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ENHANCEMENT OF COAL LIQUEFACTION REACTIVITY BY MILD ALKYLATION PRETREATMENT

By

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ABSTRACT

Enhancing coal liquefaction reactivity by mild alkylation was studied over a range of liquefaction conditions in a microautoclave reactor system. THF soluble conversion of alkylated coal was compared with that of untreated coal. Wyodak subbituminous, Beulah-Zap lignite, and Illinois #6 and Pocohonatas #3 bituminous coals were alkylated with alkyl alcohol and a small concentration of acid catalyst. The extent of alkylation varied from 0.5 grams to 9.8 grams of alkyl groups per 100 grams of coal depending upon the type of alcohol used and the coal being alkylated. It was found that the alkylation procedure developed was most effective on lower rank coals with higher oxygen contents, and that higher alcohols such as isopropanol alkylated the coal to a greater extent than methanol or ethanol. The reactivities of these alkylated coals were compared to the reactivities of the corresponding untreated coals by measuring conversion to THF and toluene soluble products at various reaction conditions. The largest percentage increases in THF and toluene conversions for the alkylated coals were seen at low severity conditions (315 ^{o}C) where the Wyodak coal showed a fourfold increase in conversion. Wyodak coal and Beulah-Zap lignite showed the largest increases in reactivity after alkylation. At higher severity conditions (350 to 400 ^{o}C), the increase in THF conversion after alkylation was not as large and the toluene conversion decreased up to twenty percent as the alkylation pretreatment caused an apparent repolymerization of the coal derived liquids. Photoacoustic infrared spectroscopy was used to study the chemistry of the alkylation procedure. By comparing the spectra of alkylated and untreated samples, it was determined that the alkylation procedure had caused a reduction in phenols and carboxylic acids while increasing the number of ethers and esters in the coal. This evidence led to the conclusion that the coal alkylation was an O-alkylation that reacted at oxygen functionalities within the coals.

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INTRODUCTION

The first significant coal liquefaction process was the Bergius process developed in Germany in the early part of this century. This process involved heating the coal to extremely high temperatures (500 ^{o}C) in the presence of high pressure hydrogen gas (70 MPa). These conditions caused thermal scission of the various bonds thus destroying the coal structure. The coal radicals were then capped by hydrogen. Until the 1970's, this method of coal liquefaction was the most effective known. Since that time, several new processes have been developed to increase coal conversion while at the same time decreasing the reaction severity. The only real strides made were the use of hydrogen donor solvents to improve the hydrogen mass transfer rates and the recycle of residual coal-derived liquids to improve conversion. The reactions continued to be carried out at high severity and did not utilize any forms of selective coal conversion chemistry (1).

In recent years a great deal of attention has been focused on lower severity liquefaction. Low severity reaction conditions offer several advantages over high severity treatment of coal including:

1) less production of light gas,
2) lower hydrogen consumption,
3) less coke and char formation,
4) significant energy savings (1).

The problems associated with high severity liquefaction are especially acute among lower rank subbituminous, lignite coals and high volatile bituminous coals. These coals have a greater number of oxygen functionalities and are therefore more reactive than other types of coal. At high temperatures the stuctures of these coals are broken apart very quickly, and the resulting coal fragments are more likely to repolymerize forming high molecular weight coal liquids that cannot be easily converted to distillable liquids by further treatment. The obvious alternative is to treat the coal mildly and selectively, cleaving bonds within the coal structure prior to low severity liquefaction. This approach would take advantage of the inherent reactivity of coal and at the same time, minimize the rate and extent of retrograde product formation.

A great deal of laboratory work has been reported on methods to depolymerize coal at mild reaction conditions. However, these studies have been mainly aimed at determining the structure of coal, with very few cases of depolymerization being used as a possible pretreatment to coal liquefaction. Depolymerization involves selective bond cleavage of the coal structure which increases the extractability of the coal in organic solvents. Such a treatment disrupts the coal structure and increases the contacting between the solvent and coal. In this project, it was hypothesized that such a treatment combined with low severity liquefaction would be a promising process concept and should be studied in detail.

One common method of depolymerization is coal alkylation. While the types of alkylation reactions occuring depend upon the severity of the method used, most alkylation reactions break ether linkages and reduce hydrogen bonding in the coal by reacting with phenolic and carboxylic acid functionalities in the coal. This treatment is more effective with lower rank coals because of their higher oxygen concentrations. A number of alkylation methods have been found to be very effective in increasing the extractability of the coal. Some studies have shown alkylation to be beneficial as a pretreatment to coal liquefaction.

Project Objective

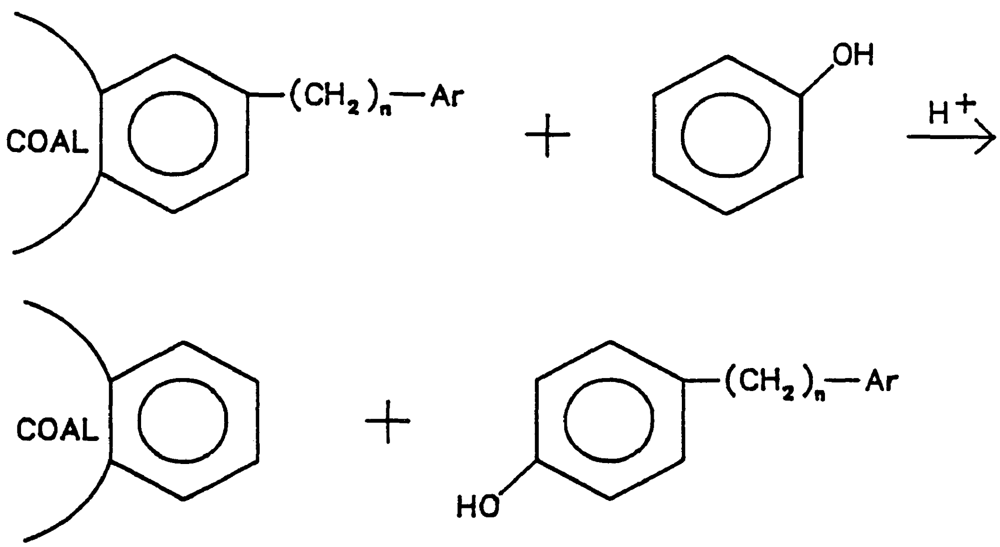
Work at the Colorado School of Mines has been undertaken to study the effectiveness of alkylation as a pretreatment to coal liquefaction. This work's primary focus was to find a mild pretreatment reaction which would not degrade coal reactivity. A mild method of alkylation was selected in order to insure minimum degradation of the coal structure. The goal was then to determine to what extent the reactivity of the coal was increased by the alkylation reaction. Coal reactivities were compared in terms of the extent to which coal was converted to preasphaltenes, asphaltenes, and oils in a liquefaction reaction. Although a range of liquefaction conditions were studied, low severity conditions were used preferentially. After determining the effectiveness of the pretreatment, experiments were done using infrared spectroscopy to determine what kind of chemical changes in the coal were caused by alkylation.

LITERATURE SURVEY

1. Depolymerization

The structure of coal has been theorized to contain a number of long polymer like chains held together by relatively weak bonds. It was therefore thought that the extractability of coal could be increased by breaking the weaker bonds, thus making the long polymeric chains more soluble in organic solvents. Several methods of depolymerization have been studied and almost all have shown coal to be composed of a number of high molecular weight organic chains which can be broken by mild chemical treatment.

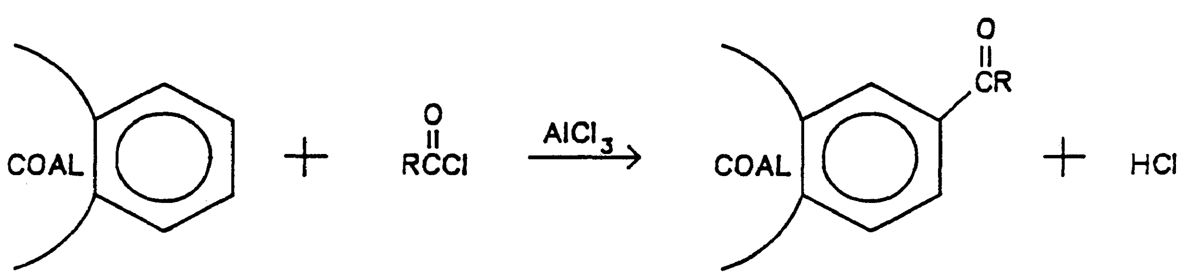
Early work in the depolymerization of coal was reported by Heredy and Neuworth (2). ~~They~~ discovered that coal could be depolymerized by using it as an alkylating agent. Coal was used to alkylate phenol using boron trifluoride as catalyst. The overall effect of this treatment was to increase the extractability of the coal in organic solvents, such as benzene and toluene. The reaction was theorized to proceed in this manner (3):



The treatment worked best on lignite indicating that the loosely bound structure was best suited for chemical depolymerization. The treatment was least effective with large polycyclic aromatic structures found in higher rank coals. The extracted coal samples contained extremely high molecular weight material which supports the theory that coal is comprised of long polymeric chains.

Subsequent experiments using this method found that extractability could be improved by using different catalysts. It was discovered that pretreating the coal with nitric acid increased the depolymerization of the coal(4). As the extracted material continued to show large molecular weights, it was theorized that the nitric acid enhanced the coal depolymerization by means of nitration and not by any additional bond cleavage. Ouchi and coworkers found that even better conversions could be attained using p-toluene sulphonic acid as the catalyst(5). This group experimented with labeled carbon in the phenol in order to determine what functionality within the coal was reacting with the phenol. Though the results were not conclusive, Ouchi suggested that the cleavage took place at ketone functionalities within the coal structure. However, other studies have concluded that the ether and sulfide bonds are broken within the coal (3).

Other experimenters have studied the possibility of depolymerizing coal by means of acylation. Hodek and Kolling (6) used carboxylic acid chlorides to acylate coals coals with an aluminum chloride catalyst. The reaction that occurs is thought to be (6):



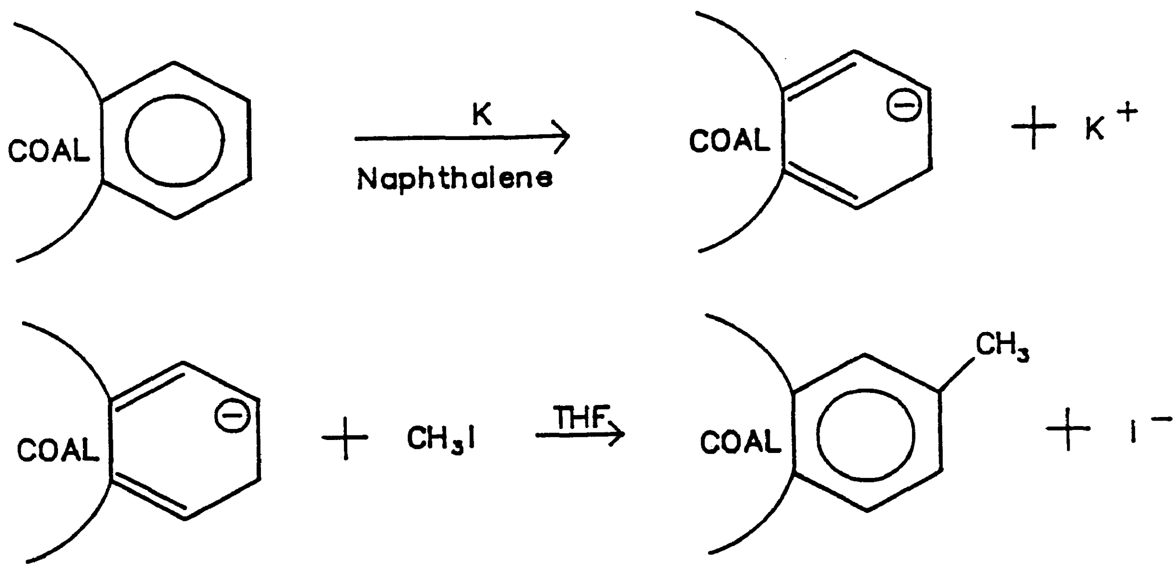
The acyl chlorides react at the surface of the coal and coats the coal particles. The long chain acyl groups then react favorably with the solvent and draw the coal polymer out of the coal structure. Acylation does not cleave any bonds, and the increase in extractability is independent of the coal-solvent interaction. However, because of the addition of the acyl chains to the coal polymers, the molecular weight of the extracted coal material is much higher than those found in any other depolymerization method (4). Depending upon the ease with which these acyl bounds can be broken, such high molecular weight material might be detrimental to further treatment such as pyrolysis or liquefaction reactions. The use of aluminum chloride is also counterproductive because of its property as a strong dehydrogenation catalyst.

Mild oxidation of coal is another method of coal depolymerization that has been tested by several researchers (7,8,9). Hessley attempted to selectively oxidize coal, forming hydroperoxides which would cleave the carbon-carbon bonds within the coal structure. Results showed that extractability was increased only a minimal amount (9). While other experimenters have shown more significant increases in extractability following oxidation, there is little evidence to suggest that oxidation would be an effective liquefaction pretreatment. Oxidation is undesirable as a pretreatment for coal liquefaction for various reasons: 1) the act of oxidation does not enhance reactivity but rather decreases reactivity by destoying many of the reactive oxygen functionalities within the coal, 2) the increase in extractibility is slight as oxidation cleaves few bonds and does little to reduce hydrogen bonding in the coal, and 3) oxidation pretreatment is more expensive in terms of hydrogen consumption during hydrogenation of coal as the addition of oxygen to the coal will increase phenol and water formation thus consuming more hydrogen during liquefaction.

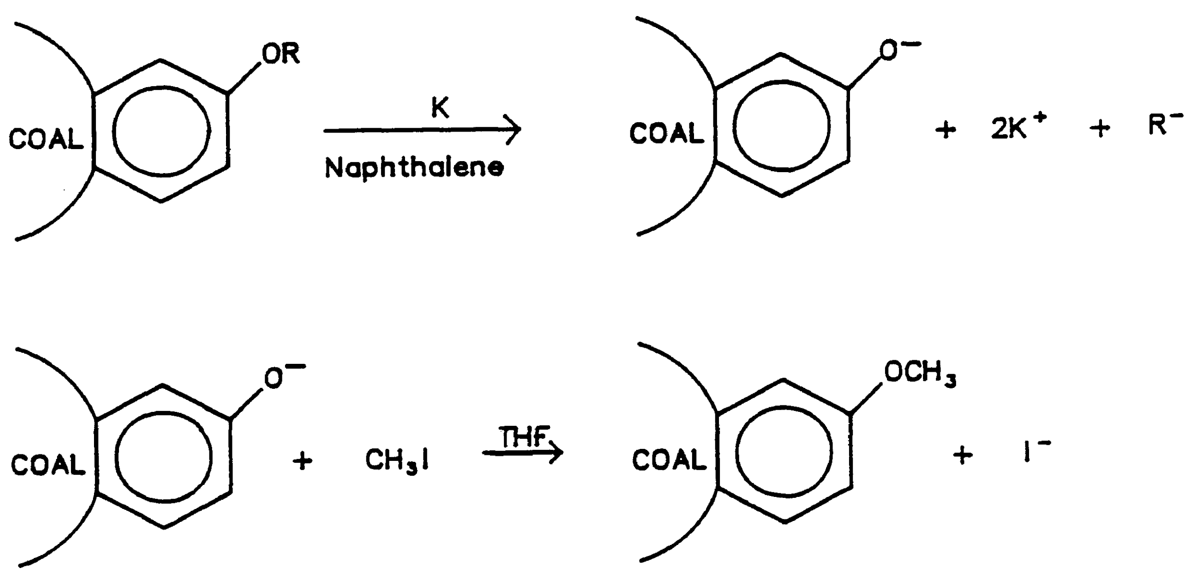
Several studies have been reported using alkali pretreatment as a method of coal depolymerization (10,11). This treatment reduces coal acidity and thus reduces the hydrogen bonding within the coal. Mirza (10) treated coal for 24 hours in a 1% aqueous sodium hydroxide solution and observed an increase in extractability of up to 25%. With a similar pretreatment, Fischer was able to convert a Texas lignite to 80-85% benzene soluble material (9). Work has been done by Chou (11) on the liquefaction of coal pre-treated with a 20-30% aqueous NaOH solution. His results showed marginal increases in conversion to benzene soluble material and a decrease in char and preasphaltene formation. The reactivity was found to increase by increasing the severity of the alkali pretreatment. The liquefaction reaction measurements were performed at high severity (410^{o} C, 6.75 MPa) which probably lessened the observed increase in reactivity due to the pretreatment. The results suggest that depolymerization is an effective pretreatment for coal liquefaction, but that more work is needed before the full value of such pretreatments will be understood.

2. Reductive Alkylation of Coal

The reductive alkylation of coal is a method of depolymerization involving the formation of a coal anion by means of an oxidation-reduction reaction. The anion is then treated with an alkylating agent which reacts to break an existing bond and forms a new bond within the coal stucture. Sternberg and Delle Donne (12,13) experimented with the oxidation of potassium to form a coal anion. The reaction was carried out in the presence of naphthalene which aids electron transfer. After the formation of the coal anion, the coal was treated with an alkyl halide as the alkylating agent. The effect of this treatment was to break bonds and disrupt the coal structure, thus increasing the coal extractability. The reaction could proceed at either carbon functionalities (14):



or at oxygen functionalites:



The extent to which coal was alkylated varied for different ranks of coal as did the extent to which coal extractability was increased. Extractability of a subbituminous coal went from 3 wt. percent to 97 wt. percent by the addition of 14 methyl groups per 100 carbon atoms in the coal. The same treatment to an anthracite coal added only 0.6 methyl groups per 100 carbon atoms in the coal and did not increase the extractability of the coal to any measurable extent.

The reason cited for the difference between extents of alkylation was the lack of oxygen functionalities in the high carbon anthracite coal. Sternberg and Delle Donne concluded that the most important action of the treatment is the cleavage of ether bonds and the O-alkylation of phenol groups. They supported this conclusion by showing that the number of alkyl groups added corresponded to the number of oxygen atoms in phenol hydroxyl groups, and in diaryl and aryl-alkyl ether bonds (13). An exhaustive review on the subject of reductive alkylation by Stock also supports this conclusion (14). While Stock has shown that other bond cleavages are occuring during alkylation, he emphasizes that the cleavage of ethers, especially aryl ethers, is the most likely reason for the increased extractability.

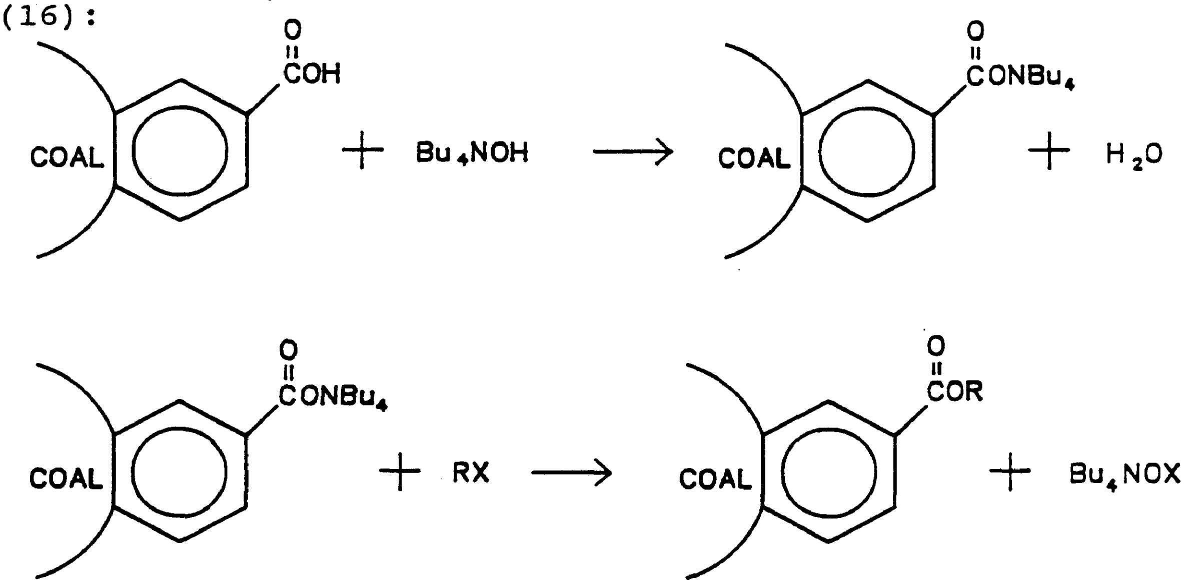
In his review, Stock cited studies which varied the reducing agent, the alkyl group, and the halide of the alkyl halide. These studies showed that the extent of alkylation decreased as the molecular weight of the alkyl group increased. However, the increase in solubility was less for the smaller alkyl groups. This effect was especially significant for the solubility in benzene and was attributed to a poor interaction between benzene and smaller alkanes. The effect was not as significant for more polar solvents. Reductive alkylation worked better with higher molecular weight halides because of their higher reactivity with the nucleophilic coal anion. Higher molecular weight alkali metals were found to be better reducing agents and therefore promoted the alkylation reaction at a greater rate.

