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Derivatization of Coal by Alkylation and Lithium Iodide Treatment

Cynthia L. Ludwig
Eastern Illinois University
This research is a product of the graduate program in Chemistry at Eastern Illinois University. Find out more about the program.

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DERIVATIZATION OF COAL BY ALKYLATION
AND LITHIUM IODIDE TREATMENT
(TITLE)

BY

Cynthia L. Ludwig

THESIS
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YEAR

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DERIVATIZATION OF COAL BY ALKYLATION
AND LITHIUM IODIDE TREATMENT

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ABSTRACT

The hypothesis that hydrogen-bonded ethers in coal could be cleaved by reaction with lithium iodide in pyridine to form new phenol groups was investigated for coals #2, 3, and 5 plus their alkylated derivatives from the Argonne Premium Coal Sample Program. Changes caused by alkylation and reaction with LiI were monitored by solvent extraction yields, solvent swelling, FT-IR and Size Exclusion Chromatography (SEC).

Solubilities of alkylated coals are rank and oxygen functionality dependent. Evidence supports the hypothesis that the solubilization mechanism is dependent on the extent of hydrogen-bonding in the coal. Elimination of hydrogen-bonds through alkylation increases toluene solubility and decreases pyridine solubility. The theory that carboxylic groups in the subbituminous coal are coordinated to divalent metal ions is supported by the observed increase in pyridine solubility upon alkylation of the subbituminous coal.

The reaction of LiI with both raw and alkylated coal caused slight increases in the -OH absorption in the FT-IR spectra. Treatment with LiI decreases toluene solubility for alkylated medium and lower rank coals. In most cases pyridine solubility decreased after LiI treatment. SEC profiles showed no change upon reaction with LiI. Data suggests that the final product does not have the proposed additional -OH groups for each cleaved ether. It is suggested that further reaction of the cleavage products with other groups in the coal occurs.
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INTRODUCTION

The United States possesses over half the coal resources in the free world. Thus, the use of coal as a fuel source is both geographically and economically sound. As with other fuel sources, such as nuclear power, coal produces significant amounts of environmentally hazardous waste. The pollutants produced by coal such as sulfur dioxide, nitrogen oxides, organic compounds, and large amounts of particulate matter can be recovered, neutralized, and returned to the environment by present means and resources. The problem with current technology for reducing pollution due to the burning of coal is cost. The cost of collection and disposal of the by-products eliminates the cost effectiveness of coal as an energy source. The logical solution to this problem is to eliminate the source of the pollution before the coal is used as an energy source. By doing so, the expense of collection would be reduced because the amount of material collected would be significantly less before combustion than after. The products removed from the coal that were considered pollutants after their combustion may be turned into marketable chemicals further enhancing the economical feasibility of using coal as an energy source. Herein lies the need for a fundamental knowledge and understanding of coal, its chemistry and characteristics. It is of interest to investigate reactions involving coal and the changes in its fundamental and derived characteristics such as swelling, solvent extraction, and others as they
may help solve the problems of coal's use as an energy source.

Coal is an aggregate of heterogeneous plant and mineral matter which have been subjected to high pressures and moderate temperatures beneath the earth for hundreds of centuries. The final result of this process, known as coalification, is the familiar black, rock-like, burnable substance which we call coal.

There are actually several steps to the process of coalification. The products of this genesis can be reasonably divided into the following categories: Plant and Minerals > Peat > Lignite > Subbituminous coal > Bituminous coal > Anthracite. As the raw materials progress toward coal, the rank, which is defined as the extent of maturation of organic materials with geological time in going from peat to anthracite, increases. As the rank increases, the carbon content of the coal increases, and the oxygen content decreases. The organic material in coal becomes increasingly aromatic as it matures.

In order to study a subject, one must be able to understand, picture, and rationalize the conceptual basis of that subject. For this reason many scientists have worked to develop models for coal. Through models, chemists hope to get insight into physical and chemical properties of coal by understanding the chemical structures of coal. There is impressive support for the theory that coalification is a depolymerization and that coals are cross-linked networks. Therefore, the use of
concepts stemming from polymer chemistry is very useful in developing models of coal. The criteria for a representative model should include that the model not only represents the physical structure accurately but also explains the physical properties, matches the elemental analysis, and behaves chemically similar to the substance being modeled. Views by Valkouie suggest that models of coal should include ether linkages, sulfide bridges, and methylene bridges of one to four carbons long. Perhaps the model which is regarded as the most representative is that of Shinn, Figure 1. When 'summed-up', the coal models suggest that coal is a three dimensional, porous, cross-linked macromolecular structure which contains in its pores varying sizes of removable micromolecular species with a wide variety of oxygen containing functional groups. The oxygen functional groups found in coal have been studied by Blom et al. They have shown that the type of functional groups found in coal depend upon the maturity of the coal which follows the rank. The quantitative determination of the oxygen containing functional groups in coal is very difficult. In general, low rank coals, subbituminous, and brown coals have a high carboxyl oxygen content. Blom and co-workers obtained values of 8.0, 5.1, 1.6, and 0.3% carboxyl oxygen in coals of 65, 72, 76, and 80% carbon.

The occurrence of methoxyl groups in coals with 65, 72, 76, and 80% carbon was found to be 1.1, 0.4, 0.3, and 0.2% of the oxygen content of coal. Heathcoat and Wheeler
Figure 1. Model of Bituminous Coal structure
determined the hydroxyl percentage in coal as a function of rank. Their results are comparable to those of Fuchs and Stengel. Several types of hydroxyl determination including standard acetylation, titration with sodium ethoxide, trimethyl silation and deuterium exchange were done. From these the following conclusions were drawn.

The hydroxyl groups in coal are predominately phenolic or at least acidic in character. There is little evidence for the presence of alcoholic or very weakly acidic hydroxyl groups in coal.

The nature of unreactive oxygen in coal has been debated by several researchers. The fact that some studies find the sum of hydroxyl, carbonyl, and carboxyl oxygen equal to the total oxygen content which suggests 'unreactive oxygen' doesn't exist. On the other hand Halleux has stated that an almost constant amount of unreactive oxygen of approximately 2.5 weight percent is present in hard coals of all ranks. He converted the unreactive oxygen with sodium metal and liquid ammonia to phenolic groups. These results indicate the presence of cleaved ether bonds. A summary of the oxygen containing functional groups and their concentrations in relationship to rank can be seen in Figure 2.
Fig. 2. Functional oxygen groups of vitrains according to rank 40
Solvent Swelling

Coal chemists use various techniques and properties to classify and describe coals. Coal, like cross-linked polymers, will swell when mixed with certain solvents. The analytical technique that measures the extent a coal sample will swell in a particular solvent produces what is known as a swelling ratio. The swelling ratios, also known as the swelling indexes, vary widely with experimental conditions. Swelling can be an indication of the extent of crosslinkage in the coal matrix. From polymer studies, it is well known that the more crosslinked a matrix is the less it will swell in a solvent that does not disturb that crosslinkage. Swelling data of coal can give insight into the extent of crosslinking in the coal matrix. Higher rank coals are more heavily crosslinked than lower rank coals. Therefore, it is no surprise to find a definite correlation between the rank of coal and its swelling properties. Each coal will have a unique swelling ratio depending on the swelling mechanisms of the solvents used. The mechanisms of swelling in coal can be divided into two categories. The first being swelling due to non-polar solvents, and the second due to basic polar solvents. The study of non-polar induced swelling in coal is hampered by two problems.

1) Swelling is relatively small due to the heavily crosslinked nature of coal which results in large margins of error.

2) The models used to interpret swelling are not
theoretically accurate enough to explain the data completely.

