon signals in the 120-130 ppm region is due to the aromatic and polycyclic aromatic species of the extract.

Detailed characterization of the polymethylenes in the THF-1 extract was done using chemical ionization mass spectrometry and tandem mass spectrometry (MS/MS) (10,11). Tandem mass spectrometry is a well-established technique for the direct analysis of complex mixtures, because it can do unaided separation and identification of the constituents of the mixtures. By using different scan types, the structure of individual components can be identified and the presence of series of related compounds can be ascertained. In particular, daughter scans identify specific constituents of the mixture on the basis of molecular weight and fragmentation behavior.

Figure 5 shows the CI mass spectrum of the THF-1 extract. In it, one can identify 14 sets of three intense peaks; each set separated by 14 amu. Based on the molecular weight, the first set of three peaks at m/z 129, 131, and 133 can be assigned to the protonated molecular ions of naphthalene, dihydronaphthalene, and tetralin. It follows that the remainder sets of three intense peaks represented the homologous series of alkylnaphthalenes, alkyl dihydronaphthalenes, and alkyl tetralins, with the polymethylene chain extending up to 14 carbons (Figure 6). In all probability, the dihydronaphthalene series and the tetralin series arise by *Birch Reduction* of the naphthalene compounds during the K-CE reaction. Therefore, only the homologous series of alkyl naphthalene compounds may be present in the coal. There are other molecular ions present but their intensities are well below that of the naphthalene-polymethylene series.

It was indeed surprising to obtain such a clean CI mass spectrum in which the polymethylene molecular ions predominate. Normally, mass spectra of coal mixtures is complex and messy and no clear-cut compound series can be identified. The reason we obtained such a clean spectrum is because the analysis was done on the THF-1 extract obtained from the second K-CE reaction. In the first K-CE reaction all the extractable material in coal and other compounds associated with coal will be removed during the THF extraction, alkali extraction and another THF extraction steps, leaving behind a *pristine* coal macromolecule. This strongly implies that the polymethylenes are not present as "trapped molecules" but as an integral part of the coal macromolecular matrix. The polymethylene chain could be present as crosslinks between aromatic clusters or as long dangling side chains on an aromatic ring.

Daughter spectra (Electron Impact) were taken for each and every member of the homologous series to confirm the structural identity of the polymethylene compounds.

Summary

The reaction of a bituminous coal with the K-CE reagent resulted in the selective snipping of the linkages in the coal macromolecular network at room temperature and atmospheric pressure. Soluble chunks of coal fragments were obtained without recourse to any thermal or pressure effects. In addition to ether cleavage reactions, a major reaction pathway in the coal/K-CE reaction is the reduction of phenolic groups to carbonyls. Analysis of the THF-1 extracts revealed the presence of a homologous series of alkyl naphthalenes and alkyl tetralins, with the methylene chain extending up to 14 carbon atoms, as the major components in the extract. These compounds are *real* and an integral part of the coal matrix and not present as *trapped molecules*. Any representation of coal structure or the development of coal process models would have to account for these pockets of aliphatic rich zones.

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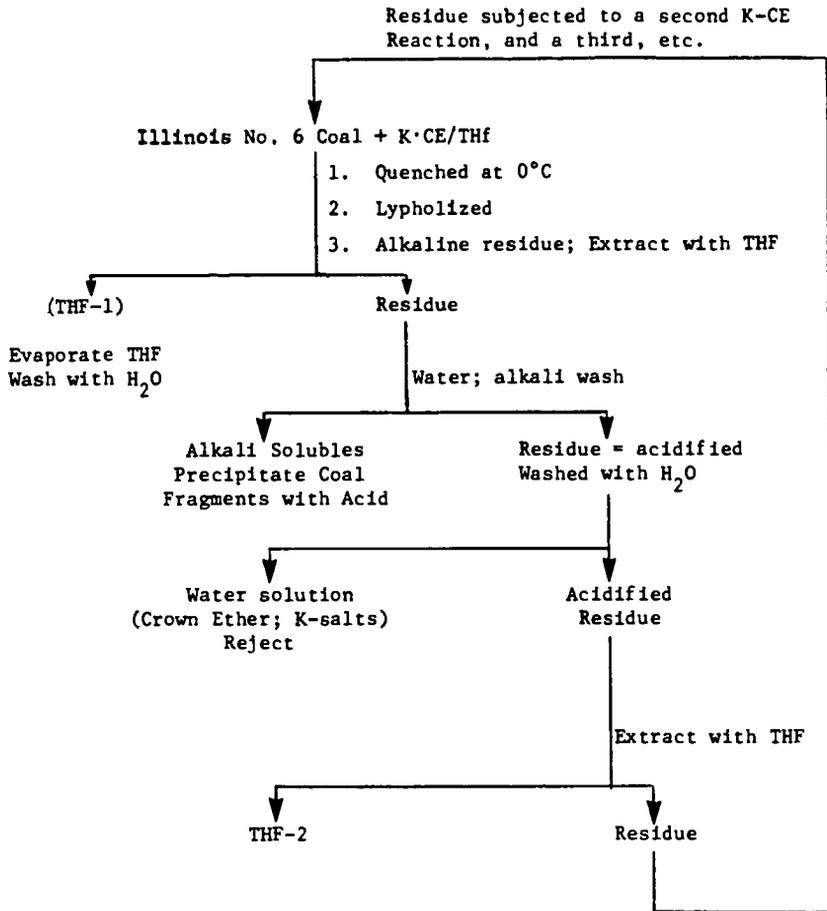


Figure 1. Work-Up of the Coal/K-CE Reaction.

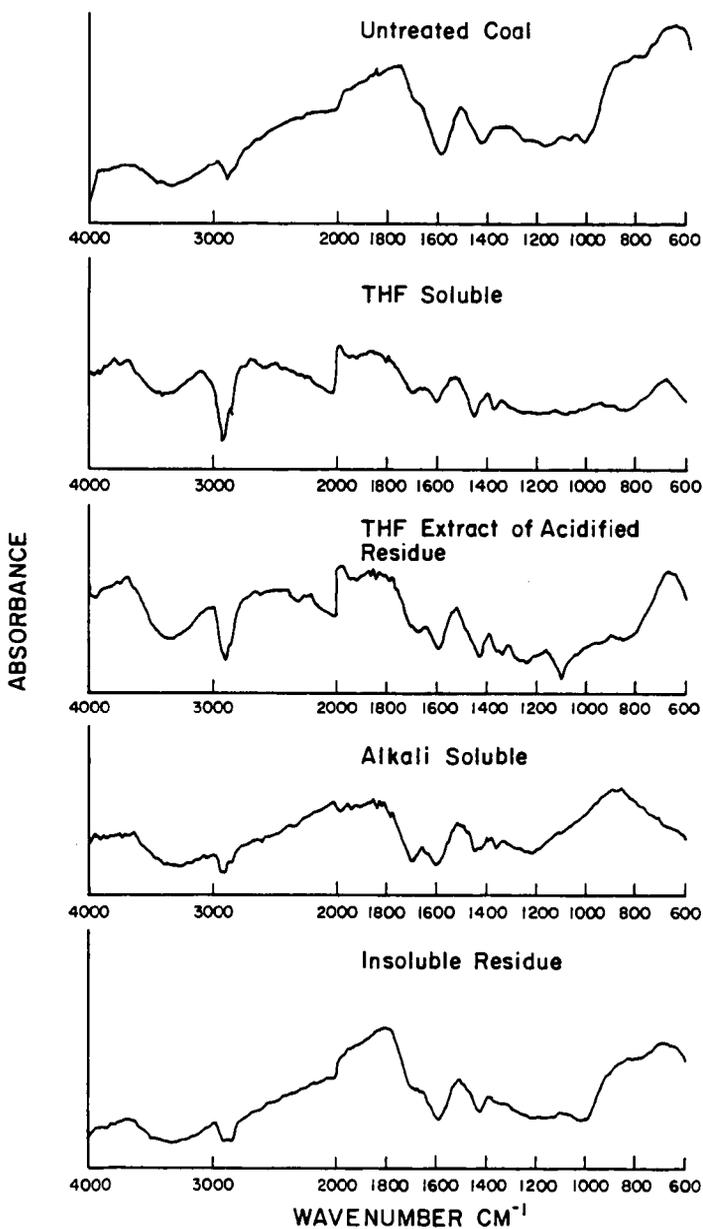


Figure 2. Infrared spectra of different fractions of K-CE treated Illinois No. 6 Bituminous Coal.

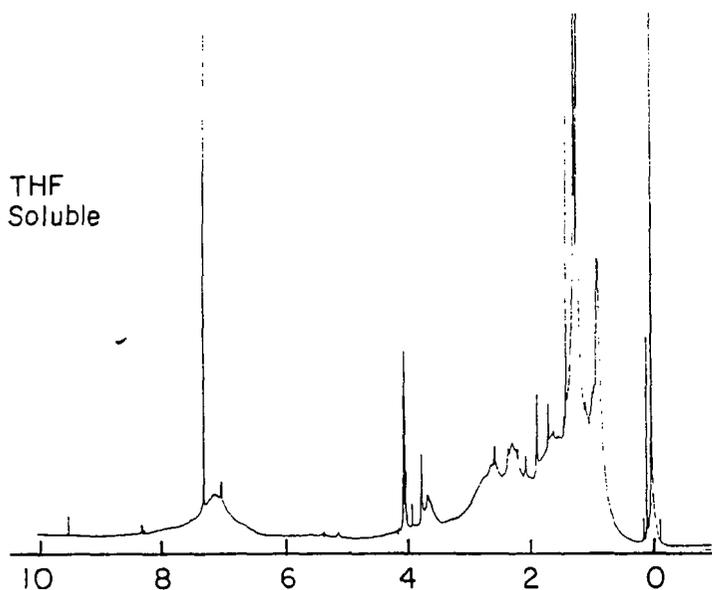


Figure 3. ^1H NMR of THF-1 extract.

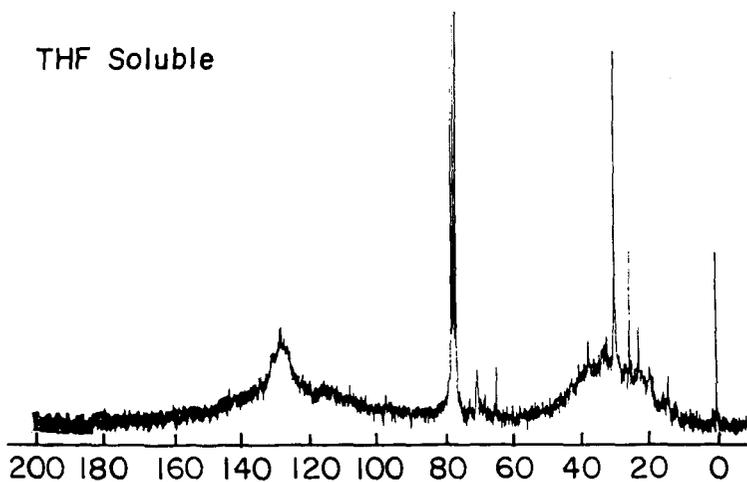


Figure 4. ^{13}C NMR of THF-1 extract.

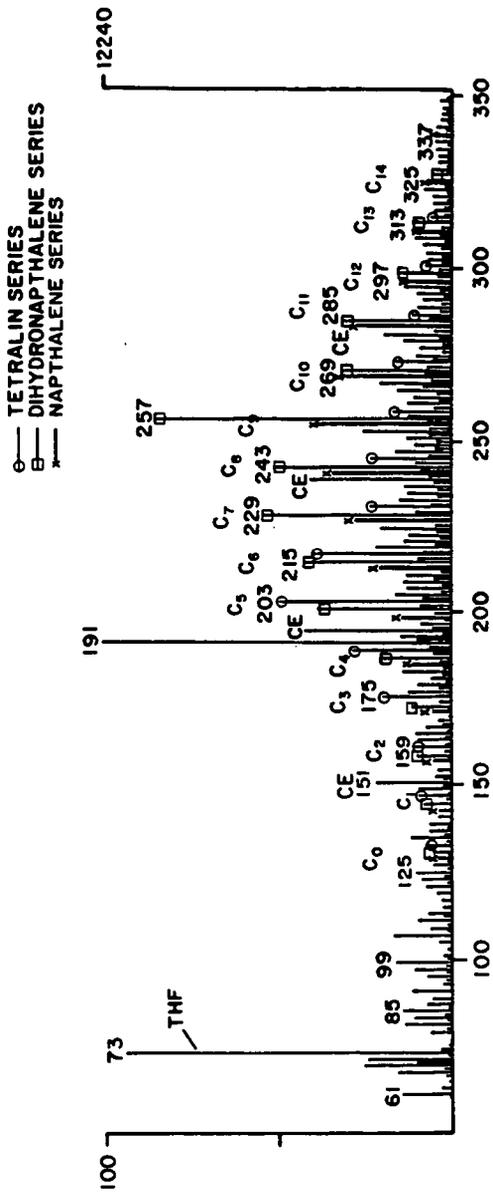


Figure 5. Chemical ionization mass spectrum.

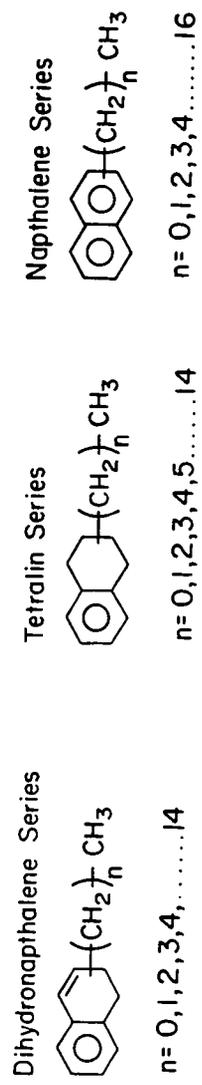


Figure 6. Polymethylene structures in coal.

MILD OXIDATIVE SOLUBILIZATION OF COAL MACERALS

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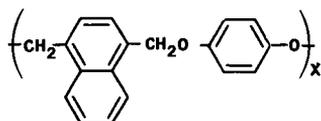
The objective of this study is to solubilize coal macerals and an Argonne Premium Coal Sample using oxidation and to characterize these soluble products. A major problem in coal characterization and in coal utilization is the intractability of the coal macromolecular network. High temperature treatments yield smaller, volatile and soluble molecules, which can be greatly altered from their original structures, along with a significant amount of a non-volatile char. Mild oxidation should provide a soluble mixture of compounds in higher yields and with structural characteristics more like the original coal. The approach described in this paper attempts to oxidatively cleave only activated benzylic sites in the coal macromolecules in a two step process. In the first step benzylic sites which are partially active due to oxygen functionality either on the aromatic ring or on the benzyl carbon are further activated by the formation of pyridinium salts at that carbon from the reaction with pyridine and iodine. In the second step this carbon is oxidized by alkaline silver oxide resulting in formation of carboxylic acid groups. This process has been described in an initial communication for whole coals (1) and the results of the first reaction on the macerals, used in this study, has been published (2). This report will focus on the yields of the oxidation step and the characterization of the products.

A few oxidative degradation studies on separated coal macerals have been published (3-5). In these studies there was extensive oxidation and only small molecules were identified. In this study, both smaller and higher molecular weight fractions which were separated on the basis of solubility have been characterized using gel permeation chromatography (GPC), GCMS, Pyrolysis MS (PyMS) the precise mass measurement mode, Fast Atom Bombardment (FAB) MS, and NMR. FAB MS has proven to be useful in the characterization of polar biological compounds. This is the first application of this technique to coal oxidation products. Since FAB is a relatively mild ionization technique, it should help to characterize products with molecular weights greater than 500. Compounds in this range are not volatile enough for GCMS and are broken down into smaller fragments by PyMS. However, the chance of rearrangements in PyMS are reduced when pyrolysing the oxidation products in comparison to the whole coals or maceral concentrates. It is interesting to note the remarkable lack of large polycyclic aromatics in the soluble products. The significance of this result will be discussed.

EXPERIMENTAL

Samples

A description of the macerals and whole coal is given in Table 1. Details of the maceral separation have been reported (2). The Upper Elkhorn and the Brazil Block samples have been separated from coals obtained from Pennsylvania State University labelled PSOC 1103 and PSOC 828, respectively. The subbituminous coal is the Argonne Premium Coal Sample (APCS) number 2, which has been recently mined and has been stored under nitrogen in sealed glass ampules. The preparation of the oxy-methylene linked polymer(I) has been described (6).



