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STEAM PRETREATMENT FOR COAL LIQUEFACTION

by

Olga Ivanenko

A dissertation submitted to the Graduate Faculty in Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

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Abstract

STEAM PRETREATMENT FOR COAL LIQUEFACTION

by

Olga Ivanenko

Adviser: Professor Robert A. Graff

The objectives of this work are to test the application of steam pretreatment to direct coal liquefaction, to investigate the reaction of model compounds with water, and to explore the use of zeolites in these processes.

Previous work demonstrated the effectiveness of steam pretreatment in a subsequent flash pyrolysis. Apparently, subcritical steam ruptures nearly all of the ether cross links, leaving a partially depolymerized structure.

It was postulated that very rapid heating of the pretreated coal to liquefaction conditions would be required to preserve the effects of such treatment. Accordingly, a method was adopted in which coal slurry is injected into a hot autoclave containing solvent. Since oxygen is capable of destroying the pretreatment effect, precautions were taken for its rigorous exclusion.

Tests were conducted with Illinois No. 6 coal steam treated at 340°C, 750 psia for 15 minutes. Both raw and pretreated samples were liquified in deoxygenated tetralin at high severity (400°C, 30 min.) and low severity (a: 350°C, 30 min., and b: 385°C, 15 min.) conditions under 1500 psia hydrogen. Substantial improvement in liquid product quality was obtained and the need for rapid heating and oxygen exclusion demonstrated. Under low severity conditions, the oil yield was more than doubled, going from 12.5 to 29 wt%.

Also chemistry of the pretreatment process was studied using aromatic ethers as model compounds. α-Benzylnaphthyl ether (α-BNE), α-naphthylmethyl phenyl (α-NMPE), and 9-phenoxyphenanthrene were exposed to steam and inert gas at pretreatment conditions and in some cases to liquid water at 315°C. α-BNE and α-NMPE showed little difference in conversion in inert gas and in steam. Hence, these compounds are poor models for coal in steam pretreatment. Thermally stable 9-phenoxyphenanthrene, however, was completely converted in one hour by liquid water at 315°C. At pretreatment conditions mostly rearranged starting material was obtained. Therefore, 9-phenoxyphenanthrene, though less reactive, is a model for ether linkages in coal.

Application of 5Å zeolite suppressed isomerization of α-BNE improving the yield of thermolysis products in steam and in inert gas. Pretreatment and liquefaction of mixtures of coal and zeolites increased yields of asphaltenes and preasphaltenes under both high and low severity conditions.

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INTRODUCTION

Processes for the direct liquefaction of coal have been under investigation for over seventy years. In these processes, coal slurried in donor solvent is heated in contact with hydrogen at elevated pressure. Catalyst may, or may not, be used. A process of this type was developed in 1920's and used by Germany during the Second World War to generate liquid fuels, primarily aviation gasoline. In the U.S., a process for coal liquefaction was first piloted after World War II, but after the 1950's interest in coal derived liquids diminished because of the availability of inexpensive oil and natural gas.

The oil embargo of 1973 revived interest in coal liquefaction as an alternative source of liquid fuel. Several processes were developed to pilot plant scale using three basic technical approaches: Solvent-refining is a noncatalytic method where coal is slurried with solvent and recycle residue at elevated temperature and pressure in the presence of hydrogen. Mineral matter contained in coal promotes coal decomposition and rehydrogenation of donor solvent. The second technical approach is also a noncatalytic coal-donor solvent slurry process, but has a catalytic stage for hydrogenation of the product middle distillate to generate donor solvent. In the third category, catalytic methods employing supported catalysts in various reactor systems are used for better control of process chemistry. In all cases, the liquefaction product is recovered by distillation and/or solvent extraction.

Over the years, yield and quality of coal-derived liquids have been significantly improved. Development of new catalysts resulted in the production of greater amounts of liquids over gas. Technological improvements have made liquefaction products obtained in the former US DOE two-stage pilot plant at Wilsonville, Alabama comparable in quality with those produced from crude oil. Even though this pilot plant scale process was successful, the cost of product in 1994 was $38-40 per barrel compared to $33-35 per barrel for similar quality products derived from crude oil (Moroni, 1994).

The considerable advances in coal liquefaction technology in recent years leading to the production of liquids superior in quality to oil refinery products were achieved mainly by increased consumption of expensive catalyst. Another major factor contributing to the higher price of coal-derived liquids is cost of capital equipment. One of the ways 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 cost savings since the liquefaction will then require less severe conditions. (Low severity conditions are usually defined as temperatures below 350°C and pressures in the range 1000-1500 psi.) Pretreatment methods include low temperature hydrogenation, chemical treatments, solvent swelling, and demineralization. It has been 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 these treatment techniques enhance liquefaction yield at low severity, none has yet been implemented 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 coal-donor solvent slurry liquefaction. An advantage of this method is that steam is among the cheapest reagents and does not leave, bound to the coal structure, undesired chemical residues. To assist in better understanding the changes occurring in coal during pretreatment, model compound reactions under steam treatment conditions are explored.