Present theories suggest that the nature of swelling of the coal matrix by non-polar solvents is due to dispersion force interactions between the coal and solvent. Non-polar solvents therefore are not believed to disrupt any of the crosslinks in the coal due to hydrogen-bonding, or covalent bonding of any type.

In contrast, the mechanism of swelling due to basic polar solvents does involve the breakage of hydrogen-bonds as well as the dispersion forces between the solvent and the coal. Therefore, an accurate description of the swelling of coal in polar basic solvents must involve two component systems accounting for both dispersion forces and hydrogen bond interaction.

Because the different solvents will be involved in disrupting different types of bonds, data from such experiments can be used to make conclusions about the extent of hydrogen bonding in a coal, and how it was changed by certain derivatizations or extractions. From the observations one can gain insight into the structure and functional groups of the coal and how certain reactions change the coal.

Solubility

Not only will coal swell in certain solvents, but it will also partly dissolve. Several theories have been developed over the years to explain why coal dissolves in certain solvents, the mechanism involved, and the nature
of that part of the coal which is soluble. The theory debated by Marzec et al. and discussed by Shinn of smaller soluble molecules held in a larger insoluble matrix has become widely accepted as a reasonable explanation. The basis of this theory is that within the coal matrix in cavities and pores, are micromolecular molecules which are not covalently linked to the macromolecular coal matrix. Shinn suggests that the portion of the coal that can be removed by pyridine in a Soxhlet extraction is hydrogen bonded to the coal matrix. Presumably a strong polar basic solvent such as pyridine disrupts these hydrogen bonds, releasing the micromolecular fraction of the coal into the surrounding solvent. Given refers to this extractable material as the mobile phase.

There is some debate as to the true amount of 'mobile' phase in coal. Marzec et al. discuss extensively the H n.m.r. data that suggests ~40% of the protons in a swollen coal are in a mobile or free environment. The two populations of protons found in coals exhibit appreciably different free inductive decay times. This data suggests that the protons have different levels of rotational mobility. Given and others explain the discrepancy between the ~20% extractable material with the ~40% alleged 'mobile' phase found by H n.m.r. techniques by indicating part of the 'mobile material' found in the n.m.r. studies is actually occluded in the coal matrix. The molecules are free to rotate or spin but are bonded to
the matrix or trapped by covalently bonded cages. Soxhlet extraction with solvents such as pyridine, which presumably do not break covalent bonds, can not liberate all of these molecules. It should be noted that some coals exhibit over 40% solubility in pyridine. Derivatized coals can have drastically different amounts of soluble material than seen in the parent coal.

It is of theoretical interest to investigate the changes in solubility of coals when certain reactions have been performed on the coal which are believed to break particular covalent bonds in the coal. An increase in solubility of the coal after reactions of this type could be partially explained by the liberation of the 'caged mobile' phase after the covalent bonds of part of the cage were broken. A more complete explanation would include the possibility of the breaking off of part of the matrix that was not considered trapped 'mobile phase', but became soluble only after breaking the bonds which linked it to the matrix.

Ether Cleavage Reactions

The presence of phenolic functionalities in higher rank coals and carboxylic acid functionalities in lower rank coals has been well established. However, the presence, nature, and spatial distribution of the ether functionalities are more elusive. Scientists have learned a great deal about ethers in coal over recent years. Major insights into both the reactions of ether groups in
the coal matrix and their spatial relationships to other functionalities have been uncovered. It is believed that ether bonds exist both in micro and macromolecular moieties of coal as unreactive cyclic ethers. Aczel and Siskin suggest that alkyl-aryl ethers in coal are the most reactive. Their pyrolysis studies indicate that diaryl and cyclic diaryl ethers are more stable under pyrolysis conditions. They did not postulate a molecular basis for their observations.

Further investigations of types of ethers that may be found in coal were done by Larsen, Liotta, and Buchanan. Although these groups approached the studies from different perspectives, they came to common conclusions. They agree that it is strongly possible that the majority of ether groups in coal are hydrogen bonded to nearby phenolic groups.

Larsen et al. concluded that the hydroxyl groups of an Illinois #6 coal are paired with another heteroatom which is most likely hydrogen bonded in the solid state. When the hydroxyl groups were derivatized with tin to form -O-SnBu\textsubscript{4} complexes, Mossbauer spectroscopy showed almost all of the tin in a trigonal bi-pyramidal coordination state. Mossbauer spectroscopy uses the fluorescence given off by the nucleus, when bombarded with gamma rays, to predict the electronic environment at the nucleus. These results would require the co-ordination of tin with a heteroatom. In a response to a question from Given about how this convenient arrangement between the two
species arose, Larsen gave two possible explanations, the most probable being that the hydrogen bonds existed from the start because it is improbable that the coal was sufficiently mobile during coalification to allow the different groups to 'find' each other. He goes on to state that coalification is a very slow and selective process. With this in mind, it would be reasonable to assume that as deoxygenation occurred with maturation, the less stable, free hydroxyl groups were eliminated faster than the hydrogen bonded counterparts. This theory remains a topic for investigation.

Buchanan, Takemura, and Sy began work on ethers in coal by first looking at model compounds containing ethers. From the generally accepted fact that alkyl-aryl, ether cleavage in acidic solution requires protonation of the ether oxygen before nucleophilic attack and other observations, they postulated that the C-O bond could be activated by intramolecular hydrogen bonding of the ether oxygen atom, eq. 1. They found that ether cleavage where alkyl ether oxygen is the acceptor atom of an intramolecular hydrogen-bonded six-membered ring could be obtained when treated with Py-HI or LiI in pyridine conditions in which protonation by free acid is impossible.
Larsen's work strongly suggests such hydrogen-bonded ethers exist in coal. Hence, there is substantial evidence to suggest that ether cleavage reactions where the specific hydrogen-bonding and protonation conditions are required, as mentioned above, are possible in coal. It should be noted that many other ether cleavage reactions are known to work on coals. A method using sodium in liquid ammonia has been well documented to cleave aryl-aryl and aryl-benzyl ethers by a radical anion mechanism. Several other methods may be used to achieve ether cleavage in coal and coal like materials including K/THF in the presence of napthalene.

Whenever reactions are performed on coal, it is necessary to develop methods to measure the extent or completeness of the desired reaction. It is well known that an increase in ether linkages in coal will reduce the swelling of the coal. Logically, if some of the ether linkages are broken, swelling should increase. It follows that the swelling in different solvents would be affected.
differently depending on the polarity and basicity of the solvent used.

From the theories of 'mobile' phase discussed earlier, it could be postulated that the solubility of a coal would be increased by an ether cleavage reaction. Not only would the parts of the matrix that were cleaved off be soluble but some of the trapped 'mobile' phase may be extractable if the ether bond was part of the cage the mobile phase was trapped in.

Alkylation

Based upon chemical and spectroscopic studies Stock and Willis claim that approximately 50% of the oxygen in Illinois #6 coal is in the form of hydroxyl groups and the remaining is involved in various types of ether linkages. These percentages are in conflict with some studies mentioned earlier. Of course, all coals will have a slightly to dramatically different composition depending on their extent of maturation and rank. Since a large part of the oxygen is classified as a hydroxyl functionality, it is of interest to investigate the possibility of doing reactions on these groups that are similar to known reactions of hydroxyl groups in model compounds.

Many studies on the alkylation of oxygen functional groups in coal (O-alkylation) have been done in recent years and will be investigated further in this study. The alkylation of three coal samples was carried out following
the Stock method. This method of alkylation was chosen over several others because of the mild conditions and literature precedence. Although several bases have been employed previously, there has been a trend toward using bases such as potassium hydroxide as opposed to the previously more commonly used tetrabutylammonium hydroxide and other bulky bases. These bases were tenaciously held in the coal matrix, disrupting and complicating the analysis of the alkylated coal. By using the inorganic base, potassium hydroxide, the problems encountered by Liotta and Matturro, with the removal of larger bulky quaternary ammonium salts after reaction have been eliminated.