Further liquefaction of reductively alkylated coal was performed by Vassalo (15), but the study was done to determine coal structure by analysis of the coal material after liquefaction. Although reductive alkylation proved to be a great analytical tool, it is impractical as an industrial treatment for several reasons. The most important reason is the impracticality of removing alkali metal ions from the coal liquids. It is not possible to leave these ions in the coal slurry because of their high corrosiveness. For this reason, no work has been done on the possibility of upgrading the reductively alkylated coal. Another major drawback is the amount of time for the oxidation-reduction reaction to take place. Sternberg and Delle Donne found that from 3 to 15 days were required for the formation of the coal anion to the extent necessary for the alkylation reaction to proceed. These two factors make reductive alkylation impractical for any large scale operation.

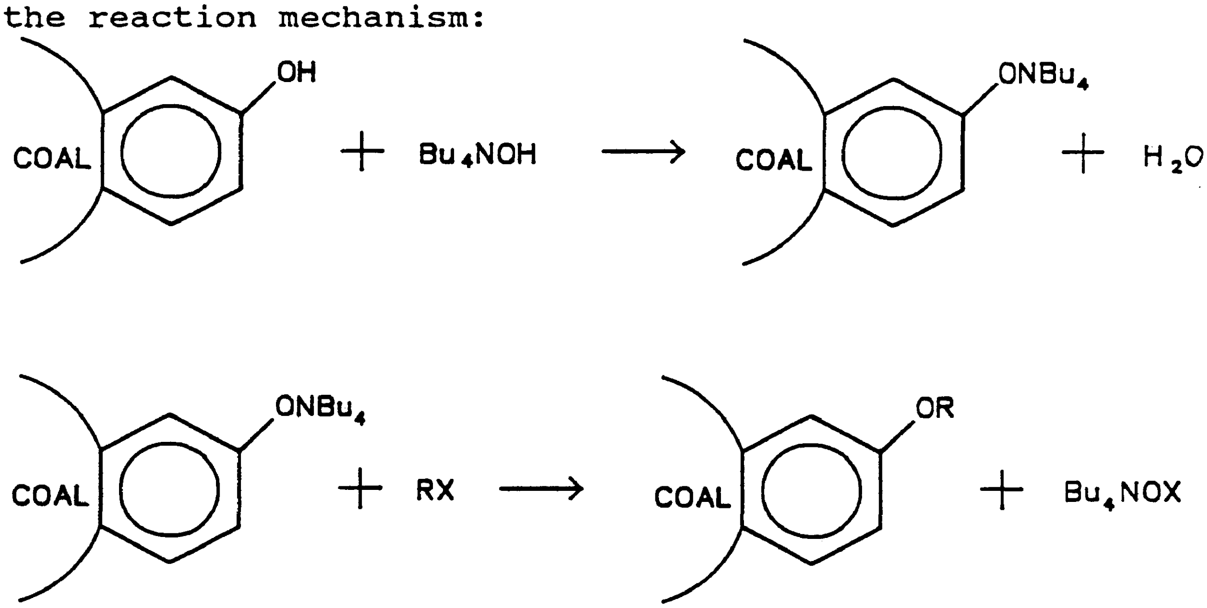
3. O-Alkylation

Because of the harmful side reactions and difficult treatment problems caused by reductive alkylation and Friedel-Kraft alkylation (which will be discussed in the next section), a more mild, selective alkylation was desired in order to cleave the necessary bonds without forming any new bonds or increasing the aromatic structure of the coal. Such a method of alkylation was developed by Ronald Liotta. His alkylation method, known as O-alkylation, was developed to concentrate on the alkylation of phenol and carboxylic acid functionalities in coal and coal derived liquids. In a number of patent reports Liotta showed that his treatment could increase the solubility of coal (16,17) and coal derived residuum (18), and could be a productive pretreatment for coal liquefaction (19) and pyrolysis (20).

The first step of Liotta's O-alkylation pretreament was to treat the coal with a quartenary base. Liotta used quartenary butyl ammonia in most of his studies. The mixture was then heated from 100° to 300° C and, after a set period of reaction, an alkyl halide was added to the mixture (16). The reaction mechanism was considered to be (16):



The reaction also occurs at carboxylic functionalities by the reaction mechanism:



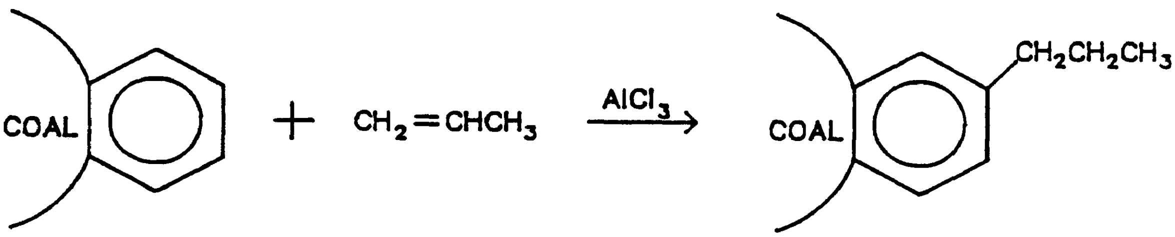
Infrared spectra indicated elimination of hydroxyl groups, and an incorporation of alkyl ether and ester carboxyl funtionalities had occurred, confirming Liotta's theory of O-alkylation (16). It was discovered by elemental analysis that the extent of alkylation was 4.5 methyl groups per 100 atoms of carbon. While the solubility of the coal was increased a significant amount by such a treatment (20-25%), a much greater increase in solubility was observed for treated coal derived residuum which showed as much as a threefold increase in solubility (18). The fact that the coal residuum was so susceptible to O-alkylation indicates that such a treatment would be extremely beneficial to the subsequent liquefaction or pyrolysis of a treated coal.

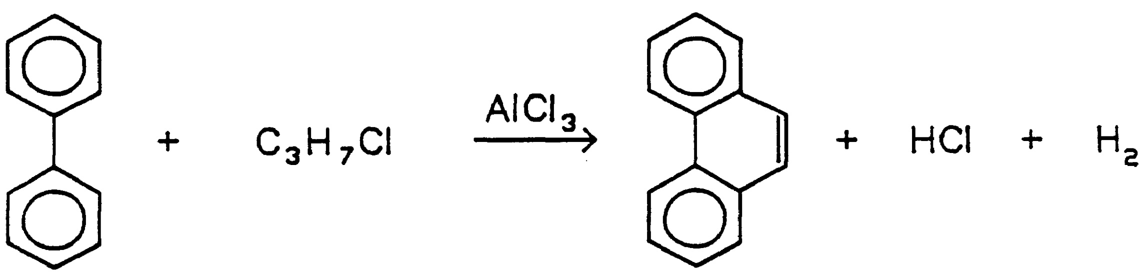
O-alkylation was tested by Liotta as a pretreatment to high severity (425° C) liquefaction (19). Pretreatment which added 4.5 methyl groups per 100 atoms of carbon to a high volatile bituminous coal increased the conversion by approximately 60 wt%. Liotta also used O-alkylation (and O-acylation) as a pretreatment for pyrolysis (20). While the alkylated coal showed a small increase in coke formation during pyrolysis, there was a significant increase in oil production and a sharp decrease in gas production. This behavior was furthur studied by Mahasay and co-workers (21). After carbon labeling of the alkylating groups and careful analysis of the pyrolysis products, it was concluded that the increase in methoxy radicals due to alkylation was the cause of the improved product yield. While the study was not extended to liquefaction of O-alkylated coal, a similar conclusion can be inferred.

While Liotta showed that O-alkylation was effective as a pretreatment for both liquefaction and pyrolysis, he did not show an industrially acceptable way to achieve such an alkylation. His alkylation method involves two reactants, quartenary ammonia and alkyl halides, which would be almost impossible to use in a large scale liquefaction operation. However, his work is extremely important in that he shows that significant increases in extractability can be achieved with very mild alkylation. It is not necessary to break any carbon-carbon bonds in order to effectively depolymerize coal. Liotta also showed that an industrially effective way to achieve mild alkylation of coal is needed .

4. Friedel-Kraft Alkylation

The Friedel-Kraft alkylation of coal is actually older than any other method of coal alkylation. In contrast to O-alkylation, the Friedel-Kraft reaction is considered a carbon alkylation, and is the organic chemical reaction that most people associated with alkylation. The alkyl group is initially in the form of an alkene and reacts with the coal in the following manner (3,22):





O-alkylation does occur during Friedel-Kraft alkylation, but it is not as important because of the ratio of carbon bonds to oxygen bonds in coal. The first coal alkylation using a Friedel-Kraft reagent was done by I. D. Kroger (3). The treatment used aluminum trichloride as a catalyst and an alkyl halide as the alkylating agent. The alkyl halide is thought to be converted to the alkene necessary for the reaction to proceed as indicated. The reaction relied on the strong acidic nature of the aluminum trichloride. Early experiments showed no evidence of bond cleavage. There was, however an increase in the coal aromaticity and a significant increase in the coal extractability. Some later experimenters concluded that the increase in solubility was due to the cleavage of methylene and ethylene linkages, O-alkylation and disruption of the coal structure. The increase in aromaticity was due to the property of aluminum chloride as a strong dehydrogenation catalyst (3).

A study was done on the possibility of upgrading coal which had been alkylated by the Friedel-Kraft method of Kroger. The purpose of this study, done by Schlosberg and coworkers (22,23), was to run alkylated coal through a Bergius type liquefaction process. The extent of alkylation varied from 4 to 12 grams of alkyl groups per 100 grams of coal depending upon the alkylation temperature and the alkyl group added. The liquefaction reaction temperature was 425^{o} C, and the reaction took place in tetralin with pressure (70 MPa) maintained by hydrogen gas. Results showed that alkylation did increase the conversion as much as 25 percent. However, conversion decreased as the extent of alkylation increased. The more highly alkylated coal had a lower reactivity because of the increase in aromaticity. Also, one would not expect to see as much an increase in conversion at such severe conditions as any bonds broken chemically at ambient conditions would probably be broken thermally at such high temperatures.

Several other types of Friedel-Kraft alkylation have been studied. The use of olefins as an alkylating agent was tried with reasonable results (4). In the reaction no bonds were cleaved, but the coal solubility was increased because of the disruption within the coal structure. In one such experiment, coal was alkylated with isobutylene using sulfuric acid as a catalyst. The reaction proceeded quite readily with twice the weight of the coal being added in isobutylene. However, the solubility of the coal decreased. It was discovered that over-alkylation of the coal had caused a great deal of cross-linking on the outer surface of the coal. This external cross-linking outweighed the effect of the internal structure disruption due to alkylation. A later study with isobutylene and hydroflouric acid showed better results with a much smaller extent of alkylation (4).

The use of hydroflouric acid as a Friedel-Kraft catalyst was also studied by Flores and coworkers (24). In contrast to all earlier work, alcohol was used as the alkylating agent. Supposedly, the alcohol is converted to an olefin by an acid catalyzed dehydrogenation reaction. The Friedel-Kraft reaction then proceeds as above. The purpose of their study was to find a milder alkylation technique to avoid the problems of dehyrogenation and cross-linking observed by other investigators (4). While this technique did show a significant increase in coal extractibility, the extent of alkylation was not measured, and no attempt was made to determine structural changes in the coal. It is therefore impossible to determine how mild the alkylation reaction was.

A similar method of alkylation was studied by Sharma and coworkers (25). In their study, they compared several types of Friedel-Kraft alkylation methods with respect to extent of alkylation and increase in extractability. The two methods of interest were the alkyl halide and aluminum chloride alkylation of Kroger and alkylation with hydrochloric acid and butyl alcohol similar to the method of Flores et al. Their results showed the alcohol and hydrochloric acid alkylation to be most effective. The extent of alkylation was 13 grams of butyl groups added per 100 grams of coal compared to 8 for the Kroger method. The net extraction for the hydrochloric acid method was twenty percent greater than the Kroger method. The milder reaction was more effective because it avoided the harmful reactivity degradation caused by aluminum chloride. Instead of dehydrogenating the coal and attacking carbon-carbon bonds, a milder Friedel-Craft reaction will simply disrupt the structure by the addition of alkyl groups to the aryl structure. It is also possible that the reaction is primarily an O-alkylation and not a Friedel-Kraft reaction as such.

Other studies have shown alcohols by themselves to be very effective alkylating agents at elevated temperatures. Makabe and Ouchi experimented with the ethylation of model coal compounds at 425-450^{o} C (26). Their results indicated that the effect of such treatment was to ethylate polar aromatics, split ether linkages and some methylene linkages, and to hydrogenate the aromatics. A similar study was done by Ouchi and coworkers using methanol (27). Methanol was used as an insitu hydrogen source in addition to being an alkylating agent. The results supported the earlier work as the same effects were observed in model compounds. While this study is not industrially important because of high severity and large alcohol consumption, it does show that alcohol is a very effective alkylating agent and does not hamper the reactivity of the coal. To the contrary, alcohol alkylation performed at the right conditions will enhance coal reactivity. While possibly not being as effective as the high temperature alkylation, an acid catalyzed reaction at room conditions will have similar effects. Such a reaction would be ideal as a pretreatment to liquefaction.

EXPERIMENTAL PROCEDURE

1. Experimental Plan

The goal of this thesis was to determine if alkylation is an effective pretreatment to coal liquefaction and, if so, to find the alkylation and liquefaction conditions which best exhibit reactivity enhancement by alkylation. The goal was not to do an exhaustive study of alkylation techniques, nor was it the goal to experimentally determine the kinetics of the liquefaction of alkylated coal. For this reason the data gathered involve a number of different parameter changes to obtain a large range of coal conversions. The important parameters that were varied were: the alkylating agent, alkylation conditions, liquefaction reaction time, liquefaction solvent, liquefaction temperature, the reducing feed gas, and the liquefaction catalyst (most reactions did not involve catalysis). These parameters were varied in hopes of showing the optimum reactivity enhancement for the coal. Once the method of pretreatment was determined, it was necessary through subsequent experiments to determine the chemistry effected by the pretreatment.

2. Coals

Early work in this study was done using a Wyodak subbituminous coal and a Kentucky medium volatile bituminous coal. However, these two coals were found to be oxidized to an extent which greatly hindered their reactivity. For this reason and also that this work could be compared with other studies, all later experiments were done with coals from the Argonne Premium Sample Bank in Argonne, Illinois. A suite of four coals, namely a Wyodak subbituminous coal, a Beulah-Zap lignite, a Pocohontas #3 low volatile bituminous coal, and an Illinois # 6 high volatile bituminous coal, were used. Available characterization data for these coals are presented in Table I.

Argonne coals are stored and shipped in nitrogen-purged glass ampules to prevent oxidation. Each ampule contains approximately five grams of coal. An ampule was left unbroken until just before use. Coal samples to be alkylated were immediately placed in the alkylation reactor. Untreated coals were dried in a vacuum oven before use in liquefaction experiments.

3. Alkylation Pretreatment Experiments

All alkylation experiments were performed at ambient conditions in a 100 ml round bottom flask. The flask was charged with approximately five grams of coal, and the coal

TABLE I: Elemental Analysis of Argonne Coals

Coal	Rank	Elemental Analysis				
		MAF Basis			MF Basis	
		%C	%H	%O	%S	%ASH
Illinois #6	HVB	77.0	5.7	10.0	5.4	16.0
Pocohontas #3	LVB	83.0	5.8	9.0	1.6	9.0
Wyodak	Subbit.	74.0	5.1	19.0	0.5	8.0
Beulah-Zap Lignite	Lignite	73.0	5.3	21.0	0.8	6.0

and flask were weighed. For purposes of alkylation, a range of alcohols from methanol to pentanol were used. Approximately 40 ml of the desired alcohol and 0.4 ml of acid catalyst (usually sulfuric or hydrochloric) were added to the coal. A water-cooled condenser was connected to the top of the flask to prevent evaporation of the alcohol. The mixture was agitated by a magnetic stirrer throughout the reaction period. At the end of the reaction period (usually three hours) the flask was detached from the condenser, and the stirring bar was removed from the mixture. The reaction conditions are summarized in Table II.

The flask containing alkylated coal was reattached to a rotoevaporation apparatus which removed most of the unreacted alcohol. The coal was then allowed to air dry approximately four hours before being placed in a vacuum oven at 60 ^{o}C and a vacuum of 20" Hg. After 24 hours in the vacuum oven, the coal was removed and cooled in a desiccator. After cooling the flask and coal were reweighed to determine weight gain due to alkylation. The coal was then stored in a glass container and returned to the desiccator until it was needed for further treatment.

Soxhlet extractions were performed to determine the

TABLE II: Alkylation Reaction Conditions

Reactor: 100 ml round bottom flask

Coal Feed: Five grams

Coal Size: -100 mesh

Alkylating Agent: Alcohol (MeOH, EtOH, PrOH, BuOH,PeOH)

Alcohol Feed: 40 ml

Catalyst: Hydrochloric acid, Sulfuric acid

Catalyst Concentration: 0.1 - 3.0 Vol %

Temperature: Ambient

Pressure: Ambient

Agitator: Magnetic stirring rod

Reaction Time: 3 - 24 hours

extractability of the untreated and alkylated coal before the liquefaction reaction. A one gram sample of coal was placed in a preweighed porous thimble. The thimble was placed in a soxhlet extractor containing either toluene or tetrahydrofuran (THF). The samples were left in the extractor for 24 hours and removed the next day. After air drying for four hours, the thimbles were placed in the vacuum oven (at the same conditions as the alkylated coal). After 24 hours the samples were removed, cooled in a desiccator, and reweighed. The weight loss of the sample indicated the percent of the sample that was extracted.

The extent of alkylation was determined by elemental analysis of both the alkylated and the unalkylated coal to determine their respective hydrogen-carbon ratios. The equation used to determine the extent of alkylation (in terms of the weight of alkyl groups added) was:

$$X = 100*(C_3 - C_1)/(C_2 - C_3)$$

Where:

X is the extent of alkylation (grams of alkyl group per 100 grams of coal)

C_1 is the normalized weight percent of carbon in the untreated coal {(wt %C)/(wt %C + wt %H)}

C_2 is the normalized weight percent of carbon in the alkyl group

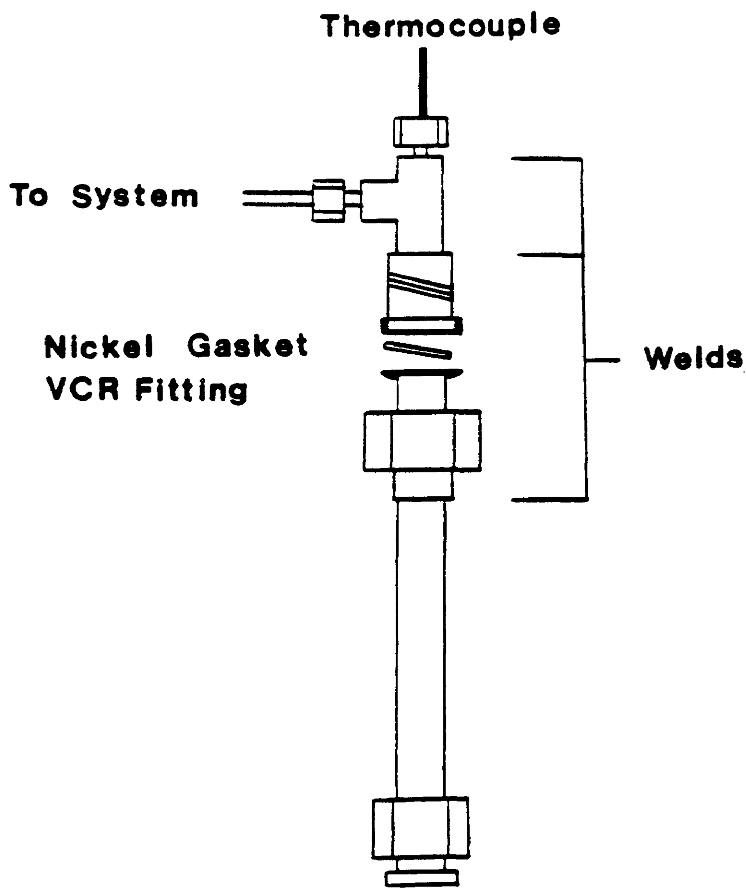
C_3 is the normalized weight percent of carbon in the alkylated coal

Elemental analyses were performed on a Carlo Erba Elemental Analyzer, model 1106, with a Hewlett Packard integrator, model 3390A. Selected analyses were performed at Huffman Laboratories.