(1)

Oxidations

The pyridinium salts of the samples were prepared by refluxing 1 g of the coal, maceral or polymer in 60 ml of pyridine with 4 g of iodine for 70 hrs (2). The reaction mixture was poured into 10% aqueous NaHSO_3 and the solution filtered. The derivatized coal was washed free of pyridine, dried and analyzed. In a typical oxidation fresh Ag_2O , prepared from 8.5 g of AgNO_3 and sodium hydroxide, was refluxed with 1.0 g of the substrate in 50 ml of 10% aqueous NaOH for 20 hrs. The silver and unoxidized samples were removed by filtration and the filtrate acidified with aqueous HCl . Products which were alkaline soluble but insoluble in the slightly acidic solution were termed humic acids. The solubles were extracted with $\text{Et}_2\text{O-MeOH}$. Yields were determined by analysing the products for carbon. The products were methylated with diazomethane for further analysis.

Characterization

Approximate molecular size distributions were determined by gel permeation chromatography using a set of three ultra-Styrigel columns with 100, 500, and 1000 Å nominal pore diameters. The samples were eluted with THF and detected by UV at 254 nm. The columns were calibrated using a set of esters of known molecular weight.

GCMS and PYMS data were obtained on a Kratos MS-25 mass spectrometer. A 60 m x 0.25 mm DB-1701 fused silica column was used in GCMS analysis. The details of the PYMS experiment have been reported (2). The samples were all heated at 50°/min on a platinum screen and the instrument was operated in the precise mass measurement mode. The FABMS data were obtained on a VG 70-250 at the University of Chicago, Chemistry Department. Argon gas was used with glycerol as the probe matrix. NMR data were taken on a Bruker AM-300 using CDCl_3 as a solvent.

RESULTS AND DISCUSSION

The yields for the oxidation step are very sample dependent as is shown in Table 1. The yields are calculated based on the carbon content of the starting material and of the products with the values given being an average of at least two experiments. The oxidation of the Illinois No. 2 vitrinite yielded 84% of the original carbon in the soluble products. This result can be contrasted with the fusinite where only 47% of the carbon has been recovered of which 40% was the $\text{Et}_2\text{O-MeOH}$ soluble fraction. If one assumes that fusinite is "fossil charcoal", then this result is expected. The number of pyridinium salts formed (1.5/100 carbons) is small and suggests that much of the oxygen occurs as heterocyclics. In addition, there were probably less benzylic carbons in this fusinite compared to the vitrinite. The lower yield for the sporinite, 62%, compared to the vitrinite may reflect

the greater aliphatic content of the sporinite which would be resistant to oxidation. The APCS #2 has a similar composition to the Illinois No. 2 vitrinite and yields essentially the same amount of solvent solubles but less humic acid material. Oxidation of the polymer gives only 1,4-naphthalenedicarboxylic acid. No evidence the naphthalene ring oxidation has been found. It is interesting to note that one naphthalene-dicarboxylic acid is formed for every pyridinium salt.

The Et₂O/MeOH soluble fraction does have a significant amount of higher molecular weight materials as is seen in the GPC data from the methyl esters presented in Figure 1. The molecular size scale is only approximate and this approach works best for comparisons. Figure 1a compares Illinois No. 2 vitrinite with fusinite. The fusinite gives a narrower distribution shifted to a larger molecular size compared to the vitrinite. A comparison of the solvent solubles and humic acid from Upper Elkhorn vitrinite is shown in Figure 1b. The humic fraction higher MW peak is significantly higher than the corresponding peak for solvent soluble. Since this is a fairly mild degradation the molecular size distribution is typically at a much higher MW compared to pyrolysis products of the sample samples. Finally, it is interesting to note the difference in Figure 1c of the output from a UV and a fluorescence detector which are in-line. The chromatograms have been normalized, but the poor signal-to-noise from the fluorescence detector is a good indication of the lack of fluorescing compounds such as polycyclic aromatics in the product.

Proton NMR data lends support to the observation of the lack of polycyclic aromatics. Since even the solvent soluble fractions contained compounds which are too large and non-volatile for GCMS, the proton NMR spectra have been taken. The methyl ester region is the most informative and is shown for the Illinois No. 2 samples in Figure 2. From the spectra of a number of known methyl esters, three regions can be assigned: 3.6-3.8 aliphatic, 3.8-4.0 single ring aromatics and heteroaromatics, and 4.0-4.2 polycyclic aromatics and heteroaromatics. Single-ring aromatics and aliphatics are the most abundant species in these samples.

Compounds that can be separated by GCMS are mostly benzene, and hydroxybenzene carboxylic acids. The total ion chromatogram for APCS #2 is shown in Figure 3. Although this is a fairly mild oxidant, tetra-, penta- and hexa carboxylic acids are still formed. Also note even the hydroxybenzene tetra- and penta-carboxylic acids are formed. More model compounds are being examined to better understand this result. In addition to benzene and hydroxybenzene carboxylic acids, furan carboxylic acids are found in significant abundance.

Fragments found by PyMS with APCS #2 and the vitrinites are dominated by aliphatics and single ring aromatics and hydroxylated aromatics. PyMS of the humic products results in volatilization at lower temperatures as compared with the coal or maceral, as is shown in Figure 4. Comparing the pyrolysis products between the two samples, the most striking difference is the reduction in aliphatics in the humic acid fraction. Figure 5 shows the distribution of hydrocarbons found as a function of Z-number (hydrogen deficiency, 0-alkane, 1-alkene, 4-benzene, etc.). However, in each case the contribution of fragments with more than 1 aromatic ring was small, 5.6% for the coal and 4.6% for the oxidation product. A milder ionization approach has been taken with some of these samples. A FAB MS spectrum for the solvent solubles from the Upper Elkhorn vitrinite is shown in Figure 6. Again, peaks which can be identified as single ring compounds dominate. However, unlike electron impact peaks are seen at M/Z > 400. The conditions for this experiment need to be optimized and a matrix more suitable than glycerol used. Also, some of these samples will be analysed using field ionization MS.

All of these results strongly suggest that for our vitrinite samples and the subbituminous coal sample the single ring aromatics dominate. Unlike many other experiments most of the carbon is characterized using this approach. More model compounds and polymers are being studied to verify the selectivity of this derivatization/oxidation procedure.

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TABLE 1. Coal and Maceral Samples.

Sample () †	Source	Rank	Empirical Formula	Py †/100°C	Ag ₂ O Oxidation Yields*	
					Organic Soluble %	Humic Acid %
APCS #2	Rawhide Seam	Subbituminous	C ₁₀₀ H ₉₇ N _{1.4} S _{0.4} O _{19.6}	4.1	~40	26
Vitrinite (95+)	Illinois #2	HvC Bituminous	C ₁₀₀ H ₉₇ N _{1.5} S _{0.8} O _{18.3}	3.8	44	40
Fusinite (95+)	Illinois #2	HvC Bituminous	C ₁₀₀ H ₆₄ N _{0.8} O _{1.1}	1.5	40	7
Vitrinite (93)	Upper Elkhorn	HvA Bituminous	C ₁₀₀ H ₉₃ N _{1.9} S _{0.5} O _{10.5}	4.6	--	--
Sporinite (91)	Brazil Block	HvA Bituminous	C ₁₀₀ H ₁₁₅ N _{1.2} S _{0.8} O _{10.7}	3.8	46	16
Polymer-I			C ₁₈ H ₁₄ O ₂	2.4	44 †	

† Maceral petrographic composition.

* Based on carbon composition.

† Mole percent.

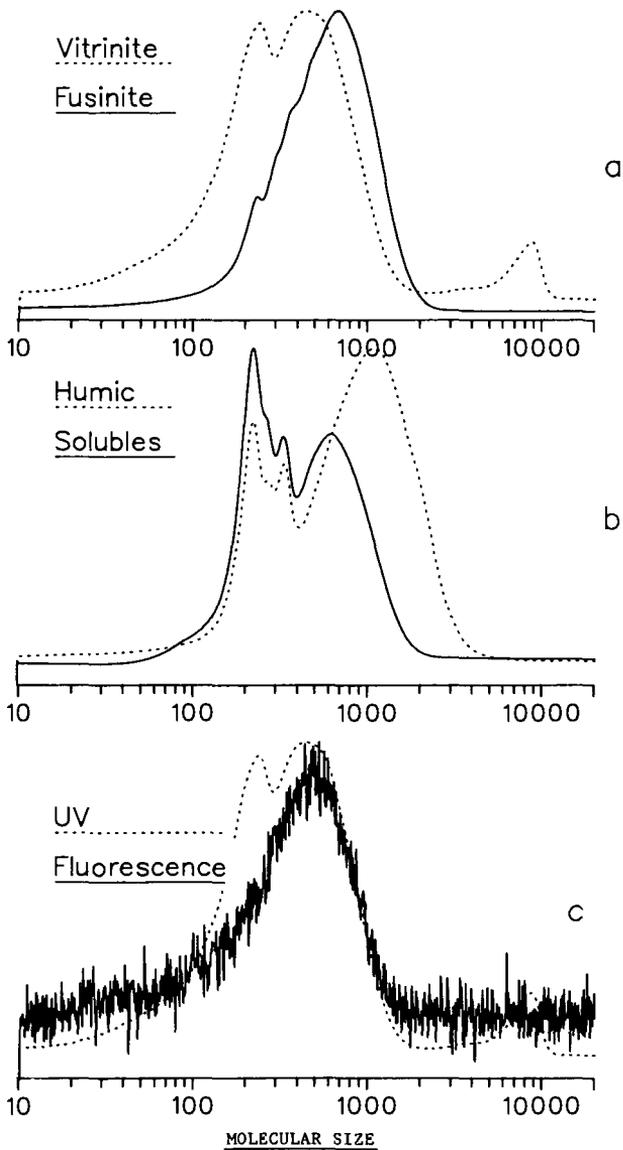


Figure 1. Gel permeation chromatograms of methyl esters: a) Illinois No. 2, solvent soluble fraction; b) Upper Elkhorn No. 3 vitrinite, and c) Illinois No. 2 vitrinite solvent soluble fraction.

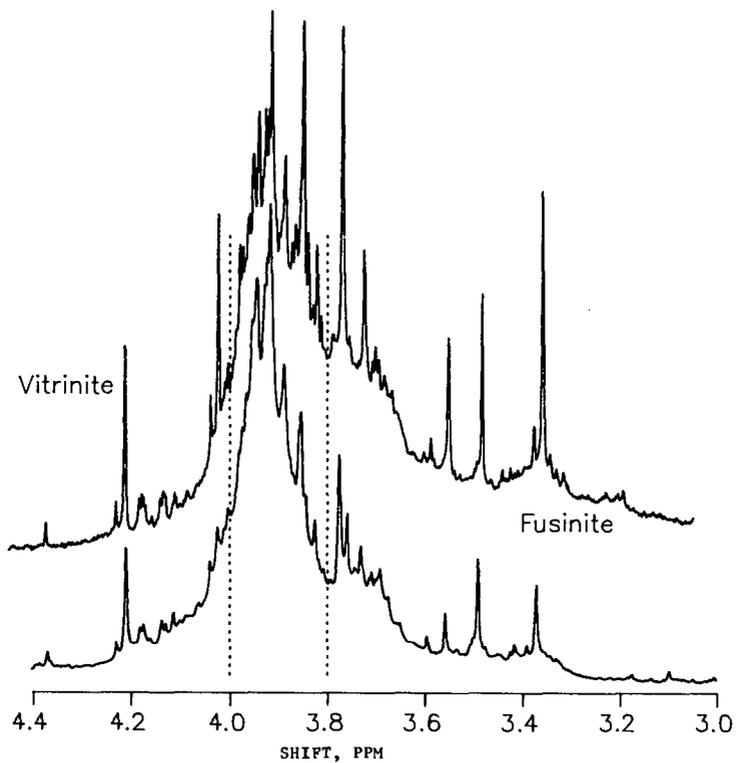


Figure 2. ^1H NMR spectra of Illinois No. 2 solvent soluble fraction, esters.

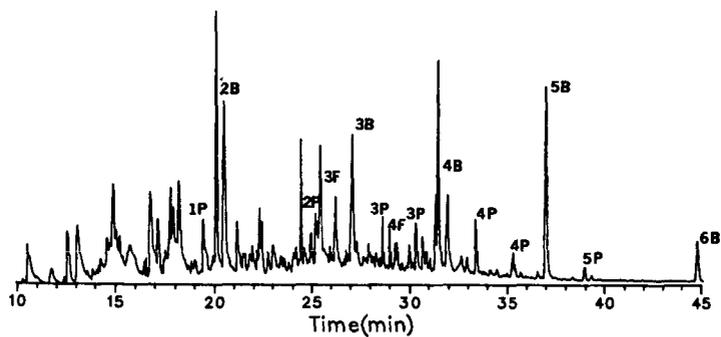


Figure 3. Total ion chromatogram of APCS #2 solvent soluble fraction, methyl esters. Major peaks: 2B-6B number of carboxylates on benzene, 2P-5P number on phenol and 2F-4F number of carboxylates on furans.

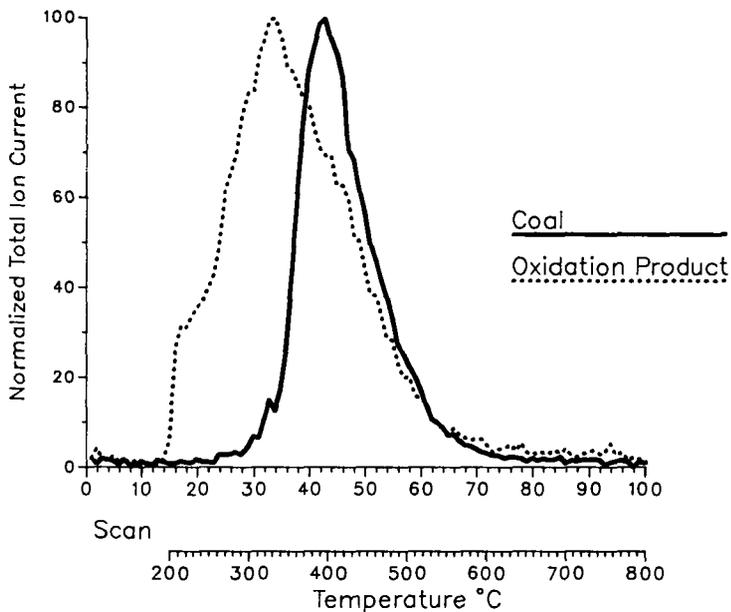


Figure 4. Total ion pyrograms for APCS #2.

