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STEAM PRETREATMENT FOR COAL LIQUEFACTION

Final Report

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ABSTRACT

The objective of this study is to demonstrate the use of subcritical steam to pretreat coal for slurry liquefaction, allowing liquefaction to be carried out at lower severity and improving product yield and quality. Although these goals have been achieved by other treatments, most involve complicated procedures, long pretreatment times and the use of exotic reagents preventing these techniques from being used as a process step.

In previous work, the effectiveness of subcritical steam was demonstrated in flash pyrolysis, not only increasing yield, but also reducing the molecular weight of the liquid product. From analyses of pretreated coal, it appears that steam ruptures nearly all of the ether links, replacing them with hydroxyl groups, leaving a depolymerized structure.

Given the success of steam pretreatment in pyrolysis, it was logical to test its application to direct liquefaction. However, all previous attempts by others to obtain an improvement in liquefaction yield by this method failed because pretreated coal was heated too slowly before reaching liquefaction temperature. Previously conducted pyrolysis research showed that heating coal above 360°C could destroy the effect of pretreatment. Therefore, it was reasoned that the heating of pretreated coal to liquefaction temperatures must be done rapidly to minimize deleterious retrogressive reactions.

Here, in order to attain rapid heating, a method is adopted in which a slurry of pretreated coal is injected into a hot liquefaction reaction vessel. Furthermore, as it is known that the benefits of pretreatment are observed only if exposure of steam treated coal to air is rigorously avoided, it is necessary to conduct all operations with pretreated coal under an inert atmosphere. To satisfy this requirement, a nitrogen filled glove bag is used for sample workup and the oxygen concentration of the bag monitored by mass-spectrometer. To verify successful pretreatment, the pyridine extraction yield is determined for each steam treated coal sample.

Samples of Illinois No. 6 coal were pretreated in 750 psia steam at 340°C for 15 minutes. These samples, as well as raw coal, were liquefied at high (400°C, 30 min.) and low (385° C, 15 min.) severity conditions under 1500 psia hydrogen with tetralin as the donor solvent. Improved yields were obtained at both conditions. (Improved yields were not obtained at a liquefaction temperature of 350°C as that put the sample into the region of retrogressive reactions) The deleterious effects of slow heating and exposure of the sample to air were demonstrated. Under low severity conditions, steam pretreatment more than doubled the oil yield, increasing it from 12.5 to 29 wt %.

Tests were also conducted with aromatic ethers as model compounds. These were exposed to inert gas and steam at pretreatment conditions and in some cases to liquid water at 315°C. α -Benzyl naphthyl ether and α -naphthylmethyl phenyl ether show little difference in conversion and product distribution when the thermolysis atmosphere is changed from inert gas to steam. Hence, these compounds are poor models for coal in steam pretreatment. The otherwise

thermally stable 9-phenoxyphenanthrene, on the other hand, is completely converted in one hour by liquid water at 315°C. At pretreatment conditions, however, mostly rearranged starting material is obtained. 9-Phenoxyphenanthrene, therefore, is a model for ether linkages in coal although it is less reactive. The improvement over the α -benzyl-naphthyl and α -naphthylmethyl phenyl ethers is a result, we speculate, of larger size of the aromatic cluster in 9-phenoxyphenanthrene.

The model compounds α -benzyl-naphthyl ether and α -naphthylmethyl phenyl ether were reacted in the presence of 5Å zeolite. Zeolite proved effective in suppressing isomerization of the starting material and improving the yield of thermolysis products, especially for the former. These results suggested that zeolites might be beneficial in steam pretreatment of coal and in coal liquefaction. Pretreatment and liquefaction of mixtures of coal and zeolites increases yields of asphaltenes and preasphaltenes.

CONCLUSIONS

The following conclusions are drawn from this work:

1. Steam pretreatment substantially improves the quality of the liquid product in coal slurry liquefaction. Under low severity conditions, the oil yield is more than doubled, going from 12.5 to 29 wt %.
2. The benefits of steam pretreatment can be realized only if the pretreated coal is rapidly heated to liquefaction temperature. This is necessary in order that the pretreated coal pass quickly through the region of retrogressive reactions. This region, in which retrogressive reactions can mitigate or even destroy the effects of pretreatment, extends downward from 360°C to perhaps as low as 320°C. The upper limit on heating time can not yet be specified, but appears to be about one minute (which was the recovery time for the low severity b series of tests). (Tubing bombs, in which improved yields after pretreatment are not obtained, require about 3 minutes to reach reaction temperature.)
3. Pretreated coal must be protected from oxygen to preserve the benefits of pretreatment.
4. The compounds α -benzyl-naphthyl ether and α -naphthylmethyl phenyl ether show little difference in conversion and product distribution when the thermolysis atmosphere is changed from inert gas to steam. Hence, these compounds are poor models for coal in steam pretreatment. The otherwise thermally stable 9-phenoxyphenanthrene, on the other hand, is completely converted in one hour by liquid water at 315°C. At pretreatment conditions, however, mostly rearranged starting material is obtained. 9-Phenoxyphenanthrene, therefore, is a model for ether linkages in coal although it is less reactive. The improvement over the α -benzyl-naphthyl and α -naphthylmethyl phenyl ethers is a result, we speculate, of the presence of the larger number of condensed aromatic rings.
5. 5Å Zeolite is effective in suppressing the formation of isomerized starting material in the thermolysis of α -benzyl-naphthyl ether and α -naphthylmethyl phenyl ether.
6. The presence of 4Å and 5Å zeolites during pretreatment and liquefaction increases yields of asphaltenes and preasphaltenes.

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INTRODUCTION

This is the Final Report for DOE Contract Number DE-AC22-90PC90052 for the period 26 September 1990 to 18 March 1995.

Development of commercially viable and environmentally sound processes for coal liquefaction remains a formidable challenge. Although advances in coal liquefaction technology in recent years have led to the production of liquids of improved quality, this improvement has been achieved mainly by increased consumption of expensive catalyst. Capital equipment costs are another major factor in the high price of the coal-derived liquids.

One way to improve the economics of direct liquefaction is to modify the coal feed prior to solubilization. The use of physically or chemically pretreated coal has a potential for savings in operating costs since the liquefaction will then require less severe conditions. (Low severity conditions are usually defined as temperature below 350°C and pressure in the range 1000-1500 psi.) Pretreatment methods include low temperature hydrogenation, chemical treatments, solvent swelling, and demineralization. It was demonstrated that treatments such as alkylation, acylation, partial oxidation and alkali hydrolysis weaken and rupture the cross-linked bonds and result in a partially depolymerized coal. Although all these treatment techniques enhance yield at low severity, none has yet been employed as a process step in liquefaction. Chemical treatment methods remain in the laboratory mainly because they employ expensive and sometimes hazardous reagents.

The work described here is based on the use of steam as a pretreatment agent in noncatalytic coal-donor solvent slurry liquefaction. Advantages of this approach are that steam is among the cheapest of reagents and does not incorporate undesired chemical residues into the coal structure.

The construction of a suitable coal liquefaction reaction system capable of providing sufficiently high heating rates was first required. Since this research is based on the hypothesis that the

heating rate of pretreated coal must be rapid, a tubing bomb or stirred autoclave (employed in the conventional way) would not be adequate to carry out liquefaction under rapid heating conditions. One way to achieve high heating rates is to use an autoclave fitted with a feed injection system. This type of equipment was developed and successfully used by Whitehurst *et al.* (1976). A stirred autoclave containing only solvent was pressurized with hydrogen and heated to the desired temperature. During this time, a slurry of coal was held at a room temperature in a barrel with a floating piston. When the autoclave reached the required temperature, the coal slurry was injected into the autoclave and rapidly dispersed by the stirrer. The heating rate for a coal slurry in such a device is approximated by the dispersion time. A system of this type, with some modifications, was designed, assembled, tested and used for the liquefaction tests.

Liquefaction tests of raw and steam pretreated Illinois No. 6 coal were made to determine the pretreatment effect on yield of liquids and on quality of product. These tests were conducted using the slurry injection autoclave described above pressurized with hydrogen and using tetralin as the donor solvent. The effect of exposure of treated coal to air and the role of coal slurry heating rate were examined at two different conditions of liquefaction severity. The experiments were also conducted using mixtures of Illinois No.6 coal and zeolite.

Several model compounds were used as surrogates for coal in steam pretreatment to investigate the chemistry of the process. Two diaryl ethers having the structure $\text{Ar}'\text{-CH}_2\text{-O-Ar}$ were first chosen to study ether linkage behavior during the steam pretreatment process. α -Benzyl naphthyl ether (α -BNE) and α -naphthylmethyl phenyl ether (α -NMPE) were synthesized and subjected to the steam treatment at the same conditions as coal. They were also reacted in inert atmosphere (nitrogen) to separate the effect of water from the thermal effect. The same set of experiments were conducted with model compound/zeolite mixtures to reduce molecular mobility, thus inhibiting isomerization of the compound.

In addition, the model compounds (pure or mixed with zeolites) were reacted under high pressure, where water is liquid, to determine the conditions required to achieve a better

cleavage of the ether linkage. The experimental procedure for these high pressure experiments are as described by Siskin *et al.* (1993), using an 11 ml stainless steel reaction tubing bomb. For comparison, 9-phenoxyphenanthrene (compound extensively studied by Siskin, *et al.*, 1991, 1993) was also synthesized and subjected to the same treatment as Ar'-CH₂-O-Ar. 9-Phenoxyphenanthrene is thermally stable in inert medium, but can be cleaved in water (Siskin, *et al.*, *op. cit.*).