4. Liquefaction Reactivity Experiments

All liquefaction reactions were performed in a micro-autoclave apparatus. The reactor itself, shown in Figure 1, consisted of 1/2" OD stainless steel tubing with a Swagelock 1/2" cap on the bottom and a Cajon VCR gland type gasket fitting at the top. The reactor head consisted of a Swagelock made run tee, a 1/8" Autoclave connector on the gas feed line, and a K type thermocouple. The head allows gas to enter the reactor and the temperature of the reactor contents to be monitored. The reactor was charged with one gram of coal, two grams of the desired solvent, and any other catalyst or reactant that was needed for the particular reaction. For some runs, carbon monoxide was used as the feed gas to promote the water-gas shift reaction. In

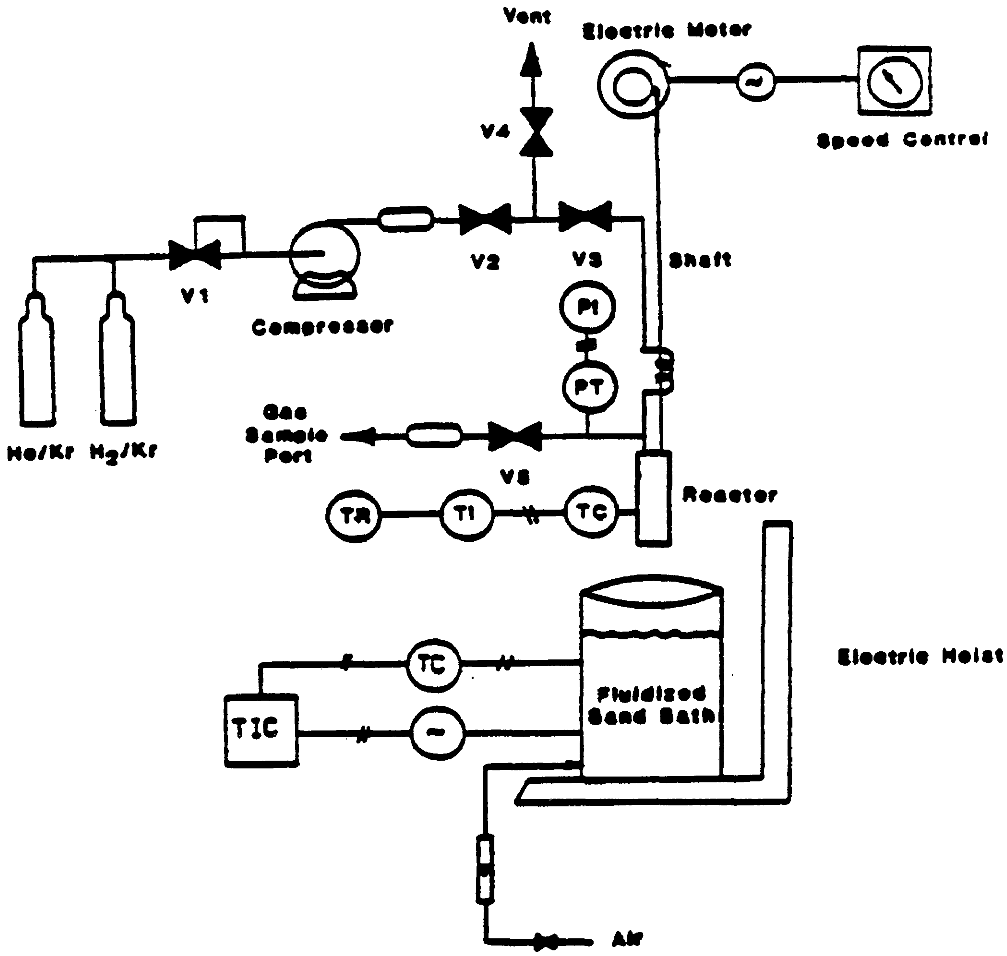
FIGURE 1: Tubing-Bomb Reactor



order to complete the reaction a 25 weight percent aqueous sodium hydroxide solution was added to the coal at a weight ratio of one to ten with the coal. In some runs, ferric oxide or cobalt-molybdenum catalysts were used. To sulfide these catalysts, a small amount of carbon disulfide was added. The ratio of coal to catalyst to carbon disulfide was a twenty to five to two weight ratio. Two small steel ball bearings were added to agitate the system internally. Before attaching the head, a disposable nickel gasket was placed between the head and the reactor to insure a better seal and reduce wear on the reactor. The threads of the reactor head were greased with Silver Goop to maintain the seal.

The reactor was then attached to the reactor apparatus (Figure 2). The system can be divided into four basic parts: the gas feed system, the gas sampling system, the heating system, and the reactor system. The reactor system has already been described. The gas feed system includes the high pressure feed gas cylinders. The gases used for this study were hydrogen and carbon monoxide. The cylinders also contained trace amounts of krypton so that gas consumption could be measured by gas chromatography, if desired. Pressure was adjusted at valve V2 before opening

FIGURE 2: Schematic of the Liquefaction Reactor System



valve V3 and pressurizing the system. The pressure could be monitored on the pressure gauge attached to the reactor system gas lines. After completion of the run, the gas could be collected in a sample bomb by opening valve V5 to the gas sampling port.

To start a run, the reactor was connected to the system gas lines and attached to the agitator, and the reactor thermocouple was connected to an external monitor. The reactor was then immersed in the heating system which consisted of a temperature-controlled fluidized sand bath, Tecam Model SBL2D. This method of heating brought the reactor to the reaction temperature in approximately three minutes. At the end of the desired reaction time, generally thirty minutes, the reactor was removed from the sand bath and quickly cooled using a compressed air line and an ice bath. After bleeding the gas lines, the reactor was disconnected from the gas lines and detached from the agitator. The reactor head was removed, and the contents of the reactor were prepared for analysis. The liquefaction reaction conditions are shown in Table III.

TABLE III: Liquefaction Reaction Conditions

Reactor: 18 cc tubing-bomb reactor

Coal Feed: 1 gram (dried)

Coal Size: -100 mesh

Solvents: 1-methylnaphthalene, dihydrophenanthrene

Solvent/Coal Ratio: 2/1 weight ratio

Temperature: 315^{o}, 350^{o}, 400^{o} C

Pressure: 900 psia (initially)

Feed Gases: Hydrogen (99% H_2, 1% Kr), Carbon Monoxide (99.5% CO, 0.5% Kr)

Shaking Speed: 120 RPM

Mixing Balls: 2

Reaction Time: 30 minutes

5. Product Analysis Procedure

After liquefaction of the coal, the coal derived liquid and solid products were analyzed to determine conversion to solvent-soluble material. The analysis used in this study was developed by Shin and can be found in detail in his thesis (28). In this method, coal conversion is defined in three ways: conversion to preasphaltenes, asphaltenes, and oils. Products which are soluble in tetrahydrofuran (THF) but are insoluble in toluene are defined as preasphaltenes. Asphaltenes are defined as the products soluble in toluene but not in hexane, and oils are the products soluble in hexane.

The quantity of THF-soluble products is determined first. At the conclusion of the liquefaction reaction the reactor was reopened and the liquefaction products were poured from the reactor into a preweighed centrifuge tube. THF was used to clean the reactor thoroughly to recover all of the liquefaction products. The treatment then given the recovered material was as follows:

1) The centrifuge tube containing the products and THF was placed in a sonicator and allowed to thoroughly mix for approximately five minutes.
2) The tube and its contents were then centrifuged for

approximately twenty minutes.

3) THF and THF soluble material were decanted off and collected, leaving behind undissolved coal and mineral matter.
4) Approximately 150 ml of THF was added to the insoluble material in the centrifuge tube.

At this point, steps 1-4 were repeated two additional times to insure that all THF-soluble products were removed. The remaining THF-insoluble material was dried for 24 hours at 100 ^{o}C and was weighed in the tube after cooling.

The decanted THF and THF-soluble products were then transferred to a rotoevaporation flask. All of the THF was evaporated in the rotoevaporation unit leaving only THF-soluble preasphaltenes, asphaltenes and oils. These materials were then extracted with toluene, placed in a centrifuge tube, and treated in the same manner as with the THF analysis. The toluene-insoluble preasphaltenes were collected in the centrifuge tube where they were dried and weighed. The decanted toluene and remaining toluene-soluble products were separated in the rotoevaporation unit. This material was then treated with hexane in the same manner. The hexane insoluble asphaltenes were collected, dried and weighed in a centrifuge tube while the hexane and hexane soluble oils were discarded.

The results of this analysis give the weights of THF insoluble material, preasphaltenes, and asphaltenes. The schematic of this analysis is shown in Figure 3. The amount of oil formed is then calculated by subtracting these weights from the total weight of the coal. Conversions can then be compared in terms of preasphaltene, asphaltene and oil formation. However, in this study reactivities compared in terms of conversion to THF-soluble material and toluene-soluble material. The conversions were calculated on a moisture and ash free basis using the following equation:

$$\text{MAF CONV} = 1 - (\text{THF}_{\text{Insol}} - \text{Coal}*\%\text{A})/\{\text{Coal}(1-\%\text{M}-\%\text{A}-\%\text{Sol})\}$$

Where:

MAF CONV is the moisture and ash free conversion

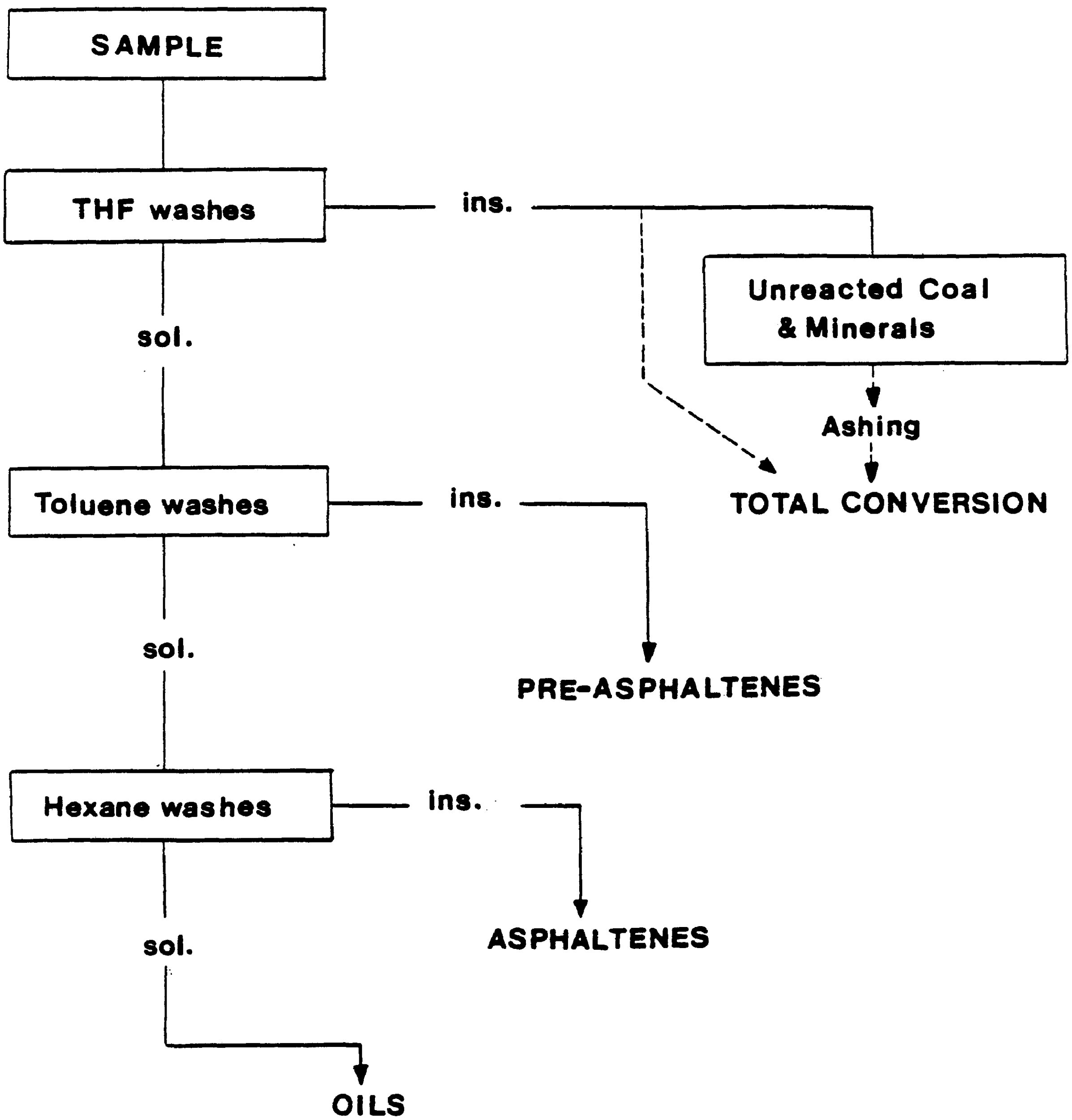
$\text{THF}_{\text{Insol}}$ is the mass of material insoluble in THF after the liquefaction reaction

Coal is the mass of coal used in the liquefaction reaction

%A is the weight percent of ash in the coal

%M is the weight percent of moisture in the coal (after drying)

FIGURE 3: Schematic of Product Separation Analysis



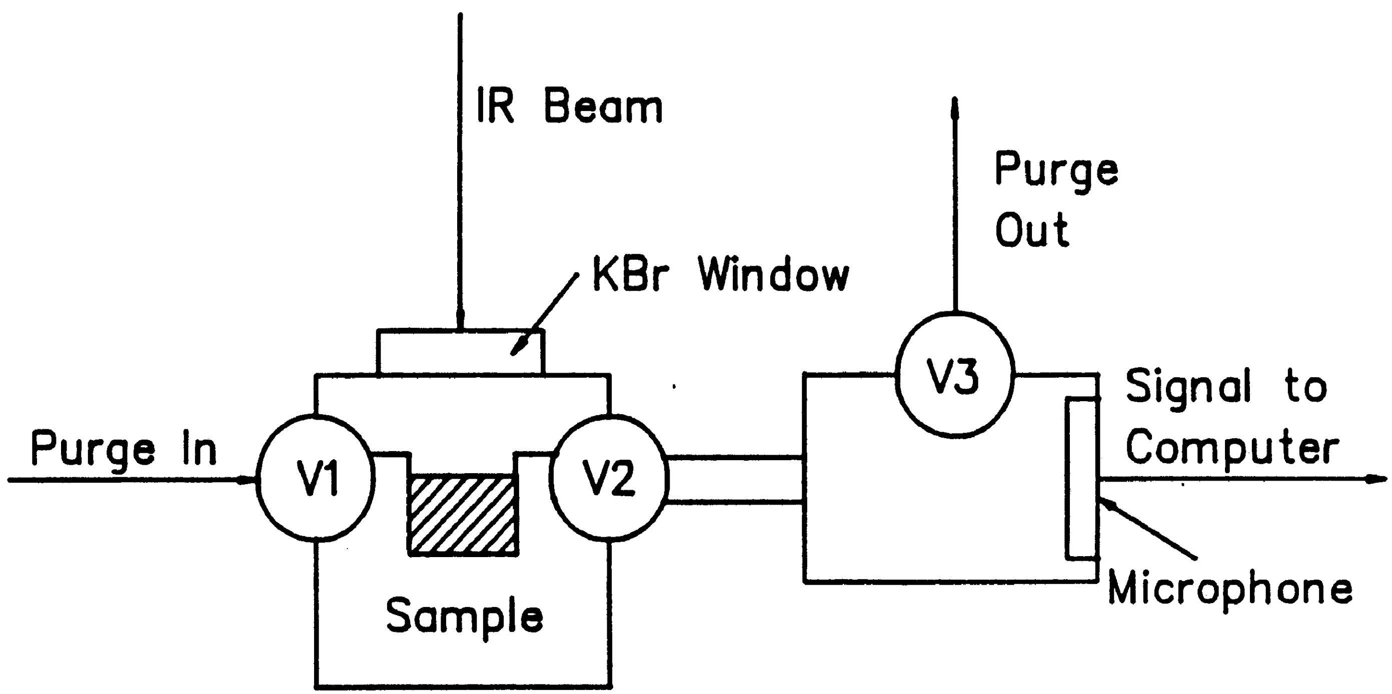
%Sol is the weight percent of THF solubles in the coal before the liquefaction reaction

The prereaction solubility was always taken as the solubility of the untreated coal in order to more clearly indicate the actual increase in conversion due to alkylation. It should be noted that conversions were not corrected for the addition of alkyl groups by alkylation. The reason for this this omission was that it is impossible to determine the extent to which the added alkyl groups were converted to THF-soluble products without elaborate laboratory techniques. If it is assumed that the alkyl groups are converted to the same extent as the rest of the coal (as indicated by Schlosberg et al. (23)), no correction is needed. It should be taken into account in cases with higher extents of alkylation that part of the increased conversion may be due to the addition of reactive alkyl groups and not an increase in coal reactivity.

6. Infrared Spectroscopy

Infrared spectroscopy was used to determine the chemical effect of the alkylation reaction on each coal sample. Because of the difficulty of measuring the spectra of solid samples with traditional transmission spectroscopy, photoacoustic spectroscopy was used with enhancement by the Fourier transformation technique. The infrared system used was a Digilab Biorad spectrometer, model FTS-40, with an interfaced 3240-SPC computer also by Digilab. The system used a Enter Computer desk top plotter, model SP600/601, for plotting spectra hardcopy. Photoacoustic spectroscopy involves the measurement of the pressure wave created when a solid sample absorbs infrared light. The pressure wave is created by the heat produced during energy absorption. A highly sensitive microphone is used to measure the pressure increase. The signal is then transformed to a standard infrared spectrum by means of Fourier transformation performed by the system computer. A schematic diagram of the sample cell and microphone system is shown in Figure 4. Since the amount of light absorbed is not directly measured, photoacoustic spectroscopy is not limited by surface morphology considerations associated with other infrared methods (29,30). However, photoacoustic spectroscopy is still believed to be primarily a measure of surface and not bulk properties. Some studies have shown that, because of the time limitations of heat transfer in a solid, photoacoustic techniques can only measure absorbances less than 40 angstroms below the solid surface (31).

FIGURE 4: Schematic of a Photoacoustic Infrared Sample Cell



To measure a spectrum, the coal sample was dried and placed in the sample cup. Sometimes a small amount of desiccate was included with the sample to absorb any water vapor produced during the run. The sample cup was then placed inside the acoustic cell. The cell was sealed with a KBr salt window and purged with helium by opening valves 1 and 3 (valve 2 is always open). After purging, the valves were closed and the beam mirror was adjusted to divert the IR beam into the cell (through the KBr window). The sample cell is contained within a larger sample compartment which was closed during operation to prevent a large amount of water vapor from interfering with the infrared beam. The sample compartment and spectrometer optical bench were purged with air until the spectrum was ready to run. The purge was then changed to dry nitrogen in order to prevent carbon dioxide and water vapor from absorbing the infrared beam and interfering with the sample spectrum.

The resolution of each spectrum was always kept at 4 cm^{-1} and the spectrum range was from 800 to 4000 cm^{-1}. The important variable in obtaining a good spectrum was the number of scans which was varied from 16 to 10,000. A computer graphic of the spectrum was produced on the computer screen after each set of scans. Because water vapor was sometimes produce during scanning, it was often necessary to run several sets of scans and purge after each set. This procedure removed any remaining water from the sample. When a good spectrum was obtained, the spectrum was plotted and saved for comparison to other spectra. It was possible to subtact spectra from different coal samples to discover any important changes in spectral information caused by alkylation. The computer graphic representation of the spectrum was also used to assign wave numbers to individual peaks. From the spectra collected in this study, it was possible to determine some of the chemical changes that had occured during alkylation pretreatment of each coal sample.