During O-alkylation of phenols by this method, the first step is rapid proton abstraction to produce a phenoxide ion nucleophile. This is followed by nucleophilic displacement of I from R-I which is the rate-determining step. Equation 2.

\[
\begin{align*}
\text{K}^+ & \quad \text{OH}^- \quad \text{Ph}-OH \\
& \quad \text{Ph}-O^- \quad \text{n-Bu}^+ \text{I}^- \\
& \quad \text{Ph}-O^-\text{n-Bu}^+ \quad \text{I}^-
\end{align*}
\]

This process has been described as a kinetically
controlled S\textsubscript{2} process which is not limited by the mass transport of the chemical reagents into the coal structure. Support for this statement includes work done by Stock and Alemany which showed that butyl chloride and bromide were clearly slower than reactions of the iodide. It is well known that methyl iodide undergoes nucleophilic displacement reactions approximately 20-30 fold more rapidly than other primary alkyl iodides. This fact and the above observations support the idea for the S\textsubscript{2} mechanism.

It was shown by Stock and Mallya that the solubility of derivatized Illinois #6 coal in THF was dramatically different between methylated and butylated coals. Previous studies by Wachowska found that the solubility of alkylated high rank coals was directly related to the size of the alkyl group involved. The proposed reasoning is that the disruption of hydrogen bonds is equally effective in the methylation and butylation cases. Presumably, the steric requirements of the butyl group are the most important factor in the enhanced pyridine extractability in these coals. The Stock study dealt with high ranking coals (>86% C) that contain more regular laminar structure. Because of the high density (~2) of these coals, it has been postulated that high rank coals have relatively few covalent crosslinks but are bonded intermolecularly by van Der Waals forces. It is of interest to investigate the changes seen by alkylating
samples containing different types of oxygen functional groups and different ranks. To further investigate the changes in solubility of derivatized coals, we chose two solvents which involve very different intermolecular associations in their solubilization mechanism: Pyridine, which will disrupt and solubilize hydrogen bonded micromolecular structures, and toluene, which only disrupts weaker intermolecular associations. By studying the changes seen in solubility in these solvents for several coals and their derivatives, it will make the structure in these coals surrounding the reaction sites readily apparent.
EXPERIMENTAL

COAL SAMPLES

Illinois #6 seam coal received from the Illinois State Geological Society's Illinois Basin Coal Sample Program, (IBC-#105) Pittsburgh #8 seam, and Wyodak-Anderson seam coals received from Argonne National Laboratories' Premium Coal Sample Program (APCSP #401 & #201) were used in this study.

Illinois #6 was prepared for use by grinding to pass 100 mesh in a nitrogen flushed ball mill with twenty ceramic grinding rods (Sargent-Welch) for three hours and fifteen minutes. The sample was stored in a nitrogen filled glove bag.

The Pittsburgh #8 and Wyodak-Anderson samples were both received in sealed glass ampoules which contained 5 grams of ground coal. The ampoules were opened by gently scoring the necks with a file and applying pressure to remove the top of the ampoule. Twelve Pittsburgh #8 and eleven Wyodak-Anderson vials were opened, similar types were combined, mixed well by shaking, and placed in a N filled glove bag for storage.

Henceforth, these prepared samples will be referred to by their assigned sample numbers found below.

Illinois #6 seam coal...........#I400
Pittsburgh #8 seam coal........#P400
Wyodak-Anderson seam coal.....#W400
Before use in all procedures, samples were dried in the following manner. After recording the weight using an Ohaus Galaxy 200 analytical balance, the coal was placed in a large Abderhalden apparatus, dried at .025 Torr for several hours or overnight at ambient temperatures, removed and re-weighed. This process, henceforth "standard conditions", was repeated successively as needed to achieve constant weight, which is defined as two successive weights that differ by less than 0.1%.

MOISTURE CONTENT

The initial samples were dried under standard conditions to determine the moisture content of each. Moisture was calculated by equation 1 and compared to the values given by the Argonne Premium Coal Sample Program handbook.

Equation 3.

\[
\text{wt. initial - wt. final} \quad \frac{\text{-----------------------}}{\text{wt. initial}} \times 100 = \% \text{ moisture}
\]

ATMOSPHERE

All samples were stored in a nitrogen filled glove bag. Unless otherwise stated, all reactions, purifications and preparations were performed under an inert atmosphere (nitrogen or argon). When it was necessary to transfer under normal atmosphere, it was done quickly and efficiently so as to minimize the time of exposure to oxygen.
SOLVENTS

All solvents were purified under nitrogen immediately before use in the following manner. Reagent grade hexane and toluene (Aldrich) were purified by simple distillation. Reagent grade THF (Aldrich) was distilled from the sodium ketyl of benzophenone. Pyridine (recovered from the SEC system using HPLC grade, Aldrich) was distilled from barium oxide. The methanol wash solution was prepared with 80% reagent grade methanol (Aldrich) and 20% Milli-Q triple de-ionized water.

REAGENTS

Reagent grade, anhydrous LiI (Aldrich) was stored in a dessicator and used without further purification. Reagent grade iodomethane (Aldrich) and bromobutane (Aldrich), whose purity was verified by physical and spectroscopic methods, were stored in a refrigerator freezer and used as received. The potassium hydroxide solution (1.5M) was prepared using A.C.S. reagent grade KOH pellets (Aldrich) and Milli-Q water.

SOXHLET EXTRACTION

Soxhlet extraction of samples followed published procedures. A representative toluene extraction of sample #W401 illustrates the method: The 250mL round bottom (RB) flask used at the bottom of the Soxhlet apparatus was filled with 200mL of toluene and 20mL was poured into the thimble compartment. The apparatus was flushed with argon for one hour. A pre-weighed thimble containing 5.5203g of sample, which had been dried under
standard conditions, was placed in the thimble compartment, and the apparatus re-assembled. The solvent was heated to reflux with a heating mantle, and the heating rate was adjusted such that the solvent siphoned approximately every fifteen to twenty minutes. The extraction was allowed to continue until the absence of color in the siphoning solvent persisted for 24 hrs.

When the extraction was complete (72hrs), the system was allowed to cool to room temperature, the solvent was removed, passed through a .45um Nylon membrane filter, and placed on the rotary-evaporator to remove the bulk of the solvent. The isolated soluble fraction was dried to constant weight .0680g under standard conditions and stored in the nitrogen filled glove bag. The residue was gravity drained of bulk solvent, dried under standard conditions to a weight of 5.5336g and returned to the glove bag.

Pyridine extractions were initiated in the same manner as the toluene, the difference was in the work-up procedure. After the initial 3.0756g of starting material was extracted with pyridine for 120hrs, the RB flask containing the soluble fraction was dried under standard conditions overnight; 100mL of 80% methanol wash solution was added to the extract in the RB flask. The flask was put under a positive pressure of argon and stirred for 6hrs. The methanol wash was removed from the sample by filtering through a .45um nylon membrane filter. The soluble fraction was dried under standard conditions.
This process was repeated as necessary until a sniff test for pyridine was negative (120hrs). The 0.2102g of isolated pyridine soluble sample was placed in a nitrogen filled glove bag for storage.

When the RB flask containing the soluble fraction was removed from the Soxhlet apparatus, it was replaced with a RB flask containing 200mL of 80% methanol wash. After Soxhlet extraction for 24 hrs, the thimble and residue were gravity drained and dried under standard conditions to a weight of 2.8972g. This process was repeated as necessary until a sniff test for pyridine was negative.