1. BACKGROUND

1.1. Oxygen Functional Groups in Coal.

O-functionalities play an important role in coal conversion processes. Oxygen content in coal may range from as low as 3% (maf) for anthracite to about 30-35% (maf) for lignite and brown coal. The total amount of oxygen is composed of organic matter, mineral matter and moisture. Organic oxygen in coal exists in a wide variety of forms predominantly in methoxyl, carbonyl, carboxyl and phenolic. During liquefaction the concentration of carboxylic, carbonylic and etheric oxygen is greatly reduced (Cronauer and Ruberto, 1977). The loss of carbonyl functional group was found to be associated with cross-linking reactions during coal pyrolysis (Solomon *et al.*, 1990). The evolution of CO₂ from carboxylate groups is related to retrogressive reactions in pyrolysis and liquefaction of low rank coals (Serio *et al.*, 1993).

Weathering of coal (exposure to air) increases the CO₂ yield and lowers fluidity and in extreme cases may result in the complete disappearance of coal coking properties due to the formation of oxygen-containing functional groups. Those groups are converted by heating to cross-links within the coal macromolecule. Oxidized bituminous coal contains greater amount of carboxyl and C-O groups and shows early cross-linking and lower tar evolution during the pyrolysis (Solomon *et al.*, 1990). Oxidation also influences the swelling ratio of coal in pyridine and decreases the yield of pyridine extract (Graff and Brandes, 1987; Brandes *et al.*, 1989).

The oxygen bridges between carbon atoms are believed to be the key cross-links in coal macromolecules. Lazarov and Angelova (1968) have shown that approximately 50% of the oxygen in coking coal is in the form of diaryl ether or arylalkyl ether. Ether cleavage during liquefaction was studied by Youtcheff and Given (1983). They proposed that slow conversion of some high oxygen content coals is a result of extensive cross-linking of ether linkages (benzylic or aryl-alkyl). Cross-link formation was suggested to be similar to benzylation of coal structure (Saini *et al.*, 1993). The influence of various treatments on ether functional groups

are further discussed in the subsequent sections.

1.2. Pretreatment Methods to Enhance Coal Liquefaction.

A variety of physical and chemical methods of coal treatment prior to low severity liquefaction have been found to significantly improve yield and quality of the product, making it superior to those obtained at high severity conditions (Shams *et al.*, 1992). There have been many studies showing that the labile cross-linked coal structure can be weakened by such treatments as alkylation, acylation, partial oxidation, alkali hydrolysis, solvent swelling, selective demineralization, water and steam treatments. As a result of the treatment, coal solubility in organic solvents such as tetrahydrofuran (THF) and toluene is significantly increased. It has been suggested that the low reactivity of many lignites and subbituminous coals is caused by excessive retrogression and lack of available hydrogen at the initial stage of liquefaction. The reactivity can be enhanced if the coal structure is partially disrupted or modified by pretreatment.

Sternberg and Delle Donne (1974) demonstrated that subbituminous and bituminous coals can be partially depolymerized by alkylation at ambient conditions. Coal structure was partially disrupted by adding ethyl groups and some of the etheric and phenolic hydroxyl groups were cleaved. A method for selective O-alkylation was developed by Liotta (1979). Baldwin *et al.* (1991) showed that both pretreatment methods, selective (Liotta) and non-selective (Sternberg and Delle Donne) alkylation, improved coal reactivity under liquefaction conditions. These experiments were carried out using Wyodak subbituminous and Illinois No.6 bituminous coals. The greatest effect is at low severity (350°C, 5 min), and for low rank (high oxygen content) coal which was selectively O-methylated. Schlosberg *et al.* (1980) alkylated Wyodak subbituminous coal and Illinois No.6 bituminous coal under Friedel-Crafts conditions using aluminum chloride and methyl chloride. Results of high severity (427°C, 1500 psi) liquefaction showed 10-21% increase in cyclohexane soluble material for the alkylated coals. Use of alkali hydrolysis to pretreat lignite, subbituminous coal and bituminous coal resulted in increased yield of asphaltenes and oils in high severity (410°C, 1000 psi) liquefaction (Chow, 1983).

The alteration of coal structure by solvent-swelling pretreatment is also reported to improve liquefaction conversion. Baldwin *et al.* (1991) demonstrated that pre-swelling in acetone very effectively promotes additional conversion with increase in the yield of hexane solubles for the swollen coals. They suggest that this effect is due to rupture of some of the weak bonds, such as hydrogen and ionic, holding the macromolecule together. Joseph (1991) demonstrated that pre-swelling of bituminous and lower rank coals (Illinois No.6 bituminous, Wyodak subbituminous, Kinneman Creek lignite) with suitable solvent, followed by the removal of the swelling agent, significantly improves liquefaction yield and product quality. Maximum improvement in liquefaction yield was achieved for bituminous coal. The explanation offered is that the macromolecular structure of coal is expanded by pretreatment and is more accessible to hydrogen donor solvent. Accessibility of the liquefaction solvent to the coal reactive sites promotes capping of free radicals, thus reducing retrogressive reactions, and increases solvent-induced bond cleavage. Artok *et al.* (1992) investigated the influence of pre-swelling on catalytic liquefaction. The combined effect of swelling and catalyst addition enhances the conversion of lignite by factor of two. Some swelling agents, if not removed from the coal after pretreatment, decompose to a good solvent inside the pores, significantly improving the yield of catalytic liquefaction for both lignite and bituminous coal (Artok *et al.*, 1993).

Generally, all of the above methods of enhancing coal reactivity somewhat improve liquefaction yield. Most involve complicated procedures, long pretreatment times and use of exotic reagents, preventing these techniques from being employed as a process step. Other pretreatment procedures are based on the use of water (liquid or steam) which is a relatively cheap and readily available pretreatment reagent.

1.3. Pretreatment in Aqueous Medium.

1.3.1. Liquid Water Pretreatment.

Steam has been considered inert to heavy complex hydrocarbon systems at relatively moderate temperatures. However, based on work by Allred (1979) and Lewan *et al.* (1979), Tyler (1981) showed that shale oil can be cracked in supercritical steam at temperatures not exceeding 425°C and pressures up to 100 atm yielding material with significantly reduced average molecular weight. Model compounds studies gave evidence of the chemical activity of water toward coal linkages. It was shown that the ether bond in anisole, a model for ether-aryl linkages in coal, can be disrupted by steam at 400°C and 184 atm (Ross *et al.*, 1982).

Carbon monoxide pretreatment of Wyodak subbituminous coal in aqueous medium at 300°C reportedly improves conversion and oil yield in subsequent liquefaction (Lim *et al.*, 1994). A sufficient amount of water was present during pretreatment to maintain a liquid phase at reaction temperature. Comparison of treated and untreated coal suggested that partial decarboxylation occurred during this pretreatment. Elemental analysis of the water insoluble product showed a 36% reduction in oxygen content. For pretreated coal, the yields of CO and CO₂ during liquefaction were significantly reduced.

Hydrothermal treatment of Wyodak coal with liquid water for 5 hours at 350°C resulted in extensive hydrolysis of the coal structure due to a virtual elimination of both phenol and catechol groups (Ross *et al.*, 1991). The effect of hydrothermal pretreatment on liquefaction of Illinois No.6 bituminous coal was studied by Pollack *et al.* (1991). Pretreatment was performed in microautoclave at 300°C under 500 psig initial nitrogen pressure using 1:2 coal to water ratio. After pretreatment was completed, the autoclave content was filtered to separate coal from the water. Liquefaction of this pretreated coal was then conducted. The pretreatment resulted in small (up to 8%) but consistent improvement in the methylene-chloride and the heptane solubles. It was also observed that hydrothermal pretreatment increased the ratio between the rate constant

of formation soluble product and the rate constant of formation insoluble product.

The effect of liquid water pretreatment on pyrolysis and liquefaction of low rank Zap lignite and Wyodak subbituminous coal and later on Illinois No.6 coal was studied by Serio *et al.* (1991, 1992a). Pretreatment was carried out at 4000 psig and temperatures 250°C, 300°C, and 350°C in a 20 ml tubing bomb reactor. For low rank coals (Zap and Wyodak) the tar yield in pyrolysis was sharply increased at relatively short pretreatment times (up to 1 hour) and deteriorated at longer pretreatment times. The effect was less dramatic for Illinois No.6 coal. However, there is a monotonic increase in pyridine extractables, especially in case of Illinois No.6 coal, and decrease in formation of CO, CO₂ and H₂O. Pretreatment of Illinois No.6 bituminous coal resulted in more than doubling of pyridine extraction yield for a freshly opened sample. The concentration of hydroxyl groups in the bulk declined with increase of pretreatment time. The yields of toluene and pyridine solubles in donor solvent liquefaction of low rank coals were decreased at short pretreatment times and were improved at longer times, but not exceeding the yields from raw coal. The results of liquefaction of Illinois No. 6 coal were inconsistent due to extreme sample sensitivity to "aging".

Aqueous pretreatment of Zap lignite and Rawhide subbituminous coal resulted in an increase in hexane solubles (Tse *et al.*, 1991). When the pretreatment was followed by co-processing with a Maya crude at 425°C, a 6 to 8% increase in hexane solubles was obtained.

The effect of water treatment was also tested in catalytic liquefaction. Catalytic pretreatment of low rank Mo impregnated coals showed an increase in liquefaction yields (Serio *et al.*, 1993). Adding a small amount of water reportedly had a dramatic promoting effect on catalytic liquefaction at 350°C, but a significant inhibiting effect occurred if reaction was carried out at 400°C (Song *et al.*, 1993). The negative effect at higher temperature was attributed to water/catalyst interactions. Analysis of oils obtained from liquefaction with added water showed more phenolic compounds compared with liquefaction without water (Song and Saini, 1994).