RESULTS AND DISCUSSION

1. Alkylation of Different Coals

The alkylation pretreatment method discussed earlier was performed on the Illinois #6, Pocohontas, and Wyodak coals and Beulah-Zap lignite, and the extents of alkylation were measured. The alcohol used for alkylation was propanol, the acid used was hydrochloric at a one percent volume concentration, and the alkylation reaction conditions were 3 hours at ambient temperature and pressure. The pH of the reaction solution was checked at intervals to verify that the acid was not consumed by minerals in the coal. The acid concentration was found to remain essentially constant throughout the reaction. The results from these experiments are summarized in Table IV. The results of all alkylation experiments are shown in Table A-1 in the appendix. As shown the pretreatment is much more effective on the lower rank subbituminous and lignite coals. There are two possible reasons which would cause this behavior. First, it is possible that the reaction is taking place at oxygen functionalities. Since the lower rank coals have much higher oxygen contents, their alkylation reactivity would be higher. Figure 5 shows the extent of alkylation as a function of oxygen weight percent. While there is not

TABLE IV: Extents of Alkylation for Various Argonne Coals

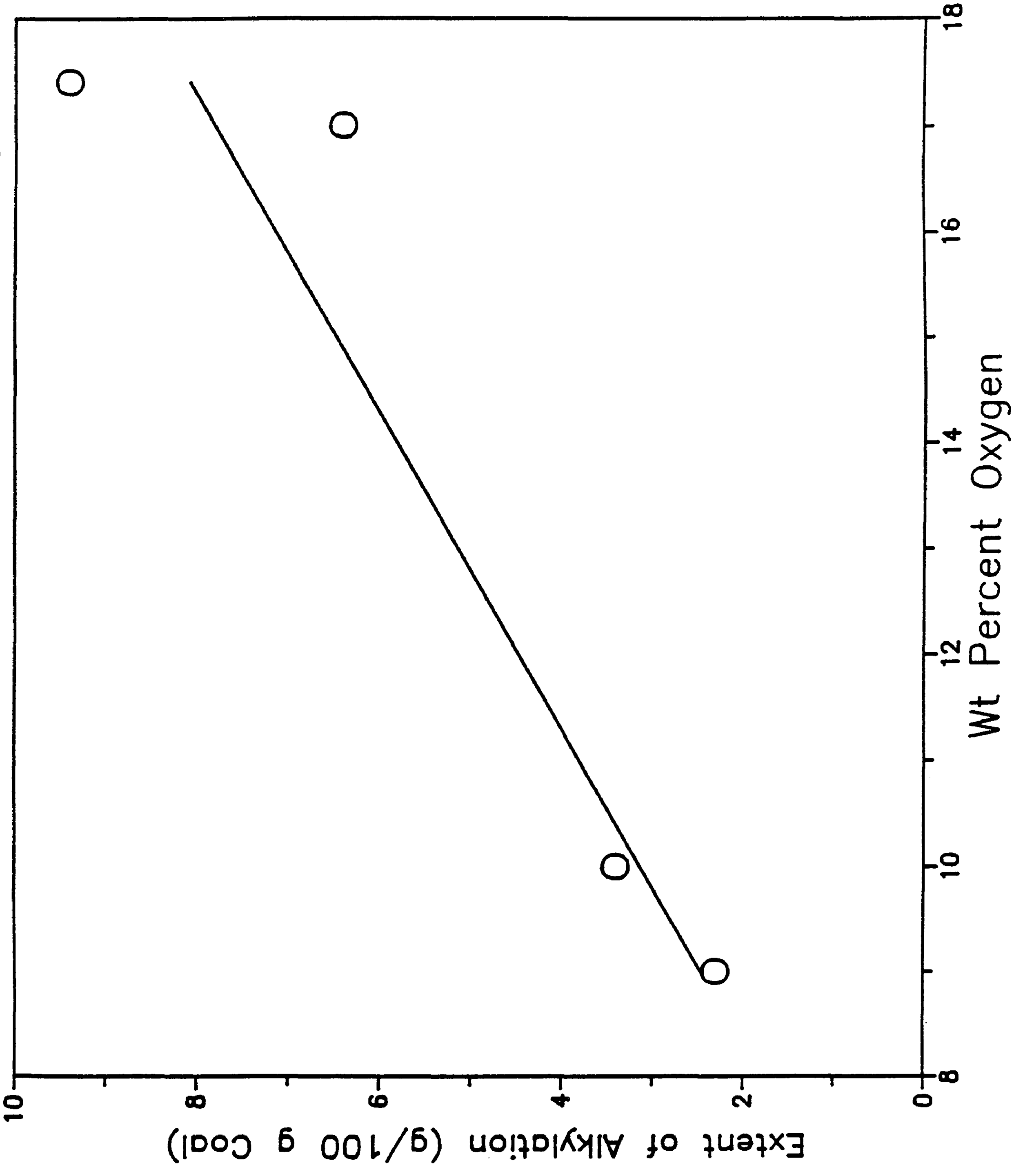
COAL	EXTENT OF ALKYLATION	
	Gms/100 gms of coal	Alkyl grps/100 carbon atoms
Illinois (Propylated)	3.4	1.23
Pocohontas (Propylated)	2.3	0.73
Lignite (Propylated)	6.4	2.66
Wyodak:		
Methylated	0.57	0.67
Ethylated	1.06	0.64
Propylated	9.4	3.78

Conditions

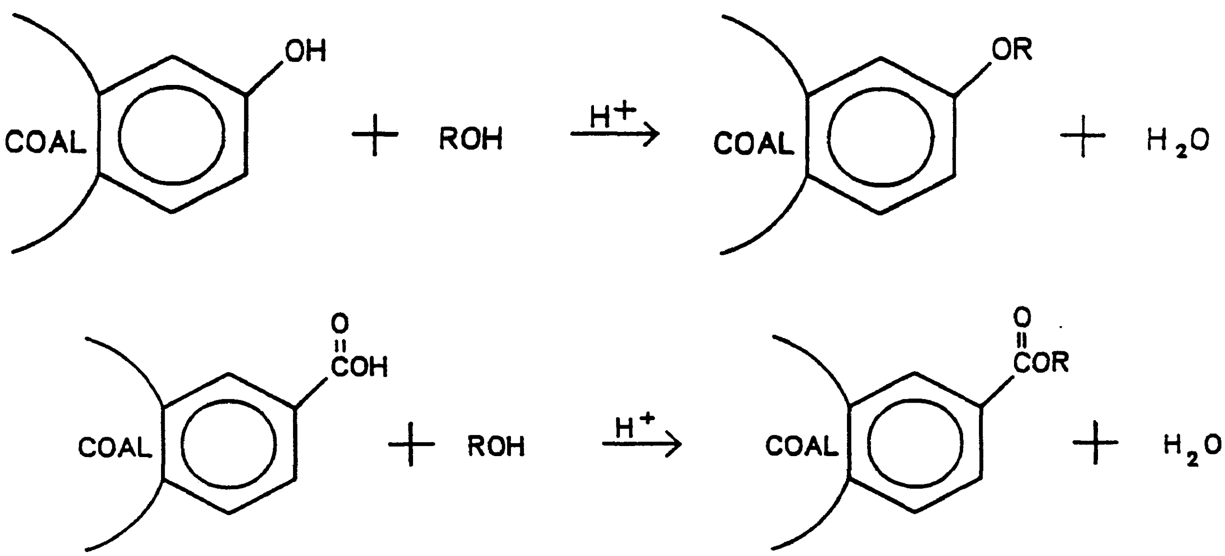
Reaction Time: 3 hours
Temperature: Ambient
Pressure: Ambient
Acid: Hydrochloric
Acid Concentration: 1 Vol %

-7

FIGURE 5: Effect of Oxygen Content on the Extent of Alkylation



enough data to say that a correlation exists, these data support the hypothesis that an oxygen alkylation is taking place. If so, the alkylation reactions that are occurring would be the dehydration of two alcohols to form an ether and the esterification of a carboxylic acid by an alcohol. These common organic reactions (32) proceed as:



It is also possible that the lower rank coals alkylate more easily because of a less dense structure. It would be easier for an alkyl group to diffuse into the interior of a lower rank coal, increasing the reactive surface area.

The alkylation conditions were varied, and the resulting extents of alkylation were measured as shown in Table V. The extents of alkylation were smaller for these runs because they were performed with a Wyodak coal which

TABLE V: Effect of Alkylation Reaction Conditions on the Extent of Wyodak Coal Propylation

Time (hrs)	Acid Conc. (Vol%)	Extent of Alkylation (gms/100 gms of coal)
3	0.1%	0.4
3	1.0%	5.3
3	2.0%	4.0
3	3.0%	6.5
6	1.0%	8.4
24	1.0%	7.8

was not from the Argonne sample bank and, therefore, was probably more oxidized and less reactive than the alkylated coals shown in Table IV. The acid concentration was varied from a volume concentration of 0.1 vol % to 3.0 vol%. As shown in Table V, the extent of alkylation generally increases directly with the acid concentration. It is important to verify that the reaction is acid catalyzed because Liotta (15) states that an O-alkylation reaction must be catalyzed by a strong base. Later, it will be shown that O-alkylation is occurring. Therefore, this particular O-alkylation method, in contrast to Liotta's, is acid catalyzed. As expected, the extent of alkylation increases with time until about six hours at which time no additional alkyl groups could be added. The fact that the reaction is relatively slow is not a major economic hindrance as the reaction rate can easily be increased with a mild increase in the reaction temperature.

Table VI shows the solubility of the coals in THF and toluene before and after alkylation pretreatment. In all cases a significant increase in extractability was observed generally in proportion to the extent of alkylation. However, the lignite showed the largest increase in both THF and toluene solubility, despite the fact that Wyodak coal

TABLE VI: Initial Solubilities of the Alkylated and Untreated Coals

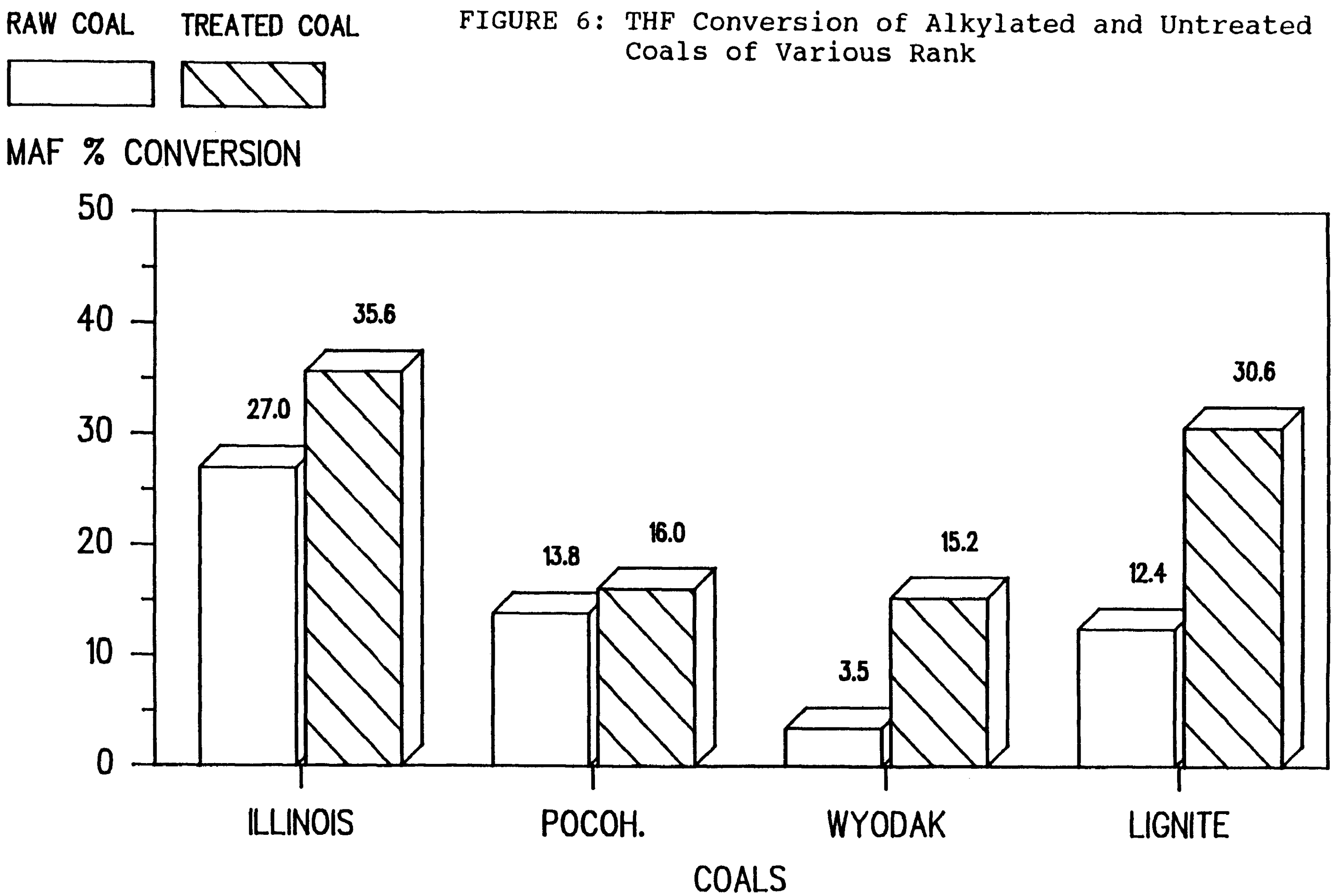
COAL	THF Solubilities (wt%)		Toluene Solubilities (wt%)	
	Treated	Untreated	Treated	Untreated
		Soxhlet Extraction		
Illinois	16.9	12.1	0.0	0.4
Pocohontas	3.5	1.6	0.5	0.1
Wyodak	9.8	2.3	2.6	0.0
Lignite	10.9	1.6	9.2	1.3
		Ambient Extraction*		
Illinois	7.0	3.1	0.0	0.0
Pocohontas	2.5	1.6	0.0	0.0
Wyodak	9.0	1.0	1.4	0.0
Lignite	8.5	0.8	7.2	0.0

* Sonication in a ultrasonic bath for 5 minutes followed by centrifugation (3 repititions)

had the largest extent of alkylation. The other solubility increases were in line with their respective extents of alkylation. Since MAF liquefaction conversions were measured in terms of unalkylated coal solubilities only, it must be noted that some of the increase in conversion was not due to an increase in reactivity but to the initial increase in solubility caused by alkylation.

The propylated Argonne coals described in Table IV were then liquefied and the THF-soluble conversions measured. Untreated samples of the Argonne coals were liquefied for comparison purposes. These experiments were run at 315 ^{o}C in 1-methylnaphthalene solvent for thirty minutes. Hydrogen gas was added at an initial pressure of 900 psia. A comparison of the THF conversion results for untreated and alkylated coals is shown in Figure 6. A compilation of all the experimental data from liquefaction runs is shown in Table A-2 in the appendix. The reason low conversions were obtained was, of course, the low temperature of the reaction and the poor quality liquefaction solvent. The Pocohontas coal showed an almost negligible increase in conversion because of either a low extent of alkylation or more likely, because it is not reactive under any conditions. Illinois #6 coal showed a much greater increase in reactivity,

FIGURE 6: THF Conversion of Alkylated and Untreated Coals of Various Rank

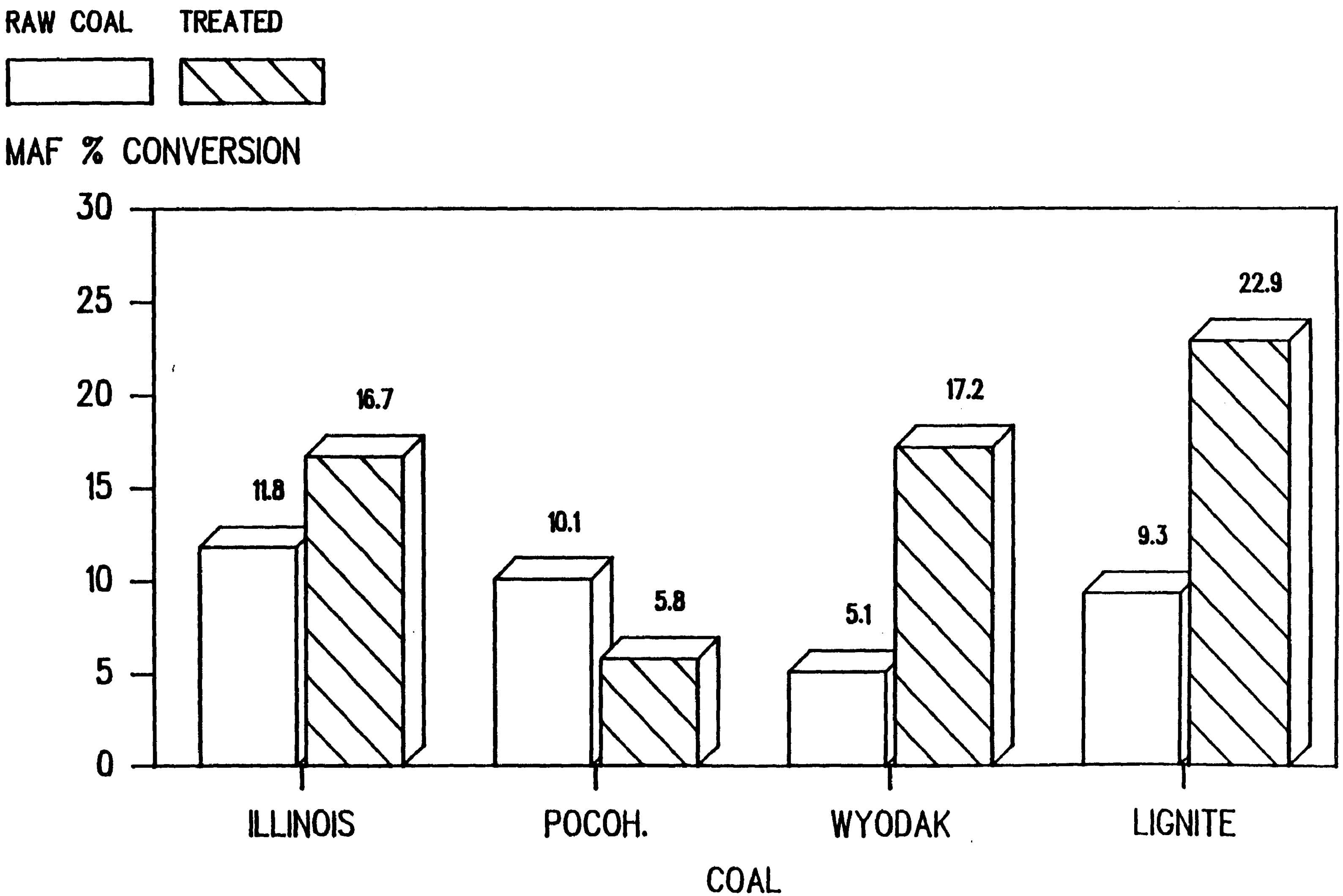


CONDITIONS: 1-MN, 315 Deg C, 30 minutes
Hydrogen Gas, 900 psia

possibly because it is a high volatile coal and had a higher initial reactivity. However, the lower rank coals both showed a tremendous increase in reactivity after alkylation pretreatment. Wyodak coal, which was the least reactive untreated coal, shows a fourfold increase in conversion after mild alkylation. It is interesting to note that the lignite showed the greatest increase in conversion while the Wyodak coal had the largest extent of alkylation. Since the lignite is inherently more reactive, it is possible that alkylation increases reativity somewhat in proportion to the initial reactivity. Such behavior might be explained by assuming that reactivity is increased by propyl-oxy radicals as described by Mahasay et al. (21). These initiators, created by O-alkylation would react at other reactive sites within the coal. Therefore, the more reactive the coal, the larger the conversion increase after alkylation would be.

Figure 7 shows toluene conversion results for the same coals. In the case of the Wyodak coal, the toluene conversion was higher than the THF conversion, but this does not mean that the conversion to toluene-soluble products is greater than the conversion to THF-soluble products. The increase in toluene conversion occurs because the MAF conversion is calculated with respect to the initial solubil-

FIGURE 7: Toluene Conversion of Alkylated and Untreated Coals of Various Rank



CONDITIONS: 1-MN, 315 Deg C, 30 minutes
Hydrogen gas, 900 psia

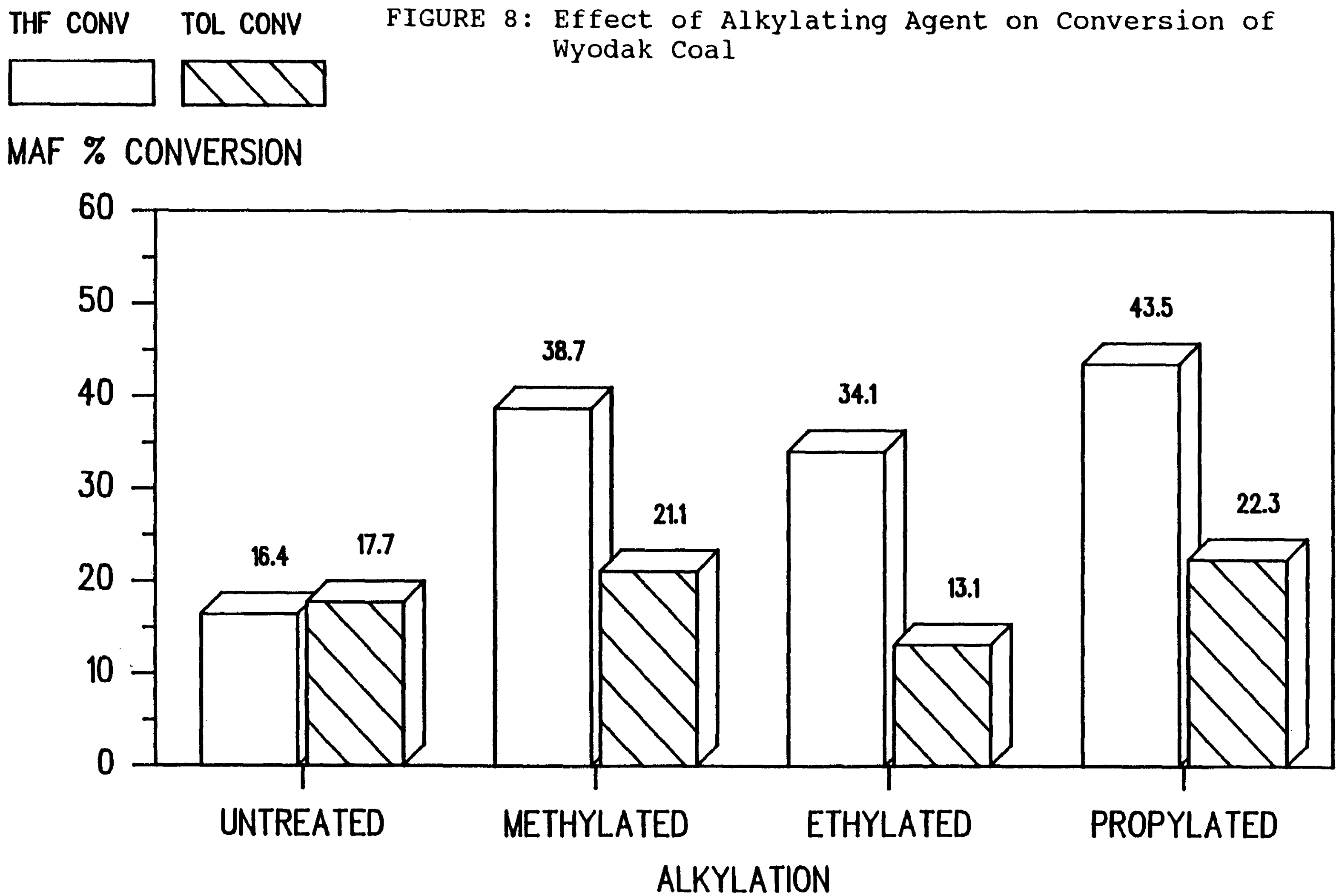
ity and the initial THF solubility was significantly higher than the toluene solubility. Except for the Pocohontas coal, the toluene conversion results indicate the same trends as the THF conversion results. The decrease in the Pocohontas toluene conversion after alkylation might be due to a slight repolymerization of coal derived products caused by the increased reactivity of the alkylated coal. This behavior may become more prevalent at higher severity conditions.