SWELLING

The volumetric method originally used by Liotta et al. and further perfected by Larsen and Green was used to obtain the swelling index ratios of the coal samples. Glass tubes (8mm i.d.) were filled with residues from solvent extractions to a height between 2cm and 3cm from the bottom of the tube, dried under standard conditions, and centrifuged at 2700 rpm for 30 mins to ensure uniform packing. The height of the coal was measured with a ruler to the nearest 0.05cm and recorded as the initial height. The coal was loosened and excess solvent was added from the bottom of the tube upwards with a long needle attached to a 20mL syringe. The tubes were stoppered and shaken daily until equilibrium was achieved. From literature references, 3 days at ambient temperatures was determined to be sufficient time to achieve equilibrium. After this time, the tubes were centrifuged and the height
recorded as the final height. The swelling ratio (R) was calculated by dividing the final height by the initial height.

ETHER CLEAVAGE

The ether cleavage reactions were done in a 250mL three-neck RB flask equipped with a condenser, a septum, and a glass stopper. The apparatus was under nitrogen atmosphere with magnetic stirring and the flask was suspended in an electrically heated oil bath. The RB flask was filled with 200mL of pyridine and purged by needle with argon for 30 min. while stirring. A 7.4028g coal sample was added to the RB flask followed by twice that weight of LiI. The mixture was heated with an oil bath to 100°C and allowed to react for five days. The reaction was cooled to room temperature. A 50 mL wash of 5% NHCl solution was added to the reaction mixture and stirred two hours. The contents of the three-neck RB flask was transferred to a single-neck RB flask so the bulk solvent could be removed by a rotary-evaporator. The nearly dry reaction mixture was transferred to a Soxhlet thimble and extracted with 80% methanol wash solution until a silver nitrate test for halide ions was negative. The first 80% methanol wash solution was removed and replaced with fresh 80% methanol wash solution after 2hrs. The second 80% methanol wash solution was checked every 2hrs for halide ions until the test was negative (12hrs).

ALKYLATION

The procedure developed by Stock for alkylation of
bituminous coals was used. A suspension of 14.4998g of coal in THF at a 1g:20mL ratio in a 500mL, three-neck RB flask was purged with nitrogen for one hour while stirring. To the suspension, 2.6mL of 1.5M KOH per gram of coal was added through a funnel into the neck of the RB flask that the glass stopper had occupied. The reaction was heated to 50°C and allowed to equilibrate for 15 hrs (one hour per gram). The alkylating agent (iodomethane or bromobutane) was added by needle through the septum at a 4.5 mmol per gram of coal ratio. The reaction proceeded at 50°C for 48 hrs and the cycle was repeated. The reaction was quenched with 5% NH₄Cl solution in 50mL aliquots until the reaction mixture remained at a pH of 2 after magnetic stirring for two hours from the last addition of 5% NH₄Cl solution. From there, the work up procedure used was the same as that used in the ether cleavage reaction.

Fourier Transform - Infrared Spectroscopy (FT-IR)

FT-IR spectra were taken on a Nicolet-20DXB FT-IR spectrophotometer using KBr pellets which were prepared by combining 3 mg of sample with 0.3g of dry KBr in a Wig-L-Bug capsule. The mixture was ground to uniform consistency with a Wig-L-Bug (45 s). The colored powder was placed in a 1.3cm diameter press and subjected to 100lbs/sq. inch pressure for 1 min. A vacuum was instituted and the pressure was raised to 6000lbs/sq. inch for three min. The pellets were dried under standard conditions and placed in a desiccator.

A background spectra using 27 scans was taken before
data collection using 50 scans was performed. The instrument gain was optimized for individual samples and the FT-IR raw data was stored on a floppy disk.

SIZE EXCLUSION CHROMATOGRAPHY

All size exclusion chromatography (SEC) was performed following published procedures by Buchanan. The system consisted of a Rheodyne 7125 injector connected to a 3-column series of ASI ultragel SE columns with 100, 500, and 1000A pore sizes, pumped by a Beckman 110B solvent delivery module. A Knauer Model 98.00 refractive index detector was interfaced with a Apple IIE micro-computer for data manipulation.

The sample dilution ratio was 6mg of soluble fraction to 1mL HPLC grade pyridine (Aldrich). The solutions were put through a 0.45um Nylon-66 filter to remove any matter which may clog the system. A 100uL aliquot of the filtered sample was injected onto the column for analysis using a flow rate of 1.8mL/min pyridine with the refractive index detector sensitivity set at 32. The raw data was stored on a floppy disk and the summation of manipulated data was plotted as a molecular size profile.

Calibration of the SEC was performed according to the procedure described by Mai using coal extracts to develop a calibration curve.
Results & Discussion

Characteristics of Coals

The analyses of the coals used in this study are given in Table 1.

Table 1. Elemental Analysis* (moisture ash free)

<table>
<thead>
<tr>
<th>Sample #</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%S</th>
<th>%O(dif)</th>
<th>%Moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td>P400</td>
<td>83.20</td>
<td>5.32</td>
<td>1.64</td>
<td>2.41</td>
<td>8.83</td>
<td>1.65</td>
</tr>
<tr>
<td>I400</td>
<td>77.67</td>
<td>5.00</td>
<td>1.37</td>
<td>5.63</td>
<td>13.51</td>
<td>7.97</td>
</tr>
<tr>
<td>W400</td>
<td>75.01</td>
<td>5.35</td>
<td>1.12</td>
<td>0.67</td>
<td>18.02</td>
<td>28.09</td>
</tr>
</tbody>
</table>

* Values obtained and calculated using The Argonne Premium Coal Sample Program Handbook

As seen from Table 1, the carbon content decreases from P400 to W400, while the oxygen content increases. This can be summed by stating that the rank of each coal decreases from P400 to W400.

The determination of oxygen is done by difference. This method of oxygen determination includes in it all the errors incurred in the determination of the other elements (C,H,N,S and ash). Oxygen content should be regarded as a somewhat unreliable number and can vary depending on the reliability of the other determinations.

Changes in FT-IR with Alkylaiton of Coals

FT-IR is a powerful tool in the study of coal and coal derivatives because of its accuracy, reproducity, sensitivity and ability to deal with coal's heterogeneous
nature. Painter and Coleman illustrate how FT-IR can be utilized in studying mineral composition, organic functionality and changes in coal due to weathering. The most common method employed for obtaining spectra of coal utilizes KBr pellet sampling. The presence of residual OH absorption seen in the 3200cm⁻¹ -3600cm⁻¹ region is a problem when using KBr because of the hydroscopic nature of the salt. Many researchers have attempted to completely eliminate the reoccurring presence of water with little success. The drying methods used to remove the water included extended time using vacuum and heat. In nearly all cases, a small persistent absorption indicated water remained after the drying procedures. This fact will be important later when the loss of an O-H region absorption is used to help determine the success of alkylation reactions. All of the KBr pellets analyzed in this study were dried under standard conditions overnight immediately prior to use. The problem of water absorption will be consistent through the spectra.

Because of the heterogeneous nature of coal, the FT-IR spectra tend to have steep base lines and are difficult to interpret. Spectra of all samples were obtained. Only the most useful spectra are shown, but copies of all the spectra are available. Except where noted, each Figure will contain spectra of similar samples from the three parent coals. The order of the coals and derivatized samples will always be W400-bottom, I400-middle, P400-top.
There are literally hundreds of specific absorptions that are of interest on the IR spectrum. It is of use to try to separate the entire spectra into regions of similar types of absorptions to simplify the interpretation process.

1) 3200-3600 cm\(^{-1}\) -OH absorption: This can be an indication for the presence of water, phenol, alcohol, -NH, etc.

2) 3050-3010 cm\(^{-1}\) Aromatic -CH absorptions: This has been linked to the rank of the coal and is sometimes overshadowed by a strong -OH absorption.