1.3.2. Steam Pretreatment.

Exposure of coal to subcritical steam leads to significant changes in coal structure and behavior in subsequent processing. Steam treatment of Illinois No.6 coal in the temperature range 300-370°C at 50 atm was studied previously by Graff and Brandes (1987). These temperatures have significance since it is in this region that softening of plastic coals occur, and, coincidentally, aromatic hydrocarbons become highly soluble in water at about 100 atm. In this work two types of tests, pyridine extraction and flash pyrolysis, were conducted with raw and steam treated coal. It was observed that the pyridine extraction yield from steam treated coal gradually increases and reaches maximum at 340-350°C. At temperatures above 370°C the effect is extinguished. Yield of liquids in coal pyrolysis was more than doubled and the total volatiles yield was increased by about 20%. The optimum pyrolysis temperature was determined to be 740°C. The effective steam pretreatment temperatures were established to be between 320 and 360°C. Treatment in helium showed slight changes in pyridine extraction yield but not above values for raw coal. As a result of pretreatment, coal, initially ground to pass 200 mesh, was lightly agglomerated, contrary to the helium treated coal which remained unagglomerated. If steam treated coal was exposed to ambient air, both pyrolysis and extraction yields were reduced to the level of raw coal. Based on the experimental results, it was concluded that coal is partially depolymerized as a result of steam treatment.

Analysis of pyrolysis liquids from raw and pretreated Illinois No.6 coal showed a decrease in molecular weight as large as 31% (Graff *et al.*, 1988). The oxygen content considerably increased, although nitrogen content decreased by 27%. In order to further understand the structural changes occurring during pretreatment solvent swelling, diffuse reflectance infrared spectroscopy (DRIS), O-alkylation, and elemental analysis were performed (Brandes *et al.*, 1989). Swelling ratios in pyridine benzene and water were measured for raw steam treated and helium treated coal. Raw coal swelled more than steam treated coal and helium treated coal swelled less than steam treated coal in pyridine which is a strong hydrogen-bond-breaking solvent. Since benzene does not break hydrogen bonds, the ratio between degree of swelling in pyridine and in benzene was used to indicate the relative number of hydrogen bond cross-links present in the

sample. Raw coal was found to have more hydrogen bond cross-links than steam treated and helium treated coal. In water, the swelling ratio is doubled by steam treatment. This shows that steam treatment makes the coal more hydrophilic. DRIS spectra of raw and steam treated coal showed changes in the hydroxyl region. The number of derivatized OH sites obtained by O-alkylation was twice that of raw coal. Elemental analysis showed that steam treatment reduces organic oxygen by 28%. Considering the combined results of swelling, DRIS and O-alkylation studies, it is evident that the absolute number of OH groups, especially phenols, is substantially increased by steam pretreatment. It was concluded that during steam pretreatment new hydroxyl groups are introduced. As a result, the covalent cross-links in the coal structure are greatly reduced yielding a partially depolymerized coal, potentially an improved feedstock for liquefaction processes.

Steam and helium treatment tests were also conducted using Mississippi lignite at 50 atm (Graff *et al.*, 1988). Despite chemical differences between this coal and Illinois No.6, similar trends were observed. Improved pyridine extraction yield was obtained for steam treated coal compared to helium treatment in the range 300-360°C with a maximum at 320°C.

Studies of the steam treatment of Wyodak coal at 250°C and 50 atm in a semiflow microreactor were conducted by Bienkowski *et al.* (1987). After pretreatment, coal was liquefied with supercritical steam. As a result of pretreatment, conversion at 400°C increased by 32%. (These results, however require verification since the procedure followed may have allowed explosive steam evolution, resulting in particle comminution and, consequently, an increase in yield for that reason.) Analysis of the toluene extracted products showed an increase in the hydrogen and oxygen content. A significant amount of oxygen in the extract was present in a form of dihydroxy aromatics. The highly condensed residue contained less hydrogen and oxygen compared to starting coal. Steam treatment of low rank coal reduced the concentration of methoxy, phenolic, aliphatic carbonyl and carboxyl groups in coal (Khan *et al.*, 1989). After steam treatment, phenols were the major components found in the water phase.

The effect of steam on the products obtained by low temperature pyrolysis was studied by

Minkova *et al.* (1991, 1992). The yields of liquid obtained by steam pyrolysis were significantly higher than those obtained in a stream of argon. It was suggested that the water vapor penetrates into the pores, accelerates the diffusion of low molecular weight components, and disrupts hydrogen bonds and donor/acceptor interactions. The steam prevents cracking of the volatile products and deposition of carbon on the solid surface leading to the formation of a highly developed pore structure.

An improvement in quality of the slurry liquefaction products following steam pretreatment at 250°C and 38 atm was reported by Ross and Hirschon (1990). The toluene soluble liquefaction product obtained from steam treated coal was more fluid and more volatile compared to the product from raw coal.

1.4. Reactions of Ether Model Compounds.

Model compounds have been used by many investigators to imitate functional groups found in coal and to investigate the reaction pathways of these functionalities in coal conversion processes. Since coal is a solid of limited solubility with randomly arranged organic and inorganic fragments, analysis of its structure may involve disruption of the network. The characterization of liquids obtained from coal conversion provides information about product molecular structure and is a window into the original coal pattern (Farcasiu, 1977). By examining the functional groups identified in a product, the type of the covalent links involved in bond scission can be established. Although many studies are focused on carbon-carbon bond breaking free radical reactions, the mechanism may require oxygen-center radical at the initiation step. Such chain initiating radicals are produced by ether scission (Chawla *et al.*, 1990). Benzyl phenyl ether was also shown to promote hydrogen transfer between tetralin and diphenylmethane under thermolysis conditions (Sharma and Mizra, 1984).

The thermolysis of arylmethyl aryl ethers under relatively mild conditions was studied by Chawla *et al.* (1990). Four ethers, α -naphthylmethyl phenyl ether (α -NMPE), α -benzyl naphthyl ether

(α -BNE), β -naphthylmethyl phenyl ether (β -NMPE), and β -benzyl naphthyl ether (β -BNE) were thermally reacted in evacuated glass ampoules at the temperatures from 250°C to 350°C for 30 minutes. The major products obtained were ArOH, Ar'CH₃, and isomers of the starting ethers Ar'CH₂ArOH. The minor amount of Ar'CH₃CH₂CH₂Ar', ArCH=CHAr', ArCH₂Ar and "dehydrocompounds" were also produced. The relative rates of thermolysis were found to be:

$$\alpha\text{-BNE} \gg \beta\text{-BNE} > \alpha\text{-NMPE} > \beta\text{-NMPE}$$

$$42 \quad : \quad 2 \quad : \quad 2 \quad : \quad 1$$

The products were formed by homolysis of the CH₂-O bond followed by recombination of the resulting radical. The difference in the relative reaction rates was explained by the stability of the radicals produced from each ether. The replacement of glass ampoule by a stainless steel reactor reduced product isomerization. All of the four ethers studied showed up to 80% conversion at these relatively mild conditions.

The analysis of the structural changes in coal macromolecular network due to the steam treatment and earlier model compounds studies showed that covalent bonds, particularly ether linkages, are readily cleaved in presence of steam (Ross *et al.*, 1982; Bienkowski *et al.*, 1987; Graff *et al.*, 1988; Khan *et al.*, 1989; Brandes *et al.*, 1989). Water can no longer be treated as an inert medium for coal and organic compounds (except under relatively low temperatures) but rather as an active participant in bond disruption reactions. Since attention was brought to aqueous organic chemistry, extensive studies with various model compounds have been performed to better understand the cleavage mechanism of coal cross-links in aquathermolysis.

Recent studies with model compounds containing various functional groups and structures found in coal indicate an ionic pathway in aquathermolysis under mild conditions (from 250 to 350°C). The earlier work on thermolysis of ethers with and without water at about 400°C considered the free radical mechanism most favorable (Ross *et al.*, 1982). The contribution of ionic chemistry was not apparent due to the high temperature employed in the experiments. Siskin *et al.* (1990) were able to demonstrate the distinction between ionic and free radical pathway for ethers and esters by a comparison of reaction products. Experiments with three diaryl ethers (diphenyl ether, dibenzofuran and 4-phenoxyphenol), three alkyl aryl ethers (cyclohexyl phenyl ether, benzyl

phenyl ether and 4-[benzyloxy]phenol) and an ester (methyl 1-naphthoate) were carried out at 250°C for 5.5 days and 343°C for 2 hours in presence or absence of liquid water at about 1500 psi. In the latter case water was replaced by decalin or nonane. Diphenyl ether and dibenzofuran were unreactive at both aqueous (ionic) and thermal (free radical) treatments. For benzyl aryl ethers ionic reactions were found to be competing with radical reactions. The activated aryl ether 4-phenoxyphenol and ester methyl 1-naphthoate were unreactive at thermal conditions even at 343°C, but the presence of liquid water provided an ionic pathway for cleavage of the carbon-oxygen bond. The product formed in aquathermolysis of 4-phenoxyphenol consisted of large amounts of phenolic products. More reactive benzyl aryl ethers generated more alkylated products under ionic conditions. For the ester, methyl 1-naphthoate, water acted as an acid or as a basic catalyst at higher temperature.

Two other extensively studied model compounds are the diaryl ethers 1-phenoxy-naphthalene and 9-phenoxyphenanthrene (Siskin *et al.*, 1991; 1993). These covalent cross-links are thermally stable under coal depolymerization to obtain liquids. However, in the presence of water at 315°C the diaryl ethers are cleaved to phenol, and 1-naphthol and 9-hydroxyphenanthrene respectively. The rate of cleavage of the diaryl ethers increased with increasing numbers of aromatic rings in the structure. The reactions were catalyzed by water which is a stronger acid at the temperatures employed and were inhibited by alkali halides which at high temperature behave as salts of strong bases and weak acids in water.

2. LIQUEFACTION OF STEAM PRETREATED COAL

2.1. Overview of Experimental Methods.

Liquefaction experiments are conducted with raw coal, steam treated coal and steam treated coal exposed to air under rapid heating, and slow heating conditions. Samples of Illinois No.6 coal (DECS-2) from the Pennsylvania State University Sample Bank are used in this work. The coal is refrigerated and stored under an inert atmosphere to avoid oxidation. Pretreatment and liquefaction experiments are carried out with these samples ground to pass 200 mesh or using coal as received (-20 mesh particle size).