2. Alkylation by Different Alkyl Groups

Experiments were done with the Wyodak coal to determine the effect of varying the alkyl alcohol on the reactivity. The resulting extent of alkylation results were shown earlier in Table IV. The extent of alkylation was approximately the same (in terms of molar alkyl groups added) for the methylated and ethylated coals while the propylated coal was much more alkylated. There are several possible explanations for this behavior. Propanol is much more easily protonated than either methanol or ethanol, and protonation is the first step in the dehydration of alcohols to form ethers. Therefore, the increase in the extent of propylation could be attributed to the fact that the propanol reacts more readily with the coal phenols in the dehydration of alcohols reaction.

Figure 8 shows the liquefaction reactivity results for Wyodak coal alkylated with methanol, ethanol, and isopropanol. These experiments were performed in dihydrophenanthrene (DHP), a hydrogen donor solvent, to insure sufficient hydrogen capacity so that the reactivity differences caused by the presence of different alkyl groups could be seen more easily. The temperature was 315 ^{o}C, the hydrogen gas pressure was again 900 psia initially, and the reaction time was thirty minutes. Despite the fact that the propylated coal has about five times as many alkyl groups per 100 carbon atoms (Table IV), it gave only slightly higher THF and toluene soluble conversion than the methylated and ethylated coals. Suprisingly, the methylated coal has a higher conversion than the ethylated coal. If the primary pretreatment reaction occuring is O-alkylation, then it can be deduced that the increased conversion is only dependent on the reduction of hydrogen bonding or some other chemical enhancement of coal reactivity caused by alkylation and not upon disruption of the coal structure by larger alkyl groups. If the latter were the cause of the increased conversion, the pretreatment effect would be more pronounced for larger alkyl groups. As approximately the same number of groups were added for the ethylated and methylated samples, it can be inferred that the size of the alkyl group

FIGURE 8: Effect of Alkylating Agent on Conversion of Wyodak Coal



CONDITIONS: DHP, 315 Deg C, 30 minutes
Hydrogen gas, 900 psia

has little or no effect on conversion. The fact that the propylated coal shows only a slight increase in conversion also supports this conclusion.

Toluene conversion of Wyodak coal in DHP was not increased a great deal by alkylation. The combination of alkylation and a donor solvent seems to strongly favor the production of preasphaltenes at the expense of asphaltene and oil production. The reason for this behavior is not clearly understood and there are many possible explanations. The most obvious reason would be that the increase in reactivity due to alkylation involves oxygen funtionalities. When liquefied, the products would be highly polar oxygen-containing compounds which, while being soluble THF, are insoluble in toluene.

3. Variations of Liquefaction Reaction Conditions

To test the flexibility of alkylation as a pretreatment technique, some of the liquefaction reaction conditions were varied. The alkylated coal for this study was a propylated Wyodak coal. Figure 9 shows the THF conversion data for these runs while the toluene conversion data are shown in Figure 10. Reaction conditions for these experiments are shown in Table VII. The first parameter varied was the

FIGURE 9: Effect of Liquefaction Conditions on THF Conversion of Alkylated and Untreated Wyodak Coal

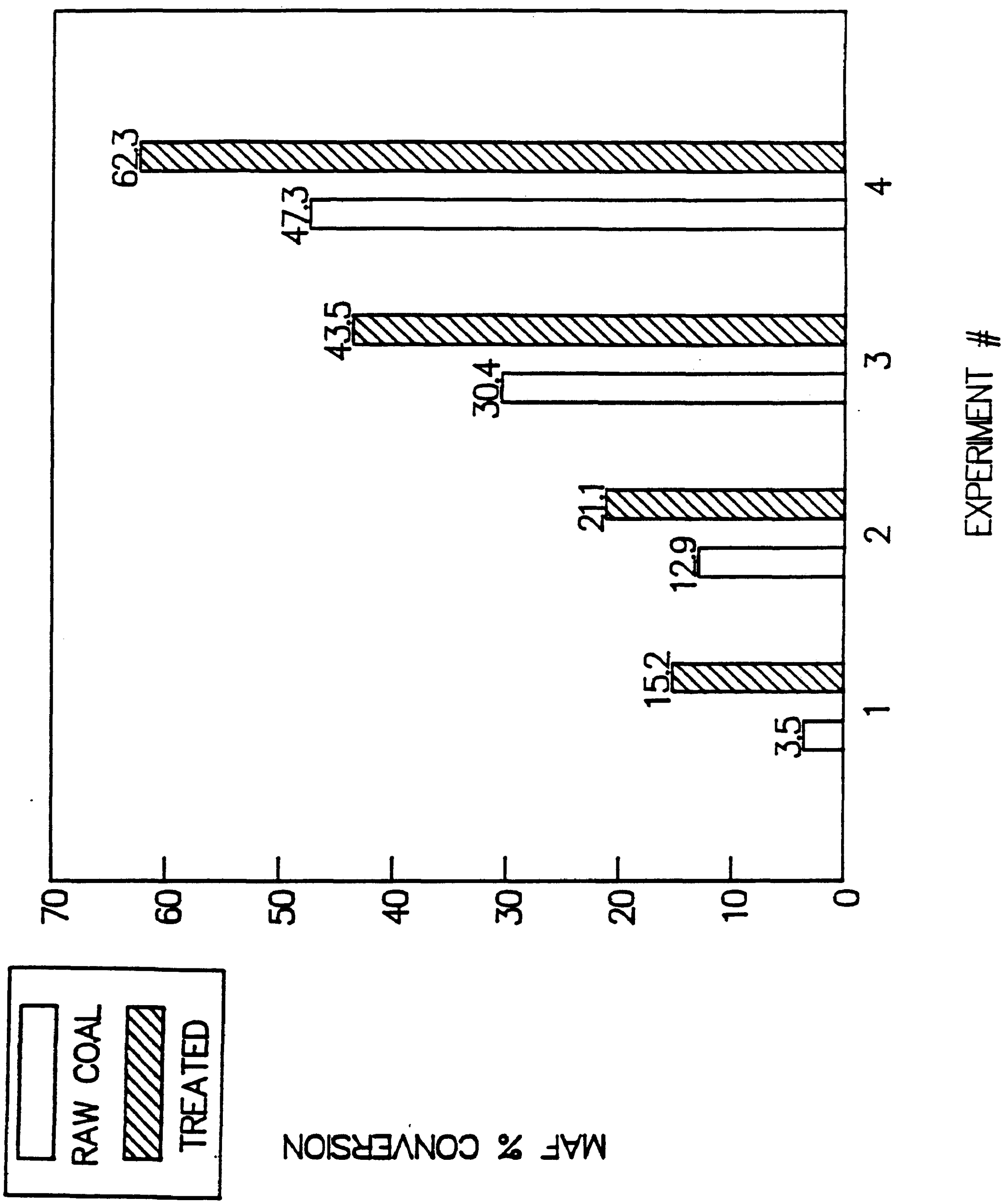


FIGURE 10: Effect of Liquefaction Conditions on the Toluene Conversion of Alkylated and Untreated Wyodak Coal

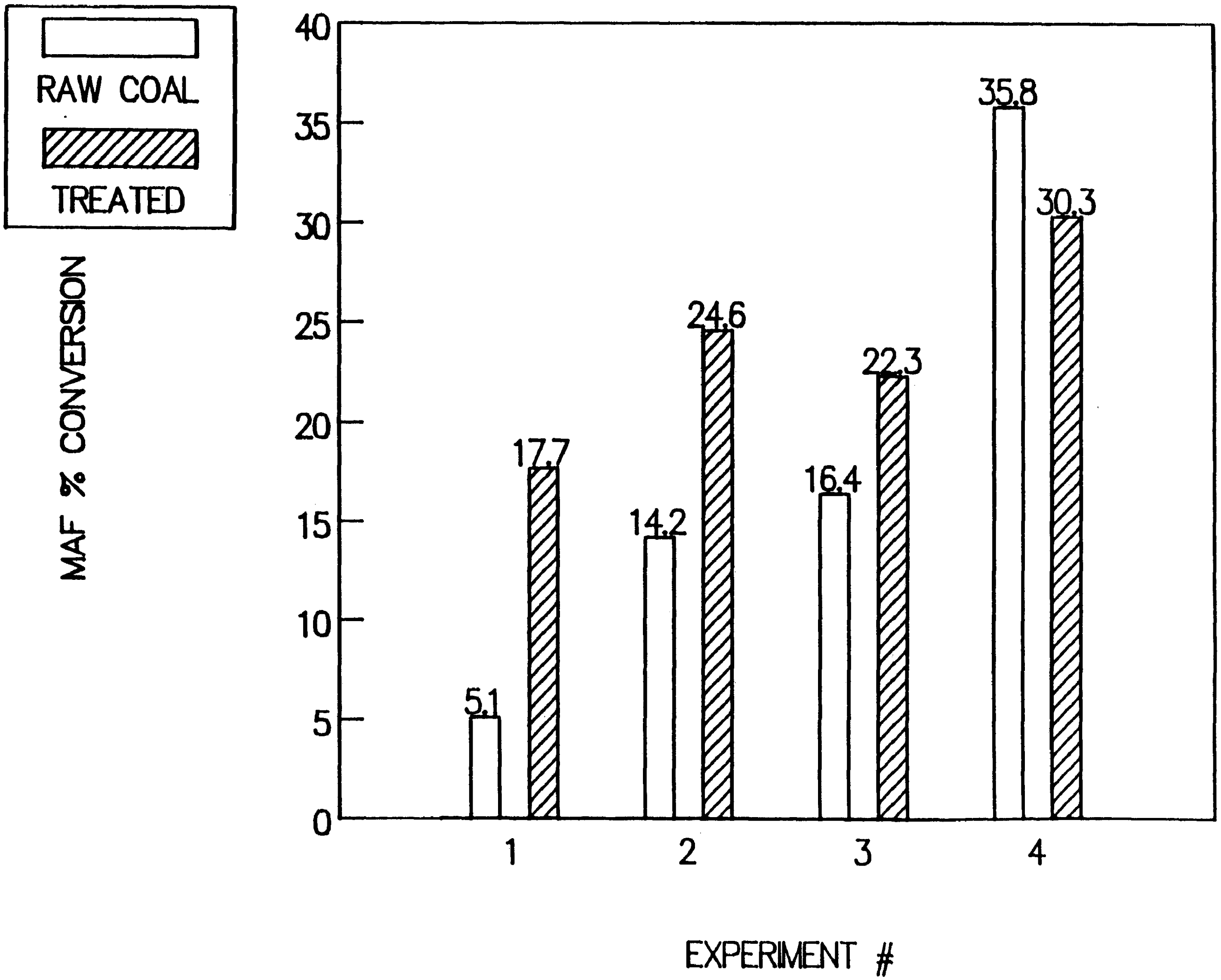


TABLE VII: Liquefaction Conditions for Figures 9 and 10

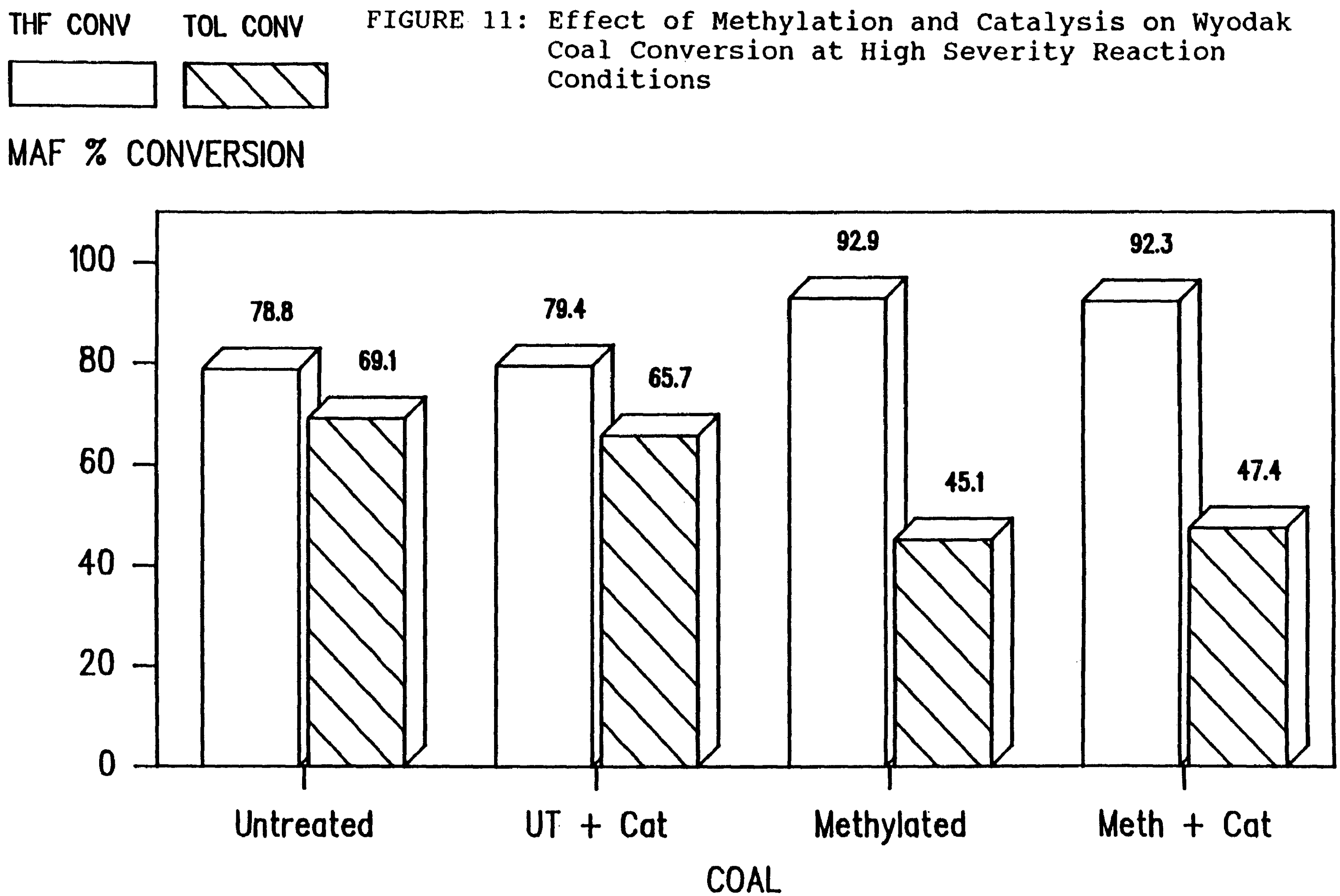
All Experiments	Coal: Wyodak Alkylation Method: Propylation Pressure: 900 psia (initially) Time: 30 minutes
Experiment #1	Solvent: 1-Methylnaphthalene Feed Gas: Hydrogen Temperature: 315° C
Experiment #2	Solvent: 1-Methylnaphthalene Feed Gas: Carbon Monoxide Temperature: 315° C
Experiment #3	Solvent: Dihydrophenanthrene Feed Gas: Hydrogen Temperature: 315° C
Experiment #4	Solvent: Dihydrophenanthrene Feed Gas: Hydrogen Temperature: 350° C

feed gas which was changed from hydrogen to carbon monoxide. It has been theorized that at lower severity reaction conditions, carbon monoxide, via the water-gas shift reaction, would be a cheaper source of hydrogen than hydrogen gas. To promote the water-gas shift reaction, an aqueous sodium hydroxide solution (25 weight percent) was added to the coal as described in the experimental section. The conversion of the alkylated coal using CO/H_2O (experiment #2) did show an increase compared with alkylated coal conversion using hydrogen gas (experiment #1). However, the conversion increase due to alkylation was lower in the carbon monoxide experiment. The water-gas shift reaction is reported to have the advantage of producing more available hydrogen for radical capping reactions. This increase may outweigh the effect of alkyl-oxy radicals produced from alkylation.

Dihydrophenanthrene was studied as a liquefaction solvent because of its strong hydrogen donor characteristics. Since most liquefaction processes involve the recycle of coal liquids which contain strong hydrogen donors, it was logical to use a solvent that somewhat imitates the behavior of these liquids. The initial experiments at 315 ^{o}C (experiment #3) showed a significant increase in THF conversion compared with the base case (experiment #1). They also showed a slightly larger increase in THF conversion after alkylation than the experiments in 1-methylnaphthalene. To see if alkylation would be as effective at higher temperatures, the reaction temperature was raised to 350 ^{o}C (experiment #4). This temperature is still considered to be low severity for liquefaction reactions. The higher temperature drastically increased THF conversion but lessened the increase in conversion due to alkylation. At higher severity conditions, the increased reactivity due to alkylation may partially serve to cause repolymerization of the products as indicated by the lower toluene conversion values.

A set of higher severity liquefaction experiments were performed at 400 ^{o}C in DHP. The reaction time and initial hydrogen pressure remained constant at 30 minutes and 900 psia, respectively. The effect of methylation of Wyodak coal was compared to the catalytic effect of ferric oxide which is commonly used to improve liquefaction conversion. The catalyst was sulfided by the addition of carbon disulfide as described in the experimental procedure section. Because of either the high temperature used or the strong donor solvent present, the addition of catalyst had a negligible effect on coal reactivity as shown in Figure 11.

FIGURE 11: Effect of Methylation and Catalysis on Wyodak Coal Conversion at High Severity Reaction Conditions



CONDITIONS: DHP, 400 Deg C, 30 minutes
Hydrogen Gas, 900 psia

Methylation, however, increased the THF conversion by approximately thirteen percent despite the high initial conversion. As shown earlier, the increased reactivity of the alkylated coal results in lower toluene conversion, possibly by the formation of highly polar coal-derived products.

4. Infrared Spectroscopy Studies

There was some ambiguity as to the chemical reactions that were taking place during acid-catalyzed alcohol alkylation. The literature, in particular Flores and coworkers (24), asserts that the alkylation of coal by alcohol and acid is a typical Friedel-Kraft reaction, suggesting that the alkyl groups are added to carbon functionalities in the coal. However, results of experiments in this study support the assertion that the alkyl groups attach to the oxygen functionalities in the coal, suggesting an O-alkylation mechanism as reported by Liotta (17-21). To better understand the chemistry involved in this work, photoacoustic infrared spectra were taken of the alkylated and untreated coal samples.