3) 2975-2853 cm\(^{-1}\) Aliphatic -CH\(_2\), methylene, and -CH\(_2\) groups. 2960 cm\(^{-1}\) -methyl groups attached to alkyl chains, 2926 cm\(^{-1}\) aliphatic -CH, 2853 cm\(^{-1}\) -symmetrical -CH\(_2\) stretching.

4) 1500-1800 cm\(^{-1}\) There are a large number of functionalities which absorb in this region including aldehydes, carboxylic acids, esters, and ketones. In general the C=O and C=C groups are seen here.

5) 1500-1300 cm\(^{-1}\) Various symmetrical and asymmetrical -CH stretching bands. Dolomite and carbonate absorb in this region.

6) 1300-1100 cm\(^{-1}\) -CO single bond stretch: This area contains groups such as ethers, and esters. 1261 cm\(^{-1}\) is characteristic of Ar-O-CH or CH-O-CH.

7) <1100-400 cm\(^{-1}\) Mineral matter.
Spectra of the parent coal samples, Figure 3, show several differences. The W400 has a much stronger absorption in the -OH region. The aliphatic carbon absorption becomes increasingly more intense as the rank of the coal increases. The C=C absorption peak becomes more distinct with an increase in rank. The W400 coal has a less intense absorption in the various mineral matter areas.

Comparing the methylated coals, Figure 4, to the corresponding parent coals, Figure 3, it is readily apparent that the ratio of aliphatic -CH absorption peak to the -OH absorption peak has increased most dramatically in the W400 coal, moderately in the I400 coal and negligibly in the P400 coal. This is most likely due to the fact that there are more reactive sites for alkylation in the lower rank W400 coal than the higher rank coals I400 and P400. The changes due to the alkylation will be more noticeable in the coal with the most sites available for reaction. The increase in the -CO absorption peak seen in all the coals indicates the formation of ether type bonds due to the reaction. The W400 coal shows a dramatic change in C=O indicative of an increase in C=O content in the methylated and butylated samples. There are several possibilities to explain this. Upon alkylation, the esters formed may shift the C=O absorption of the previous acid C=O absorption and cause it to be more apparent. In addition, there could be a side reaction in which C=O is formed instead of the expected ether. The W400
subbituminous coal is known to have a much higher percentage of carboxylic acid functional groups than the other bituminous coals. The chemistry will be somewhat different in this coal than the others.

The butylated coals exhibit the same changes as the methylated coal with the additional peak at 2960 cm\(^{-1}\) due to the methyl groups attached to an alkyl chain which is consistent with the change of alkyl substituent from methyl to butyl.

The spectra of the toluene soluble fractions of all these coals, Figure 6, are very similar. They have small \(-\text{OH}\) absorptions, large aliphatic \(-\text{CH}\) absorptions, moderate \(\text{C}=\text{C}\) and \(\text{C}=\text{O}\), and no mineral matter adsorptions. In order to make reasonable comparisons in the size of the absorption peaks in coal spectra, the size of the aromatic \(\text{C}=\text{C}\) stretch, which is presumed to be unchanging for each coal, is compared to the peak in question.

Equation 4.

\[
\text{Comparison Ratio} = \frac{V_{x^*}}{V_{\text{C}=\text{C}}} 
\]

* Reaction

The change in the ratio from the coal to the derivatized sample is used in the comparisons. The actual calculations will not be shown. They are not for quantitative analysis but are for qualitative comparisons of the reactions performed on the coals.

Figure 7 contains spectra of the toluene soluble
fractions of the methylated coals. There is little or no change in the -OH region suggesting that alkylation doesn't change the -OH containing toluene extractable material in the coal or that the material that is now extractable, doesn't contain an increased number of -OH functional groups. The reaction has presumably converted the majority of the -OH groups into ether groups. The toluene extraction does not disrupt hydrogen-bonds, therefore a large number of -OH functional groups are not expected in the extracted material. There is no recognizable trend in the changes observed in that region. The -OH absorption that is present is most likely primarily due to residual water that hasn't been removed from the KBr pellet by the drying process.

The aliphatic region in the toluene soluble fractions of the methylated and butylated coals have larger aliphatic -CH/-C=C ratios than the parent coals. The individual peaks of the region, 2960cm$^{-1}$, 2926cm$^{-1}$, 2853cm$^{-1}$, differ noticeably in intensity. The butylated coals again show an increase in the 'aliphatic' peaks consistent with a methyl group attached to an alkyl chain. Failure of this peak to be more intense in the methylated coal than in the parent coal is proof that the reaction is proceeding by o-alkylation, not C-alkylation. The methylated coal and butylated coal show an increase in C=O absorption in the toluene extracts as well as an increase in the absorption due to ethers at 1261cm$^{-1}$.

An example of the FT-IR of the residue of a toluene
extraction is shown in Figure 9. I400 coal (bottom) its methylated derivative (middle) and its butylated derivative (top) are shown as a representative case. The other residues are very similar and do not reveal any additional pertinent information.

Figure 10 contains the spectra of the pyridine soluble fractions of P400, I400, and W400 coal. The most important features in these spectra are the increases seen in -OH absorption region as compared to the toluene soluble fractions. Pyridine extraction disrupts the hydrogen-bonded structures in the coal removing material which contains -OH groups. The aromatic -CH region is more prominent in the two higher rank coals. The aro-CH / ali-CH ratio increases as the rank increases consistent with theory that higher rank coals have increased aromaticity.

The spectra of the pyridine soluble fractions of the methylated coals, Figure 11, differ from those of the parent coal in intensity of the aliphatic -CH absorption. The relative intensities of the -OH absorption and the region between 1200cm⁻¹ and 1700cm⁻¹ are less in the derivatized coal than in the parent coal. The pyridine soluble fractions of the butylated coals, Figure 12, are very similar to the methylated samples with the distinct peak at 2960cm⁻¹ having an increased intensity indicative of the butyl substituent.

FT-IR spectra of the residues of the pyridine extracts do not contain any significant differences. They will not be shown, but are available from Eastern Illinois Chemistry
Department.
Figure 3. FT-IR of original coal samples
Figure 4. FT-IR of methylated coal samples
Figure 5. FT-IR of butylated coal samples
Figure 6. Toluene soluble fraction of coal
Figure 7. Toluene soluble fraction of methylated coal
Figure 8. Toluene soluble fraction of butylated coal
Figure 9. Toluene residues of 1400 coal$^a$, methylated$^b$, butylated$^c$
Figure 10. Pyridine soluble fraction of coal
Figure 11. Pyridine soluble fraction of methylated coal
Figure 12. Pyridine soluble fraction of butylated coal
Changes in Solubility upon Alkylation of Coals

Toluene and pyridine extractions were performed on all the coals, the methylated coals, and the butylated coals. A representative scheme of an alkylation and subsequent extraction with toluene and pyridine is shown in Scheme 1.

Scheme 1. FLOW CHART OF PYRIDINE AND TOLUENE EXTRACTIONS OF METHYLATED COAL W400

The results of the extractions of all the raw coals, the methylated coals, and the butylated coals, are listed in Table 2. Parallel extractions were done on the 1400 series to check the reproducibility of the method. The differences found in the duplicates were all well within experimental error. Repeat extraction of a pyridine residue produced <1.0% additional extractable material. From this data, it was concluded that the initial
extraction process removed essentially all of the extractable material. The 80% methanol wash recovered from washing the pyridine extraction residues was slightly orange in color and negligible in amount for the I400 and P400 series coals. The W400 series coal gave a very dark colored solution which was concentrated and gave at most 2% by weight. This material is thought to be a conglomeration of acids which may be precursors to coal.