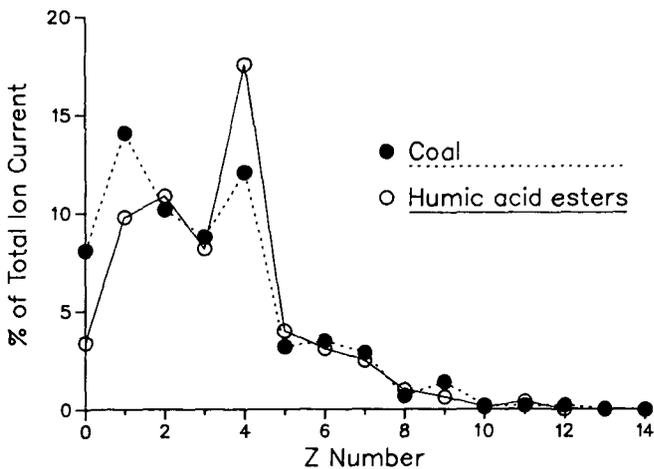
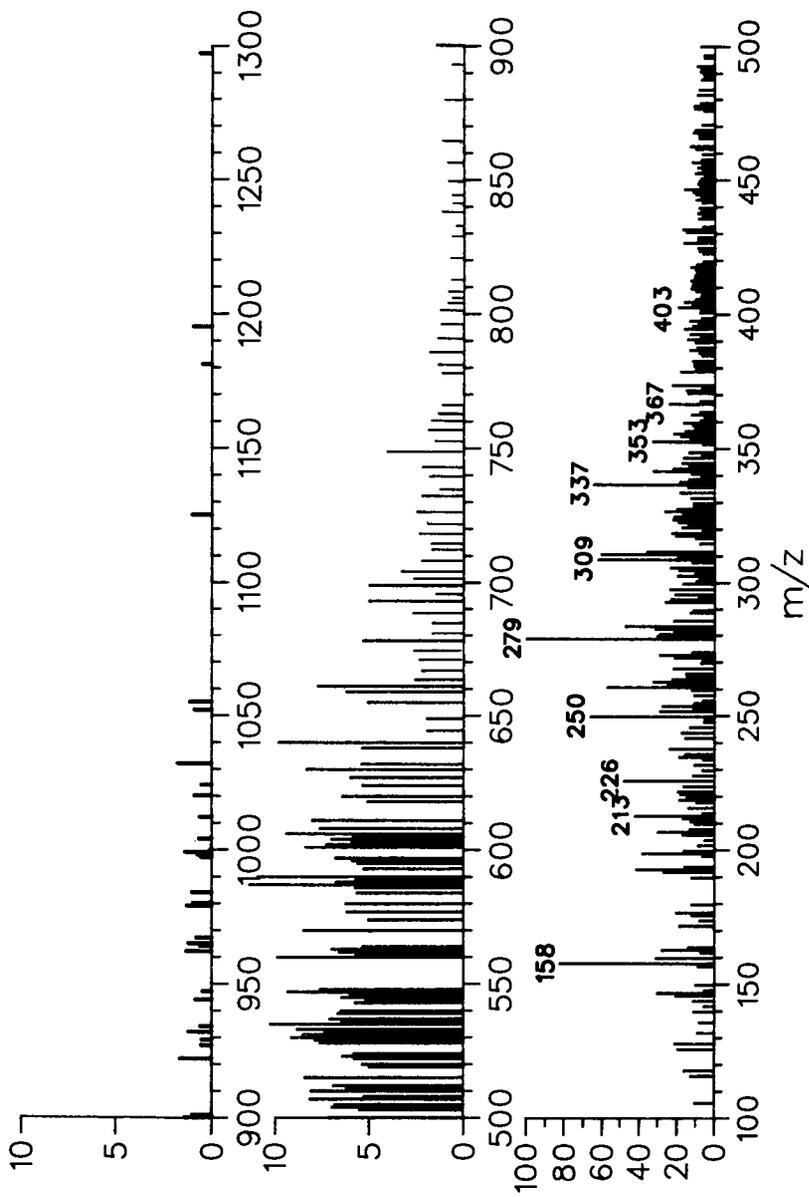


Figure 5. Distribution of hydrocarbons with Z-number for average of the data shown in Figure 4.

Figure 6. FAB mass spectra of Upper Elkhorn No. 3 vitrinite solvent soluble fraction, methyl esters.



Coal Oxidation and Thermal Chemistry

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I. Introduction

The physical and chemical properties and processing characteristics of most coals are extremely sensitive to storage conditions.(1-3) Both drying and the air induced oxidation are known to produce substantial changes to coal. Consequently, they have been the subject of study throughout the history of coal research. In this paper we discuss some of the recently obtained data indicating that these processes involve a few simple chemical transformations which are closely coupled by virtue of their kinetic behavior. In-situ FT-ir analysis used to examine the overall chemical changes is examined herein. Light and neutron scattering were used to examine the concomitant structural changes thereby providing some information on the location of some of the reactive functionality within the coal matrix. These studies will appear elsewhere.(4-7)

Drying is believed to result principally in the loss of adsorbed water, though some studies suggest that chemical alterations occur. That drying produces some alteration is evidenced by the routine use of drying prior to almost all coal studies or processing. The de-facto standardization leads to a coal having reproducible characteristics. Despite considerable study, similar standardized procedures to mitigate the effects of oxidations are not currently available.

Since oxidation of coal is generally believed to influence many coal properties, the resulting literature is extensive. The principal cause of changes associated with the "weathering" of coal is attributed to oxidation. From a utilization standpoint, air oxidation alters properties of the coal which, depending upon the particular end-usage of the coal, may either be detrimental or advantageous. For example, the heat content of coal decreases upon oxidation resulting in increased amounts of coal being needed in any particular application. However, oxidation increases the heteroatom content of the coal resulting in a greater number of sites available for chemical reaction and catalyst binding. Changes to the swelling and fluidity properties of coals are correlated to oxidation. This implies that oxidation alters the fundamental geometrical structure of the coal in addition to the chemical composition and will likely have a secondary effect on all coal chemical reactions through induced alteration of mass and thermal transport through the "semi-solid" coal.

In order to understand these complex reactivity/structure relationships, we have examined both the chemical and structural changes which occur when a sub-bituminous (Rawhide - SBB) and a bituminous (Illinois No. 6 - HvC) coal are reacted at low-temperature (<150°C). In brief we find that drying produces chemical alterations which compete with some of the chemical reactions which occur during the oxidation. Oxidation consists of at least two separate sets of reactions which are distinguishable by their time and/or temperature dependencies. Correlations between the reactivity studies and structural studies carried out with scattering methods suggests the species which react both thermally and oxidatively reside on void surfaces and are readily accessible to the environment.(7-9)

In this paper we review some of our evidence supporting the presence of multiple competing thermal and oxidation reactions. The correlated structural studies are available elsewhere.(8,9)

II. Experimental

Experimental procedures employed are described elsewhere.(4,5,7) As previously describes, samples employed for FT-ir studies are thin sections having a nominal thickness of 0.4 micro-meters and an area of approximately 1 mm². Analytical data representative of the samples are contained in Table 1. A two-dimensional matrix of these sections is prepared using serially cut sections to obtain the desired total sample area on an appropriate substrate.

III. Results and Discussion

We have found that several reactions take place at low-temperature when dry coal is either heated or exposed to oxygen. In order to examine the oxidation chemistry, it is first necessary to remove the effects of drying. We therefore discuss the thermally induced changes prior to dealing with the oxidation.

Drying Results in decarboxylation/decarbonylation

The effect of drying on thin-section samples of Rawhide (SBB) and Illinois No. 6 (Hv-C) coals were examined in a series of experiments. The coal thin-sections were dried at room temperature by subjecting them to a moderate vacuum ($>10^{-5}$ torr) for at least 12 hours. Observation of the hydroxyl stretching region indicates that the physisorbed water is removed within the first hour. We believe that such vacuum drying is able to remove most of the water for two reasons: 1) O'Rourke and Mraw found that room-temperature "drying" of coal using a highly desiccative environment was capable of removing greater than 98% of the adsorbed water from powdered samples of similar coals¹⁰ and 2) we find that subsequent drying by heating under vacuum at 100°C does not further reduce the hydroxyl stretching region intensity.

An example of the effect of heating such a dried Illinois No 6 coal sample for ca 6 hours under vacuum is shown in Fig. 1. Only the region of the ir spectrum indicating carbonyl content (C=O stretch and -C-O-H modes) is shown. The difference spectrum clearly indicates loss of carbonyl intensity at ca 1707 cm⁻¹. This region of the spectrum does not uniquely identify the specific carbonyl species lost. We assign the loss to hydrogen bonded or dimerized aliphatic carboxylic acids based upon several lines of reasoning. These will be discussed subsequently.

The observed frequency loss at ca 1707 cm⁻¹ is generally assigned (9) to the C=O stretch in dimers of aliphatic carboxylic acids in which the aliphatic chain is contains more than 3 carbons.(11) It can also be assigned to a variety of ketone and aldehyde species. It is unusual for aromatic carbonyls to absorb at such a high frequency. This fact together with surface functionality information obtained from neutron small-angle scattering (8) makes an assignment to aromatic carbonyl functionality less plausible. Despite the possibility that the absorption is due to non-carboxylic acid carbonyl species, the weight of the evidence summarized below is in favor of the carboxylic acid assignment. A more complete discussion of alternate assignments is available elsewhere.(6)

A spectral loss is observed at 1285 cm⁻¹ which is observed to follow the same kinetics as the 1707 cm⁻¹ loss feature. Therefore these two absorptions probably result from different vibrational modes of the same species. When present in addition to a carbonyl stretch, the 1285 cm⁻¹ mode is diagnostic for carboxylic acid dimers. We have attempted to determine whether the reactive functionality was located on the void surface or inside the organic matrix by performing solvent permeation studies and examining the induced structural changes and permeability restrictions using neutron and light scattering techniques. Neutron scattering measurements suggest that aliphatic carboxylic acid species are present on the void (pore) surface.(8) In view of our spectroscopic assignments above, we believe the thermally reactive carboxylic acid species to be located at the pore surface.

Restricted mobility of both of reactant and product molecules within the coal matrix is expected. Indeed, higher temperature pyrolysis of coal shows that different chemical transformations occur when carried out under vacuum as compared to a closed atmosphere.(12) This is understandable when the overall reaction is the result of secondary reactions of some initially formed reactive intermediate. We investigated this by carrying out the same thermal reaction in a closed cell under a static helium atmosphere. The overall thermal reaction was unchanged. Only minor changes in some of the relative intensities of the absorption losses were seen. This indicates that mass transport limited secondary reactions are not important under these conditions. Therefore the thermal reaction is either 1) bimolecular between two topologically adjacent portions of the matrix or 2) sequential with the first step being the formation of a reactive species by a unimolecular decomposition followed by reaction with a nearby portion of the matrix surface. The available data does not uniquely determine either possibility.

Available functional group analysis of the Illinois No. 6 coal used for the experiments discussed above indicates that only a relatively small amount of carboxylic acid functionality (0.5 COOH per 100 carbon atoms) is present. We are not currently able to quantify the number of carbonyl groups which we observe since an extinction coefficient for these vibrations is not available for species present in a similar environment. Therefore we were particularly interested in observing the thermal behavior of a lower rank coal containing a larger carboxylic acid content. Rawhide coal containing ca 3.2 COOH per 100 carbon atoms was used.

In contrast to that observed for the Illinois coal, a significant loss of intensity which could be assigned to a loss of C=O species was not seen. There are several possible explanations: 1) carboxylic acid species are unreactive; 2) the predominant carboxylic species are not dimers and the carboxylic acid species which do react form some other carbonyl containing species (e.g., ketones or aldehydes); or 3) the absorptivity of the affected carbonyls is small. We discount 3) since observed C=O stretching intensities are strong in liquid, polymer and solid systems. In order to distinguish between 1) and 2), we employed pyridine as a spectroscopic titrant for acid functionality.

Several of the ring-based carbon vibrations of pyridine are sensitive to the existence and strength of any hydrogen-bonds formed with the unpaired electrons on the nitrogen. Such spectroscopic information has been used for investigations of acidic functionality on surfaces.(13) We show the dependence of some of the pyridine-based vibrations on thermal treatment in Fig. 2. Absorptions at 1485 and 1465 cm^{-1} characterize pyridine which is hydrogen bonded to two types of sites which differ in the strength of the hydrogen bond formed. Only one type of hydrogen bonded pyridine is seen prior to thermal treatment (1485 cm^{-1}). After thermal treatment two pyridine binding sites are seen. The original 1485 cm^{-1} absorption is narrower following thermal treatment. Therefore thermal treatment has converted part of the acid functionality associated with the 1485 cm^{-1} vibration to an acid center characterized by the 1465 cm^{-1} absorption and having a greater hydrogen bond strength than the original species. It is generally believed that the only significant acidic functionality present is phenolic and carboxylic.(1) Concomitant spectroscopic changes indicating phenolic reaction (e.g., 1600 cm^{-1} loss) is not observed. In addition the frequency loss (1485 cm^{-1}) indicates that the original species bound to pyridine have similar hydrogen bond strength. Therefore we assign the acid group loss to carboxylic species. Since corresponding loss in the C=O stretching region does not occur, we conclude that a reaction of the type



occurs. If the species which reacts with the carboxylic acid is a part of the "solid" matrix, a new covalent "cross-link" will be formed at the expense of one hydrogen-bonded "cross-link".

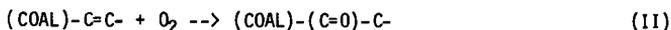
Oxidation of thermally treated coal at 100°C produces new oxygen functionality

The effect of O₂ oxidation of Illinois No. 6 coal at 100°C was examined. An example of the spectroscopic changes resulting from O₂ oxidation at 100°C is shown in Fig. 3 for a sample which had been thermally treated at 100°C to remove the reactive carboxylic acid species. The dependence of the oxidation changes on prior treatment (thermal, closed cell or ambient oxidation) was examined. The principal changes could be attributed to the same oxidation reactions indicating that the 100°C oxidation is reasonably independent of sample history.

The principal changes observed are absorption increases which occur in regions attributable to oxygen functionality on carbonaceous substances. Intensity increases in the carbonyl stretching region (1650 to 1750 cm⁻¹) indicates aldehyde, ketone or carboxylic acid formation. The observation that most of the intensity increase is broadly centered at 1670 cm⁻¹ suggests that oxygen addition to aromatic or unsaturated carbon residues has taken place. Intensity increases occur in the "ether" region (1000 to 1150 cm⁻¹) which, though not diagnostic for ether formation, are suggestive.

The reaction of coal with O₂ to form thermally unstable hydroperoxide intermediates has been frequently proposed as the principal air and/or O₂ oxidation reaction. Definitive spectroscopic evidence showing hydroperoxides has not been reported. Compelling non-spectroscopic evidence is reported by deVries, et al.(14) Our spectroscopic changes are consistent with the formation of all of the expected decomposition products of transient hydroperoxides with the exception of alcohols. Hydroperoxide decomposition proceeds by two parallel pathways: one leads to carbonyl formation while the other leads to alcohol formation. deVries found, and our data supports, the conclusion that the alcoholic pathway is not important in coal oxidation.

We do not believe that significant numbers of carboxylic acids are formed either. An increase in intensity in the OH stretching region associated hydrogen-bonding is not seen. Nor does acid group titration using pyridine indicate a change in the number of acidic groups as a result of oxidation. The principal reaction can be summarized as

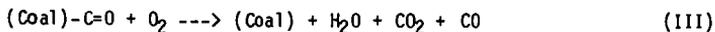


where we have indicated the reaction having occurred with unsaturated carbon as noted above.

A new oxidation reaction is found at room-temperature

The effect of lengthy O₂ on Illinois No. 6 coal was examined spectroscopically. While some changes were seen, they were of low intensity and difficult to resolve. Since the 100°C oxidation and the thermal decarboxylation are obviously independent reactions, we expected the room-temperature oxidation to have no effect on any thermal chemistry. This did not prove to be correct. Lengthy room-temperature oxidation eliminated all evidence of the thermal decarboxylation reactions. The room-temperature oxidation reactions, though not resulting in any striking absorptivity changes, have a dramatic reactivity effect.

We propose the existence of a hitherto unrecognized reaction which is competitive with the thermal decarboxylation reaction. The reaction is summarized as:



We have examined the kinetic behavior of this new oxidation reaction and find that the reaction is rapid by 50 to 60°C. On the other hand, the thermal decarboxylation

reaction is negligible below 60 to 70°C. Therefore there is a temperature "window" from approximately 50 to 80°C in which the reactions will compete and the overall spectroscopic and chemical changes are extremely sensitive to temperature and atmosphere. In addition we predict that any experiment employing a temperature-jump encompassing this temperature "window" will be heating rate dependent. Such a temperature-jump is routinely employed in coal drying procedures. A survey of the literature examining the low-temperature oxidation of coal reveals many statements that the coal used must be carefully predried under precisely defined conditions (see, for example, deVries, et al.(14) and the discussion and references in 7). We take this to be a consequence of the need to control these competing reactions. The sensitivity to the pre-oxidation conditions suggests that the reactivity differences arising from the thermal and room-temperature oxidation are significant even though the i.r. spectroscopic changes are relatively weak and non-specific.

Oxidation Mechanism

Based upon the above evidence with additional confirmation from studies not included herein, we propose the following "mechanism" for the low-temperature oxidation of coal. The oxidation at any moderate temperature is comprised of a combination of the reactions observed in the single-step procedures which we have discussed and summarized as I-III. Thermal decomposition results in loss of carboxylic acid functionality (I). These can be partially replenished during oxidation by the formation of a variety of new carbonyl species (II) resulting from the decomposition of transient hydroperoxide intermediates. The variety of carbonyl species formed is larger than lost due to the thermal decomposition. If the oxidation is allowed to proceed for a long time, the net change in carboxyl absorbance can approach zero. Consequently the net result of the thermal oxidation is to convert carboxylic acid functionality into a more extensive variety of oxygenated species. The oxygen-to-carbon ratio will be less sensitive to these changes than might be expected on first consideration since carbon may be lost through the production of CO and CO₂ and the change of carbonyl functionality will depend upon both the length of time allowed for reaction and the heating rate. A second oxidation reaction (III) occurs at a significant rate slightly above room temperature. Over some temperature ranges, this reaction occurs simultaneously with the thermal decomposition reaction (I) and is either competitive or involves a common intermediate species. Since the absorbance changes associated with II are relatively weak, reaction I will dominate the i.r. difference spectra when it is present.