Figure 12 shows the spectrum resulting from the subtraction of an untreated Wyodak coal sample spectrum from the

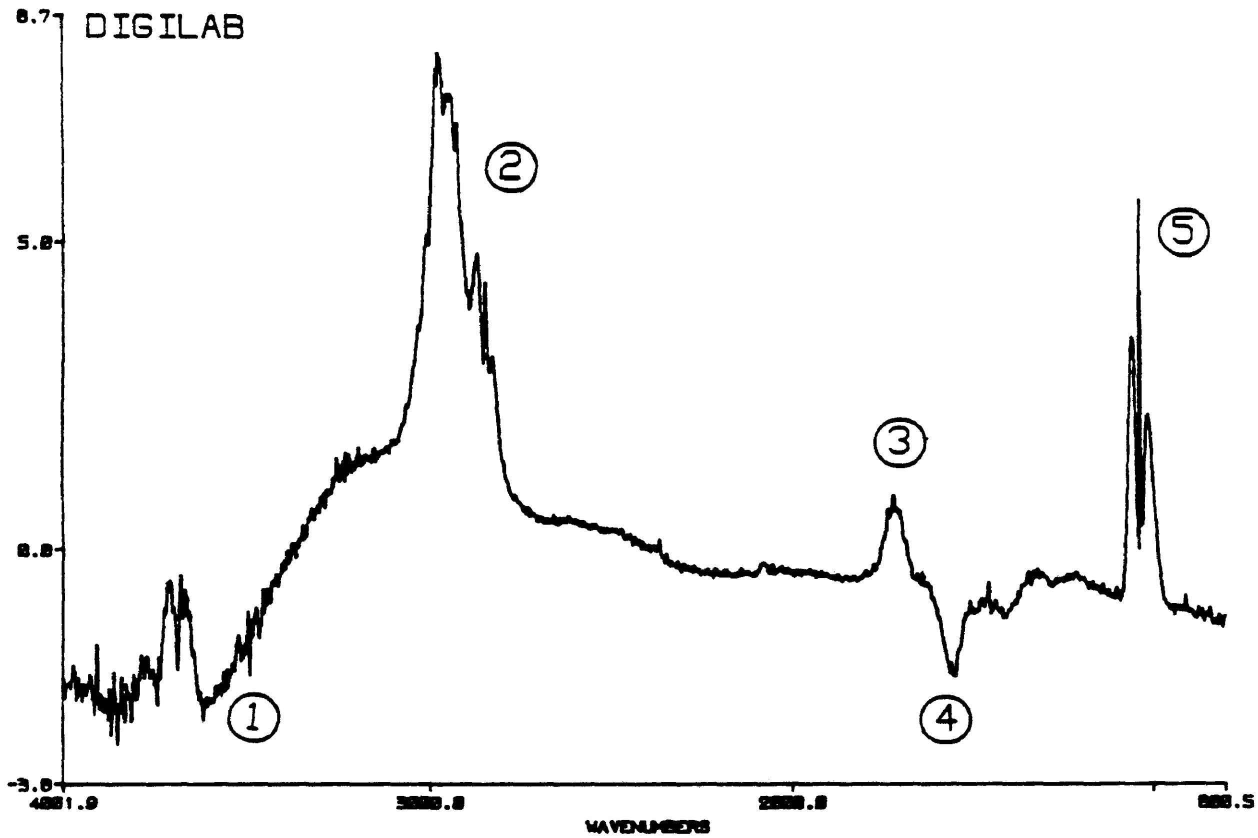


FIGURE 12: Subtractive Spectrum of an Unoxidized Propylated Wyodak Coal

1. O-H stretch (3200-3600 cm^{-1})
2. C-H aliphatic stretch (2800-3000 cm^{-1})
3. C=O ester stretch (1700 cm^{-1})
4. C=O carboxylate ion stretch (1550 cm^{-1})
5. C-O aliphatic and aromatic stretch (1000 cm^{-1})

propylated Wyodak sample spectrum. Because of the tendency of coal to oxidize when exposed to air for long periods, the sample spectra were run within twenty four hours of the initial exposure. Of particular interest are the sharp peaks in the 1000 wavenumber region which represent carbon-oxygen single-bond stretches. Since these peaks are positive, their presence indicates an increase in ether groups, especially alkyl ether linkages in the alkylated coal. The wide negative peak at about 3500 cm^{-1} indicates a decrease in oxygen-hydrogen stretches which means a reduction in phenol groups caused by alkylation. An important reaction in O-alkylation as reported by Liotta is the conversion of phenols to ethers. Another important reaction is the conversion of carboxylic acids to esters. The proof of this reaction is shown by the two peaks between 1500 and 2000 wavenumbers. These peaks are both carbon-oxygen double bond stretches. The negative peak at 1550 cm^{-1} represents the down shift in the stretch of either a carboxylic acid or a carboxylate functionality. The upshifted positive peak at 1700 cm^{-1} represents the ester functionality carbon-oxygen double bond stretch. As the two peaks are approximately the same size, they would seem to indicate that there is a conversion of carboxylic acids to esters caused by alkyation.

The peak at about 3000 cm^{-1} represents the aliphatic carbon-hydrogen stretch caused by the addition of alkyl groups to the coal. One would hope to see a single peak instead of the wide band of peaks which occurs. However, the only acceptable explanation is that the additional alkyl groups are shifted in different ways resulting in a spread of peaks instead of one sharp peak. Some might assert that the spread in the peaks is caused by the fact that carbon alkylation is taking place in addition to the O-alkylation that is observed, but if carbon alkylation was taking place, one would expect to see a distinctive positive peak in the range of 1200-1500 cm^{-1} indicating an increase in aromatic carbon-aliphatic carbon stretches. Since the only other changes seen in the spectrum are attributed to oxygen functionalities, it must be concluded that O-alkylation is the primary reaction that is occurring.

Figure 13 shows the subtractive spectrum of an untreated Illinois coal sample spectrum from the propylated Illinois sample spectrum. The positive peaks above 3000 cm^{-1} are probably caused by incomplete drying of the alkylated sample. There is a small peak at 2350 cm^{-1} which indicates a small amount of carbon dioxide in the cell during the scan of the alkylated sample. Again, increases in the ether

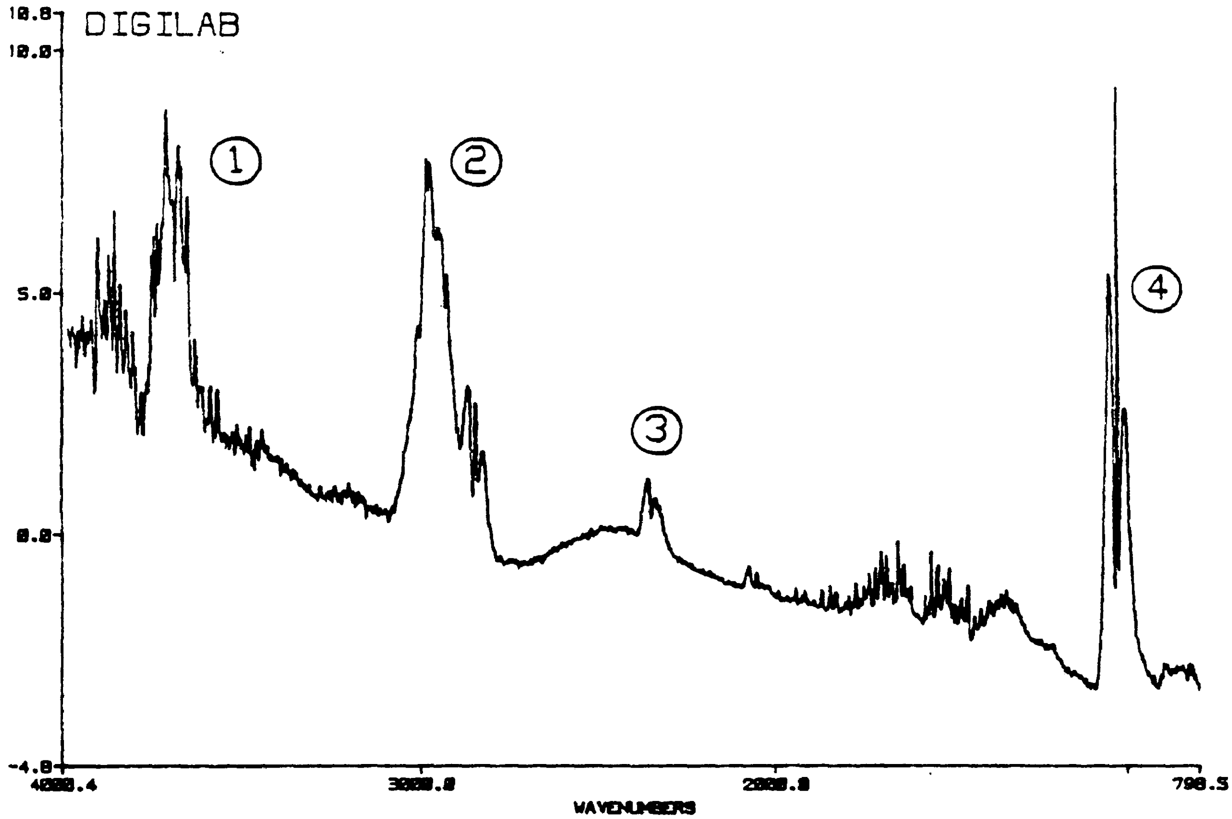


FIGURE 13: Subtractive Spectrum of an Unoxidized Propylated Illinois Coal

1. O-H stretch indicating water (3600 cm^{-1})
2. C-H aliphatic stretch (2800-3000 cm^{-1})
3. Carbon Dioxide Stretch (2400 cm^{-1})
4. C-O aromatic and aliphatic stretch (1000 cm^{-1})

linkages at 1000 cm^{-1} and alkyl carbon-hydrogen stretches at 3000 cm^{-1} are noted. There is no indication of the conversion of acids to esters, but since there is less oxygen in Illinois coal, there are probably not enough carboxylic acid functionalities to react to an extent that would be indicated on the spectrum. Once again, there are no indications of carbon alkylation reactions occurring.

Figure 14 shows the subtractive spectrum for the propylated lignite coal. These samples were not as fresh as the Wyodak and Illinois samples, however, which may explain the increase in noise and why the peaks are not as sharp. The negative peak at 1550 cm^{-1} probably indicates that the untreated coal was more oxidized (possibly because of more phenol groups) as shown by Lynch et al. (33). Because of the presence of this peak, it is impossible to see any conversion of carboxylic acids to esters. There are, however, strong indications of a reduction in phenols due to the large negative band at about 3300 to 3600 cm^{-1}. The fact that the increase in ethers is not as obvious as in the previous spectra can also be attributed to oxidation. The alkyl carbon-hydrogen peak is present at 3000 cm^{-1} as expected. Oxidation makes it impossible to say much about changes in carbon-carbon stretches, but it is expected that

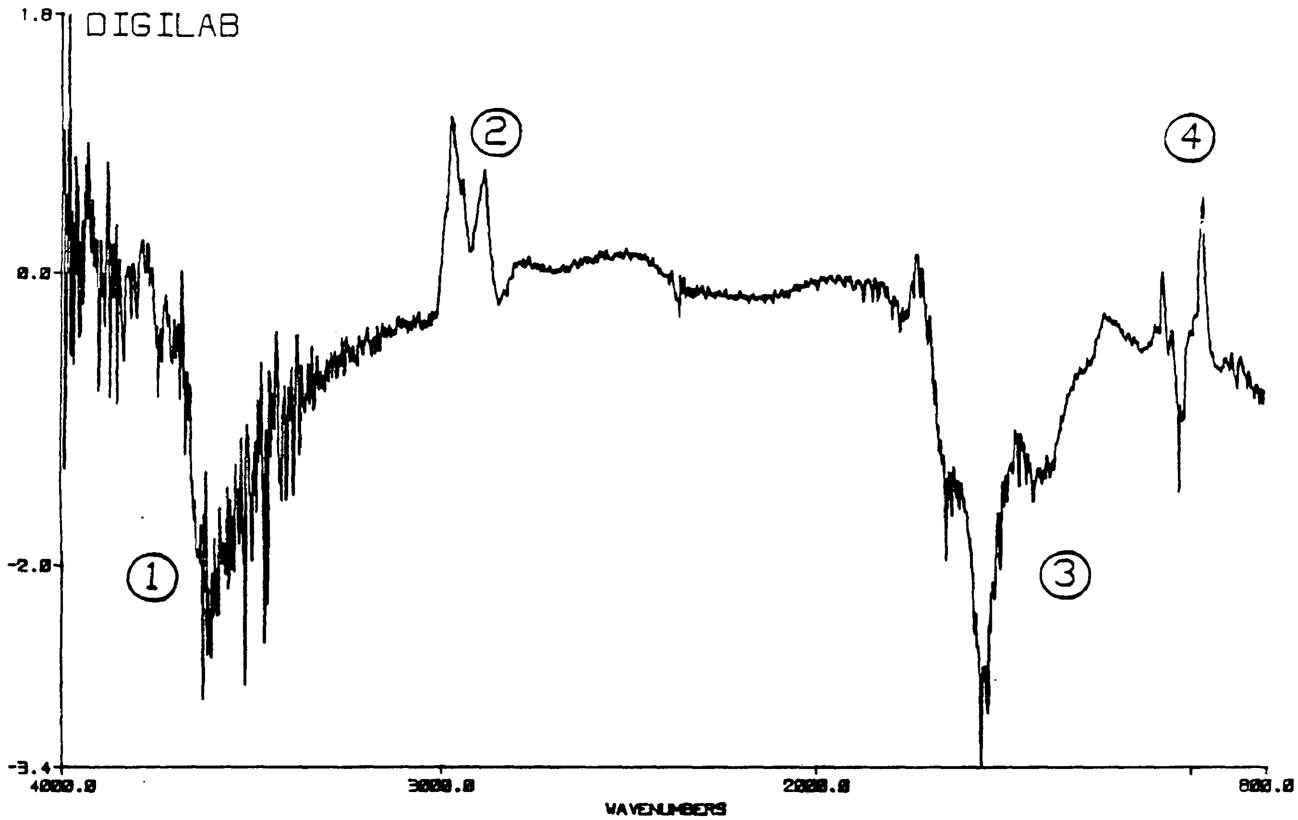


FIGURE 14: Subtractive Spectrum of an Oxidized Propylated Lignite

1. O-H phenol stretch (3200-3600 cm^{-1})
2. C-H aliphatic stretch (2800-3000 cm^{-1})
3. C=O stretch from oxidation (1300-1700 cm^{-1})
4. C-O aromatic and aliphatic stretch (1000 cm^{-1})

lignite would undergo changes similar to the Wyodak coal.

Another fact supporting O-alkylation is the similarity of the spectra shown in Figures 15 and 16. Figure 15 is the subtractive spectrum of a methylated Illinois while Figure 16 is the subtractive spectrum of a propylated Illinois coal. Since these coals are not as fresh as the coal sample used to generate Figure 13, there are large differences which indicate the importance of using fresh samples. The important fact is that the methylated and propylated spectra are almost exactly the same. If carbon alkylation, as reported by Schlosberg et al. (22), was occurring, it could not possibly occur during methylation as methanol cannot undergo the dehydrogenation reaction to form an alkene. If carbon alkylation was occurring at all, it would occur during the propylation reaction. Since the spectra in the Figures 15 and 16 are very nearly the same, it can be concluded that carbon alkylation is not occurring to any great extent. The combined evidence from the infrared spectra serves to support the conclusion that the reaction which is occuring is O-alkylation of phenols and carboxylic acid groups within the coal. This treatment has the effect of reducing hydrogen bonding within the coal, and generally increasing coal reactivity during liquefaction.

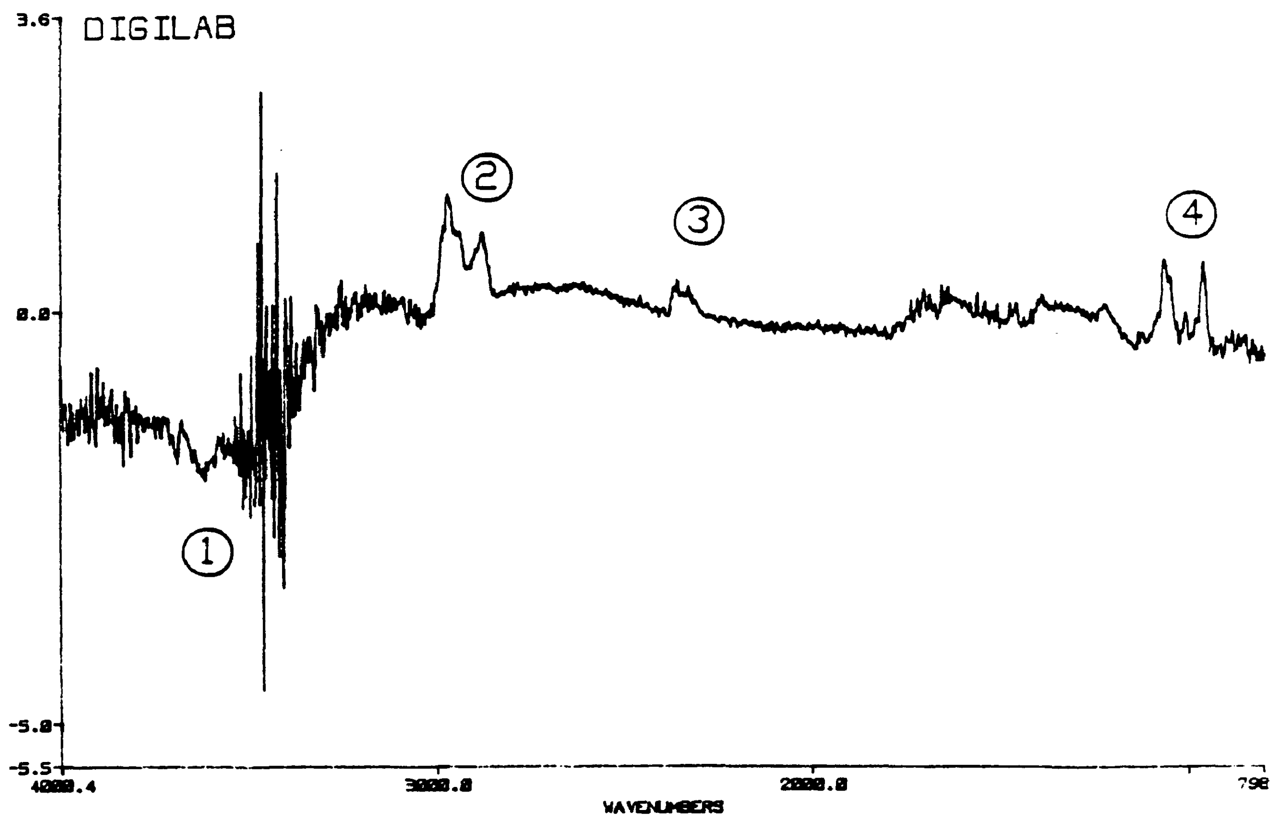


FIGURE 15: Subtractive Spectrum of an Oxidized Propylated Illinois Coal

1. O-H phenol stretch (3200-3600 cm^{-1})
2. C-H aliphatic stretch (2800-3000 cm^{-1})
3. Carbon Dioxide Stretch (2400 cm^{-1})
4. C-O aromatic and aliphatic stretch (1000 cm^{-1})

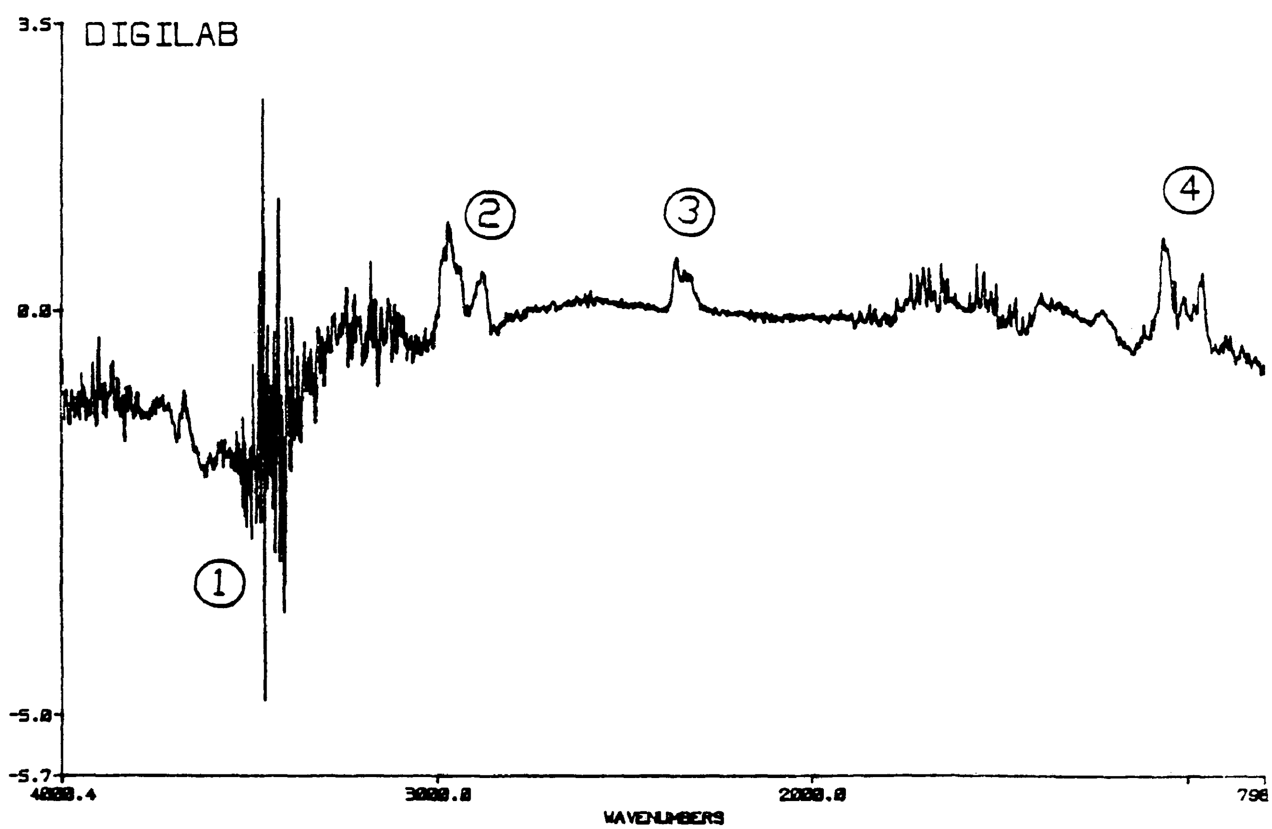


FIGURE 16: Subtractive Spectrum of an Oxidized Methylated Illinois Coal

1. O-H phenol stretch (3200-3600 cm^{-1})

2. C-H aliphatic stretch (2800-3000 cm^{-1})

3. Carbon Dioxide Stretch (2400 cm^{-1})

4. C-O aromatic and aliphatic stretch (1000 cm^{-1})

CONCLUSIONS AND RECOMMENDATIONS

Based on the work performed , the following conclusions can be made:

1. Acid-catalyzed alcohol alkylation of coal results in the formation of ethers from phenols and esters from carboxylic acids which are defined in the literature as O-alkylation reactions.