Table 2. Toluene and Pyridine Extraction Results

<table>
<thead>
<tr>
<th>Coal #</th>
<th>Description</th>
<th>wt % Tol sol</th>
<th>% Mat Bal</th>
<th>wt % Py sol</th>
<th>% Mat Bal</th>
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<tbody>
<tr>
<td>W400</td>
<td>Coal</td>
<td>1.2</td>
<td>101.5</td>
<td>6.8</td>
<td>101.0</td>
</tr>
<tr>
<td>I400</td>
<td>Coal</td>
<td>5.3</td>
<td>103.2</td>
<td>23.1</td>
<td>100.0</td>
</tr>
<tr>
<td>P400</td>
<td>Coal</td>
<td>1.7</td>
<td>100.9</td>
<td>33.4</td>
<td>100.4</td>
</tr>
<tr>
<td>W400</td>
<td>Methylated</td>
<td>8.1</td>
<td>99.7</td>
<td>17.8</td>
<td>99.6</td>
</tr>
<tr>
<td>I400</td>
<td>Methylated</td>
<td>11.0</td>
<td>99.2</td>
<td>21.1</td>
<td>100.9</td>
</tr>
<tr>
<td>P400</td>
<td>Methylated</td>
<td>10.8</td>
<td>98.6</td>
<td>24.4</td>
<td>99.2</td>
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<tr>
<td>W400</td>
<td>Butylated</td>
<td>7.7</td>
<td>99.3</td>
<td>9.7</td>
<td>98.4</td>
</tr>
<tr>
<td>I400</td>
<td>Butylated</td>
<td>11.9</td>
<td>100.4</td>
<td>16.0</td>
<td>99.8</td>
</tr>
<tr>
<td>P400</td>
<td>Butylated</td>
<td>14.6</td>
<td>98.1</td>
<td>30.2</td>
<td>96.4</td>
</tr>
</tbody>
</table>

The methylation and butylation of all three coals increases the toluene extraction yields. The difference between the methylated and butylated toluene extractions yields is negligible in the I400 and W400 coals. The P400 coal shows a marked difference between methylated and butylated samples. This can be readily seen by Graph 1.,
which illustrates the results of the toluene extractions. The cleaved samples refer to LiI treated coals which will be discussed later. The x-axis is labeled according to the parent coal for those samples shown directly above the series number. The y-axis is the weight percent soluble in the solvent listed at the top of the graph. Note that the scales for toluene (Graph 1) and pyridine (Graph 2) are different.

During the alkylation reaction, hydrogen-bonds of the -OH functional groups which are not disrupted by toluene extraction, are replaced with ether bonds by the addition of alkyl substituents. This results in the increase in toluene solubility because the coal matrix has less hydrogen-bonding, and more organic like material which the toluene will solvate. These factors work together resulting in increased solubility in toluene.

The toluene solubility of the butylated P400 coal is much greater than the methylated P400 coal. This is consistent with the findings of Stock and Wachoska. The lower rank coals do not follow the trends of the higher rank coals because the lower rank coals are less aromatic. Because of the low aromaticity, differences in methylated and butylated substituents are negligible.
The pyridine extract yields were decreased by methylation and butylation of the P400 and I400 coals. The subbituminous W400 coal's solubility in pyridine was increased markedly by methylation and moderately by butylation. These results are illustrated in Graph 2.

When the -OH functionalities were changed to -O-Alkyl in the alkylation, the strong hydrogen-bonding interactions between the -OH and pyridine were eliminated and only the much weaker Van der Waals interactions remained. This accounts for the decrease in solubility seen in P400 and I400. The previous argument of disrupting the aromatic stacking forces is responsible for the differences in methylated and butylated samples of each coal. While both are decreased, the butylated sample appears less effected because of the opposing factors which increase its solubility.

The I400 series shows a steady decrease in solubility with increase in chain length or 'organic nature' of the substituent. This is consistent with the previous argument in that the differences in size of the butyl and methyl groups do not effect the solubility of less aromatic coals in pyridine.
Extraction Solubilities

Toluene Extractions    P400, I400, W400

Graph 1. Percent extractable material using toluene for P400, I400, and W400 coals.
Extraction Solubilities

Pyridine Extractions  P400, I400, W400

Graph 2. Percent extractable material using pyridine for P400, I400, and W400.
Changes in Swelling Ratio due to Akylation

The solvent swelling ratio of each solvent extracted residue of the coals and their alkylated derivatives are listed in Table 3. The experimentally determined reproducibility of this method is $\pm 0.05$.

Figure 22 illustrates the swelling ratio of toluene extracted residues of coals W400, I400, and P400 and their derivatives. The solvent used for the swellings is listed on the x-axis directly below the set of samples it relates to. The y-axis is the swelling ratio and all the solvent swelling graphs are the same scale (0-3).

The alkylated I400 and P400 samples show an increase in the swelling ratios upon alkylation in both the methylated and butylated samples. The rationale for this finding is that toluene is better able to solvate the -O alkyl groups compared to the -OH group Incorporations more solvent into the coal hence increasing the swelling ratio. The larger ratios found in the butyl groups over methylated samples can be attributed to the larger butyl group being able to accommodate a larger solvent cluster than a methyl group.

The toluene swelling ratio of the W400 methylated sample doesn't differ more than experimental error from the raw coal sample. However, the butylated sample swelled in toluene, and both samples swelled in THF and follow the same trend as the other coals. The trend may be due to the fact that the methyl group is much smaller than the butyl group. Methylation may not have a strong
Solvent Swellings

Toluene residues of P400 series coal

Toluene residues of I400 series coal

Toluene residues of W400 series coal

Graph 3. a) P400 solvent swelling ratios b) I400 solvent swelling ratios c) W400 solvent swelling ratios.
enough affect on the coal to show an increase in swelling with the non-polar toluene solvent. Arguments could be made that complexation of the carboxylic oxygen with divalent cations could exist in the coal. This complex may decrease the extent of alkylation. Therefore, even though alkylation has occurred in -OH groups, some of the carboxylic groups do not react under the mild conditions used during alkylation.

W400 shows a slight increase in the toluene swelling ratio upon butylation. The addition of an alkyl group, which interacts more favorably with toluene than the hydrogen-bonding moieties they replaced, will cause more swelling in the non-polar solvent.

The differences in the swelling ratio between the butylated and methylated samples of the W400 coal may be due to the difference between the solvation of the methyl and butyl ether and ester species in toluene and THF. Further investigations need to be done to test these hypotheses.

Pyridine swelling ratios of toluene residues were obtained. However, due to the additional amount of material which is soluble in pyridine and not toluene, these swelling ratios are not reliable. The differences in solubility between the two solvents depends upon the particular coal or derivatized coal. These results will not be discussed further.

The swelling ratios of pyridine residues do not show the same trend found in the toluene residues. The
pyridine extraction and swelling process effects the hydrogen-bonding in the coal and derivatized samples unlike the toluene extraction and swelling process. The complex nature of the hydrogen-bonding in coal and how it is affected by alkylation reactions makes interpretation of the swelling ratios of these samples very difficult.

Pyridine extraction substantially effects the structure of the coal. Pyridine disrupts both principal types of cohesion forces (Van der Waals and hydrogen-bonding) found in coal. After extraction and removal of pyridine from the coal, it is not precisely known what percentage of the material capable of hydrogen-bonding is left in the coals or the extent of the reformation of hydrogen-bonds. The Van der Waals attractions obviously still exist but have undoubtably undergone rearrangement in the extraction process.

There is a general leveling effect seen in the toluene and THF swellings of all three coals. The leveling is probably due to the fact that any subtle changes that are occurring are somewhat overwhelmed by the harsh effects of pyridine extraction of the coal.