The effect on liquefaction yields when zeolite is added to the coal sample is also examined. Three zeolite samples with different pore size are tested in this work: 5Å, 4Å, and 13X (materials obtained from Aldrich Chemical Company, Inc.). The zeolite powder is used "as received" (undried). Before each run, the moisture content of the molecular sieve is determined separately from the coal sample. Tests with zeolite are carried out following the same procedure as used in experiments with a coal alone. In some tests, zeolite is added to the coal sample prior to the steam pretreatment. After the treatment, zeolite is not removed, but carried over to the liquefaction stage. In other tests, zeolite is added only after pretreatment.

Steam pretreatments are conducted in a stainless steel tubular reactor which can be charged with up to 30 grams of sample. The procedure is described by Graff *et al.* (1988). The coal pretreatment is conducted in the continuous flow of steam at 50 atm and 340°C for 15 minutes while the reactor is submerged in a fluidized bed heater. These conditions were previously found to be an optimum for Illinois No.6 coal. After steam pretreatment is completed, the reactor is placed in a nitrogen filled glove bag where all manipulations of the treated sample are performed. If raw coal is used in the liquefaction tests or exposure of the steam pretreated sample to air is required, the inert atmosphere is not used. The room temperature pyridine extraction yield is determined for each steam treated sample to verify successful pretreatment. The rapid heating

slurry liquefaction with this steam treated sample is then conducted using deoxygenated tetralin as a hydrogen donor solvent.

The liquefaction apparatus consists of a 300 ml stirred autoclave and coal slurry injection system (loading reservoir and rupture disc). After a portion of solvent is preheated in the autoclave to the desired temperature, a coal slurry prepared from the steam treated coal and tetralin is charged into the loading reservoir. Application of hydrogen pressure causes the rupture disc to burst injecting slurry into the reaction vessel. This procedure provides a rapid heating of the coal sample.

After the liquefaction run is completed and the reactor cooled down, coal conversion is determined as described by Joseph (1991) and the liquid product classified as hexane solubles (oils + gases), toluene solubles (asphaltenes), and THF solubles (preasphaltenes) (Joseph, 1991).

In later runs, after cool down, vent gas from the autoclave is analyzed by mass-spectrometer. The total gas yield, including volatiles loss during pretreatment, is then subtracted from the value of hexane solubles (oil + gas) to obtain the yield of oils alone.

2.2. Sample Preparation.

2.2.1. Coal Sample Preparation.

The work is conducted with Illinois No.6 coal samples (DECS-2) from the Pennsylvania State University Sample Bank. The coal was received in two batches (designated 27 and 31) of three packets each. After receipt, these samples were stored under refrigeration in their unopened sealed foil packets. The as received samples have a particle size of -20 mesh and an elemental composition (weight percent on a dry basis) of:

Ash	16.16
Carbon	65.49
Hydrogen	4.56
Nitrogen	1.11
Sulfur	4.52
Oxygen	8.16

Samples for pretreatment and liquefaction are ground to pass 200 mesh. Grinding is conducted in a nitrogen filled glove bag using a Trost Air Impact Pulverizer, operated with inert gas. Ground coal is riffled, placed in a glass jars, flushed with inert gas, sealed, and refrigerated.

2.2.2. Zeolite Powder and Coal/Zeolite Mixtures.

Zeolites with three different pore sizes were chosen for this work: 5Å (average particle size 3-5 μm), 4Å (average particle size 2-3 μm), and 13X (average particle size 2 μm , average pore size 9-10Å). These were purchased from the Aldrich Chemical Company, Inc.

The unit cell of zeolite A contains 24 tetrahedra, 12 AlO_4 and 12 SiO_4 . The ratio Si/Al is slightly less than one (Breck, 1974). The zeolite 4Å has the unit cell content $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 27\text{H}_2\text{O}$, when fully hydrated (oxide formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4.5\text{H}_2\text{O}$). The zeolite 5Å is a modified 4Å in which the blocking sodium cations have been partially replaced by calcium. The unit cell formula, when fully hydrated, is $\text{Ca}_{4.8}\text{Na}_{2.4}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 28\text{H}_2\text{O}$ (oxide formula $0.8\text{CaO} \cdot 0.2\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4.7\text{H}_2\text{O}$). The chemical formula of fully hydrated 13X zeolite is $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 264\text{H}_2\text{O}$ (oxide formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{SiO}_2 \cdot 6\text{H}_2\text{O}$). The molecular sieve of 13X zeolite has higher Si/Al ratio and, therefore is more organophilic than the A type zeolite.

The coal/zeolite mixture is prepared prior to the steam pretreatment by mixing the zeolite powder with the coal sample in a glass beaker. In all calculations the zeolite part of the mixture is

considered to be of constant weight and is added to the amount of ash in coal.

2.3. Experimental Equipment.

2.3.1. Steam Treatment Apparatus.

The apparatus used for steam pretreatment is made up of a steam generation section and a steam treatment section (Figure 2.1). The steam generation section includes a water reservoir, pump, furnace and boiler. This assemblage produces steam at pressures from one to fifty atmosphere by altering the rate at which water is pumped into the boiler and by adjusting the boiler vent valve. The furnace has three heating zones (Lindberg, model #54256-A). The boiler is made of a 28-inch long, 1-inch ID, 1-1/2-inch OD stainless steel tube with reducing fittings welded to each end. Steam from the boiler is supplied to the pretreatment section through a heated stainless steel transfer line.

The pretreatment section consists of a fluidized bath heater and a steam preheating coil where steam from the boiler is brought to the temperature of the bed. The pretreatment reactor is connected to the preheating coil (20-foot long, 1/4-inch OD stainless steel tube) and submerged into an electrically heated fluidized sand bath (Techne model #IFB-200). Excellent temperature stability was demonstrated using this fluid bed sand bath. Reactors of different size may be used according to amount of coal to be pretreated. The smallest is 4 inches long, 1/2 inch OD and holds 3 grams; the largest is 14 inches long, 1 inch OD and holds 30 grams. Steam is vented from the pretreatment reactor through a needle valve. If treatment in an inert gas is desired instead of steam, the inert gas (nitrogen) at the reaction pressure is supplied to preheated steam delivery line from a high pressure tank.

Figure 2.1. Steam Pretreatment Apparatus.

2.3.2. Liquefaction Apparatus.

The rapid heating liquefaction apparatus consists of a 300 ml stirred autoclave and a coal slurry injection system (Figure 2.2). The autoclave (Autoclave Engineers EZE-Seal, model #P-419) is made of Hastelloy C and equipped with a packless magnetic stirrer drive. The coal slurry injection system includes a stainless steel slurry reservoir, loading line and a rupture disc assembly. The coal slurry and washing solvent are loaded into reservoir through a valve from two syringes. The slurry syringe is of 50 cc capacity and solvent syringe is of 30 cc capacity. A 1000 psia rupture disk separates the reservoir from the autoclave. Nitrogen and hydrogen are supplied from cylinders. Nitrogen is used for pressure testing of the system and hydrogen is used in the liquefaction process.

Figure 2.2. Stirred Autoclave with Coal Slurry Injection (Shown Prior to Coal Slurry Injection).

In runs where the liquefaction gas is analyzed, this is done by sampling the gas vented from the autoclave as pressure is relieved after completion of the run. The vent gas is continuously sampled directly into a mass spectrometer (Extranuclear Laboratories, Inc.; Model C50) through a 69 cm long, 0.05 mm id, capillary tube (Figure 2.3). The gas transfer line downstream of the reactor outlet valve is equipped with a 90 μm filter and a needle valve to control the flow. Two shut off valves, installed directly before and after the capillary tube, allow a bleed of reaction gas to be conducted into the source of the mass-spectrometer. The vented excess flow is monitored by a ball flow meter. Hydrogen gas is used to sweep the transfer line from air prior to sampling of the reaction gas.

Figure 2.3. Gas Analysis Equipment.

2.4. Experimental Procedures.

2.4.1. Steam Pretreatment of Coal.

For each batch of coal used in pretreatment, the moisture content is determined by drying about one gram of sample for 18 hours in a vacuum oven at 90°C. A portion of coal to be pretreated is loaded into the reactor, flushed with nitrogen and the reactor is sealed. About 30 grams of undried coal are pretreated in each batch. After the fluid bed is preheated to a desired temperature, the pretreatment reactor is connected to the steam preheating coil and is held above the bed. Nitrogen at treatment pressure is passed through the reactor while it is heated above the condensation point of the steam. Temperature is monitored by a thermocouple attached to the reactor. After the reactor is preheated, nitrogen is switched off, replaced by steam and the reactor is submerged into the fluidized bath. Pretreatment in steam is continued for 15 minutes. Then reactor is removed from the bed, steam is replaced by a flow of nitrogen and the reactor is allowed to cool. When there is no detectable moisture at the outlet of the reactor the valves directly before and after the reactor are sealed. The reaction tube is disconnected from the coil and removed from the system.

The yield of volatile matter during pretreatment is determined in a separate experiment. About one or two grams of coal is used for this test. A weighed coal sample of known moisture content is loaded into a boat, 2-1/2 inches long and 1/4 inch wide. This boat is then placed in a 1/2 inch diameter reactor tube and a pretreatment is carried out the same way as described above. After treatment, the sample is weighted again and yield of the volatiles is determined from the weight loss.

In this work, Illinois No.6 coal is pretreated at optimum conditions: 340°C and 51 atm (750 psia). At this temperature, pressure was found to have no effect on the yield of volatile matter up to 750 psia (Graff *et al.*, 1988). The dependance of the volatiles yield on steam flow rate was also established (Graff *et al.*, 1988).