Sensitivity to water content

We have observed that the relative contribution of the three indicated reactions is sensitive to water. This has not been systematically explored in our experiments. Similar dependencies have been reported.(14,15) deVries, et al.(14) point out that water will influence the hydroperoxide decomposition reactions. Marinov finds evidence for multiple reactions in the low-temperature chemistry of coal.(15) Marinov further finds that water is both a product and a reactant in the low-temperature chemistry of coal. Comparison of the conditions employed by Marinov and ourselves indicates that the two sets of observed reactions may be the same. Therefore water is likely involved in two or more of the reactions which we observe and will lead to extremely complex time-temperature-water content dependencies.

The conditions which we have employed and those of the other cited studies were carried out in the temperature range and using coals which are subject to "spontaneous" ignition. These complexities associated with water content will be one of several factors which will contribute to the initiation of such an uncontrolled oxidation. We believe that our results are suggestive of several new approaches which might be beneficial in preventing "spontaneous" ignition and, more generally, improving the stability of dry coal. Hydroperoxide oxidation is not important until relatively high temperatures and is endothermic in model compounds. Our identification of two additional reactions which occur at much more modest

temperatures and are competitively coupled provides specific reaction-types which might be amenable to control. It is likely that interrupting either reaction will to improved coal stability and may even be effective in reducing or eliminating a key reaction leading to spontaneous ignition.

V. Conclusions

Analysis of FT-ir difference spectra obtained when coal is subject to different oxidation and thermal conditions indicates that thermal oxidation consists of at least three reactions all of which occur in a low-temperature (25 - 100°C) oxidation region. Reaction types (I-III) account for the observed data. Two of the reactions involve oxygen directly; the third is a thermal decarboxylation or decarbonylation reaction which proceeds in the absence of oxygen. Oxidation at 100°C results in the formation of a variety of oxygenated species. The principal products are believed to be carbonyl species which result from the decomposition of thermally unstable hydroperoxides formed by oxygen addition to some species in the coal. In contrast, oxidation at 25°C results in a net loss of absorbance which we interpret as a loss of carbonyl species. The thermal process results in significant i.r. absorption loss at frequencies which are characteristic of carboxylic acid species. Since carbonyl species can either be lost or gained depending upon which pathway dominates, the time-temperature profile employed in oxidation studies will have a significant effect on the overall composition of the oxidized coal. Commonly employed coal pre-drying procedures prior to oxidation is expected to alter the composition of the final oxidized coal since such pre-drying is similar to the thermal step examined in this work.

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Table I

Analytical data for coals representative of the samples utilized⁽¹⁾

PARAMETER	ILLINOIS No. 6	EMWIDE
Rank	HR-C	SAB-C
S Carbon (DMF)	29.44	73.40
H/C	0.944	0.836
O/C	0.999	0.201
COON (per 100 carbon)	0.5 ⁽²⁾	3.2 ⁽³⁾
Organic S (DMF)	3.08	0.93
Phenolic OH (per 100 carbon)	4.5 ⁽²⁾	4.4 ⁽³⁾
Total S (Dry)	3.94	0.92
Pyritic S. (Dry)	1.17	0.01
Mineral Matter	10.94	7.00

1. All analysis (except as noted) are from data from similar samples contained in the Coal Characterization Library of the Exxon Coal Research Laboratory, Baytown, Texas. Sample to sample variations are expected as well as differences due to sample preparation. The numbers, therefore, are useful only in addressing trends.

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3. Analyses were kindly provided by Dr. R. Liotta and obtained from samples representative of those utilized.

Fig. 1 - FT-ir difference spectrum of Illinois No. 6 coal subjected to vacuum drying at 100°C showing absorption losses relative to the coal before heating.

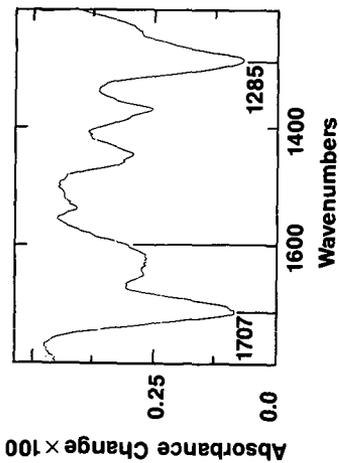


Fig. 2 - Pyridine adsorbed on Rawhide coal (A) before and (B) after having been subjected to vacuum drying at 100°C. The 3 indicated absorptions are pyridine specific.

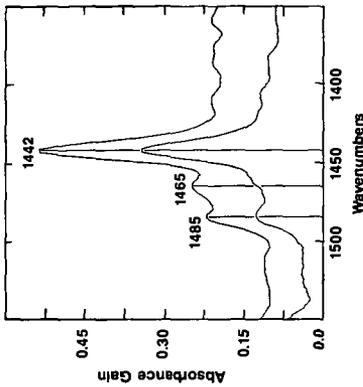
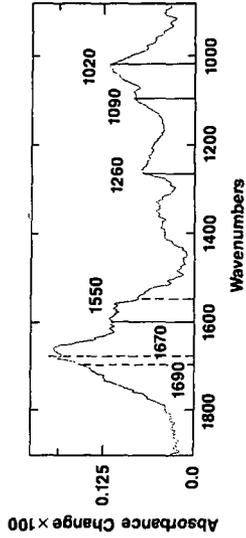


Fig. 3 - FT-ir difference spectrum of Illinois No. 6 pretreated by vacuum drying at 100°C and subjected to O₂ treatment at 100°C. Absorption increases of the oxidized coal as compared to the dried (100°C) starting coal are shown.



The Structure and Plastic Properties of Coals Following
Low-Temperature Catalytic Hydrogenation

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Abstract

Following earlier work, studies have been continued in examining the physical and chemical changes which occur in coals following low-temperature ($\leq 400^{\circ}\text{C}$) catalytic hydrogenation. Reactions were conducted with a series of coals ranging in rank from subbituminous to low volatile bituminous and using a dispersed Mo catalyst in the absence of solvent. With progressive hydrogenation, the yield of extractable liquids substantially increased for all coal samples except the low volatile bituminous coal. There were corresponding increases in the coal fluid properties. Low-temperature hydrogenation was also found to negate the adverse effects of air oxidation on coal fluid behavior.

Although hydrogenation improved coal fluidity, it essentially eradicated any swelling properties of the parent coal. Experiments using blends of hydrogenated coals and hydrogenated coal extracts with parent coals showed that dilatation could be greatly improved for a bituminous coal by the addition of hydrogenated bituminous coal extract. No other blends exhibited swelling properties. It is suggested that the phenomenon of swelling is due to a particular chemical interaction between the mobile liquids (indigenous or extraneous) and the chemical structure of the coal macromolecular network.

Introduction

It has been known for several decades that heating certain coals, at or near their softening point, may result in a several fold increase in the content of extractable liquids (1-8). Furthermore, it has been demonstrated that the fluid properties of the parent coals correlate with the yield of extractable liquids from the heat treated coals (most often when chloroform was used as the extracting solvent) and that both of these characteristics passes through a maximum in coals between 85 to 88% carbon content (5,6,9,10).

The effect of the low molecular weight, hydrogen-rich, chloroform-soluble material on the plastic behavior of coal has been explained by the hypothesis that the development of plasticity is a transient, in-situ, hydrogen-donor process (11). These lighter molecular weight substances not only play an essential role in plasticity development, but also are influential in coal liquefaction (12,13).

A decrease in the yield of extracts (14) and a significant decrease in plastic properties (14,15) can be effected by mild oxidation. Ignasiak et al. (16) have suggested that the incorporation of reactive oxygen groups (as phenolic, acidic, or ketolic oxygen) may act as the agents responsible for the formation of cross-linkages during the heating of the coal, leading to an overall reduction in the internal mobility of the coal molecules. Conversely, hydrogenation of oxidized or high oxygen content coals can result in the development of plastic properties (17-19).

In earlier reported research (13,20), which was directed towards deriving coal structural information through low-severity catalytic coal liquefaction in the

absence of solvent, it was found that, as the yield of extractable liquids increased, the coals became progressively more fluid. Further investigations have since been made of the relationship between the catalytically generated liquids and coal fluid properties for a series of coals of different rank. The findings are presented in this paper.

Experimental

1) Coal Properties and Preparation

The coals studied were obtained from the Pennsylvania State Coal Sample Bank and were selected to cover a range of rank from subbituminous to low volatile bituminous; each containing over 80% vitrinite. Properties of the coals are shown in Table 1.

The coals were ground to -20 mesh under conditions to minimize oxidation and were subsequently stored under nitrogen and used without drying. For catalytic hydrogenation experiments, the coals were impregnated with 1% wt (dmmf) Mo by slurring with an aqueous solution of ammonium tetrathiomolybdate. After slurring, the excess water was removed by drying under vacuum below 100°C.

A high fluidity coal (PSOC-1296) was chosen for studies to examine the effects of oxidation on plastic properties. The coal was oxidized under mild conditions by passing air through a bed of the finely ground coal (-40 mesh) at 50°C for four days.

2) Catalytic Hydrogenation

Hydrogenation reactions were conducted in tubing bomb reactors under an initial (cold) hydrogen pressure of 7 MPa and at temperatures between 250 and 400°C for times of 5 to 60 min. The yields of light gases were determined by volumetric measurement and gas chromatographic analysis.

In some cases, the reacted coals were extracted in chloroform, using a Soxhlet apparatus, to obtain a partition into soluble extract and residue. More detailed descriptions of the experimental procedures have been reported (13,20,21).

3) Analytical

The fluid properties of coals, hydrogenated coals and blends of coals with coal extracts were studied using an automated Gieseler plastometer, following the ASTM standard procedure (22), and a pressure microdilatometer. The latter was operated at a heating rate of 20°C min⁻¹ from ambient under 0.1 MPa of nitrogen.

Results and Discussion

The yields of gases and chloroform-soluble extract obtained upon catalytic hydrogenation of the coals for 60 min at 350 and 400°C are given in Table 2. Reaction at 350°C caused a significant increase in the yields of chloroform-soluble extract over that obtained from the parent coal, the greatest response being obtained with the subbituminous coal, PSOC-1403. This observation is consistent with reported data showing that, under these reaction conditions, low-rank coals were more reactive than bituminous coals (13). At 400°C, high extract yields were obtained with all of the coals except the low volatile bituminous coal, PSOC-1325. It is supposed that the structure of a coal at this stage of metamorphism contains such a high proportion of strong covalent bonds that it is difficult to break down into lower molecular weight species, even in the presence of an active catalyst.

Mild oxidative treatment of the hvA bituminous coal, PSOC-1296, reduced the yield of extractable liquids, a commonly observed phenomenon. However, the subsequent catalytic hydrogenation of this coal appeared to have more than counteracted the effects of oxidation.

The results of Gieseler plastometer measurements on catalytically hydrogenated and unextracted coals are shown in Figures 1(a) - (c). The effect of reaction time on the fluidity of an hvA coal can be seen in Figure 1(a). With increasing reaction time at 400°C, which corresponds to a progressive increase in the content of extractable liquids, the coal softening temperature was lowered and the maximum fluidity was increased. For times longer than 15 min, the maximum fluidity exceeded the measurable range of the instrument. Similarly, reaction for 60 min at 400°C introduced fluid behavior to subbituminous coals which, in their parent state, produced no response in the Gieseler plastometer, Figure 1(b).

In parallel with the measured effects of oxidation of the hvA bituminous coal in lowering the yield of chloroform-extractable liquids, the fluid properties were also suppressed, Figure 1(c). Catalytic hydrogenation of the oxidized coal was instrumental in increasing the fluidity above that of the original coal.

The development of fluidity in these coals, as measured by the Gieseler plastometer, is not to be confused with the swelling behavior shown by coking coals. Examination of the treated coals in the microdilatometer showed that, consistent with the Gieseler measurements, the coal softening temperature had been reduced. However, all of the samples underwent a volume contraction with increasing temperature, even those which had exhibited a net volume expansion or dilatation prior to treatment. These results were interpreted to mean that the catalytic hydrogenation had increased the coal fluidity to such an extent that, in the melted state, the viscosity was so reduced that volatile pyrolysis products could freely escape without causing the coal to swell. In effect, the volume contraction meant that, upon becoming fluid, the density of the coal sample had increased.

A number of experiments were then conducted, using a bituminous and a subbituminous coal (PSOC-1266 and PSOC-1403, respectively) to determine whether blending the hydrogenated products with untreated coals could influence swelling behavior. Mixtures of unextracted hydrogenated coals with the parent coal, in which the concentration of the former was increased up to 50% wt did not appreciably influence the swelling behavior of either coal, although, for the bituminous coal, there was a steady reduction in softening temperature with increasing concentration of the treated coal.

Blending the extract from the hydrogenated bituminous coal with the parent coal had a dramatic effect upon swelling properties, Table 3. This effect was not found with any other combination of the parent bituminous or subbituminous coal with either extract from the hydrogenated coals, although blending did reduce the initial softening temperature and increase the volume contraction in each case.

It is assumed that the extracts from the hydrogenated coals and in particular the bituminous coal will contain a reasonable proportion of hydroaromatic structures. The presence of H-donor compounds is thought to enhance the plastic behavior of coals (11). The results presented here suggest that the phenomenon of swelling is attributable to a particular combination of (possibly) H-donor properties of the mobile liquids within coals (and added liquids such as the extract from the hydrogenated bituminous coal) together with the structural configuration of the coal macromolecular network.

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TABLE 1

COAL PROPERTIES

Penn State Sample Bank Number	PSOC-1325	PSOC-1296	PSOC-1022	PSOC-1266	PSOC-1403	PSOC-1414
Seam	L. Kittanning	L. Kittanning	L. Kittanning	L. Kittanning	Anderson	Beulah-zap
County	Somerset	Armstrong	Lawrence	Mahoning	Campbell	Mercer
State	Pennsylvania	Pennsylvania	Pennsylvania	Ohio	Wyoming	N. Dakota
ASTM	LV	HVA	HVA	HVA	SUBBIT B	SUBBIT C
Mean-Maximum Reflectance of Vitrinite (R _{max} , %)	1.63	0.87	0.80	0.83	0.40	no data
Moisture Content (a.r., % wt)	1.2	1.1	3.8	3.4	17.8	25.4
Mineral Matter (dry, % wt)	13.5	20.3	17.2	6.1	11.9	10.8
Elemental Composition (% dmmf)						
Carbon	90.0	85.7	82.9	83.2	73.0	71.0
Hydrogen	5.0	5.5	5.7	5.0	4.5	6.6
Oxygen	2.8	5.8	7.7	8.6	20.4	21.1
Nitrogen	1.6	1.5	1.6	2.1	1.2	0.7
Organic Sulfur	0.6	1.4	0.6	0.5	0.9	0.6
Petrographic Composition (mineral-free, % vol)						
Vitrinite	96	88	81	91	87	83
Exinite	0	2	13	3	2	2
Inertinite	4	10	6	6	11	15

TABLE 2

YIELDS OF GASES AND CHLOROFORM-SOLUBLE EXTRACT (% dmfm) FROM CATALYTICALLY HYDROGENATED COALS
(1% wt Mo (dmfm); no solvent; 60 min reaction; 7 MPa cold H₂ pressure)

Coal	ASTM Rank	CHCl ₃ Extract for raw coal	Reaction Temperature (°C)					
			350			400		
			CHCl ₃ -solubles	CO _x	C ₁ -C ₄	CHCl ₃ solubles	CO _x	C ₁ -C ₄
PSOC-1325	lvB	0.6	12.9	0.2	0.4	12.8	0.1	0.7
PSOC-1266	hVA	0.9	8.8	0.2	0.0	59.1	0.3	0.8
PSOC-1022	hVA	2.5	13.3	0.7	0.3	54.3	1.8	1.5
PSOC-1296	hVA	5.0	--	-	-	49.6	0.5	0.8
PSOC-1403	Sub. B	4.3	33.4	7.2	0.8	52.3	12.4	4.0
PSOC-1414	Sub. C	2.3	--	-	-	37.0	17.2	4.1
*PSOC-1296	hVA	0.6	--	-	-	54.5	1.3	4.1

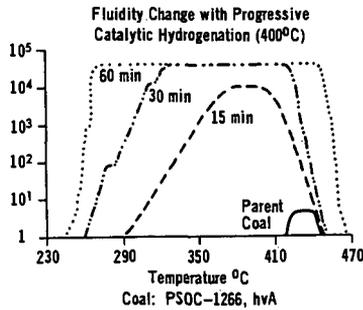
* Pre-oxidized coal

TABLE 3

DILATOMETRIC PARAMETERS FOR MIXTURES OF BITUMINOUS COAL (PSOC 1266)
WITH THE CHLOROFORM-SOLUBLE EXTRACT OF THE HYDROGENATED COAL

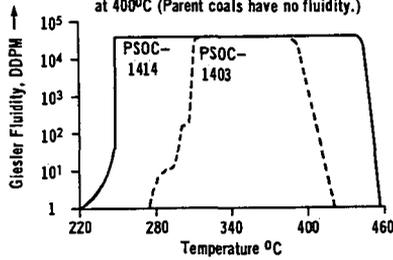
wt% hydrogenated extract in mixture	0	5	10	20
Softening temperature, °C	435	410	395	367
Temperature of maximum contraction, °C	477	460	450	435
Temperature of maximum expansion, °C	500	487	480	485
Resolidification temperature, °C	---	---	500	495
% maximum volume* contraction	21	24	21	26
% maximum volume* expansion (net)	23	52	129	349
% volume expansion* on resolidification (net)	---	---	80	349

* measured relative to original coal volume



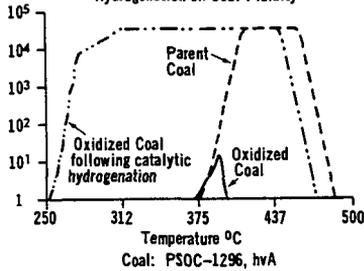
(a)

Fluidity of Subbituminous Coals Catalytically Hydrogenated at 400°C (Parent coals have no fluidity.)