Some variety can be seen in the toluene swellings of the I400 and P400 series. The explanation for these findings is similar to that discussed for the increased swelling of alkylated samples in toluene. However, the effects have been subdued due to the pyridine extraction.
Solvent Swellings

Pyridine residues of P400 series coal

Pyridine residues of I400 series coal

Pyridine residues of W400 series coal

Graph 4. d)P400 solvent swelling ratios e)I400 solvent swelling ratios f)W400 solvent swelling ratios.
The THF swelling ratios of all three coals show very slight if any trends upon alkylation. Again, the preparation of the samples by pyridine extraction has masked any information by reducing any changes to nearly within experimental error. The pyridine swelling ratios of the W400 series show little or no change upon methylation or butylation of the coal. It has the largest amount of oxygen of the three coals and presumably, the most hydrogen-bonding species. The leveling effect will be a major factor as illustrated by the Graph 2, scan f.

The I400 and P400 series show nearly identical behavior. The swelling ratio for the methylated coal is markedly lower than for the coal. An argument supporting this data is that when the -OH group is replaced with an -O-alkyl group, the strength of the interaction between the oxygen containing group and the pyridine is reduced from a hydrogen bond (strong) to a Van der Waals interaction (weak). It follows that the weaker Van der Waals interaction created by alkylation would not swell the coal as much in pyridine. The opposing effect of introduction of a longer chain alkyl group discussed earlier explains the restoration of the swelling ratio to nearly that of the original coal when the substituent is changed to a butyl group. In effect, the loss of -OH hydrogen bonding is replaced equally by the addition of Van der Waals forces of a four carbon chain but not by a one carbon chain.
Changes in SEC upon Alkylation of Coals

Size exclusion chromatography (SEC) profiles were analyzed as evidence for reaction completeness in the alkylated coals. The profiles of the toluene and pyridine soluble fractions of P400 coal are shown, Profile 1, as a representative example. The W400 and I400 profiles change in the same manner as the P400 samples. The change in the shape of the curve is an indication of a reduction in the molecular weight or in the -OH functionality of the soluble fraction of the coal. From the shift to the right of the major portion of the curve seen in the pyridine soluble fraction, but not present in the toluene soluble fraction, a change in the amount of -OH functionality is presumed to be the explanation of the changes in the curve. The pyridine soluble fraction is known to remove -OH functionalities from the coal that are undisturbed by toluene because of the hydrogen-bonding involved. The shift seen only in the pyridine fraction suggests that the molecular weight of the material removed did not actually change during the alkylation process, but that the -OH material was converted into an ether material which will cause the observed shift. From this evidence, it is concluded that -OH functionalities in the coals were converted into -O-alkyl functionalities by the reaction.
Profile 1. SEC Profiles of Toluene and Pyridine soluble Fractions of Raw Coal, Methylated, and Butylated Samples.
Changes in FT-IR upon LiI treatment of coals

All coals and their alkylated derivatives were treated with LiI under previously described reaction conditions. The LiI treated coals were subjected to the same analyses as the alkylated samples and raw coals.

Comparison of Figure 3, raw coal, with Figure 13, LiI treated (henceforth cleaved) coal shows an increase in the -OH / -C=C ratio for the W400 cleaved coal. The I400 treated coal shows a slight increase in -OH absorption but no other apparent changes from the parent coal. The P400 has a prominent increase in -OH absorption upon treatment of the parent coal.

Spectra of the cleaved, methylated W400, I400, and P400 coals, Figure 14, differ from the spectra of the raw coals, Figure 4, in exactly the same manner as the untreated methylated samples differ from their parent coals. The ratio of -OH absorption to -CH absorption in the IR increased after methylation. The development of the -CO absorption peak at 1261 cm⁻¹ indicates the formation of ether type bonds. The differences found between the treated butylated coals, Figure 15, and the untreated butylated coals, Figure 5, are negligible.

One might expect to see a decrease in absorbance at 1261 cm⁻¹ indicative of a removal of ether bonds. However, the LiI treatment is only effective on hydrogen-bonded aromatic-O-alkyl ethers. The ether bonds formed during alkylation aren't necessarily in this environment. The addition of alkyl groups to the -OH groups should
eliminate many of the hydrogen-bonds necessary for the cleavage of pre-existing coal ethers to proceed as proposed.

The W400 sample in Figure 16, of the toluene soluble fractions of treated coals, shows no differences from the spectra of the same samples of untreated coals. The lower ranked coal contains a lower percentage of its oxygen in aro-O-alkyl ethers than the other coals. Therefore, the cleavage reaction wouldn't be expected to be as effective.

The spectra of the toluene soluble fractions of P400 and I400 cleaved coals, Figure 16, show reductions in the 1261 cm$^{-1}$ and 800 cm$^{-1}$ peaks as compared with the spectra of the toluene soluble fraction of the untreated coals, Figure 6. These coals are known to contain the required ether structures. Presumably the loss at the ether peak indicates that cleavage takes place. The appearance of a 'product' peak which would be characteristic of the final cleavage product is annoyingly absent. A dramatic increase in phenol content would be expected if the aqueous work up procedure displaced the iodide with -OH, and neutralized the phenoxide ion as seen on page 12. Increases in -OH content would range from 2-3 times the original number if -OH groups replaced the iodide and phenoxide ion. Spectra of the the toluene soluble fraction would not show an increase in -OH because of toluene's inability to remove hydrogen-bonded material from the coal.

Spectra of the toluene soluble fraction of the
methylated coals, Figure 7, and the toluene soluble fraction of the cleaved methylated coals, Figure 17, show similar changes as those between Figure 6 & 16. There is a loss of absorption at 1261 cm$^{-1}$ and 800 cm$^{-1}$ as seen in the toluene soluble fractions of the raw coal, Figure 6, as compared to the toluene soluble fraction of the methylated coal, Figure 16.

The spectra of the toluene soluble fractions of the cleaved butylated coals are shown in Figure 18. There are no apparent differences between these spectra and those of the same fraction from the raw coals, Figure 8. Evidently any changes in the toluene soluble fraction that may occur with the lithium iodide treatment have been nullified by the alkylation procedure or are not apparent in the toluene soluble fraction.

The spectra of the pyridine soluble fractions of the P400, and I400 cleaved coals, Figure 19, show a general increase in the -OH absorption over the pyridine soluble fraction of the raw coals, Figure 10. The I400 has the biggest increase followed by the P400 series. The W400 shows no changes. The differences in the spectra are evidence to suggest that lithium iodide reaction is most effective on the coal believed to have the largest number of the type of ethers that will be susceptible to treatment. It follows that the other two coals which have less of the necessary ether functionalities do not react to the same extent.

From Figure 20, the pyridine soluble fraction of
cleaved methylated coals, it is apparent that cleavage of the methylated samples of I400 and P400 affects the pyridine soluble fraction of the sample when compared to the pyridine soluble of the raw coals, Figure 11. Note, there is no apparent change in the W400 coal. The change seen in the P400 and I400 occurs in the relative intensities of the peaks in the -CH aliphatic region. It appears that some materials containing alphatic groups that were not soluble before treatment have become soluble in pyridine after treatment with LiI.

Unlike the methylated derivatives, none of the coals show important differences between the spectra of the pyridine soluble fractions of the butylated raw coals, Figure 12, and the butylated cleaved coal.
Figure 13. Cleaved Coals

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Figure 14. Cleaved Methylated Coals
Figure 15. Cleaved Butylated Coals
Figure 17. Toluene Soluble of Cleaved Methylated Coals
Figure 18. Toluene Soluble of Cleaved Butylated Coals
Figure 19. Pyridine Soluble of Cleaved Coals
Figure 20. Pyridine Soluble of Cleaved Methylated Coals
Figure 21. Pyridine Soluble of Cleaved Butylated Coals
Changes In Solubility Upon LiI Treatment

LiI treatment of the P400 series of coal samples has little or no effect on the toluene solubility for the raw coal as seen in Graph 1. Conversely, treatment of the I400 series reduces the toluene solubility dramatically in each case. The W400 raw coal seems to be unaffected by treatment unlike its alkylated derivatives which are reduced significantly. This could be attributed to the already extremely low solubility of this coal in toluene.