If coal is to be pretreated with a zeolite powder, the following procedure is employed: The moisture content is determined separately for coal and molecular sieve. To determine the amount of moisture absorbed by a zeolite, about one gram of the powder is dried in a vacuum oven at 90°C for 18 hours. This time is sufficient to dry the zeolite to a constant weight. Equal amounts of coal and zeolite (both undried) are mechanically mixed together in a glass beaker before the steam pretreatment run is conducted. About 30 grams of the coal/zeolite mixture is loaded into the reactor and is treated in the same way as a coal sample. After the run is completed, zeolite is not separated from the mixture.

2.4.2. Room Temperature Pyridine Extraction.

After steam treatment is completed, the pretreatment reactor is placed in a nitrogen-filled glove bag where the following operations are carried out:

The pretreated coal is removed from the reactor, crushed in a ceramic mortar and weighted. About 1.5 grams of sample are transferred to 250 ml flask for pyridine extraction following the procedure of Graff and Brandes (1987).

2.4.3. Liquefaction Tests.

Slurry liquefaction tests are conducted using tetralin as a hydrogen donor solvent. Before the tests are carried out, tetralin is bubbled with nitrogen for 1 hour to exclude air dissolved in the solvent. The rapid heating liquefaction of steam pretreated coal (or steam pretreated coal/zeolite mixture) is conducted as follows:

Sixty grams of deoxygenated tetralin is placed into the reaction vessel and the autoclave is sealed. After the system (Figure 2.2) is leak tested with nitrogen at 2000 psia with the bypass line valve open, the reactor is flushed with hydrogen at atmospheric pressure and then heated using an electric furnace and keeping the bypass line valve closed. While the reactor is heated, slurry is prepared in a nitrogen filled glove bag from the pretreated coal and the solvent. The slurry is

made of 1/3 part of coal and 2/3 parts of solvent using about 20 grams of coal. (In some experiments, where noted, slurry was made of equal amounts of coal and solvent.) When the autoclave has been preheated to operating temperature, two syringes are filled, one with about 40 ml of slurry and one with 20 ml of solvent. The syringes are attached to the loading line, the loading valve is opened, and the slurry reservoir is sequentially filled with 10 ml of solvent, coal slurry (full contents of the syringe), and, finally, 10 ml of solvent. The loading valve is then sealed and hydrogen at the desired pressure is applied. This causes the rupture disc to burst, injecting slurry into the reactor and pressurizing the system. The valve above the reservoir is then closed. The reaction temperature is maintained with $\pm 5^{\circ}\text{C}$ accuracy. The run continues for 30 minutes measured from coal injection. Then the heater is turned off, removed from the autoclave and the run is terminated. When the reactor has cooled to ambient temperature the magnetic stirrer is turned off. After the reaction gas is vented, the autoclave is opened and liquid product analysis are performed.

For the tests where exposure of pretreated coal to air is desired, all manipulations of with coal are done under ambient air. If liquefaction of raw coal is to be carried out slurry can also be prepared under ambient air. In slow heating liquefaction the same procedure is employed except that slurry is injected when the autoclave is at room temperature. The reaction mixture is then heated to operating temperature in approximately 35 minutes and the run continued for additional 30 minutes.

2.4.4. Liquid Product Characterization.

After the autoclave has reached atmospheric pressure, it is opened and the contents transferred to a weighed predried cellulose Soxhlet thimble (double thickness). Material remaining in the reactor and on the stirrer is washed off with 200 ml of hexane and transferred to the same thimble. After the liquid has drained off at ambient temperature, the thimble is placed in a Soxhlet extraction apparatus. The residue is first extracted with hexane for 18 hours to obtain the oil yield. After the thimble has been dried in the vacuum oven and weighed, the asphaltenes are extracted with toluene for 18 hours and the dried residue is weighed. Finally, the residue is

extracted with THF for 18 hours to obtain the preasphaltenes yield.

The amount of coal injected into the reactor is calculated as the difference between the amount of coal used to prepare the slurry and the amount of coal not loaded into the autoclave. To determine the amount of the latter unloaded coal, the slurry remaining in the syringe after injection is transferred to a weighed filter paper. Syringes and injection line are washed with hexane. The washings are then filtered through the same filter paper. The content of the filter paper is dried in air, then placed in the vacuum oven at 90°C and dried to a constant weight. The weight of this unloaded coal is subtracted from the weight of coal used to prepare the slurry.

Yields are calculated based on the raw coal maf charge. The amount of coal charged for pretreatment and then used in the liquefaction is determined based on amount of treated coal loaded into the autoclave and on the amount of volatiles lost during pretreatment. The yield of hexane solubles include liquefaction gas and oils. According to Joseph (1991), the gas yield from raw Illinois No.6 coal in slow heating liquefaction is less than 5% (400°C, 1100 psia hydrogen, 30 minutes).

2.4.5 Gas Analysis.

In later runs, analyses of liquefaction gases were conducted by mass-spectrometer. After completion of the liquefaction run and cooling of the reactor to room temperature, gas from the autoclave was vented and a sample of this stream fed by capillary into the mass-spectrometer (Section 2.3.2).

The mass spectrometer was calibrated for quantitation. Several preliminary mass scans of the reaction gas were taken and the major components were identified as CO, CO₂, H₂S, CH₄, C₂H₆, C₂H₄, C₃H₆, C₄H₁₀. A calibration mixture was made up of these compounds in hydrogen based on concentrations reported in the literature (Serio *et al.*, 1992b). In addition, neon was added as a reference gas. No attempt was made to analyze for hydrogen sulfide as adsorption of this gas on walls of the transfer line and other internal surfaces makes its quantitation unreliable. The

composition of the calibration mixture is as follows:

Component	CO	CH ₄	Ne	C ₂ H ₄	C ₃ H ₈	C ₂ H ₆	C ₃ H ₆	C ₄ H ₁₀	CO ₂	H ₂
Concentration, mol %	0.483	0.530	0.930	0.466	0.452	0.469	0.462	0.473	2.820	bal.

The reference gas neon was also added to the hydrogen used for liquefaction in the amount of 0.464 mole %.

The mass spectrometer is used to determine N_i , the total number of moles of each component i flowing through the vent line during the entire time of discharge of the autoclave

$$N_i = \int F C_i dt \quad (1)$$

where F is the total vent gas flow rate (volume/time), and C_i is the concentration of component i (mole/volume).

The peak intensity (I_i) obtained for component i depends on the sensitivity of the mass spectrometer to that component, but is proportional to the rate of flow of that material into the instrument. Since the capillary samples the vent gas at constant (atmospheric) pressure, the flow rate of component i into the mass spectrometer is proportional to its concentration in the vent line. Therefore

$$I_i = C_i / k_i \quad (2)$$

The response constant k_i takes into account both the sensitivity of the mass spectrometer and the characteristics of the sampling capillary.

Combining equations (1) and (2) at constant vent gas flow rate gives

$$N_i = k_i F \int I_i dt \quad (3)$$

The integral $\int I_i dt$ (in arbitrary units) is computed by integrating the peak intensity for component i over the entire time of venting of the mass spectrometer. Dividing Equation 3 by the same equation written for neon

$$\frac{N_i}{N_{Ne}} = K_i \frac{\int I_i dt}{\int I_{Ne} dt} \quad (4)$$

where K_i is the ratio of the response constant k_i to that for neon. The use of Equation 4 requires only that the vent gas flow rate be constant, its value need not be known.

The response factor for each component is determined by the application of Equation 4 to a flow of the calibration mixture through the vent line. In that case N_i/N_{Ne} is equal to the ratio of the concentrations of the two substances.

When analyzing the gaseous product, the gas is released from the cooled autoclave into the vent line previously flushed with hydrogen. Initially, the autoclave pressure is between 750 and 850 psia. The peak intensities of the selected compounds are monitored continuously for 20 minutes at a constant gas flow rate. At the end of the analysis the autoclave pressure is below 100 psia.

To apply Equation 4 to the calculation of liquefaction gas yields, N_{Ne} is determined from the autoclave charging pressure, temperature, and volume using the perfect gas law.

3. MODEL COMPOUND STUDIES

3.1. Experimental Methods

According to Chawla *et al.* (1990), the α compounds, α -benzylnaphthyl ether (α -BNE) and α -naphthylmethyl phenyl ether (α -NMPE), are more reactive at relatively mild temperatures than the β compounds, β -benzylnaphthyl ether (β -BNE) and α -naphthylmethyl phenyl ether (β -NMPE). For this reason, the steam treatment studies in this work focused on the reactions of α compounds.

Ether model compounds α -NMPE and α -BNE were synthesized according to the procedures described by Maslak and Guthrie (1986) along with 9-phenoxyphenanthrene, the compound extensively studied by Siskin *et al.* (1993), (Figure 3.1).

Figure 3.1. Ether Model Compounds.

The model compounds are reacted in steam and under inert gas utilizing the same method as in coal pretreatment (Sections 2.3.1, 2.4.1). The experiments are conducted in a stainless steel tubular reactor of 2 inch length and 3/8 inch OD. The reactor is connected to a steam supply line and submerged into the fluidized bed preheated to desired temperature. Since the compounds are volatile, the reactor scheme utilizing continuous flow of steam is replaced by non-flow open operation where steam at 51 atm is continuously supplied into the reactor equipped with an inlet

valve on one end and a cap on the other. This semi-flow reactor arrangement was first tested using Illinois No.6 coal. The pyridine extraction yield obtained from coal pretreated in non-flow open reactor agreed with results obtained in continuous flow operation. Since the reactor walls may effect conversion, model compounds tests are carried out in both stainless steal and Pyrex-lined vessels. If the compound is to be treated under inert atmosphere, steam is replaced by a flow of nitrogen gas supplied from a high pressure tank.