2. The alkylation pretreatment occurs to the greatest extent in lower rank coals with high oxygen contents.

3. Coal liquefaction reactivity as measured by conversion to THF and toluene soluble products is significantly increased by the mild alkylation of the oxygen functionalities.

4. Alkylation as a reactivity enhancement pretreatment for coal is more effective for lower rank coals and coals which have a higher intrinsic reactivity prior to alkylation.

5. The increase of reactivity due to alkylation is most noticeable and least degradative at low severity conditions (315 to 350 °C reaction temperature). At higher severity the pretreatment increases reactivity to a lesser extent and causes a decrease in asphaltene and oil production.

6. At high severity conditions (400 °C reaction temperature) coal reactivity is increased more by the alkylation of the coal than by the addition of iron oxide catalyst to the coal slurry.

7. Coal reactivity enhancement caused by alkylation is independent of the molecular weight of the alkyl group being added. It is also insensitive to the number of alkyl groups added.

The experiments performed in this study also suggest the following recommendations for future work in this field:

1. Work should be done upon the effect that alkylation has on insoluble organic material that remains unconverted after a coal liquefaction reaction.

2. A thorough study of the effect of alkylation conditions and the resulting extents of alkylation on coal reactivity should be performed to indicate to what extent the reactivity is controlled by the alkylation reaction. Such a study should also indicate the optimum alkylation conditions for future liquefaction reactions.

3. A kinetic analysis of the liquefaction of a range of alkylated coals might indicate to what extent the oxygen content of the coal affects the increase in reactivity caused by alkylation.

4. Alkylated coal should be liquefied in a two-stage reaction system to indicate how easily the products of the first reaction can be upgraded to distillable material.