(b)

Effects of Mild Oxidation and Subsequent Catalytic Hydrogenation on Coal Fluidity



(c)

Figure 1. GIÉSELER PLASTOMETRY MEASUREMENTS OF HYDROGENATED AND PARENT COALS.

DISTRIBUTION OF IMPREGNATED METAL HALIDE CATALYSTS IN COAL GRAINS

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INTRODUCTION

Metal halides such as stannous chloride and zinc chloride are known to be effective coal hydrogenolysis catalysts (1-3). Weller et al. (1) examined a number of potential catalysts and found zinc and tin chlorides to be among the best. Although stannous chloride is generally recognized to be more active than zinc chloride, zinc chloride has been chosen as the catalyst in a number of coal liquefaction systems. These include processes developed in Japan (4), molten salt reactors (2,3) and short residence time reactors (5-7).

The metal halides appear to be active in cleaving bridges between groups of condensed aromatic rings (unit structures) under liquefaction conditions. This results in a progressive depolymerization of the coal, ultimately to isolated unit structures, with little reaction of the condensed ring systems themselves (8-10). This results in less hydrogen consumption and a soluble product that can be further upgraded. Weller et al. (1) suggested that a metal sulfide was formed, which was the active catalytic species. Zielke et al. (2) proposed a complex of zinc chloride and water to form a Friedel-Crafts type acid, for the case of zinc chloride catalyzed liquefaction. Bell and coworkers (11-14) studied the cleavage in model compounds with ether and carbon-carbon bonds, species that are thought to form bridges between unit structures in coal. They proposed a similar active species. This conclusion was supported by a study of Beishline et al. (15). The hydrogenolysis reaction begins at the surface of coal grains and proceeds towards the center (16,17). As the bridges are broken, the coal softens and reacts. The metal halides lower the temperature at which the coal softens (18) and also the temperature at which the exothermic coal hydrogenation reaction occurs (19).

Contacting of the metal halide with the bridging structures is required for the liquefaction reaction to proceed. At the temperatures of liquefaction processes, the coal softens and both thermal and catalytic bond cleavage occurs. The reactions are rapid, but may lead to retrogressive reactions if sources of hydrogen are insufficient or the catalyst is not present (20,21). The semi-coke formed by the retrogressive reactions is less reactive to liquefaction and increases the reaction time and severity of conditions required for high conversions. Partial liquefaction under hydrogen deficient conditions may induce sufficient fluidity for mesophase to form. Recently, the liquefaction of coal at mild conditions, below the normal softening temperature, has been studied (22). The process involves two steps: hydrotreating of metal halide impregnated coal and base catalyzed depolymerization of the products. The temperature of the process is kept below 275°C. Under these conditions, the fluidity of the system is low and it is important to have good contact between the metal halide catalyst and the bridges that are to be cleaved. The catalytic reactions must occur and the thermal reactions must be suppressed. It is therefore important that a good dispersion of the catalyst throughout the coal grains be achieved. The effect of impregnation method on the dispersion of the catalyst is the subject of this report.

EXPERIMENTAL

Four coal samples were studied in these experiments. The ultimate analysis of the coals is shown in table 1. The preparation of the samples for analysis is shown schematically in figure 1. The coals were ground to -60/+100 mesh and extracted with THF in a Soxhlet extractor. Some samples used for X-ray analysis were demineralized by HCl and HF. Water, acetone and methanol were used as solvents for impregnation of the metal halides. Reagent grade $ZnCl_2$, $FeCl_3$, $NiCl_2 \cdot 6H_2O$, $SnCl_2 \cdot 2H_2O$ and $SnCl_4 \cdot 5H_2O$ were impregnated on the coals. The solvent, metal halide and coal were mixed in the desired amounts. The mixture was stirred and agitated in an ultrasonic bath for two hours. The coal/metal halide mixture was then dried to remove the solvent.

Grain mounts were prepared with epoxy mounting medium, ground and polished to expose cross sections of the coal grains. A Hitachi (model S-500) scanning electron microscope was used to examine the samples. The electron energy was 20,000 KeV. A Kevex energy-dispersive spectrometer was used to map fluorescent X-rays from the metal atoms and the chlorine. X-ray diffraction was used to measure changes in the spacing of clusters of condensed-ring aromatic groups. The assignment of X-ray diffraction peaks was by comparison with the diffraction pattern of graphite.

RESULTS AND DISCUSSION

Polished grain mounts of the metal halide-impregnated coal samples were examined with the scanning electron microscope. Grinding and polishing of the grain mounts exposes a cross section of the coal grains. Fluorescent X-rays, emitted from the surface of the mount, were measured with the energy dispersive detector as the sample was scanned. A narrow band of X-rays, corresponding to a specific atom, were recorded on photographic film as the sample was scanned. The distribution of the given atom in the coal grain was thus obtained. The metal atom and chlorine atom distributions for various impregnation conditions were determined. If the metal halide is uniformly distributed throughout the coal grain, the photograph will show a uniform exposure throughout the cross section of the coal grain. If the metal halide is poorly distributed throughout the coal grain, the photograph will show exposure at the edge of the cross section and along cracks, but not in the center of the grains. Some background exposure will be seen in areas where the epoxy mounting medium is exposed at the surface. Electron micrographs of the coal grains were also obtained. The X-rays mostly originate near the surface, since the depth of penetration of the electrons is not great.

The distribution of the metal halides within coal grains is qualitatively shown in figure 2. The interpretation is subjective and is based on observation of several grains for each sample. Good dispersion of the metal halides is achieved with organic solvents. Both methanol and acetone are effective in dispersing the metal halides and under the conditions of these experiments, it is impossible to determine if one is better than the other. Both of these solvents are known to swell coals. Stannous chloride is the most easily dispersed of the metal halides tested. Nickel and iron chlorides are more difficult to disperse from aqueous solution. The effectiveness of dispersion of the metal halides varies with the coal samples, but does not follow rank.

Beall (23,24) has reported the possible formation of intercalation compounds of coal with the chlorides of iron, chromium, and copper at temperatures from 215°C to 150°C. The formation of intercalates has been suggested as a possible mechanism in the catalysis of coal hydrogenolysis by metal halides. The possible formation of intercalates was investigated by X-ray diffraction of the impregnated samples. Formation of an intercalation complex would be expected to shift the 002 diffraction peak, corresponding to a larger interplanar spacing in the clusters of condensed-ring aromatic groups. Demineralized samples were studied to remove the interference from diffraction peaks due to mineral matter. Impregnation of metal halides decreased the intensity of 002 diffraction peaks due to scattering of X-rays by the metal atoms, but the peaks were not shifted. Although the formation of intercalates cannot be ruled out by these experiments, there is no evidence to support intercalate formation.

Acetone and methanol swell coals and are also effective in impregnating metal halides throughout the coal structure. Examination of swollen coals, from which the solvent has been removed, by X-ray diffraction show no changes in the 002 diffraction peak. The solvent is apparently imbibed by the amorphous regions surrounding the clusters of condensed-ring aromatic units, but does not disrupt the clusters. The metal halides appear to be deposited in these amorphous regions as the solvent is evaporated. Water does not swell coal, but it is adsorbed on coal surfaces within pores. Impregnation from aqueous solution is not as effective as from organic solution and depends strongly on the coal and the metal halide properties. Impregnation of stannous chloride from aqueous solution at room temperature can be quite effective in achieving high dispersion at the microscopic level, which is the limit of resolution of these techniques. The dispersion at the molecular level for impregnation from either aqueous or organic solutions cannot be measured by these procedures.

CONCLUSIONS

Impregnation of metal halides throughout coal structures is more effective from organic solutions than from aqueous solutions. High dispersion of the metal halide is attributed to the ability of the solvent to penetrate the coal structure and cause swelling. A minimum solubility of the metal halide in the solvent is also required. No evidence for the formation of intercalation compounds between the metal halides and condensed-ring aromatic structures in the coal has been found.

Good dispersion of potential coal hydrogenolysis catalysts throughout the coal is expected to be important in low-severity coal liquefaction processes. Liquefaction may be expected to be achieved below the normal softening temperature of the coal. Good dispersion may also prevent the formation of less-reactive semicoke during liquefaction at higher temperatures. Under conditions of good catalyst dispersion and hydrogen accessibility, depolymerization of coal to soluble products may be expected to occur rapidly.

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Table 1. Ultimate Analysis of Coal Samples

	<u>Wyodak</u>	<u>Burning Star</u>	<u>Elkhorn</u>	<u>Coal Basin</u>
Carbon, %	76.0	78.9	85.4	90.3
Hydrogen, %	5.4	5.4	5.1	5.4
Nitrogen, %	1.4	1.2	1.8	2.2
Sulfur, %	0.6	4.4	0.7	0.7
Oxygen, % (dif)	16.6	10.1	7.0	1.4

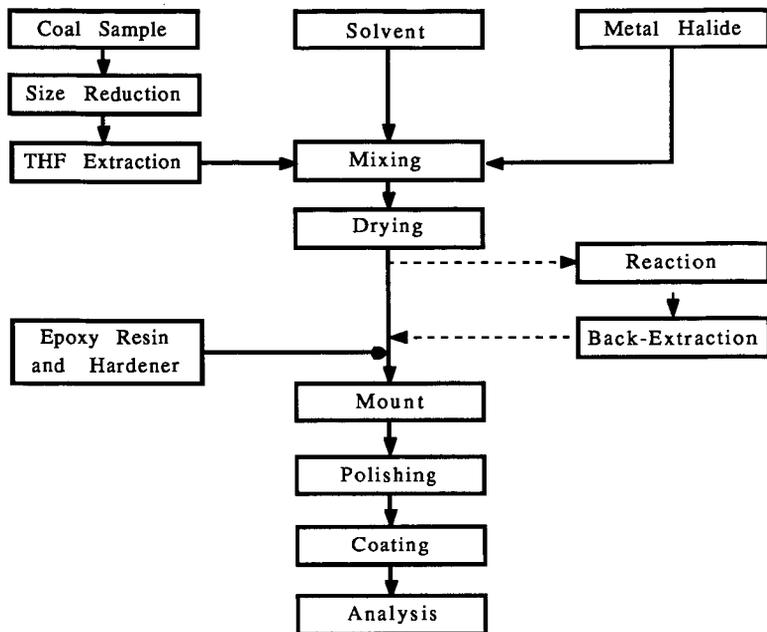


Figure 1. Flowchart for SEM Mount Preparation

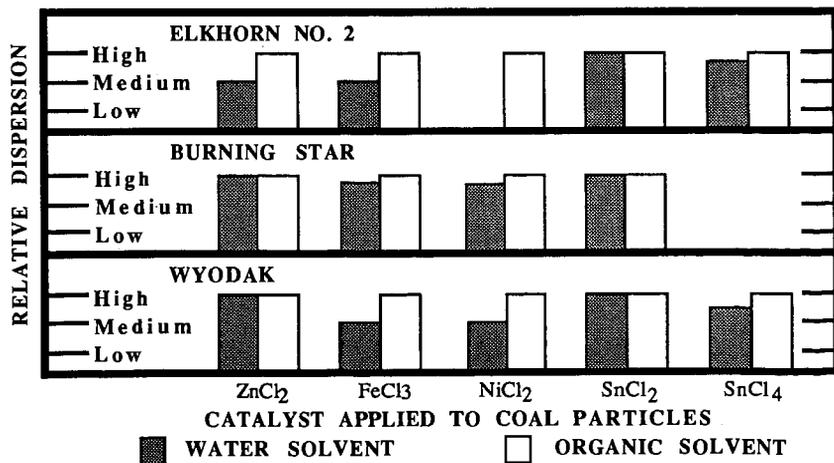


Figure 2. Catalyst Dispersion

A PSEUDOKINETIC STUDY OF COAL LIQUEFACTION

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All approaches to the study of the chemistry of coal liquefaction are handicapped to one degree or another by the inability to accurately measure the detailed structure of the primary reagent -- coal. Recent work at PETC has focused on utilizing quantitative ^{13}C NMR together with elemental balances to obtain an improved picture of the molecular level chemistry of hydrogen in realistic conversion environments. The method divides total hydrogen incorporated into the organic products into that consumed in hydrogenation, heteroatom removal, and hydrogenolysis. The details of this approach have recently been discussed [1]. To date, the approach has proven useful in describing the influence of reaction temperature [1,2] and catalyst [3] on the utilization of hydrogen. This work describes efforts to determine the relative rates of hydrogen-consuming reactions -- hydrogenolysis, hydrogenation, and heteroatom removal.

Experimental

All reactions were done on a shaking microautoclave system, which has the capacity to simultaneously immerse five 40 milliliter microreactors into a preheated fluidized-bed sandbath. This system has a heat-up time of approximately 5 minutes. Prior to reaction the microreactors were charged with 4 g of Illinois No. 6 hvC (River King) bituminous coal and 7 g of a heavy coal-derived distillate (240°C-450°C cut from the SRC-II Process), and pressurized to 1200 psig with hydrogen at ambient temperature. This loading procedure results in a hydrogen pressure of approximately 2000 psig at reaction temperature. Catalytic runs were accomplished by loading the coal with 0.006 g of either molybdenum (as ammonium heptamolybdate) or tin (as SnCl_4). Reactions were run at 0-, 5-, 10-, 20-, 30-, and 60-minute reaction times (time at 380°C).

Following reaction the headspace gas was quantitatively collected and analyzed by gas chromatography. The total reaction product was removed to a Soxhlet thimble and separated via CH_2Cl_2 extraction into soluble and insoluble fractions. Both product fractions were analyzed for elemental composition via microanalytical procedures by Huffman Laboratories.

Both ^{13}C and ^1H high-resolution NMR spectra were obtained in CD_2Cl_2 on the soluble fractions using a Varian XL-100 spectrometer. The ^{13}C NMR

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

spectra of the feed coal and the CH_2Cl_2 insolubles were obtained via crossed polarization magic angle spinning, CP/MAS, techniques using a Brücker CXP-100 instrument.

Results and Discussion

The hydrogen utilization profiling method involves measurement of the ^{13}C NMR aromaticity change during reaction as a direct quantitative measure of the degree of hydrogenation of the feed slurry. The total hydrogen incorporation is obtained from the elemental analysis, and the amount incorporated in heteroatom removal is estimated from the change in organic heteroatom content. In these low-temperature reactions (380°C), negligible amounts of light hydrocarbon gases were produced. Thus any hydrogenolysis observed must involve cleavage of slurry matrix bonds to yield smaller solid and liquid fragments. It must be remembered that because there is no means of counting bonds, the amount of hydrogen incorporated via hydrogenolysis must be obtained by difference:

$$\text{Total hydrogen} - (\text{hydrogenation} + \text{heteroatom removal}) = \text{hydrogenolysis.}$$

The data in final form are simply the number of hydrogens, per 100 carbons of feed slurry, that are incorporated into organic products via hydrogenation, heteroatom removal, and hydrogenolysis (bond cleavage) reactions.