The steam (or inert gas) treatment experiments are carried out at 320°C and 51 atm (750 psia) for 15 minutes using 100-300 mg of material. After the run is completed the steam (or nitrogen) pressure is increased by about 2 atm, the reactor is sealed and detached from the steam supply assembly. After the treatment vessel is cooled to the room temperature, the reaction mixture is taken for analysis.

The series of treatment experiments with α -NMPE and α -BNE are also conducted in the presence of 5Å zeolite to prevent the formation of isomeric starting material. The model compounds are mechanically mixed with zeolites using 1:5 compound to zeolite ratio. The experiments are carried out following the same procedure as where no zeolites present. The effect of zeolite on the model compound cleavage product is studied in steam and in inert atmosphere using only the stainless steel reaction vessel. The glass lined reactor is not used for coal/zeolite treatment experiments.

Model compounds are also reacted at a high pressure when water is present in liquid phase. It has been previously discovered by Siskin *et al.* (1993) that 9-phenoxyphenanthrene, while unreactive at 315°C and 350°C in inert medium, can be cleaved at this temperatures in water. The aquathermolysis is carried out according to the procedure described by Siskin *et al.* (1993) in a 11 ml stainless steal reaction tubing bomb using from 100 mg to 1g of material. The desired amount of model compound and 7 ml of deoxygenated deionized water is placed in the reactor under inert atmosphere and the vessel is sealed. The reactor is then submerged in a fluid bath at 315°C for 1 hour. At this reaction temperature a liquid water phase is maintained and pressure reaches 105.1 atm (1545 psia).

3.2. Product Analysis.

The reaction products are analyzed using the following instrumental methods: nuclear magnetic resonance (nmr) spectra recorded on Bruker 200 or 300MHz instruments in CDCl_3 as solvent. High performance liquid chromatographic (HPLC) analysis are carried out on a Hewlett-Packard 1090 chromatograph using a μ -Porasil column 4.5 x 250 mm. Gas chromatography-chemical ionization mass spectral analyses (GC-CIMS) are conducted on a Finnigan SSQ-70 instrument using ammonia as reagent gas. Preparative GC experiments are carried out on a Hewlett-Packard 5890 gas chromatograph equipped with a thermal conductivity detector.

The condensable reaction products are washed from the reactor using 4 x 3 ml portions of methylene chloride (CH_2Cl_2) per 0.1 gram of sample pyrolyzed. The methylene chloride is then evaporated under a stream of nitrogen to establish recovery yield. The material obtained is then analyzed by GC-CIMS using a fused silica capillary column (Supelco). The ^1H nmr spectrum and GC-CIMS of the mixture is also determined to verify that no decomposition occurs during separation step. If decomposition of the product is detected the mixture is separated by preparative GC on a porous polymeric column Tenax-GC (Alltech). The peaks obtained from GC runs are collected and pure compounds undergo ^1H , ^{13}C nmr and CIMS analysis.

4. EXPERIMENTAL RESULTS

4.1. Liquefaction Studies.

4.1.1. Coal.

Liquefaction runs were conducted with Illinois No. 6 coal at three sets of conditions:

High severity: 400°C, 1500 psia, 30 minutes,

Low severity a: 350°C, 1500 psia, 30 minutes, and

Low severity b: 385°C, 1500 psia, 15 minutes.

The first set of liquefaction runs were conducted at the high severity conditions of 400°C and 1500 psia for 30 minutes. The results are shown in Table 4.1.1, classified according to the liquefaction conditions employed. All yields are calculated based on moisture, ash free (maf) raw coal charge. Pyridine extraction yields include the volatiles lost in pretreatment. Oil yield from the liquefaction experiments also includes gaseous products produced.

The steam pretreatment and liquefaction experiments were conducted using a coal sample CFI No.27 (A and B) of Illinois No.6 coal. First, raw coal was examined under slow (run C2) and rapid (runs 2 and 8) heating liquefaction conditions. Then, a series of tests with steam treated coal were conducted: runs 6, 7, 9 and 12 were carried out under rapid heating conditions. However, runs 7 and 9 were made with tetralin from a bottle which was previously opened and not protected against oxygen absorption. The importance of preventing the exposure of pretreated coal to oxygen (run 11) and the importance of rapid heating (run 10) for the liquefaction were also demonstrated.

The total yield of liquid product from raw coal obtained at rapid heating conditions appears to be slightly lower than at slow heating due to the longer overall reaction time in a slow heating run. The yield of oils, however, is increased and preasphaltene yield is decreased.

Table 4.1.1.
High Severity Liquefaction of Illinois No.6 coal. Sample 27 (A, B).
(400°C, 1500 psia, 30 minutes)

Run No.	Conditions	Conversion (%wt)				Pyridine Extraction Yield(%wt)
		Total	Oils	Asph.	Preasph.	
C2	raw coal slow heating	81.6	37.0	16.9	27.7	18.3
2	raw coal	73.8	42.2	10.0	21.6	----
8	rapid heating	80.0	48.7	16.7	14.6	20.3
10	steam treated coal slow heating	73.8	35.2	14.4	24.2	35.1
6	steam treated coal	85.7	60.1	17.2	8.4	----
12	rapid heating	79.3	55.8	14.7	8.8	34.7
7	steam treated coal, rapid heating, tetralin contains	91.6	56.0	14.2	21.7	35.2
9	dissolved oxygen	85.2	47.5	17.3	20.4	38.9
11	steam treated coal, exposure to air, rapid heating	66.3	38.6	19.8	7.9	32.4

No improvement in the yields was observed when steam pretreated coal was subjected to the liquefaction under slow heating. Compared to raw coal, a lower total yield as well as a lower yield of each fraction were obtained.

Rapid heating liquefaction of steam pretreated coal with deoxygenated tetralin showed a definite improvement in oil yield and a decrease in preasphaltene yield. In the case where tetralin was not protected against oxygen absorption, a pronounced increase in preasphaltene yield was observed.

When steam treated coal was deliberately exposed to ambient air for one hour before slurrying with deoxygenated tetralin the pretreatment effect deteriorated. The oil yield decreased even below the value for raw coal with rapid heating. Total yield also decreased. Asphaltene yield is higher and preasphaltenes yield is lower when an exposure to air was prevented.

In rapid heating liquefaction of raw and steam pretreated coal, a potentially important difference in temperature history was observed after injection of coal into the autoclave. When pretreated coal was injected (run 12) the temperature drop was 41°C . In raw coal liquefaction, temperature dropped by 88°C in run 2 and by 71°C in run 8. A large temperature drop (60°C) was observed in a simulated test in which solvent without coal was injected. After an initial temperature drop, caused by injection, the recovery time was substantially shorter for steam pretreated coal. In run 12, for example, temperature reached its initial value in 1 minute. After raw coal was injected, temperature was recovered in 2.5 minutes. Moreover, the rate of recovery was about the same for raw and steam treated coal for the first 30 seconds, then the recovery process for raw coal slowed down. The absence of a large temperature drop as well as a short temperature recovery time may indicate the occurrence of exothermic reactions in pretreated coal under hydrogenation conditions.

Several additional high severity runs were made with a different batch of Illinois No. 6 coal (CFI No. 31A). This batch gave slightly different results (Table 4.1.2) than the previous one (No. 27, Table 4.1.1) In rapid heating liquefaction, steam pretreatment of sample 31A greatly enhanced

the total yield and the oil yield. These yields were only slightly diminished by slow heating. Exposure of steam treated coal to air also decreased the total yield and the oil yield and, in addition, raised the yield of preasphaltenes.

Although coal samples 27 A,B and 31A respond similarly to steam pretreatment, each must be considered separately because the baseline case (raw coal, rapid heating) is different for each batch. Evidently, these liquefactions are affected by some rather subtle differences in coal properties.

Table 4.1.2.
High Severity Liquefaction of Illinois No.6 coal. Sample 31 A.
(400°C, 1500 psia, 30 minutes)

Run No.	Comments	Conversion (wt%)				Pyridine Extraction Yield(wt%)
		Total	Oils	Asph.	Preasph.	
22	raw coal rapid heating	72.3	39.2	13.2	19.9	20.9
24	steam treated coal	81.4	51.9	13.6	18.6	31.2
25	slow heating	84.9	55.0	15.5	14.4	32.6
23	steam treated coal rapid heating	88.9	57.8	13.7	17.5	33.1
26	steam treated coal, rapid heating, exposure to air	85.7	48.4	12.0	25.3	31.2

The second set of the liquefaction tests with Illinois No.6 coal was conducted under conditions of reduced severity (low severity a): the reaction temperature was decreased to 350°C and the

pressure and the reaction time were kept unchanged (1500 psia, 30 minutes). Raw and steam pretreated coal were tested under rapid heating conditions. In addition to the liquid product characterization, the gas formed in the process was also analyzed. Liquefaction yields are shown in Table 4.1.3. and the gas composition in Table 4.1.4.

Having the gas yield makes it possible to calculate the oil yield. The yield of hexane solubles determined according to the liquid product characterization procedure, is difference between the weight of the starting DAF coal sample and the weight of the residual dry solid after hexane extraction. In addition to the oils extractable by hexane, this weight loss is comprised of the volatiles lost in steam pretreatment (8 wt% at the conditions used) and gas formed in the liquefaction process (determined by mass spectrometry). This breakdown of the hexane solubles is given in Table 4.1.3.

All yields are calculated based on moisture, ash free raw charge. Gas composition is given based on the amount of liquefaction gas produced. The pyridine extraction was carried out prior to each liquefaction run and yields were determined to be: 20.0 % in run no.28 (raw coal), 30.7 % and 32.3 % in runs 29 and 30 (steam treated coal).

Table 4.1.3.