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APPENDIX

Infrared Spectra and Experimental Data

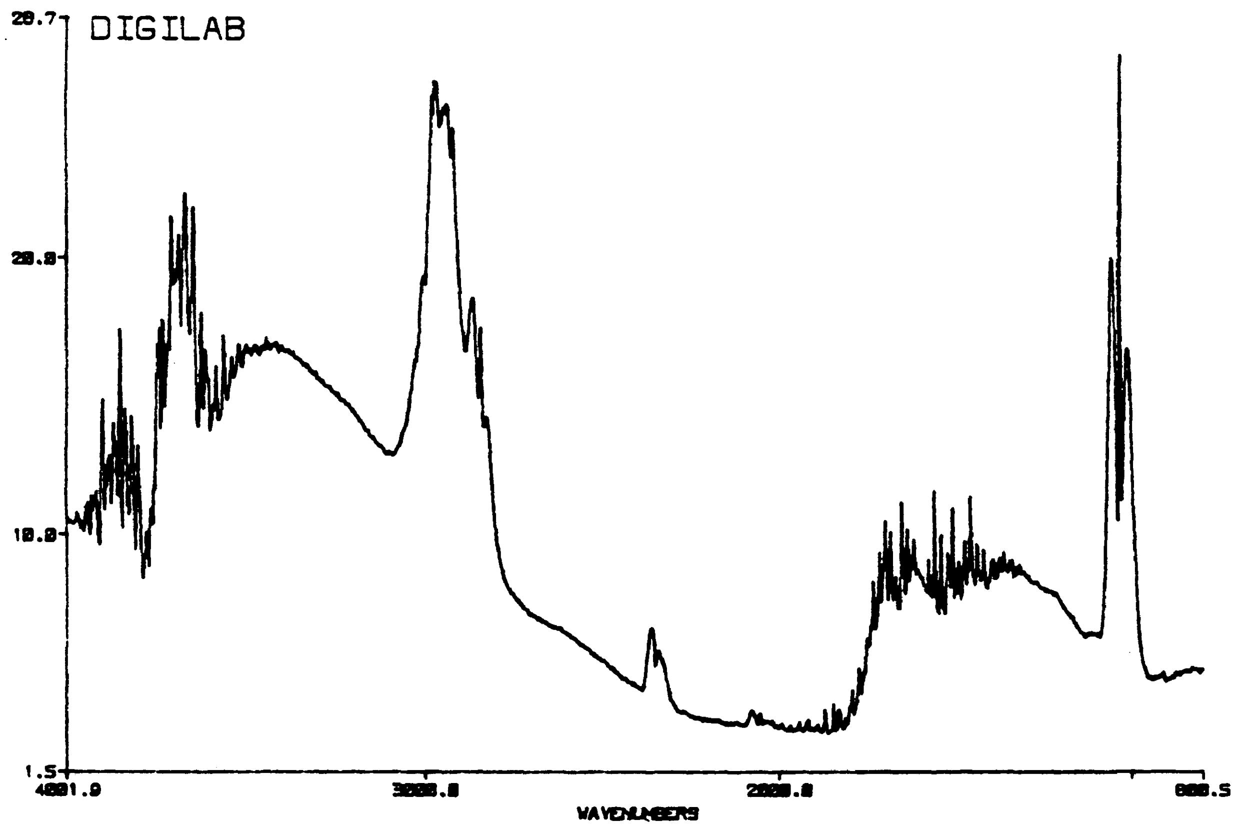

FIGURE A-1: Infrared Spectrum of Unoxidized Propylated Wyodak Coal

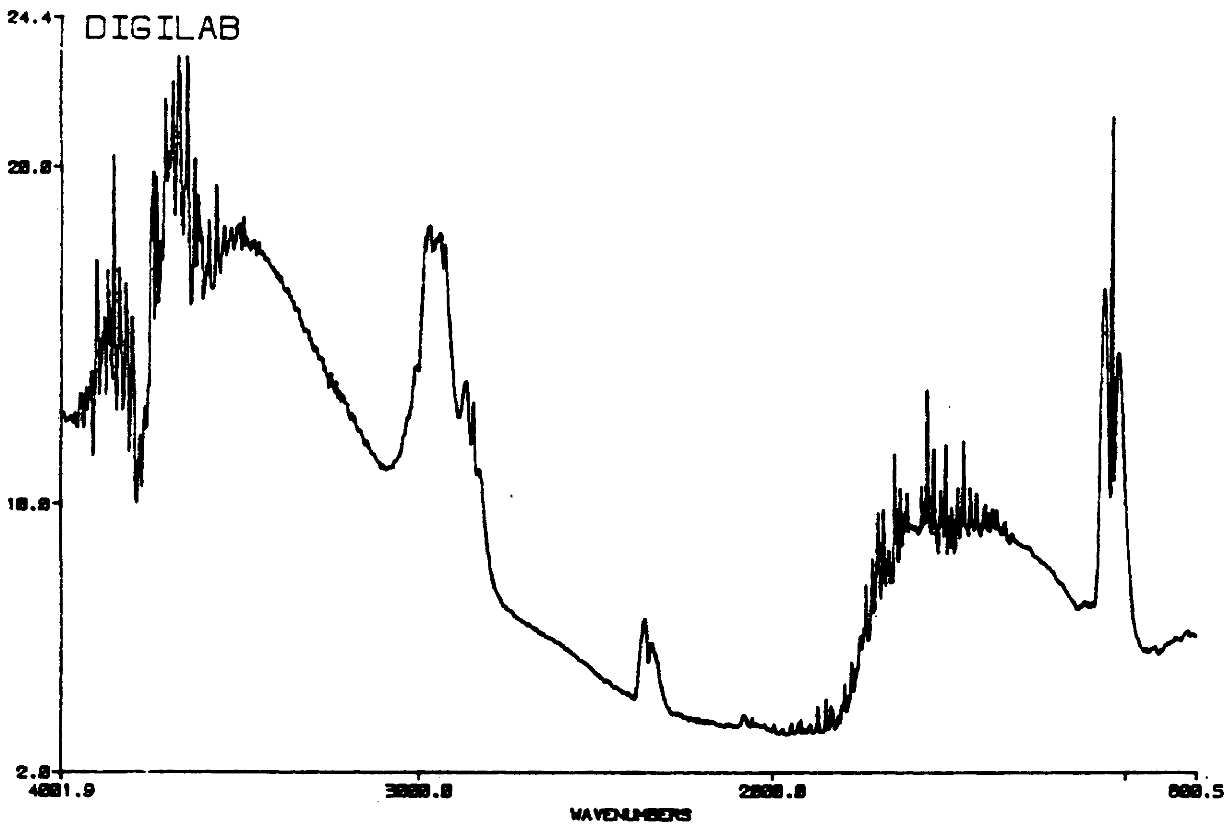

FIGURE A-2: Infrared Spectrum of Unoxidized Untreated Wyodak Coal

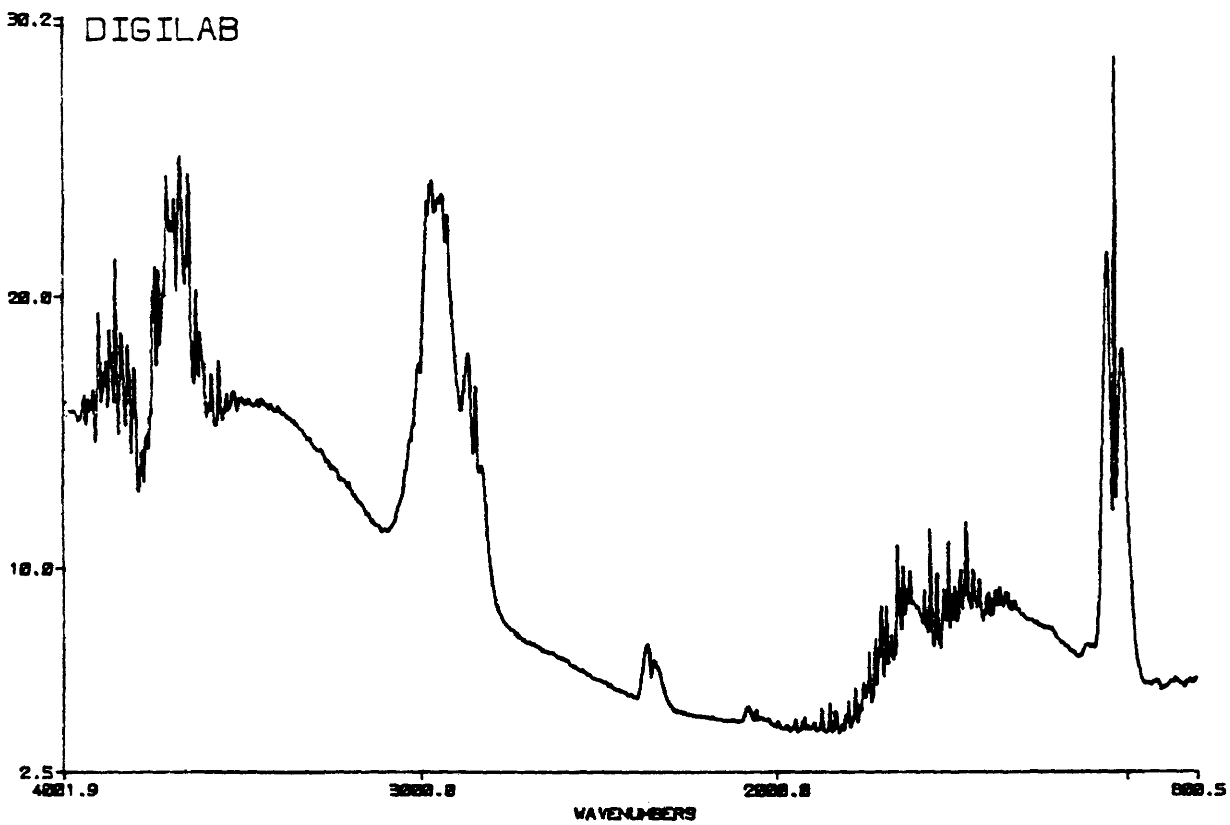

FIGURE A-3: Infrared Spectrum of Unoxidized Propylated Illinois Coal

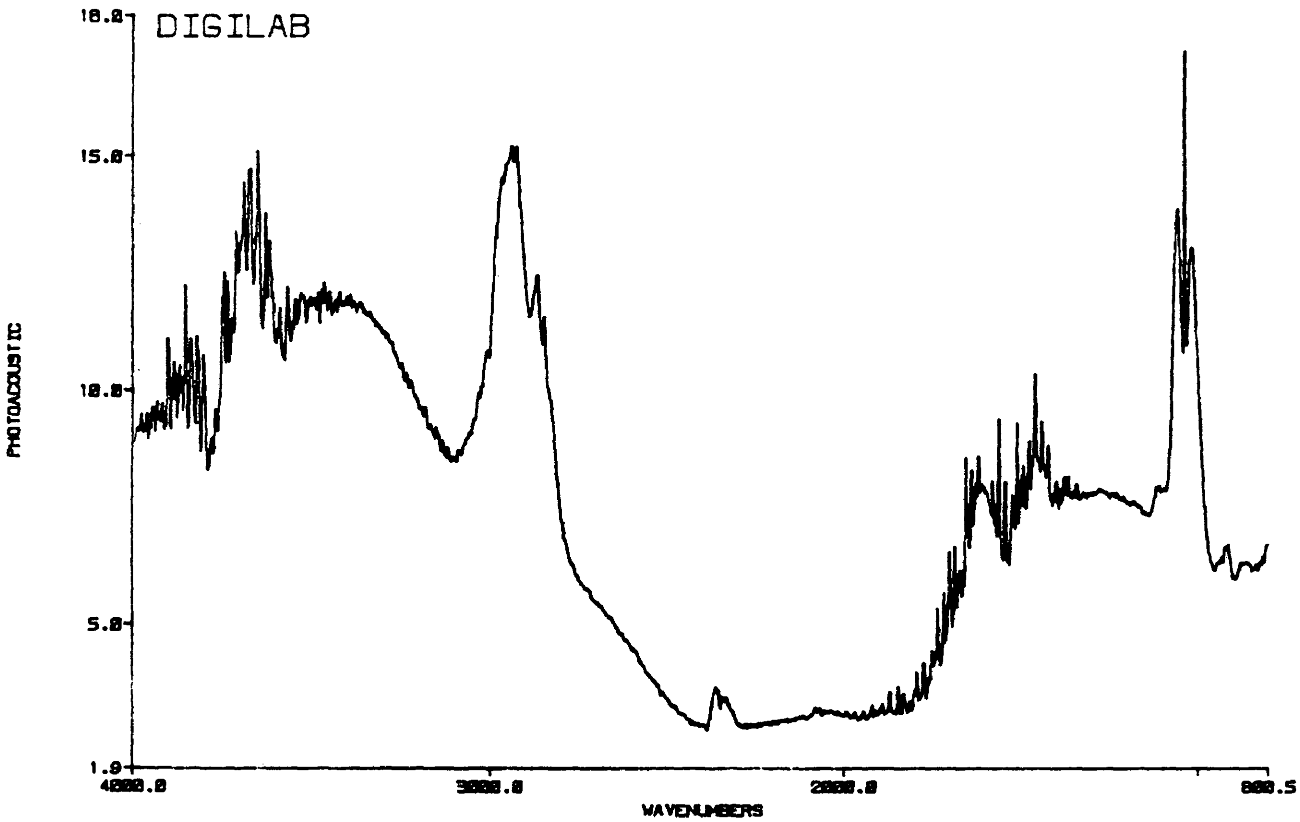

FIGURE A-4: Infrared Spectrum of Unoxidized Untreated Illinois Coal

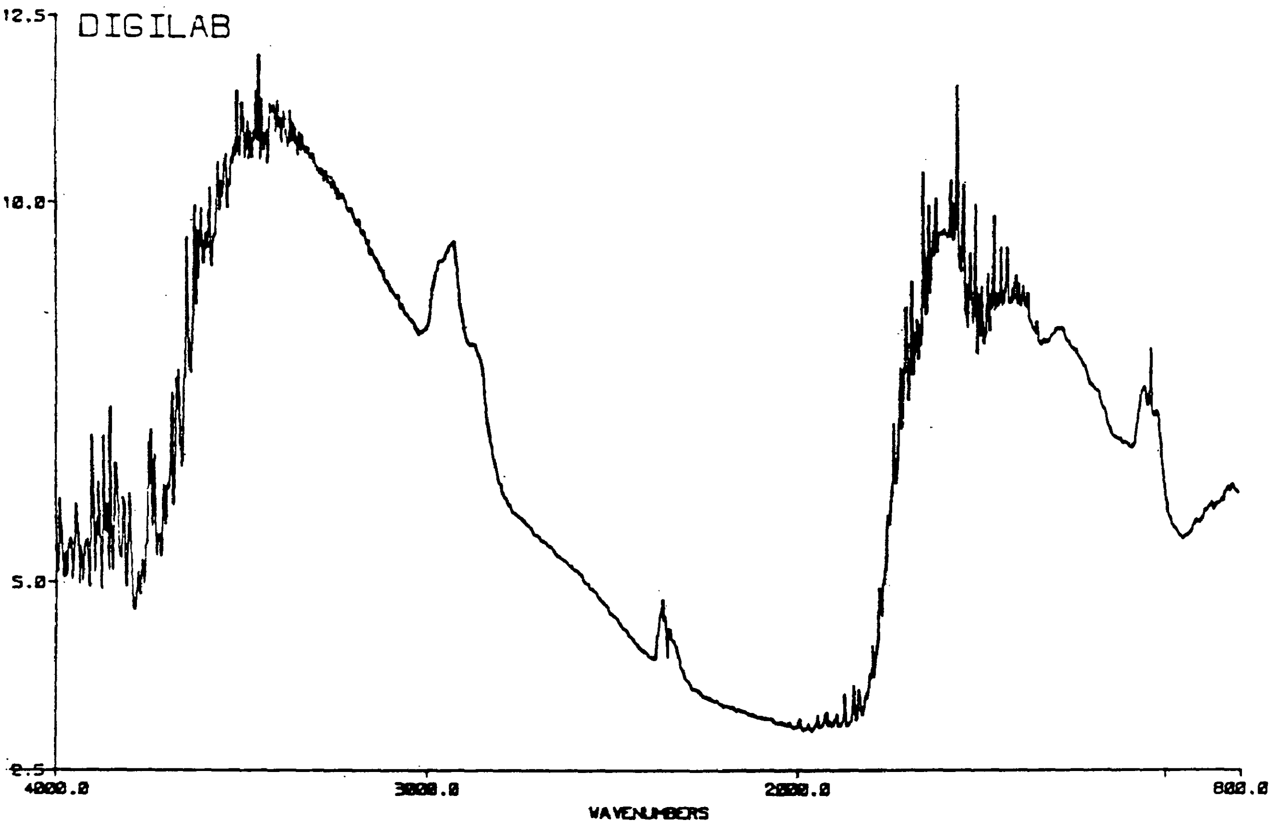

FIGURE A-5: Infrared Spectrum of Oxidixed Propylated Lignite

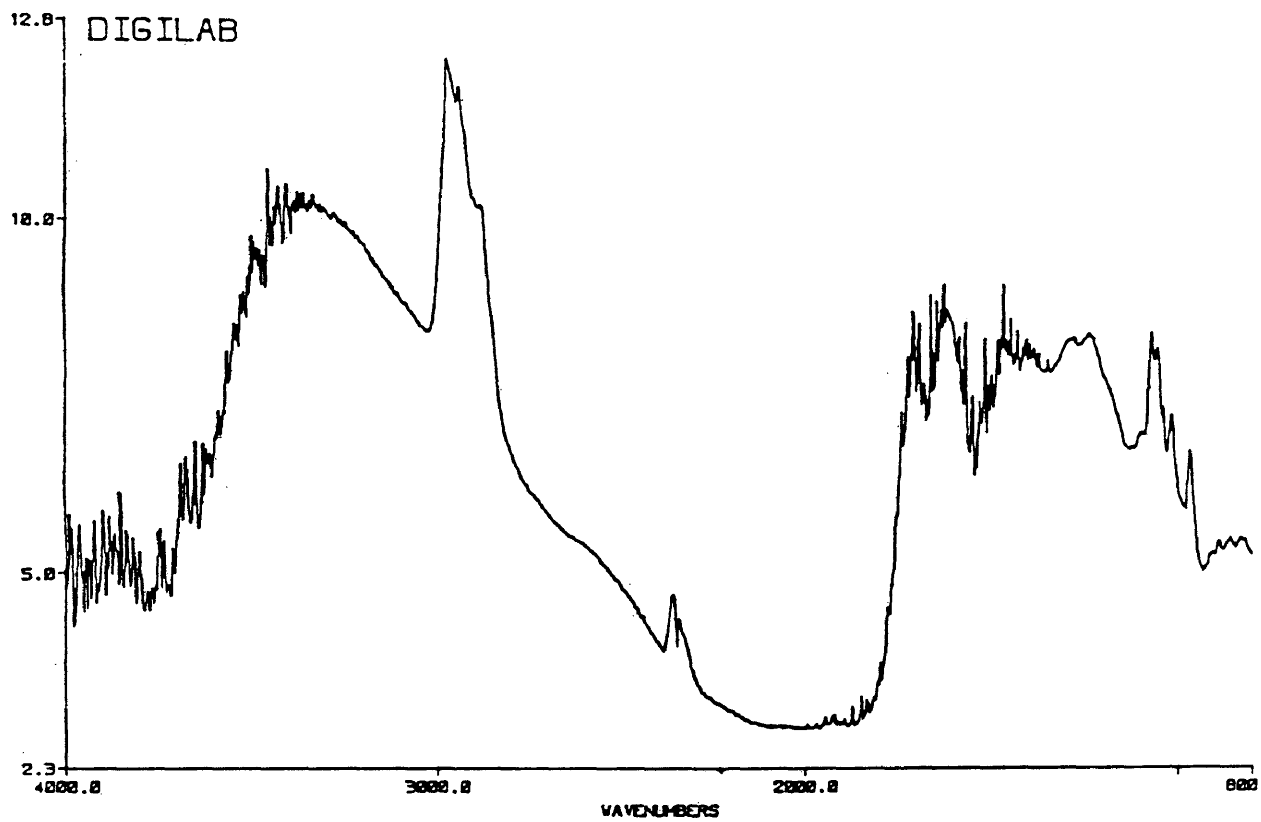

FIGURE A-6: Infrared Spectrum of Oxidized Untreated Lignite

TABLE A1: Alkylation Experiments

Run #: A-W1
Alcohol: Propanol
Acid: Hydrochloric
Coal: Wyodak
Concentration: 1 Vol %
Coal Source: Lab
Reaction Time: 3 Hours
Extent of Alkylation: 5.3 gm/100 gm coal

Run #: A-W2
Alcohol: Propanol
Acid: Hydrochloric
Coal: Wyodak
Concentration: 2 Vol %
Coal Source: Lab
Reaction Time: 3 Hours
Extent of Alkylation: 3.9 gm/100 gm coal

Run #: A-W3
Alcohol: Propanol
Acid: Hydrochloric
Coal: Wyodak
Concentration: 3 Vol %
Coal Source: Lab
Reaction Time: 3 Hours
Extent of Alkylation: 6.5 gm/100 gm coal

Run #: A-W4
Alcohol: Propanol
Acid: Hydrochloric
Coal: Wyodak
Concentration: 0.1 Vol %
Coal Source: Lab
Reaction Time: 3 Hours
Extent of Alkylation: 0.43 gm/100 gm coal

Run #: A-W5
Alcohol: Propanol
Acid: Hydrochloric
Coal: Wyodak
Concentration: 1.0 Vol %
Coal Source: Lab
Reaction Time: 6 Hours
Extent of Alkylation: 8.43 gm/100 gm coal

Run #: A-W6
Alcohol: Propanol
Acid: Hydrochloric
Coal: Wyodak
Concentration: 1.0 Vol %
Coal Source: Lab
Reaction Time: 24 Hours
Extent of Alkylation: 7.8 gm/100 gm coal

Run #: A-W7
Alcohol: Propanol
Acid: Sulfuric
Coal: Wyodak
Concentration: 0.25 Vol %
Coal Source: Lab
Reaction Time: 3 Hours
Extent of Alkylation: 1.84 gm/100 gm coal

Table A1 (Continued)

Run #: A-W8
Alcohol: Isobutanol Acid: Hydrocholoric
Coal: Wyodak Concentration: 1.0 Vol %
Coal Source: Lab Reaction Time: 3 Hours
Extent of Alkylation: 2.19 gm/100 gm coal

Run #: A-W9
Alcohol: Isobutanol Acid: Sulfuric
Coal: Wyodak Concentration: 1.0 Vol %
Coal Source: Lab Reaction Time: 3 Hours
Extent of Alkylation: 1.41 gm/100 gm coal

Run #: A-W10
Alcohol: Isopropanol Acid: Hydrocholoric
Coal: Wyodak Concentration: 1.0 Vol %
Coal Source: Lab Reaction Time: 3 Hours
Extent of Alkylation: 1.84 gm/100 gm coal

Run #: A-W11
Alcohol: n-Butanol Acid: Hydrocholoric
Coal: Wyodak Concentration: 1.0 Vol %
Coal Source: Lab Reaction Time: 3 Hours
Extent of Alkylation: 12.98 gm/100 gm coal

Run #: A-W12
Alcohol: Pentanol Acid: Hydrocholoric
Coal: Wyodak Concentration: 1.0 Vol %
Coal Source: Lab Reaction Time: 3 Hours
Extent of Alkylation: 6.36 gm/100 gm coal

Run #: A-W13
Alcohol: Ethanol Acid: Hydrocholoric
Coal: Wyodak Concentration: 1.0 Vol %
Coal Source: Lab Reaction Time: 3 Hours
Extent of Alkylation: 3.58 gm/100 gm coal

Run #: A-W14
Alcohol: Propanol Acid: Hydrocholoric
Coal: Wyodak Concentration: 1.0 Vol %
Coal Source: Argonne Reaction Time: 3 Hours
Extent of Alkylation: 9.4 gm/100 gm coal

Table A1 (Continued)

Run #: A-W15
Alcohol: Methanol Acid: Hydrocholoric
Coal: Wyodak Concentration: 1.0 Vol %
Coal Source: Argonne Reaction Time: 3 Hours
Extent of Alkylation: 0.57 gm/100 gm coal

Run #: A-W16
Alcohol: Ethanol Acid: Hydrocholoric
Coal: Wyodak Concentration: 1.0 Vol %
Coal Source: Argonne Reaction Time: 3 Hours
Extent of Alkylation: 1.06 gm/100 gm coal

Run #: A-IL1
Alcohol: Propanol Acid: Hydrochloric
Coal: Illinois #6 Concentration: 1.0 Vol %
Coal Source: Argonne Reaction Time: 3 Hours
Extent of Alkylation: 3.4 gm/100 gm coal

Run #: A-IL2
Alcohol: Methanol Acid: Hydrocholoric
Coal: Illinois #6 Concentration: 1.0 Vol %
Coal Source: Argonne Reaction Time: 3 Hours
Extent of Alkylation: NA

Run #: A-P1
Alcohol: Propanol Acid: Hydrocholoric
Coal: Pocohontas #3 Concentration: 1.0 Vol %
Coal Source: Argonne Reaction Time: 3 Hours
Extent of Alkylation: 2.3 gm/100 gm coal

Run #: A-L1
Alcohol: Pentanol Acid: Hydrocholoric
Coal: Lignite Concentration: 1.0 Vol %
Coal Source: Argonne Reaction Time: 3 Hours
Extent of Alkylation: 6.4 gm/100 gm coal

TABLE A2: Liquefaction Experiments

Run #: L-W1

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .91 gms
Toluene Insolubles: .92 gms
Hexane Insolubles: .96 gms
Alkylation: None
Feed Gas: Hydrogen
Temperature: 315 ^{o}C
Time: 30 min

Run #: L-W2

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .79 gms
Toluene Insolubles: .86 gms
Hexane Insolubles: .89 gms
Alkylation: A-W1
Feed Gas: Hydrogen
Temperature: 315 ^{o}C
Time: 30 min

Run #: L-W3

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .79 gms
Toluene Insolubles: .81 gms
Hexane Insolubles: .87 gms
Alkylation: A-W2
Feed Gas: Hydrogen
Temperature: 315 ^{o}C
Time: 30 min

Run #: L-W4

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .85 gms
Toluene Insolubles: .88 gms
Hexane Insolubles: .94 gms
Alkylation: A-W4
Feed Gas: Hydrogen
Temperature: 315 ^{o}C
Time: 30 min

Run #: L-W5

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Catayst: Cobalt/Moly
Coal Feed: 1 gms
Time: 30 min
THF Insoluble: .80 gms (no cat.)
Toluene Insolubles: .80 gms
Hexane Insolubles: .85 gms
Alkylation: None
Feed Gas: Hydrogen
Temperature: 315 ^{o}C
Catalyst Feed: 0.2 gms
CS_2 Feed: 0.1 gms

TABLE A2 (Continued)

Run #: L-W6

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Catalyst: Cobalt/Moly
Coal Feed: 1 gms
Time: 30 min
Alkylation: A-W1
Feed Gas: Hydrogen
Temperature: 315 ^{o}C
Catalyst Feed: .2 gms
CS_2 Feed: 0.16 gms
THF Insoluble: .84 gms (no cat.)
Toluene Insolubles: .77 gms
Hexane Insolubles: .76 gms

Run #: L-W7

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gm
Time: 30 min
Alkylation: None
Feed Gas: CO
Temperature: 315 ^{o}C
20% NaOH Feed: .20 gms
THF Insoluble: .76 gms (including sodium salts)
Toluene Insolubles: .79 gms
Hexane Insolubles: .81 gms

Run #: L-W8

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gm
Time: 30 min
Alkylation: A-W8
Feed Gas: CO
Temperature: 315 ^{o}C
20% NaOH Feed: .20 gms
THF Insoluble: .86 gms (including sodium salts)
Toluene Insolubles: .88 gms
Hexane Insolubles: .94 gms

Run #: L-W9

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
Alkylation: A-W5
Feed Gas: Hydrogen
Temperature: 315 ^{o}C
Time: 30 min
THF Insoluble: .88 gms
Toluene Insolubles: .88 gms
Hexane Insolubles: .88 gms

TABLE A2 (Continued)

Run #: L-W10

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .79 gms
Toluene Insolubles: .82 gms
Hexane Insolubles: .86 gms

Alkylation: A-W8
Feed Gas: Hydrogen
Temperature: 315 °C
Time: 30 min

Run #: L-W11

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .80 gms
Toluene Insolubles: .80 gms
Hexane Insolubles: .81 gms

Alkylation: A-W9
Feed Gas: Hydrogen
Temperature: 315 °C
Time: 30 min

Run #: L-W12

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .82 gms
Toluene Insolubles: .83 gms
Hexane Insolubles: .89 gms

Alkylation: A-W10
Feed Gas: Hydrogen
Temperature: 315 °C
Time: 30 min

Run #: L-W13

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .83 gms
Toluene Insolubles: .83 gms
Hexane Insolubles: .91 gms

Alkylation: A-W11
Feed Gas: Hydrogen
Temperature: 315 °C
Time: 30 min

Run #: L-W14

Coal: Wyodak (Lab)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .81 gms
Toluene Insolubles: .82 gms
Hexane Insolubles: .84 gms

Alkylation: A-W12
Feed Gas: Hydrogen
Temperature: 315 °C
Time: 30 min

TABLE A2 (Continued)

Run #: L-W15

Coal: Wyodak (Argonne)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
Time: 30 min
THF Insoluble: .62 gms
Toluene Insolubles: .63 gms
Hexane Insolubles: .71 gms
Alkylation: None
Feed Gas: Hydrogen
Temperature: 315 °C
Coal Cond.: Wet

Run #: L-W16

Coal: Wyodak (Argonne)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .80 gms
Toluene Insolubles: .80 gms
Hexane Insolubles: .86 gms
Alkylation: A-W14
Feed Gas: Hydrogen
Temperature: 315 °C
Time: 30 min

Run #: L-W17

Coal: Wyodak (Argonne)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
Time: 30 min
THF Insoluble: .84 gms
Toluene Insolubles: .84 gms
Hexane Insolubles: .91 gms
Alkylation: None
Feed Gas: CO
Temperature: 315 °C
NaOH Feed: 0.20 gms

Run #: L-W18

Coal: Wyodak (Argonne)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
Time: 30 min
THF Insoluble: .89 gms
Toluene Insolubles: .89 gms
Hexane Insolubles: .93 gms
Alkylation: None
Feed Gas: Hydrogen
Temperature: 315 °C
Coal Cond.: Dry

Run #: L-W19

Coal: Wyodak (Argonne)
Solvent: 1-MN
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .76 gms
Alkylation: A-W14
Feed Gas: CO
Temperature: 315 °C
Time: 30 min

TABLE A2 (Continued)

Toluene Insolubles: .76 gms
Hexane Insolubles: .84 gms

Run #: L-W20

Coal: Wyodak (Argonne)
Solvent: DHP
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .79 gms
Toluene Insolubles: .80 gms
Hexane Insolubles: .81 gms
Alkylation: None
Feed Gas: Hydrogen
Temperature: 315 ^{o}C
Time: 30 min

Run #: L-W21

Coal: Wyodak (Argonne)
Solvent: DHP
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .56 gms
Toluene Insolubles: .76 gms
Hexane Insolubles: .82 gms
Alkylation: A-W14
Feed Gas: Hydrogen
Temperature: 315 ^{o}C
Time: 30 min

Run #: L-W22

Coal: Wyodak (Argonne)
Solvent: DHP
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .54 gms
Toluene Insolubles: .65 gms
Hexane Insolubles: .77 gms
Alkylation: None
Feed Gas: Hydrogen
Temperature: 350 ^{o}C
Time: 30 min

Run #: L-W23

Coal: Wyodak (Argonne)
Solvent: DHP
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gm
THF Insoluble: .40 gm
Toluene Insolubles: .69 gm
Hexane Insolubles: .78 gm
Alkylation: A-W14
Feed Gas: Hydrogen
Temperature: 350 ^{o}C
Time: 30 min

TABLE A2 (Continued)

Run #: L-W24

Coal: Wyodak (Argonne)
Solvent: DHP
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gm
THF Insoluble: .60 gm
Toluene Insolubles: .77 gm
Hexane Insolubles: .78 gm

Alkylation: A-W15
Feed Gas: Hydrogen
Temperature: 315 ^{o}C
Time: 30 min

Run #: L-W25

Coal: Wyodak (Argonne)
Solvent: DHP
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gm
THF Insoluble: .64 gm
Toluene Insolubles: .84 gm
Hexane Insolubles: .90 gm

Alkylation: A-W16
Feed Gas: Hydrogen
Temperature: 315 ^{o}C
Time: 30 min

Run #: L-W26

Coal: Wyodak (Argonne)
Solvent: DHP
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .26 gms
Toluene Insolubles: .35 gms
Hexane Insolubles: .61 gms

Alkylation: None
Feed Gas: Hydrogen
Temperature: 400 ^{o}C
Time: 30 min

Run #: L-W27

Coal: Wyodak (Argonne)
Solvent: DHP
Coal/Solvent Ratio: 1/2
Catalyst: Fe_2O_3
Coal Feed: 1 gms
Time: 30 min
THF Insoluble: .33 gms (plus cat.)
Toluene Insolubles: .43 gms
Hexane Insolubles: .49 gms

Alkylation: None
Feed Gas: Hydrogen
Temperature: 400 ^{o}C
Catalyst Feed: 0.05 gms
CS_2 Feed: 0.06 gms

Run #: L-W28

Coal: Wyodak (Argonne)
Solvent: DHP
Coal/Solvent Ratio: 1/2
Coal Feed: 1 gms
THF Insoluble: .14 gm
Toluene Insolubles: .56 gm
Hexane Insolubles: .57 gm

Alkylation: A-W15
Feed Gas: Hydrogen
Temperature: 315 ^{o}C
Time: 30 min

TABLE A2 (Continued)

Run #: L-W29

Coal: Wyodak (Argonne)	Alkylation: A-W15
Solvent: DHP	Feed Gas: Hydrogen
Coal/Solvent Ratio: 1/2	Temperature: 400 °C
Catalyst: Fe_2O_3	Catalyst Feed: 0.07 gms
Coal Feed: 1 gms	CS_2 Feed: 0.06 gms
THF Insoluble: .60 gms	Time: 30 min
Toluene Insolubles: .77 gm	
Hexane Insolubles: .78 gm	

Run #: L-W30

Coal: Wyodak (Argonne)	Alkylation: A-W15
Solvent: DHP	Feed Gas: Hydrogen
Coal/Solvent Ratio: 1/2	Temperature: 400 °C
Coal Feed: 1 gms	Time: 5 min
THF Insoluble: .27 gm	
Toluene Insolubles: .77 gm	
Hexane Insolubles: .88 gm	

Run #: L-IL1

Coal: Illinois (Argonne)	Alkylation: None
Solvent: 1-MN	Feed Gas: Hydrogen
Coal/Solvent Ratio: 1/2	Temperature: 315 °C
Coal Feed: 1 gms	Time: 30 min
THF Insoluble: .67 gms	
Toluene Insolubles: .88 gms	
Hexane Insolubles: .94 gms	

Run #: L-IL2

Coal: Illinois (Argonne)	Alkylation: A-IL1
Solvent: 1-MN	Feed Gas: Hydrogen
Coal/Solvent Ratio: 1/2	Temperature: 315 °C
Coal Feed: 1 gms	Time: 30 min
THF Insoluble: .61 gms	
Toluene Insolubles: .84 gms	
Hexane Insolubles: .98 gms	

Run #: L-IL3

Coal: Illinois (Argonne)	Alkylation: None
Solvent: DHP	Feed Gas: Hydrogen
Coal/Solvent Ratio: 1/2	Temperature: 315 °C
Coal Feed: 1 gms	Time: 30 min
THF Insoluble: .55 gm	
Toluene Insolubles: .86 gm	
Hexane Insolubles: .90 gm	

TABLE A2 (Continued)

Run #: L-IL4

Coal: Illinois (Argonne)	Alkylation: A-IL1
Solvent: DHP	Feed Gas: Hydrogen
Coal/Solvent Ratio: 1/2	Temperature: 315 ^{o}C
Coal Feed: 1 gms	Time: 30 min
THF Insoluble: .51 gm	
Toluene Insolubles: .87 gm	
Hexane Insolubles: .96 gm	

Run #: L-L1

Coal: Lignite (Argonne)	Alkylation: None
Solvent: DHP	Feed Gas: Hydrogen
Coal/Solvent Ratio: 1/2	Temperature: 400 ^{o}C
Coal Feed: 1 gms	Time: 5 min
THF Insoluble: .83 gm	
Toluene Insolubles: .86 gm	
Hexane Insolubles: .90 gm	

Run #: L-L2

Coal: Lignite (Argonne)	Alkylation: A-L1
Solvent: 1-MN	Feed Gas: Hydrogen
Coal/Solvent Ratio: 1/2	Temperature: 315 ^{o}C
Coal Feed: 1 gms	Time: 30 min
THF Insoluble: .67 gms	
Toluene Insolubles: .74 gms	
Hexane Insolubles: .81 gms	

Run #: L-P1

Coal: Pocohontas (Argonne)	Alkylation: None
Solvent: 1-MN	Feed Gas: Hydrogen
Coal/Solvent Ratio: 1/2	Temperature: 315 ^{o}C
Coal Feed: 1 gms	Time: 30 min
THF Insoluble: .86 gms	
Toluene Insolubles: .90 gms	
Hexane Insolubles: .95 gms	

Run #: L-P2

Coal: Wyodak (Argonne)	Alkylation: A-P1
Solvent: DHP	Feed Gas: Hydrogen
Coal/Solvent Ratio: 1/2	Temperature: 315 ^{o}C
Coal Feed: 1 gms	Time: 30 min
THF Insoluble: .84 gm	
Toluene Insolubles: .94 gm	
Hexane Insolubles: .99 gm	