The results of this study of hydrogen utilization are presented in Figure 1. Figure 1a shows the total net hydrogen incorporation into organic products as a function of time for uncatalyzed and tin- and molybdenum-catalyzed reactions. The catalyzed systems appear to incorporate hydrogen more rapidly than the uncatalyzed reactions (note 20- and 30-minute reaction times), but at the longest reaction time (60 minutes), there is no difference between the total net hydrogen incorporation in catalyzed and uncatalyzed reactions. For the catalyzed reactions the results suggest that product hydrogen content actually decreases from 30 to 60 minutes, whereas in the noncatalyzed reaction, hydrogen is still being incorporated during this time period. This may indicate that retrogressive reactions are important at longer reaction times in the catalyzed reactions. Analysis of headspace gas composition after reaction indicates that this decrease in hydrogen content is not due to hydrogen starvation. The behavior shown in Figure 1 at short reaction times, ≤ 10 minutes, is seemingly erratic. However, it does suggest that in general the chemistry is different, either in rate or in the nature of the reactions, from that observed at longer reaction times.

The data in Figure 1b indicate that there is essentially no dependence of heteroatom removal on either catalyst addition or reaction time under these conditions.

The amount of hydrogen incorporated into products via hydrogenation reactions is measured directly by measuring the change in aromaticity during reaction. The data obtained for incorporation of hydrogen by hydrogenation are presented in Figure 1c. It first must be stressed that optimistic error limits on measurement of the change in aromaticity, Δf_a , are ± 0.02 . This error translates directly into an error of ± 2 hydrogens per 100 carbons.

With this caution, the data in Figure 1c indicate no significant change in degree of hydrogenation with reaction time. However, it is intriguing to note that all three sets of data -- molybdenum-catalyzed, tin-catalyzed, and uncatalyzed -- show evidence of hydrogenation at 10-minute reaction times and show a drop in the degree of hydrogenation between 10 and 20 minutes. Both catalytic runs also exhibit slightly higher levels of hydrogenation than the noncatalyzed reaction from 20 minutes to 60 minutes of reaction. These small differences are within the limits of error of the method.

The most difficult (and error-prone) mode of hydrogen utilization to measure is the hydrogen incorporated into the system via hydrogenolysis or bond cleavage chemistry. This mode of utilization is determined by difference and incorporates the sum of the errors of the other analyses (total hydrogen, heteroatom removal, and hydrogenation). With this qualification, the data that describe hydrogen incorporation in bond cleavage chemistry are very interesting (see Figure 1d). They indicate that for the first 10 minutes of reaction, there is progressively more net bond formation (condensation). This is followed by a period, 10-30 minutes, during which bond cleavage predominates. Both catalytic systems appear to reach their peak in hydrogenolysis consumption at 30 minutes under these conditions. This maximum is followed by a slight decrease in net hydrogenolysis on going to 60-minute reaction times. The data in Figure 1d suggest the existence of a sequential mechanism for conversion under these conditions. At short reaction times, the apparent internal hydrogen redistribution is based on condensation (bond-making) chemistry, while at longer reaction times, bond cleavage (hydrogenolysis) chemistry appears to predominate.

The hydrogen utilization profile data in Figure 1 can be contrasted with the conversion data shown in Figure 2. The conversion data were obtained on samples generated under conditions identical to those used for generation of Figure 1. Neither of these solubility-based conversion plots seem consistent with the hydrogen utilization data, particularly at short reaction times. The solubility data do not indicate any substantial effect of added catalyst and show no apparent qualitative differences between short reaction times and long reaction times. In particular, the time dependence of conversion based on solubility in the two solvents appears to be substantially different. The THF solubility shows an abrupt change at short reaction time, while cyclohexane solubility is essentially a linear function of reaction time. This lack of correspondence between solubility-based conversion values and hydrogen utilization profiles is probably an indication that the two techniques are measuring different properties of the liquefaction system. It seems likely that solubility, especially in strong solvent systems, might be sensitive to physical changes in the system that are not probed by the chemical methods used in hydrogen utilization profiling. It is possible that the hydrogen utilization profile approach may prove to be more useful in investigations of the detailed chemical mechanism of liquefaction.

Conclusions

The hydrogen utilization profiles as a function of reaction time indicate that two different time regimes of reactivity may exist under these mild reaction conditions. At short reaction time the data suggest that

hydrogenation and condensation reactions are operative with minimal net hydrogen incorporation. (The possibility exists that the hydrogen generated in condensation during this time period is being shuttled into more reactive regions of the slurry via hydrogenation). After this initial period of hydrogen redistribution, the major chemistry appears to be bond breaking (hydrogenolysis) that results in significant net hydrogen incorporation into the slurry. This description is consistent with a set of two sequential reactions being responsible for liquefaction under these conditions. The data in this study clearly indicate that both tin and molybdenum accelerate the incorporation of hydrogen into the reacting slurry and imply that the major net effect of the catalysts is to make hydrogen more readily available for hydrogenolysis reactions.

Acknowledgments

The authors would like to express their appreciation to Walter L. Lipinski for his help in operating the autoclave system and to Marjorie R. Hough and Richard F. Sprecher for obtaining the NMR data.

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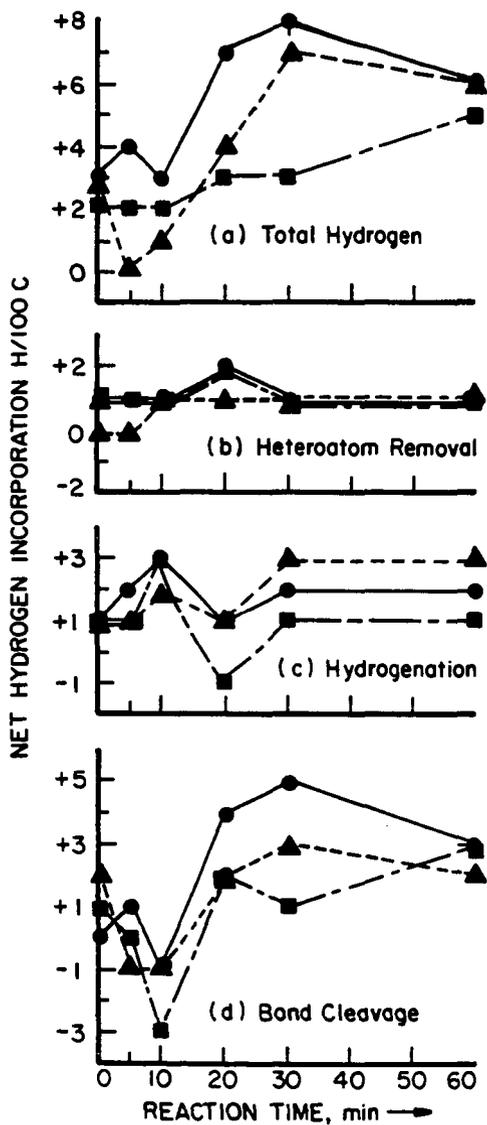


Figure 1 - Hydrogen Utilization as a Function of Reaction Time.

- — Sn Catalyzed
- - - - Mo Catalyzed
- ▲ - - - Uncatalyzed

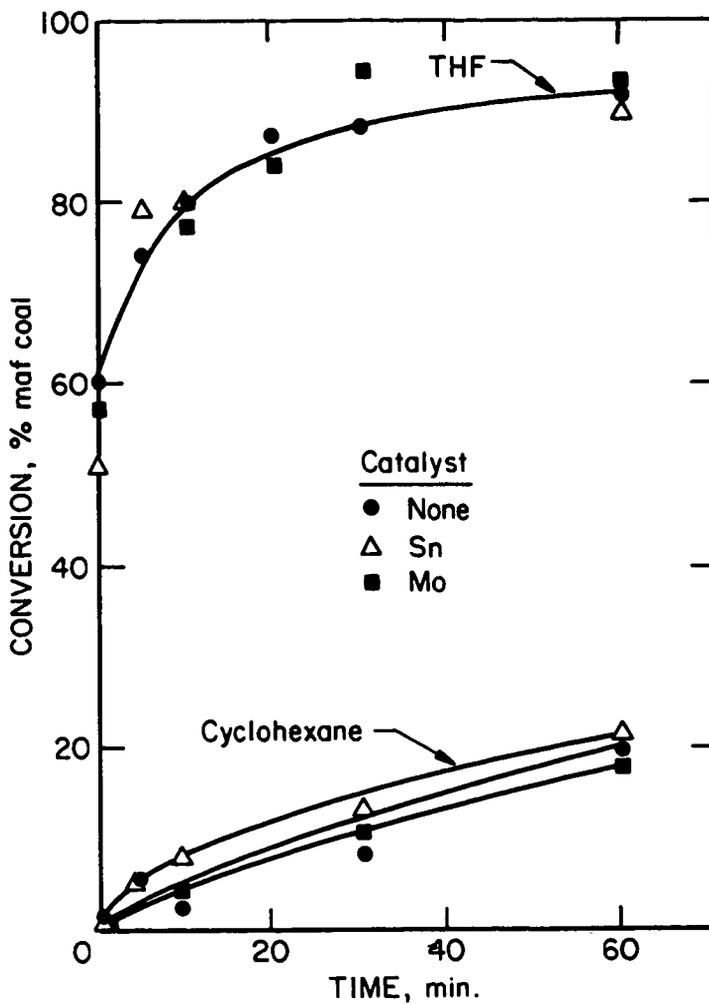


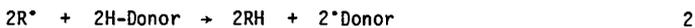
Figure 2 - Conversion of Illinois No. 6 coal at 380°C.

An Electron Spin Resonance Investigation of Free Radicals
in Lignite Formed Using Programmed Temperatures, H₂S, CO and H₂

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INTRODUCTION

The conversion of low-rank coal to liquid products has traditionally been performed in organic donor solvents at constant reactor temperatures. In one view of coal liquefaction, the thermolysis of weak bonds in the coal structure is followed by H transfer to the coal-derived radicals by hydrogenation atom donor molecules, reactions 1 and 2. To minimize addition and allow organic



materials to enter the product stream, we have recently developed a new donor solvent, H₂O-H₂S with CO and H₂, as a substitute for the organic slurrying solvent (1,2) and reducing gases. For ZAP lignite, volatile product conversion for the reaction performed in H₂O-H₂S-H₂-CO at 420°C is 42.8%; and, for H₂O-H₂-CO, it is 37.4% (1). Our current research into the chemistry of liquefaction has yielded considerable progress using the linear temperature programmed reactions, 300-500°C. The conversion to volatile products using H₂O-H₂S-H₂-CO is equal 59.3% (3).

A number of investigators have applied ESR to examine radicals formed during pyrolysis of coal (4-11). Since the method of electron resonance is a very sensitive, we have chosen this technique to investigate mutual interactions of coal-derived radicals with reducing gases.

EXPERIMENTAL

The ZAP lignite (Table 1) was ground to less than 37 μm. About 30-50 mg of lignite sample was inserted in a 2 mm i.d. Pyrex tube together with 20-30 mg of glass wool. The samples were dried in vacuum 1 Torr at 50°C for 3 hrs. The liquefaction was performed under reducing gases using the linear programmed temperature range of 300-500°C over the period of 1 hr in the batch autoclaves.

When the temperature 500°C was reached, the reactors were vented to remove oil and gas, cooled down in water (20°C) and next in ice.. The samples were immediately sealed under argon, and the ESR measurements were carried out within 10-15 min at room temperature. According to Petrakis (12), upon cooling to room temperature, spin concentrations in coal are, in general, the same as at the high temperature. The spin concentrations and g values were determined by the sample interchange method. DPPH was employed as the standard. Spin concentrations were calculated on final and initial amounts of lignite. The spin concentration (SC) data was employed to calculate the conversion to distillate products by using the equation 3. The calculated conversion (SC)

$$\% \text{ conversion (SC)} = \frac{\text{SC}(\text{final}) - \text{SC}(\text{initial})}{\text{SC}(\text{final})} \times 100\% \quad \underline{3}$$

has been correlated with similar conversion values into volatile products independently determined by employing the traditional techniques (1).

All ESR spectra were recorded using a Bruker ER-420 spectrometer. Duplicate samples were prepared for all different sets of liquefaction conditions to check reproducibility.

RESULTS AND DISCUSSION

(a) The effect of H₂S on stabilization of coal-derived radicals

The typical ESR spectrum of a ZAP lignite sample is a single symmetric signal without hyperfine structure (Figure 1). This signal is distinguishable by its g-value, linewidth and spins g⁻¹. For unreacted coal, they are 2.0021, 8.3 G and 1.8 x 10¹⁹ spins g⁻¹, and for pyrolyzed coal linear programmed over 300-500°C for 1 hr, the values are 2.0011, 6.8 G and 20.2 ± 1.9 x 10¹⁹ g spins g⁻¹, respectively. Decreases in ESR g value is known to be a consequence of the evolution of heteroatom-containing gases such as CO₂ and H₂O which are formed during the pyrolyses (13). The decrease in linewidth of the sample can be attributed to the dehydrogenation reactions known to be occurring concurrently.

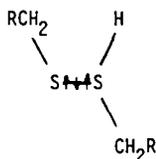
A representative spectrum of ZAP lignite which has been reacted with H₂S is reproduced in Figure 2. This spectrum consists of two symmetric signals:

one is positive (+) and one is negative (-). The positive signal can be attributed to coal-derived and some organo-sulfur radicals. It is close to Lorentzian in shape. The observed negative curve has a Gaussian shape, and it represents radicals associated a variety of, organo-sulfur bonds. The existence of the negative signal suggests an altered magnetic environment of these unpaired electrons.

More recent measurements of the ^{33}S hyperfine structure have revealed three basic forms of sulfide radicals: $\text{RCH}_2\text{S}^\cdot$, $\text{RCH}_2\text{SS}^\cdot$ and $(\text{RCH}_2\text{SSCH}_2)^\cdot$ (14). The g tensor, which has proven to be widely applicable for identification of sulfur-centered radicals, does not provide a critical distinction between the monosulfide and disulfide forms of these radicals. There seems to be agreement (15) that the disulfide radical anion forms from RS^\cdot by reaction 4. The



unpaired electron is weakly bounded to the $\text{S}=\text{S} \sigma_{3p}^*$ antibonding molecular orbital since it contains a major $3p+3p$ element. The disulfide radical anions can be protonated (16) to give I.



I

This molecule still has the unpaired electron in the $\text{S}=\text{S} \sigma_{3p}^*$ orbital. The S-S bond will probably be weaker than that of the anion.

In this system, one can expect the diffusion of H_2S inward in the coal particle during the heating. This may cause production several kinds of organo-sulfur bonds which can vary with different concentration of H_2S . It is reasonable to assume that charged organo-disulfide radicals can be also formed

in the interior of coal's grain and be distributed as paramagnetic impurities partly stabilized by environment.

By computer analysis of the spectra, it was possible to separate experimental ESR curve into two component spectra. The positive one belongs primarily to coal-derived radicals (positive) and the other to organo-disulfur radicals.

The relationship of spin concentrations per gram to the pressure of H_2S is shown in Figure 3. The lines assigned as I and II were determined by the division of the spin concentration values by the amount of charged lignite and recovered solid material from the reactor, respectively. There is a significant rise of spin density with increasing concentrations of H_2S . The differences in spin concentrations between the two plots I and II represents the amount of coal-derived radicals which have been converted to oil and gas. The line described as theoretical has been calculated from the computer separated signals, and represents the total number of radicals.

The variation of g-value with pressure of H_2S is presented in Figure 4. The g values increase significantly with H_2S pressure. It is related to the amount of heteroatoms incorporated (23). Thiophenolic forms like phenolic forms are effective at causing g-shifts (11).

Figure 5 shows the variation of the ESR line width (ΔH_{pp}) as a function of H_2S pressure. Overall the principal contributor to the positive signal is coal-derived radicals, $\Delta H_{pp} \approx 5$ G and for signal (-) some kind of organo-disulfur compounds $\Delta H_{pp} > 15$ G. The results indicate that hydrogen content in the coal radicals is unchanged with pressure of H_2S . For organo-disulfur compounds, the linewidths fall within the range 14.1-16.6 G with increasing of H_2S pressure. This suggests that other effects may also influence on the ESR linewidth such as electron-proton interactions (13).

It is worthwhile to note that negative ESR signal disappears when previously sulfurized ZAP lignite is exposed to H_2 or CO atmospheres at 500°C. The g-values and linewidths concomitantly decrease to 2.0016 and 5.8 G, respectively.

(b) Effect of H₂S and H₂ (CO) on hydrogenation of coal-derived radicals.