The I400 series and W400 alkylated coal data are consistent with the theory that lithium iodide treatment introduces hydrogen-bonding \(-\text{OH}\) species into the coal, which would lead to a reduction in toluene solubility. The coal which has the largest number of the ether types affected by the lithium iodide treatment, I400, shows the most dramatic reduction in toluene solubility.

Graph 2, pyridine solubilities of the coal samples, shows a similar extent of reduction in solubility with lithium iodide treatment of all samples in the P400 and I400 series. Because the pyridine disrupts the hydrogen bonding in the coal, the possibility that \(-\text{OH}\) functionalities may have been introduced into the coal should not effect extractability in pyridine as it does toluene. The reason for the decrease in pyridine solubility seen in the I400 and P400 upon cleavage is unclear.

Because the W400 series does not have a large
percentage of its oxygen in the required environment any lithium iodide reaction would be very limited in extent. This explains the small effect on solubility observed between the cleaved and raw samples.

Changes in Swelling Ratios upon Li-I Treatment

Table 3, page 52, lists all the swelling ratios of the cleaved raw and alkylated samples. The information is presented in Graph 3, page 51, which has been previously discussed.

The W400 series, a), shows a reduction of swelling ratio in THF for alkylated samples and for the butylated sample in toluene upon cleavage. The mechanism for THF solvent swelling, which involves hydrogen-bonding, has been inhibited by the cleavage of the alkylated sample but not the raw coal. This would suggest that the alkyl groups that are responsible for the increased swelling have been altered by cleavage in such a way that the increase in swelling has been eliminated. The toluene swelling differences can be explained in the same manner keeping in mind that it is believed the methyl group is not large enough to noticeably increase the swelling ratio of the coal in toluene. Neither of the swelling ratios change in the raw coal and cleaved coal. The lack of change is consistent with the belief that this coal does not contain the ethers required for reaction. This may also suggest that the alkylated products do contain newly formed hydrogen-bonded ethers which undergo reaction with lithium iodide.
The swelling ratios seen for the I400 series, b), suggest that the cleavage reaction changes the hydrogen-bonding functionalities in such a way as to reduce the interactions with THF and increase the swelling ratio of the coal upon cleavage. The swelling of the alkylated samples are decreased, butyl more than methyl, upon treatment. The reaction appears to be reducing the swelling ratio to the same extent that the aklylation increased it.

The P400 series, c), shows less obvious trends upon the lithium iodide treatment. It important to keep in mind P400 coal has a very low percentage of oxygen. The reaction reduces the butylated swelling ratio in toluene while increasing that of the methylated and raw coal samples. It is unclear exactly what type of reaction products would produce these swelling results. There is little or no effect seen in the THF swelling ratios of the P400 series, Graph c). This is most likely due to the low oxygen content of the coal not providing many possibilities for THF to interact and swell the matrix. Evidently, the reaction does not provide any increase in interactions for THF in the coal or alkylated sample.

The swelling ratios of the pyridine extracted samples are shown in Graph 4. The P400 series, d), shows little change upon cleavage as would be expected from its low oxygen content. The W400 series, f), shows the overwhelming leveling effect that pyridine extraction has on the high oxygen containing coal.
The coal samples from the I400 series, do not show differences in the swelling ratio between raw or cleaved sample. This is probably due to the fact that the pyridine extraction disrupts the hydrogen-bonds in coal, and thus we can not see any effects due to the reaction. The alkylated samples have absolutely no related trends that are consistent with any of the previous theories on alkylation. Further investigation will have to be done for reasonable hypotheses to be made as to what the final products of the lithium iodide reaction with coal and alkylated derivatives of coal are.

Changes in SEC upon Li-I Treatment

As seen in Figures 23,24,25,26,27,28, there are no apparent changes in any of the SEC profiles upon treatment with lithium iodide in pyridine. The I400 series is shown as representative example which P400 and W400 follow. This could be evidence for no reaction or that the reaction is not so drastic that it changes molecular weight or functionalities of the coal enough to show up in the profiles. There is the possibility that the cleavage reaction doesn't show changes in the SEC profiles because although reaction did occur, the reaction causes more of a 'rearrangement' of the coal than the formation of a drastically different species. This is consistent with the theory of the reaction intermediate reacting with the surrounding coal during the work-up procedure.
Figure 22. SEC profiles of toluene soluble fractions of raw coal -vs- cleaved coal, methylated -vs- cleaved methylated, and butylated -vs- cleaved butylated for P400 coal.
Figure 23. SEC Profiles of Toluene Soluble Fractions of Raw Coal -vs- Cleaved Coal, Methylated -vs- Cleaved Methylated, and Butylated -vs- Cleaved Butylated for I400 coal.
Figure 24. SEC profiles of toluene soluble fractions of raw coal -vs- cleaved coal, methylated coal -vs- cleaved methylated and butylated -vs- cleaved butylated coal for the W400 coal.
Figure 25. SEC profiles of pyridine soluble fractions of raw coal -vs- cleaved coal, methylated coal -vs- cleaved methylated and butylated coal -vs- cleaved butylated coal for P400 coal.
Figure 26. SEC Profiles of Pyridine Soluble Fractions of Raw Coal -vs- Cleaved Coal, Methylated -vs- Cleaved Methylated, and Butylated -vs- Cleaved Butylated.
Figure 27. SEC profiles of pyridine soluble fractions of raw coal -vs- cleaved coal, methylated coal -vs- cleaved methylated and butylated coal -vs- cleaved butylated coal for the W400.
Conclusions

Alkylation of coals is easily achieved under mild conditions in THF with methyl iodide or bromobutane. The extent to which alkylation effects the solubility of the sample in toluene is more dependent on the alkyl group in higher ranked coals than lower ranked coals. Butylation increases the toluene solubility of the P400 coal by approximately one third more than methylation. The lower rank coals showed no difference between methylation and butylation. The difference is possibly due to the amount of aromatic stacking that is disrupted by alkylation that is not present in the lower rank coals. The swelling mechanism of toluene residues in toluene and THF involves the ability of the coals to accommodate a solvent cluster in the coal matrix. Upon alkylation the added methyl or butyl groups are better solvated than the -OH groups they replaced thus increasing the swelling ratio of the alkylated samples.

Pyridine solubilities are decreased by alkylation in bituminous coals but increased in the subbituminous coal. Hydrogen-bonding in bituminous coals is 'turned off' by alkylation therefore decreasing its solubility in the polar basic solvent pyridine. The -OH species that existed in the bituminous coal before alkylation were very susceptible to hydrogen-bonding with pyridine. This strong interaction enabled a large amount of material to be solubilized by the pyridine. When these groups were replaced with -O-alkyl groups, the strong interaction was
eliminated along with the hydrogen. The result is a decrease in the solubility in pyridine. The same effect is not seen in the subbituminous coal because it contains a large number of carboxylic groups that may be complexed with divalent metals in a salt formation. These formations block hydrogen bonding in the pyridine extraction of the raw coal. These complexes are broken by the addition of base in the alkylation procedure thus enabling alkylation to occur. The newly formed esters are more soluble in the pyridine than the salt complexes therefore an increase in solubility is observed.

The lithium iodide reaction in pyridine does not replace hydrogen-bonded ethers in coal with additional -OH groups as was proposed by equation 1. The coal product from this reaction exhibits properties quite different from the original sample. It is believed that the products first formed in the reaction go on to react with other groups in the coal, but it is unclear as to exactly what types of reactions occur.
REFERENCES


Amsterdam 1987, 741.


41) Wang, S.H.; Griffiths, P.R. Fuel 1985, 64, 229.