Low Severity a Rapid Heating Liquefaction of Illinois No.6 Coal. Sample 31 B.C.
(350°C, 1500 psia, 30 min)

Run No.	Conditions	Conversion (wt %)					
		Total (liquid + gas)	Hexane Solubles Total	Gas	Oils	Toluene Solubles Asphaltenes	THF Solubles Preasphalt
28	raw coal	73.9	47.4	5.52	41.88	10.9	15.6
29	steam treated	71.3	47.1	13.52	33.58	9.5	14.7
30	coal	70.9	42.6	12.02	30.58	11.0	17.0

These results, obtained under reduced severity conditions, show no improvement in the

liquefaction yields between raw and steam pretreated coal. (That the pretreatments were successful is confirmed by the increased pyridine extraction yields.) Steam pretreatment did, however, increase gas yield at the expense of oil. The liquefaction gas composition shows a decrease in the yield of carbon dioxide and an increase in the yield of propane and butane for steam treated coal.

Table 4.1.4.
Low Severity a Rapid Heating Liquefaction Gas Composition.
(350°C, 1500 psia, 30 min)

Run No.	Conditions	Gas Yield, wt %		Liquefaction Gas Composition (%wt)						
		Total	Liq. Gas	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈ +C ₄ H ₁₀
28	raw coal	5.52	5.52	1.77	74.12	8.32	3.03	0.80	2.77	9.19
29	steam	13.52	5.52	1.44	63.39	6.88	3.81	0.79	6.00	17.69
30	treated coal	12.02	4.02	1.44	63.08	10.02	4.08	1.19	3.35	16.84

A possible explanation for the lack of improvement in yields after steam pretreatment may be found in the temperature history in the autoclave. The coal slurry (made of raw or steam treated coal) was injected into the autoclave preheated to 350°C. In all cases the injection caused the temperature to drop below 300°C. This was followed by a recovery to 350°C in about 1.5 minutes. Consequently, sample has passed through a region below 360°C where retrogressive reactions occur, resulting in low yield of the liquid product and in a higher yield of gas. Perhaps, the chosen reaction temperature itself, 350°C, is where retrogressive reactions occur.

To keep the reaction temperature higher after slurry injection and during the reaction, the low severity liquefaction conditions were modified (low severity liquefaction b). The temperature was increased to 385°C (which is above the upper limit of pretreatment), the reaction time reduced to 15 minutes, and the pressure was left unchanged at 1500 psia. The procedure was also slightly

modified: the autoclave was initially preheated to 400°C. After the temperature drop caused by the slurry injection, the temperature was raised to 385°C.

A third series of liquefaction tests were conducted under these low severity b conditions. The results are shown in Table 4.1.5. (yield of liquid product) and 4.1.6. (gas composition). In all rapid heating liquefaction experiments the reaction temperature never dropped below 320°C. Recovery time was between 1.5 minute for raw coal and 1 minute for steam treated coal. The pyridine extraction yields were determined for each type of coal sample used in the liquefaction experiments, raw, treated and treated exposed to air, and were found to be 20.0 %, 32.5 % and 23.3 % respectively (average values).

Table. 4.1.5.
Low Severity b Liquefaction of Illinois No.6 Coal. Sample 31 B.C.
(385°C, 1500 psia, 15 min)

Run No.	Conditions	Conversion (% wt)					
		Total (liquid + gas)	Hexane Solubles			Toluene Solubles	THF Solubles
			Total	Gas	Oils	Asphaltenes	Preasphalt
32	raw coal	71.6	27.7	13.7	14.0	17.9	26.0
33	rapid heating	71.3	26.5	15.5	11.0	20.2	24.6
31	steam treated coal	71.3	41.8	11.9	29.9	16.4	19.3
34	rapid heating	70.9	38.9	10.3	28.6	15.8	21.5
35	steam treated coal,	71.3	30.5	14.9	15.6	18.9	23.3
36	exposure to air	70.9	31.2	13.8	17.4	17.1	23.1
37	steam treated coal	71.3	35.2	16.4	18.8	20.0	19.7
38	slow heating	70.9	34.1	19.2	14.9	18.6	27.2

These low severity liquefaction tests show a strong improvement in the yields of liquids resulting from steam pretreatment under rapid heating conditions (runs no. 31 and 34 compared to runs no. 32 and 33). The yields of hexane solubles were increased with a slight reduction in the total gas make. Remarkably, the oil yields are doubled while preasphaltenes are reduced. This improvement in the liquid quality occurred together with an increase in the total yield of liquids.

Exposure of steam treated coal to air (runs no. 35 and 36) resulted in a drop in the yield of hexane solubles and oils almost to the level of raw coal. The total yield of liquids also decreased.

In slow heating liquefaction (runs no. 37 and 38), the total yield of liquids has dropped compared to rapid heating, but is still higher than raw coal under rapid heating. Of the three liquid fractions, only hexane solubles are distinctly affected by heating rate. Under slow heating conditions the highest total gas make was observed, the total yield of hexane solubles and oils alone have intermediate value between raw and steam treated coal under rapid heating. The higher total yield under slow heating liquefaction may result from a longer reaction time (it takes up to 30 minutes to preheat autoclave to 385°C), since the liquefaction process starts before the reactor temperature reaches 385°C, even under low pressure.

Comparing the yields of liquefaction gas (Table 4.1.6), the lowest yield among treated samples was observed under rapid heating and the highest under slow heating, the sample exposed to air has an intermediate value. A significant reduction in liquefaction gas yields from steam treated coal compared to raw coal can be explained by the volatile matter, lost in the steam pretreatment process, which otherwise contributes into the amount of liquefaction gas produced. Steam treatment and heating rate also affect the liquefaction gas composition. More C₃-C₄ hydrocarbon gases were obtained from steam treated coal. The highest yield of carbon dioxide was produced from raw coal. It is possible that a significant amount of carbon dioxide is formed in the pretreatment process, decreasing its yield in the liquefaction gas from treated coal in contrast to the untreated. Exposure of treated coal to air also causes an increase in the yield of CO₂.

Table 4.1.6.
Low Severity b Liquefaction Gas Composition.
(385°C, 1500 psia, 15 min)

Run No.	Conditions	Gas Yield, %wt		Liquefaction Gas Composition (%wt)						
		Total	Liq. Gas	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈ +C ₄ H ₁₀
32	raw coal	13.73	13.73	2.34	51.81	14.86	5.19	1.34	3.12	21.34
33	rapid heating	15.50	15.50	1.75	54.45	17.24	5.94	1.42	4.03	15.17
31	steam trtmnt,	11.95	3.95	1.51	40.59	15.38	6.47	2.43	9.12	24.50
34	rapid heating	10.29	2.29	1.40	39.44	19.53	7.82	2.31	5.45	24.05
35	steam trtmnt,	14.93	6.93	1.38	48.15	20.97	6.85	2.27	5.06	15.32
36	expos. to air	13.86	5.86	1.04	46.23	19.19	5.59	1.99	4.70	21.26
37	steam trtmnt,	16.44	8.44	1.08	40.31	24.19	6.18	2.28	4.97	20.99
38	slow heating	19.16	11.16	0.96	40.23	23.10	6.73	2.48	4.82	21.68

The heating rate does not show any effect on the production of CO₂. More methane was produced under slow heating conditions, compared to rapid heating, contributing to the highest overall gas yield. Increased production of CO₂ as well as CH₄ may indicate the occurrence of retrogressive reactions (Solomon *et al.* 1990).

Comparison of the gas composition at the two low severity liquefaction conditions (Tables 4.1.4. and 4.1.6.) demonstrates that the amount of carbon dioxide produced at 350°C is substantially higher than the yields of other constituents, while at 385°C the relative amounts of CO₂ are reduced.

Summarizing these results, the behavior of Illinois No.6 coal in low severity liquefaction (385°C, 15 min, 1500 psia) follows the same trends as when higher temperature and longer reaction time

are used (400°C, 30 min, 1500 psia). The best results, highest total yield and yield of hexane solubles, are obtained from steam pretreated coal under rapid heating conditions. Moreover, the improvement in the hexane solubles is achieved as a result of an increase in the yield of oils and a decrease in gas yield (at least at low severity). The liquefaction yields (total yield and hexane solubles) obtained from steam treated coal under slow heating conditions have intermediate values between raw and steam treated coal under rapid heating. When steam treated coal is deliberately exposed to air, the total yield drops to the level of raw coal (rapid heating), the yield of hexane solubles is slightly higher than from raw coal under rapid heating but does not exceed the value obtained under slow heating.

4.1.2. Coal/Zeolite Mixtures.

Liquefaction tests were also conducted with steam pretreated Illinois No.6 coal mixed with zeolite powder under rapid heating conditions. The runs were carried out at 400°C and 1500 psia. Three types of zeolite, 5Å, 4Å, and 13X, were tested. Results are listed in Table 4.1.7. The molecular sieve 5Å was tested at two different coal to zeolite ratios: 1:1 (runs 13, 14 and 16) and 10:1 (run 17). Other zeolites, 4Å and 13X, were used at 10:1 ratio (runs 20 and 21).

The highest total conversion yields (95.5-98.1%) were obtained in runs 13, 14 and 16 where an equal weight of a 5Å zeolite was added to the coal sample during the steam pretreatment stage. Although consistently high yields of oils (51-63.8%) were obtained in the presence of zeolite, they are not higher than the yields obtained without zeolites. However, yields of asphaltenes and preasphaltenes are increased.

When 5Å zeolite is added to coal in proportion 1:10 the effect is less pronounced. There is, however, a slight increase in the total yield of liquids due to the increase in the yields of asphaltenes and preasphaltenes. Since the coal/zeolite mixture is prepared by simply mixing the two powders, it is possible that the surface of the zeolite particle is not fully available for reaction. The decrease in yields of liquids with reduction of the zeolite/coal ratio in the mixture can be, therefore, attributed to the lack of contact between zeolite "active sites" and coal.

Table 4.1.7.

Rapid Heating Liquefaction of Steam Treated Illinois No.6 Coal. Sample 27 C
and Zeolite Mixtures.