In H₂S-H₂ or H₂S-CO atmospheres significant differences occur in ESR spectra of ZAP lignite programmed 300-500°C (Figure 6). The line shape varies and is characterized by the disappearance of the negative signal (Figure 2) and the appearance of a narrow peak with a short width of line ~ 1 G. The spin concentration in H₂S-CO atmosphere is lower than in H₂S-H₂ (Figure 7). Therefore, CO decreases the probability of the carbon sulfur bonds formation.

The g values of the ZAP lignite in H₂S-CO also changes upon the introduction of H₂ particularly at lower pressures of H₂S (Figure 8). In the higher fractional pressure of CO (≈ 0.7) in the mixture of H₂S + CO there appears, first of all, to be CO interaction with coal radicals. This is mostly pronounced in reaction CO alone with coal radicals (Table 1), $g = 2.0026$ and suggest strong spin-orbit coupling, probably with phenoxy groups or those of the semiquinone type.

(c) Effect of water on free radicals formation and lignite conversion.

The results of the ESR measurements with water and reactant gases (CO, H₂S, H₂) are listed in Table 1. In all experiments with H₂O, the radical concentrations of ZAP lignite is low considering the very large numbers of radicals known to be formed during pyrolysis ($\approx 20.2 \times 10^{19} \text{ g}^{-1}$). The determined conversion to volatile products is varied with different pressure of CO. The maximum conversion was achieved mostly in CO = 70 MPa + H₂S = 17.5 MPa. This suggests that many of formed radicals were consumed by hydrogen transfer from shift reaction, H₂O + CO, shift reaction promoted by H₂S throughout COS intermediate compounds and as oil extracted by supercritical water or partly evaporated to reactor were removed during ventilation process. The very narrow linewidth was noted for reactions performed with H₂O and reactant gases. Using the relation between ESR spectral linewidth and hydrogen content of coals developed by Retcofsky (29), $\Delta H_{pp} = 1.6 H - 1.8$ where H is weight percent hydrogen, we can conclude that the hydrogen content in the nonvolatile residue is decreased.

SUMMARY

To increase the liquid yields of coal liquefaction, ESR spectra of unconverted coal residues are related to reactor conditions and conversion into volatile products. ESR spectra were obtained for North Dakota Zap lignite treated with various reducing gas atmospheres using a linear-programmed reactor temperature range of 300-500°C. The line shape, spin density, linewidth and g-values were all found to vary with the nature of the reducing gases employed. The spin density of the coal samples increased with increasing concentrations of H₂S in the reactor. Partially superimposed positive and negative signals were recorded when the coal was reacted with H₂S alone. When H₂S is used in conjunction with either H₂ or CO, only two positive signals were observed in the ESR spectra and the spin densities were reduced. The spin density of the reacted coal was minimum when the reaction mixture contained H₂O. The spin density of the samples were inversely related to the percent conversion into volatile products.

ACKNOWLEDGEMENTS

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Table 1. ESR Spectral Data and Distillate Conversion Results for ZAP Lignite.¹

Pressure of gases (MPa)	g value	Linewidth (G)	Spin Density ($\times 10^{19}$)		Conversion (SC) %	Distillate Conversion %
			spins g ⁻¹ (initial)	spins g ⁻¹ (final)		
Pyrolysis ²	2.0011	6.8	20.2 ± 1.9	20.2 ± 1.9	NA	NA
H ₂ = 34.4	2.0016	6.3	6.1 ± 0.3	10.0 ± 0.5	39.0	NA
CO = 34.4	2.0026	10.6	11.7 ± 0.9	18.7 ± 2.1	37.4	NA
H ₂ , CO = 34.4	2.0026	6.3	4.0 ± 0.5	7.3 ± 0.9	45.2	45.0
H ₂ S = 17.5	2.0035	two signals (+,-)	34.2 ± 3.0	45.0 ± 3.5	24.0	20.0
H ₂ S = 17.5, CO = 34.4	2.0025	6.0	6.3 ± 0.7	10.4 ± 1.2	39.4	39.8
H ₂ S = 17.5; H ₂ , CO = 34.4	2.0012	two signals (+,+)	2.8 ± 1.8	6.2 ± 2.0	54.8	47.8
CO = 34.4; H ₂ O = 0.8 g	2.0017	6.2	3.8 ± 1.2	6.6 ± 1.1	42.4	43.8
CO = 70; H ₂ O = 0.8 g	2.0016	4.4	1.3 ± 0.2	3.2 ± 0.2	59.4	60.9
CO = 70; H ₂ O = 0.8 g; H ₂ S = 17.5	2.0018	2.2	0.5 ± 0.09	2.2 ± 0.4	77.6	78.1
H ₂ S = 17.5; H ₂ , CO = 34.4; H ₂ O = 0.8 g	2.0011	3.9	1.6 ± 0.4	3.8 ± 1.0	57.9	59.9
H ₂ S = 17.5; H ₂ O = 0.8 g	2.0021	two signals (+,-)	19.2 ± 1.9	25.2 ± 3.5	23.8	22.0
S/lignite = 0.94 ^{2,3}	2.0036	6.25	11.9	11.9	NA	NA
S/lignite = 0.33 ^{2,3}	2.0036	two signals (+,-)	24.7	24.7	NA	NA

¹Experimental conditions for liquefaction, water = 0.8 g, pressure of gases are listed in the Table, reaction

²temperature, 300-500°C, reaction time 1 hr, ventilation at 500°C.

³Reactions have been performed in sealed capillary tubes with no charged gases.

Weight ratio of sulfur to lignite.

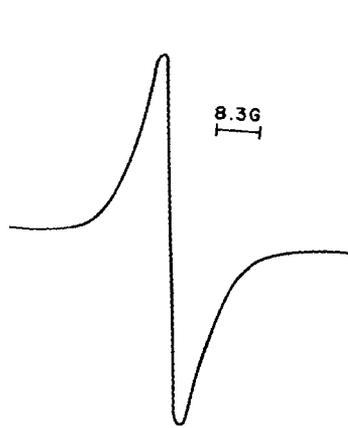


Figure 1. ESR spectrum of ZAP lignite.

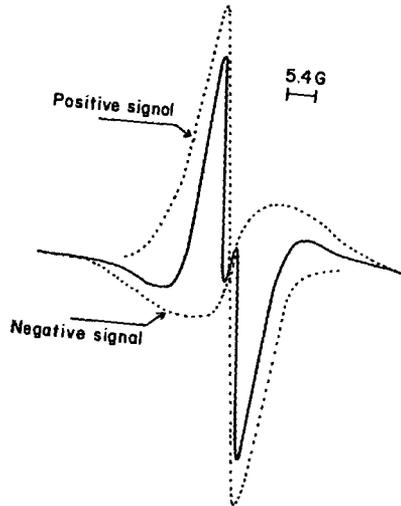


Figure 2. ESR spectrum of ZAP lignite after reaction with H_2S .

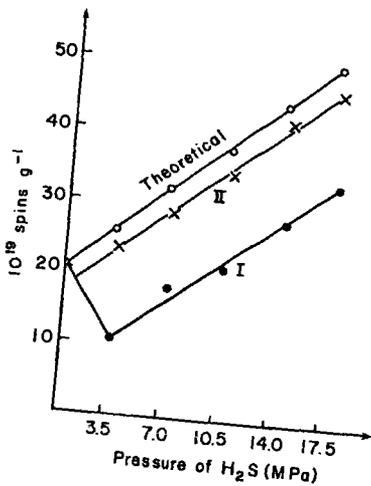


Figure 3. Variation of total radical concentration with pressure of H_2S .

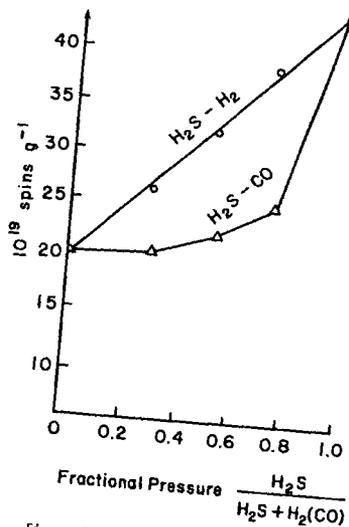


Figure 4. ESR g-value of ZAP lignite after reaction with H_2S at linear programmed temperature, 300-500°C.

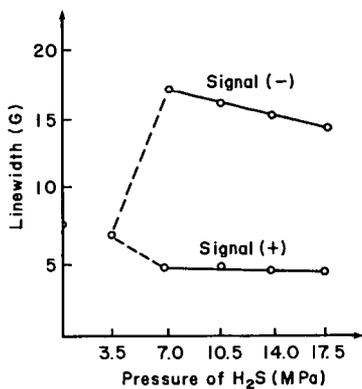


Figure 5. Variation of ESR spectral linewidth for recorded positive (+) and negative (-) signals with pressure of H₂S.

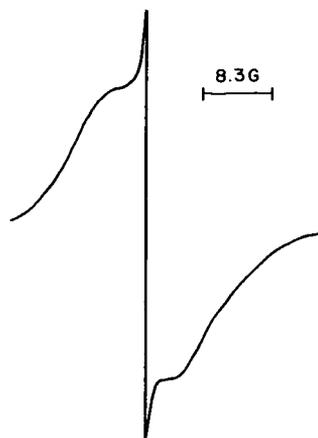


Figure 6. ESR spectrum of ZAP lignite after reaction with H₂S-H₂ at linear programmed temperature, 300-500°C.

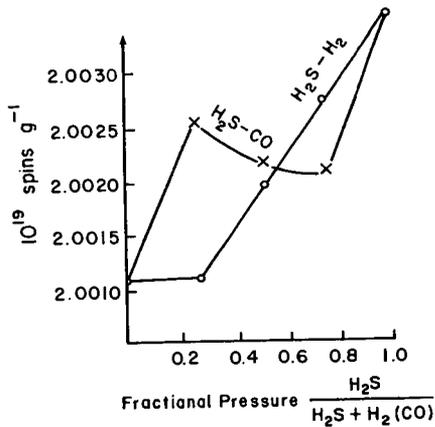


Figure 7. Variation of spin concentration with fractional pressure of H₂S.

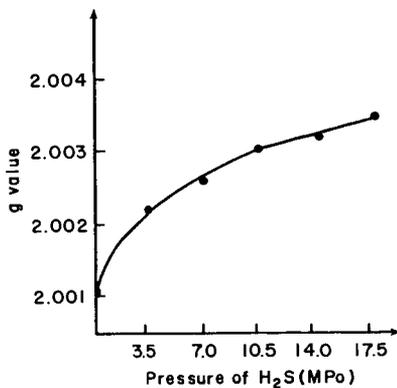


Figure 8. ESR g value of ZAP lignite versus fractional pressure of H₂S.

STRUCTURAL FEATURES OF PRODUCTS DERIVED FROM WATER-ASSISTED
LIQUEFACTION OF BITUMINOUS COALS

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INTRODUCTION

In recent years, several research teams interested in obtaining liquid fuels from coal have investigated approaches that involve adding substantial amounts of water with the coal during processing. Although the approaches taken by the different groups vary considerably, all groups cite the low cost of water -- as a reactant, extractant, or transport medium -- to be a potential advantage for aqueous liquefaction compared to more conventional processes. For some processes, the vapor pressure of water at reaction temperature makes a very considerable contribution to the total pressure required in the reaction section. Further research will show if the necessity of high pressure in aqueous systems can be avoided or if advantages in terms of product quality and yields realized through use of water will compensate for higher pressure requirements.

Work at our laboratory has investigated the interplay of organic solvent, water, and water-soluble catalysts on conversion of coal to soluble products in the presence of hydrogen gas [1,2,3]. At constant hydrogen partial pressure and temperature, conversion increases both with an increase in water density and an increase in water-to-coal ratio in the reactor. The mechanism by which water aids conversion is not known, but some experiments with deuterium oxide indicated that hydrogen-oxygen bonds in water were not being broken. In the presence of water, especially when a water-soluble molybdenum catalyst is also present, the full benefit of having an organic solvent present is achieved at solvent-to-coal ratios as low as 0.25. In addition, organic solvent, water, and catalyst are complementary in promoting conversion, and high conversions can be obtained by various combinations of these three aids to hydroliquefaction reactions.

These findings have led us to continue to conduct reactions with various combinations of coal-to-solvent and coal-to-water ratios, of temperature, and of hydrogen partial pressure. Our aim is to identify advantageous reaction conditions that may be used in a continuous process that employs a lower solvent-to-coal ratio for the feed stream than is used in current donor solvent processes. This work examines the structural features of coal liquids produced under a variety of unconventional reaction con-

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

ditions. Some questions of interest are the following: For reaction at low solvent-to-coal ratios and high water partial pressure, do liquid products resemble those from conventional donor solvent processes, or take on some characteristics of pyrolysis products? Is there evidence of incorporation of oxygen from water in the products? What is the effect of reaction temperature on product characteristics? To examine these questions, reactions were carried out with two Illinois No. 6 bituminous coals, and the liquid products were extensively analyzed.

EXPERIMENTAL

Hydroliquefaction Reactions

Batchwise liquefactions of two Illinois No. 6 bituminous coals were carried out using varying values of organic vehicle-to-coal and water-to-coal in the charge. All reactions were carried out with use of a water-soluble catalyst, ammonium heptamolybdate, in the concentration range 0.08-0.27 wt% molybdenum on dry coal. Gaseous hydrogen was employed in all runs. Ultimate analyses of the two coals, Burning Star and River King, are shown in Table 1. Two different hydrogen-donor solvents were also employed in this work. A composite Lummus solvent was derived from the 2SCT series of experiments (LCF-9 runs) with Burning Star coal on the Lummus Integrated Two-Stage Liquefaction (ITSL) Process Development Unit. A second solvent, designated HWSRC, was resid from the hydrotreater at the Wilsonville Advanced Coal Liquefaction Facility, produced during Run 242 with Burning Star coal.

Table 1. Elemental and Ash Analyses (wt%) of Illinois No. 6 Coals.

	Burning Star		River King	
	mf	maf	mf	maf
H	4.74	5.47	4.65	5.27
C	67.5	77.9	65.2	73.9
O	--	(12.1)diff.	--	(15.5)diff.
N	0.8 ₆	1.0	0.9 ₆	1.1
S	3.0	3.5	3.7	4.2
Ash	10.6	--	13.8	--

Reactions were carried out in a stirred one-liter autoclave. Reaction conditions employed are shown in Table 2. Coal, organic solvent, water, and catalyst were charged batchwise. Hydrogen was charged cold to the reactor at the desired total reaction pressure. As the reactor temperature rose during the heat-up period, hydrogen gas was vented via a back pressure control valve to maintain the total pressure. During the course of the

reaction, the partial pressure of hydrogen decreased and that of other components increased. The total pressure and the hydrogen partial pressure at reaction temperature at the end of each run are shown in Table 2. In one run (H-14), the reaction was carried out under 1900 psig partial pressure of nitrogen. Reaction times were 30 or 60 minutes and were measured from the time the desired operating temperature was established. Following a reaction, the reactor was cooled overnight to room temperature. Product gases were vented to a gas holder, then metered and sampled. Light oils (n.b.p. $\leq 293^{\circ}\text{C}$) and water were stripped from the reactor by vacuum distillation. The remaining heavy liquids and solids were dissolved in toluene and removed from the reactor. The toluene was stripped from the heavy products that were subsequently analyzed for THF-, benzene-, and cyclohexane-insolubles to determine conversions and product distributions. Asphaltenes are defined as material soluble in benzene and insoluble in cyclohexane. Heavy oils are material soluble in cyclohexane.

Chemical and Instrumental Analyses

The vacuum-stripped products were separated into methylene chloride solubles and insolubles to facilitate further analyses. Elemental analyses were performed on both the methylene chloride soluble and insoluble portions. Molecular weight determinations were performed on methylene chloride solubles by vapor pressure osmometry. Quantitative measurements of phenolic O-H, and relative concentrations of N-H in the methylene chloride soluble fractions were made by near-infrared procedures. High resolution ^1H and ^{13}C NMR spectra of the methylene chloride soluble fractions were acquired on a Varian XL-100 spectrometer.

RESULTS

Solvent Analysis

Conversions to THF and benzene solubles, and yields of hydrocarbon products are shown in Table 3. Although all reaction conditions were not varied systematically, some general observations can be made. High THF conversions (greater than 90%) and high benzene conversions (approaching 90%) were achieved with both of the coal and solvent combinations tested, River King/Lummus and Burning Star/HWSRC. Use of low hydrogen pressure results in low THF conversions (Runs H-14 and H-17). With a low temperature, high THF conversions may be obtained, but benzene conversions are reduced (Runs H-12 and H-16). In systems with solvent present, high conversions are obtained both with and without added water, but at lower pressure when water is absent (Runs H-10, H-24, and H-30).

Elemental Analyses of Feed and Product Fractions

Table 1 shows that analyses of the two coals are very similar, as expected. Tables 4 and 5 give the elemental analyses and average molecular weight of the methylene chloride soluble and insoluble fractions, respectively, of the two solvents used -- composite Lummus ITSL solvent and hydrogenated Wilsonville thermal resid (HWSRC). Essentially all the HWSRC is soluble in methylene chloride. The tables disclose several significant

Table 2. Experimental Reaction Conditions Associated with Liquefaction Products Analyzed

Autoclave Run No.	Added Solvent	Solvent/Coal	Water/Coal	Catalyst wt% Mo on Coal	Temp. (°C)	Time (min.)	Final Pressure, psig	
							P _{Total}	P _{H₂}
H-10	Lummus	0.33	0.25	0.14	427	60	4250	1750
H-12	None	0	0.44	0.10	370	30	4050	1760
H-14	Lummus	0.33	0	0.27	427	60	4510 (3160 N ₂)	520
H-16	Lummus	0.33	0.25	0.08	370	60	4690	2820
H-17	None	0	0.44	0.10	427	60	3880	720
H-24	HWSRC	0.33	0	0.10	427	60	2170	1530
H-30	HWSRC	0.33	0	0.10	427	60	1730	1180

All runs with Illinois No. 6 coal -- River King (H-10 through H-16) and Burning Star (H-17 through H-30).

Table 3. Conversion to Solubles and Yields in Liquefaction Experiments

Autoclave Run No.	Conversion (wt%, maf Coal)		Net Yield (wt%, maf Coal)			
	THF	Benzene	Asphaltenes	Heavy Oils	Light Oils	Hydrocarbon Gases
H-10	90.2	87.6	17.7	66.7	9.0	8.7
H-12	89.7	55.0	29.7	17.9	1.0	---
H-14	71.9	59.8	16.7	43.8	9.0	7.1
H-16	92.7	66.2	42.1	37.7	3.0	---
H-17	84.1	----	38.0	11.8	3.8	5.3
H-24	91.4	86.6	27.2	68.0	8.6	6.3
H-30	90.8	83.9	28.6	59.7	10.6	5.5

Table 4. Elemental Analyses and Number Average Molecular Weights of Methylene Chloride Soluble Fractions of Solvents and Heavy Aqueous Liquefaction Products.

Sample	C	H	O	N	S	H/C	\bar{M}_n^a
Composite Lummus ITSL Solvent	90.4	6.9 ₃	1.5	0.7 ₀	0.4 ₅	0.91 ₃	345
HWSRC Solvent	89.6	7.4 ₆	1.9	0.8 ₃	0.2 ₇	0.99 ₀	587
H-10	88.5	7.4 ₆	2.6	1.1	0.3 ₅	1.0 ₀	315
H-12	84.1	7.2 ₇	6.0	1.1	1.5 ₇	1.0 ₃	573
H-14 ^b	89.4	6.6 ₃	2.3	1.2	0.5 ₀	0.88 ₈	318
H-16	86.4	7.2 ₈	4.2	1.1	1.0 ₃	1.0 ₀	408
H-17	87.8	7.1 ₀	3.2	1.4	0.5 ₂	0.96 ₄	340
H-24	88.8	7.4 ₇	2.4	1.1	0.3 ₁	1.0 ₀	343
H-30	89.0	7.0 ₃	2.3	1.3	0.3 ₃	0.94 ₁	362

^aAVPO in pyridine @ 80°C.^bAverage of two determinations.

Table 5. Elemental Analyses (C,H,N) of Methylene Chloride Insoluble Fractions of Solvents and Heavy Aqueous Liquefaction Products on an Ash-Free Basis.

Sample	C	H	N	H/C
Composite Lummus ITSL Solvent	86.4	4.9 ₄	2.1	0.68 ₂
H-10	74.8	4.5 ₂	2.4	0.72 ₀
H-12	81.3	5.7 ₆	1.5	0.84 ₄
H-14	85.4	4.2 ₄	1.6	0.59 ₁
H-16	80.8	5.8 ₃	1.6	0.85 ₉
H-17	89.6	4.9 ₈	1.9	0.66 ₂
H-24	87.7	5.1 ₇	2.1	0.70 ₂
H-30	88.1	5.0 ₀	2.2	0.68 ₁

differences between the solvents. The Lummus solvent is of lower molecular weight and is less hydrogenated. The average molecular weight of the HWSRC is in the range expected for soluble nondistillate coal-derived resids.

Tables 4 and 5 also contain elemental analyses for the methylene chloride soluble and insoluble fractions, respectively, of the residual reaction products after the light oil has been stripped off. The hydrogen content of the methylene chloride soluble fractions of the products is ~7%, similar to that of the added hydrogen donor solvents. Although the relative yields of methylene chloride solubles are considerably reduced in the runs made at 370°C vs. 427°C, the H/C ratio of the solubles does not appear to be highly temperature dependent. All of the methylene chloride solubles are higher in oxygen than the added hydrogen donor solvents (which have been catalytically hydrotreated). The oxygen content of the products from the runs at 370°C is considerably higher than that of the runs at 427°C. However, excluding the 30-minute Run H-12 with added solvent in which poor conversion to methylene chloride solubles was achieved, the oxygen determinations in Table 4 are in the range expected for conventional direct liquefaction products of similar average molecular weight derived from Illinois No. 6 coal.

Heteroatomic Functionality

Infrared analyses of the O-H and N-H functionality in the solvents and heavy products are summarized in Table 6. The fraction of oxygen present as phenolic OH in the methylene chloride solubles appears to be between 0.3 and 0.4, and follows the total oxygen in Table 4 as determined by elemental analysis. The results reflect the fact that hydrogenolysis of carbon-oxygen bonds is less extensive at 370°C than at 427°C. Also, the methylene

Table 6. Dilute Solution Infrared Analyses of Methylene Chloride Soluble Solvent Fractions and Product Fractions

Solvent	%O as Free OH	Fraction of Total O as Free OH	Est.% N as N-H	Fraction of Total N as N-H
Composite Lummus ITSL	0.47	0.32	0.25	0.36
HWSRC	0.44	0.23	0.28	0.34
Autoclave Run No.				
H-10	0.97	0.37	0.32	0.30
H-12	1.7	0.29	0.20	0.19
H-14	0.88	0.35	0.44	0.40
H-16	1.3	0.32	0.27	0.25
H-17	1.5	0.47	0.48	0.35
H-24	0.99	0.41	0.43	0.40
H-30	0.94	0.41	0.44	0.34

chloride solubles from runs made without added hydrogen donor solvent tend to be higher in phenolic O-H and oxygen than from runs made with added solvents that are relatively depleted in oxygen. The estimated fraction of the nitrogen present as pyrrolic N-H is from 0.3 to 0.4, values that are consistent with similar infrared analyses of other direct liquefaction products derived from Illinois No. 6 (Burning Star) coal.

Average Structural Parameters

As a means of further comparing the heavy dewatered products, average structural parameters associated with the methylene chloride soluble solvent and product fractions have been calculated. These parameters should not be viewed as a means of constructing fictitious "average structures" for these very complex fractions but as a means of condensing a large body of diverse information into a set of correlative parameters that may prove useful for comparing samples and drawing general conclusions.

The mean structural parameters tabulated in Table 7 have been calculated by the Brown and Ladner procedure⁴ from elemental analysis, ¹H NMR, and NIR data. The aliphatic H/C ratio was assumed to be two for all groups having proton resonances in the H_α and H_β regions, and three for groups

Table 7a. Mean Structural (Brown and Ladner) Parameters of Methylene Chloride Soluble Fractions of Hydrogen Donor Solvents

	Solvent	
	Composite Lummus ITSL	HWSRC
Carbon Aromaticity, f_a	0.73	0.62
Hydrogen Aromaticity, H_{ar}^*	0.37	0.20
Degree of Aromatic Ring Substitution, σ	0.30	0.49
H/C Ratio of Unsubstituted Aromatic Units, H_{aru}/C_{ar}	0.64	0.61
Average Alkyl Substituent Chain Length, n	2.2	2.2

(mostly methyl) having resonances in the H_γ region. This "prescription" generally yields calculated aromaticity values for bituminous coal liquefaction products that agree with the direct ^{13}C NMR measurements.

The mean structural parameters of the added donor solvents are given in Table 7a. The calculated aromaticities reflect the relative hydrogen content of the solvents as determined by elemental analysis (Table 4). The degree of aromatic ring substitution (σ), which is an estimate of the fraction of aromatic ring edge atoms bearing a substituent, is higher for more hydrogenated HWSRC. In part, this is a consequence of the fact that the Brown and Ladner approach treats hydroaromatic rings as two alkyl substituents with an average carbon chain length of two. In both solvents, the estimated average alkyl substituent chain length is about two, i.e., in common with most heavy coal liquefaction products, the most prominent alkyl substituents are methyl groups and hydroaromatic rings as opposed to long chain alkyl groups. The calculated H/C ratio of the unsubstituted aromatic units (H_{aru}/C_{ar}) imply that the average aromatic units in both solvent fractions are larger than three rings and that the average size of such units is larger in the HWSRC than in the methylene chloride soluble fraction of the composite Lummus ITSL solvent. However, it should be realized that this parameter is an insensitive indicator of the exact ring cluster size for systems containing more than three aromatic rings. In addition, since the Brown and Ladner treatment does not acknowledge the presence of heterocyclic rings, care should be exercised in attaching more than qualitative significance to these results.

None of the structural parameters characterizing the methylene chloride soluble fractions of the heavy dewatered aqueous liquefaction products (Table 7b) are significantly different from those of direct liquefaction products of similar hydrogen content and molecular weight range derived from Illinois No. 6 coal. As an example, analyses of two light thermal resids

Table 7b. Mean Structural (Brown and Ladner) Parameters of Methylene Chloride Soluble Product Fractions Calculated Using $^1\text{H-NMR}$ Data

	Autoclave Run No.						
	H-10	H-12	H-14	H-16	H-17	H-24	H-30
Carbon Aromaticity, f_a	0.68	0.62	0.76	0.66	0.69	0.67	0.70
Hydrogen Aromaticity, $H_{ar}^{\#}$	0.34	0.22	0.45	0.27	0.33	0.30	0.33
Degree of Aromatic Ring Substitution, σ	0.33	0.48	0.27	0.39	0.33	0.37	0.36
H/C Ratio of Unsubstituted Aromatic Units, H_{aru}/C_{ar}	0.76	0.70	0.72	0.68	0.68	0.71	0.69
Average Alkyl Substituent Chain Length, n	1.9	2.0	1.7	2.1	2.2	2.0	1.9

(LTR's) from Non-Integrated Two-Stage Liquefaction (NTSL) experimentation at Wilsonville are summarized in Table 8. In Run 236 the dissolver was operated under "mild" severity NTSL conditions (419°C, 2000 psig H_2 , 30 lb/hr ft^3 coal space rate), while in Run 241 the dissolver was operated under "moderate" severity NTSL conditions (430°C, 2400 psig H_2 , 20 lb/hr ft^3 coal space rate). The aqueous liquefaction fractions tend to be only slightly lower in average molecular weight and slightly more hydrogenated than the light thermal resid from NTSL Run 236. After allowing for the diluting effect of the added donor solvent, the percent oxygen appears to be slightly lower in the aqueous liquefaction product fractions than in the LTR's, but the fraction of oxygen as OH is similar in both cases. Likewise, the estimated wt% nitrogen as pyrrolic N-H and fraction of the total nitrogen as N-H are similar for both types of products.

Table 8a. Elemental Analyses and Number Average Molecular Weights of Methylene Chloride Soluble Fractions of Light Thermal Resids from Liquefaction of Illinois No. 6 (Burning Star) Coal at the Wilsonville ACLTF.

Run No.	Elemental Analysis (wt%)					H/C	\bar{M}_n
	C	H	O	N	S		
236	85.1	6.7 ₀	5.5	1.6	1.1	0.938	464
241	88.1	6.1 ₉	3.3	1.6	0.8	0.836	453

Table 8b. Near-Infrared Analyses of Methylene Chloride Soluble Fractions of Light Thermal Resids.

Run No.	% O as Free OH	Fraction O as Free OH	Estimated %N as NH	Fraction N as NH
236	1.8 ₆	0.3 ₇	0.4 ₄	0.3
241	1.4 ₂	0.4 ₆	0.5 ₁	0.3

Table 8c. Mean Structural (Brown and Ladner) Parameters of Methylene Chloride Soluble Fractions of Light Thermal Resids.

	Light Thermal Resid	
	Run 236	Run 241
Carbon Aromaticity, f_a	0.70	0.75
Hydrogen Aromaticity, H_{ar}^*	0.32	0.35
Degree of Aromatic Ring Substitution, σ	0.38	0.36
H/C Ratio of Unsubstituted Aromatic Units, H_{aru}/C_{ar}	0.69	0.61
Average Alkyl Substituent Chain Length, n	1.8	1.7

DISCUSSION

From the viewpoint of general structural features such as aromaticity, hydrogen distribution, and heteroatom functionality, the methylene chloride solubles of the vacuum-stripped products from aqueous liquefaction of Illinois No. 6 coal in the presence of added Mo catalyst are remarkably similar to conventional direct liquefaction products of the same molecular weight range derived from this coal. They do not exhibit features characteristic of coal pyrolysis products, such as a predominance of highly condensed polycyclic aromatic structures with a low degree of ring substitution and low phenolic content. These results are consistent with recent reports of the product composition from dissociation of Illinois No. 6 coal in base-catalyzed CO and H₂O systems.⁵ In the latter experiments, no dramatic differences in composition of the toluene soluble product fractions were found over a wide range of conversion. Also, chromatographic profiles of the toluene solubles from liquefaction of Illinois No. 6 coal in CO and H₂ and in tetralin were similar, although the mechanism of coal dissociation in the two systems must be quite different. A distinction has been made

between thermal severity (temperature, residence time) and reduction severity (specific reactivity of the reducing species). The inference has been made that similar weak bonds in the coal macromolecular structure are being broken in both aqueous and conventional coal liquefaction systems and that the products reflect some statistical regularity or uniformity in the distribution of chemical entities that constitute the coal macromolecular structure. Thus, although increasing the reduction (chemical) severity may increase the rate of bond breaking by chemical rather than thermal mechanisms, the observed result is primarily a larger number of liberated fragments rather than a change in their character. The present work indicates a similar interpretation is consistent with the reaction systems studied here.

In the present experiments, temperature is the most obvious variable influencing both yields and product composition. There appears to be the same trade-off in the aqueous liquefaction of catalyst-impregnated coal as in conventional thermal liquefaction using hydrogen donor solvents without added catalyst. Lower reaction temperatures (<400°C) tend to favor hydrogenation over cracking and result in reduced hydrocarbon gas production, lower distillate yields, and higher yields of heteroatom-rich resid that may be soluble in polar solvents. Higher reaction temperatures (>400°C) favor thermolysis and hydrogenolysis over hydrogenation. A higher yield of distillate may result, but the remaining resid tends to become more refractory in nature, and the production of light hydrocarbon gases increases.

The chemical role of the water, if any, in the catalyst-impregnated coal and aqueous liquefaction system is not clear from the elemental and structural analyses of the products. Use of water as a vehicle with added ITSL solvent and catalyst appears to have given no better results than hydrogenation of the catalyst-impregnated coal in the presence of small quantities of a heavier, slightly more hydrogenated solvent at moderate pressures. There is no evidence for any significant net incorporation of oxygen; the water-assisted liquefaction products are not any higher in total oxygen or phenolic OH than conventional thermal-stage coal dissociation products of Illinois No. 6 coal.

In terms of H/C ratio, and carbon and hydrogen aromaticities, the methylene chloride soluble fractions of the residual liquefaction products exhibit characteristics typical of donor solvent liquefaction products. As seen in Table 7, except for Run H-14, the aromaticities of the reaction products were less than that of the Lummus ITSL solvent and comparable to that of the HWSRC. Table 8c discloses that the carbon and hydrogen aromaticities of light thermal resids produced at Wilsonville in NTSL Runs 236 and 241 are higher on average than those for the reaction products of this work. The analytical data indicate that the latter products have properties typical of similar molecular weight products that were produced in conventional donor solvent processes.

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