Run No.	Comments	Total	Conversion (wt%)			Pyridine Extraction Yield(wt%)
			Oils	Asph.	Preasph.	
5Å Zeolite						
13	coal:zeolite=1:1	95.5	51.2	25.0	19.3	40.1
14	"	96.2	53.5	17.3	25.4	33.0
16	"	98.1	63.8	18.8	15.5	35.0
17	coal:zeolite=10:1	88.0	51.4	19.4	17.2	35.0
13X Zeolite						
20	coal:zeolite=10:1	84.7	45.8	22.7	16.2	26.7
4Å Zeolite						
21	coal:zeolite=10:1	89.4	53.9	15.8	19.7	33.0

The results obtained from liquefaction of steam pretreated coal mixed with 4Å zeolite are comparable to those obtained with 5Å zeolite (at the same coal/zeolite ratio). Both 5Å and 4Å zeolites have a similar framework structure and Si/Al ratio close to one.

The use of the zeolite 13X was less successful (run 20). The pyridine extraction yield and the oil yield are at the raw coal level. This zeolite has larger Si/Al ratio than zeolite 5Å and, therefore, is more organophilic. The zeolite 13X can absorb up to 264 molecules of water and its pore size is two times larger than 5Å molecular sieve. The zeolite pores can retain extraction solvent and moisture resulting in an artificial decrease of pyridine extraction and liquefaction yields.

Results obtained with 4Å and 5Å zeolites suggest that zeolite assists in breaking down the macromolecular network in coal. In petroleum cracking processes, straight-chain reactants are selectively converted in the presence of a small pore zeolite despite the fact that the reactivity of branched-chain reactants is greater. By analogy, zeolites might enhance the reactivity of certain structural fragments in coal.

4.2. Model Compounds Studies.

A series of tests were conducted with α -benzylnaphthyl ether (α -BNE) and α -naphthylmethyl phenyl ether (α -NMPE) using two types of reaction vessel, stainless steel and glass lined. Both ethers were treated in steam and in a flow of nitrogen at 51 atm (750 psia) and $322 \pm 3^\circ\text{C}$. The condensed reaction product was fractionated by preparative GC and analyzed by combination of ^1H and ^{13}C nmr, and CI-MS. The major reaction products of α -benzylnaphthyl ether are 1-naphthol, isomeric starting material 2-benzyl-1-naphthol and 4-benzyl-1-naphthol, and minor products (Figure 4.1). The presence of toluene (a volatile compound) in the reaction product was detected, prior to GC separation, by mass spectrometry. The reaction products of α -naphthylmethyl phenyl ether are phenol, 1-methyl naphthalene, 1-naphthaldehyde, and isomeric starting material o-naphthylmethyl phenol and p-naphthylmethyl phenol (Figure 4.2).

Figure 4.1. Products Obtained from the Pretreatment of α -Benzylnaphthyl Ether.

Figure 4.2. Products Obtained from the Pretreatment of α -Naphthylmethyl Phenyl Ether.

Treatment runs in the stainless steel vessel were conducted using 200 mg of model compound; when the reaction vessel was glass-lined the amount of material was reduced to 100 mg. The results are shown in Table 4.2.1 for α -BNE and in Table 4.2.2 for α -NMPE where the reaction product distributions are based on the amount of condensed material recovered.

Table 4.2.1.

Pretreatment of α -Benzylnaphthyl Ether.

Product Distribution in Steam and in Inert Atmosphere (wt %).

Product	1-naphthol	isomeric starting material	recovered starting material	minor product
Conditions
metal	41	53	0	6
STEAM				
glass	37	58	0	5
metal	42	49	0	11
INERT				
glass	40	52	0	8

Table 4.2.2.

Pretreatment of α -Naphthylmethyl Phenyl Ether.Product Distribution in Steam and in Inert Atmosphere (wt %).

Product	phenol	1-methyl naphthalene	1-naphth aldehyde	recovered starting material	isomeric starting material
Conditions
metal	23.1	22.5	4.3	9.0	41.2
STEAM					
glass	6.3	17.1	6.0	14.2	56.4
metal	22.4	25.4	9.2	0	43.0
INERT					
glass	24.2	16.5	7.3	0	52.0

About half of the product obtained from α -BNE as well as from α -NMPE consists of isomeric starting material both in steam and in inert atmosphere. A slightly larger amount of isomeric starting material and less cleavage product is obtained in a glass-lined reactor from α -BNE. In case of α -NMPE the difference is more pronounced, especially in steam, possibly due to a catalytic effect of metal wall surface. A significant difference between glass and metal reactors, however, was not observed. Still, the glass-lined reactor is considered unsuitable for the model compound treatment since it promotes undesired isomerization.

The isomeric starting material is produced by recombination of benzyl radicals formed by homolysis. The radical recombination reaction, therefore, competes with the formation of

cleavage product and requires control. It is possible that the model compound has far more freedom to isomerize than similar structures in a coal matrix.

The use of zeolite was tested as a way to control the reaction pathway by reducing molecular mobility. Zeolite can affect the product distribution by formation of carbenium ion intermediates rather than radicals. Selective adsorption of the reactants, carbenium ions and/or products on the zeolite surface as well as steric and transport effects can modulate the product distribution and, therefore, may inhibit pathways to isomerized product.

The model compounds α -BNE and α -NMPE mixed with 5Å zeolite were reacted in steam and in a flow of nitrogen at $322 \pm 3^\circ\text{C}$ and 51 atm (750 psia). The material to be reacted was prepared by mixing 100 mg of model compound with 500 mg of zeolite. The mixture was then placed into a stainless steel reaction vessel and the run was conducted in the same way as previously in the absence of zeolite. The reaction products are shown in Table 4.2.3 for α -BNE and in Table 4.2.4 for α -NMPE.

Table 4.2.3.

Pretreatment of α -benzylnaphthyl ether in the Presence of 5Å Zeolite.

Product Distribution in Steam and in Inert Atmosphere (wt %).

Product Conditions	1-naphthol	isomeric starting material
STEAM	92	0
INERT	76	8

Table 4.2.4.

Pretreatment of α -Naphthylmethyl Phenyl Ether in the Presence of 5Å Zeolite.

Product Distribution in Steam and in Inert Atmosphere (wt %).

Product Conditions	phenol	methyl- naphthalene	naphth- aldehyde	isomeric starting material
STEAM	29	19	6.0	44
INERT	21	19	6.6	52

In the case of α -BNE, isomerization is successfully suppressed by zeolites. Only 8% of the product is isomerized starting material under inert atmosphere and none is found under steam. The effect of zeolite addition to α -NMPE was less dramatic. It is to be noted, however, that α -NMPE is the less reactive compound (Chawla *et al.*, 1990).

For both α -BNE and α -NMPE only a small difference in conversion and product distribution were observed when steam was changed to inert gas. However, the otherwise thermally stable 9-phenoxyphenanthrene, extensively studied by Siskin *et al.* (1991, 1993), can be cleaved in the presence of liquid water at 315°C. Hence, it is of interest to determine if liquid water (aquathermolysis) is generally required to cleave ethers. Accordingly, tests under aquathermolysis conditions were carried out using α -NMPE as well as 9-phenoxyphenanthrene. The reaction products obtained from cleavage of 9-phenoxyphenanthrene are shown on Figure 4.3.

Figure 4.3. Aquathermolysis of 9-Phenoxyphenanthrene.

The results of Siskin *et al.* (1991, 1993) for aquathermolysis of 9-phenoxyphenanthrene were successfully duplicated giving complete conversion of the diaryl ether to phenol and phenanthrol. When the reaction time was reduced from 1 hour to 15 minutes (the reaction time employed in the coal pretreatment by steam), the conversion was incomplete. The starting material (not isomerized) accounted for 83 % of the material recovered (recovery was close to 100%). Clearly, the ether linkages in coal are more reactive than 9-phenoxyphenanthrene even at the lower water density of steam pretreatment.

Under coal pretreatment conditions (325°C, 750 psia, 15 minutes), both with and without 5Å zeolite, 9-phenoxyphenanthrene unreactive. The product was approximately 80% rearranged starting material with the structure:

Bond cleavage is believed to occur, followed by recombination of the primary fragments to yield isomeric starting material rather than phenol and phenanthrol which would require proton abstraction from water. It is possible that the reaction follows a radical mechanism under low

pressure, even in the presence of steam, rather than the ionic pathway proposed by Siskin *et al.* for the aquathermolysis.

The studies were then conducted with α -NMPE under conditions of aquathermolysis. The results are shown in Table 4.2.5. along with values obtained under steam treatment conditions and under inert atmosphere with and without 5Å zeolite.

Table 4.2.5.
Conversion of α -Naphthylmethyl Phenyl Ether (% wt).

Product Conditions	phenol	methyl naphthalene	naphth- aldehyde	isomeric starting material	starting material
Inert	22.4	25.4	9.2	43.0	0.0
Steam	23.1	22.5	4.3	41.2	9.0
Inert, Zeolite	21.0	19.0	6.6	52.0	0.4
Steam, Zeolite	29.0	19.0	6.0	44.0	2.0
Aquathermolysis	20.0	8.0	7.0	65.0	0.0

In all cases there is a substantial amount of isomeric starting material present. The major difference between results obtained at the conditions of aquathermolysis and obtained at low pressure (750 psia) is in the yield of methyl naphthalene and isomeric starting material. When water is present in the reactor in the liquid phase, the amount of methyl naphthalene is greatly reduced while the yield of isomeric starting material is increased.

α -NMPE is, evidently, a poor model for ether bonds in coal since its course of thermolysis is

little affected by the presence of water even when the liquid phase is present. 9-Phenoxyphenanthrene is a better model, at least at aquathermolysis conditions, cleaving only in the presence of water, and then almost quantitatively. Cleavage by aquathermolysis appears to have considerable discriminatory power in identifying coal-like ether linkages in model compounds.

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