1. BACKGROUND

1.1. Theory of Coal Structure

It is now generally accepted that coal is predominantly of vegetal origin. Because of this, coal is a non-homogeneous, almost non-volatile, non-crystalline material composed of fossilized plant debris (macerals) and mineral matter. Macerals are microscopically visible components of the organic portion of coal with various physical and chemical properties (Haenel, 1992).

Although coal structure is still imperfectly understood, the organic part is commonly viewed as a three-dimensional cross-linked macromolecular network embedded with relatively small molecules of various structures and molecular weights (Solomon, 1981; Shinn, 1984; Given *et al.*, 1986; Given and Marzec 1988; Derbyshire *et al.*, 1989). These small molecules are called the "mobile phase" and are extractable. The "immobile phase" is composed of macromolecules of aromatic, hydroaromatic and polycyclic structure containing heteroatoms and bound together to form a network. Nuclear magnetic resonance analysis has shown that two different types of hydrogen atoms are associated with the "mobile" and "immobile" phases. According to the method, 30-50% of the protons detected correspond to the "mobile" phase. However, the amount of material extractable by solvents from a coal sample is usually considerably smaller. This fact was explained by ascribing part of the "mobile" hydrogen atoms to sufficiently mobile long side-chains and weaker cross-linked segments of the macromolecular structure.

The macromolecular network is held together by covalent bonds. In addition, non-covalent interactions are considered of great importance (Nishioka and Larsen, 1990; Larsen and Mohammadi, 1990). These links are (in order of decreasing bond strength): ionic bonds, hydrogen bonds, and aromatic-aromatic interactions. These interactions can hold together different coal macromolecular segments and therefore act as cross-links. For lower rank coals the number of non-covalent cross-links is much larger than that of covalent cross-links. For example, the ratio of the hydrogen-bonded cross-links to covalent cross-links of Illinois No.6 coal is reported to be more than 5 (Larsen *et al.*, 1985).

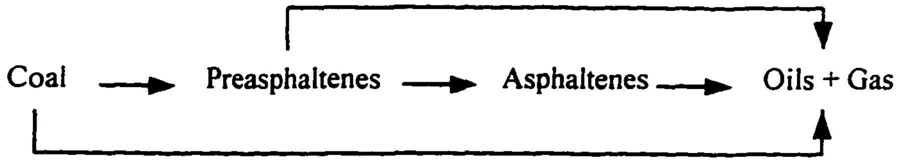
Coal conversion is characterized by the breaking of the coal macromolecular network and the formation of lower molecular weight products. The reactivity of coal in liquefaction processes generally depends on the strength of the bonds linking the lower molecular weight substructures together as well as on the process conditions and the amount of donatable hydrogen available (Stephens and Kottenstette, 1991).

1.2. Mechanism of Thermal Coal Liquefaction

The objective of the coal liquefaction process is to convert coal into a clean liquid fuel. This requires addition of hydrogen and removal of heteroatoms such as sulfur, nitrogen, and oxygen. Hydrogen addition is accomplished by direct hydrogen addition, by a hydrogen donor solvent or other hydrogen transfer agent. A slurry of coal in a hydrogen donor solvent is typically heated to temperatures between 375°C and 465°C in hydrogen at high pressure.

At these temperatures, pyrolysis or thermal decomposition of coal becomes important. Structures that are physically joined together or joined by weak unstable covalent bonds are thermally disrupted, forming free radicals. These free radicals are then stabilized by hydrogen transfer from donor solvent (Curran *et al.*, 1967), preventing retrogressive reactions which otherwise would lead to higher molecular weight products. Under liquefaction conditions a number of competing chemical processes occur simultaneously: coal pyrolysis, coking, hydrogen transfer from solvent to coal and to extract, solvent rehydrogenation, and direct interaction of molecular hydrogen with elements of the coal structure. Hydrogen donor solvent has the essential role of transferring the hydrogen from the gas phase to the coal as well as the dissolving the products. Hydrogen is consumed at a high rate early in the reaction sequence (Stephens and Kottenstette, 1991).

The dissolution step is considered to be of great importance in coal liquefaction. It involves the transition from solid coal to initial dissolved products during the reaction with hydrogen and/or solvent under elevated temperature and pressure. Dissolution is a relatively fast process which includes both chemical and physical changes, which begins to occur at temperatures as low as 300°C (Schindler *et al.*, 1983). Thermal rupture of weak bonds takes place simultaneously with coal swelling by hydrogen donor solvent resulting in formation of initial depolymerized product of high molecular weight called "preasphaltenes" (Sternberg, 1975). The lower molecular weight material is produced by series of reactions involving cleavage of stronger bonds, resulting in formation of "asphaltenes" and "oils". The process is accompanied by generation of gas consisting of CO, CO_2, H_2S, and C_1-C_4 hydrocarbons (McMillen *et al.*, 1987; Malhotra and McMillen, 1990). The reaction of coal dissolution can be generally described by the reaction scheme (Keogh *et al.*, 1991)



The reaction of hydrogen with highly reactive free radicals, formed in the process, leads to desirable low molecular weight products. Reactions with aryl-free radicals produce undesirable materials of high molecular weight which reduce liquid yield and deactivate any catalyst employed (Stohl and Stephens, 1987).

Of all the hydroaromatic compounds suitable for application in liquefaction as hydrogen donors, tetralin is used most extensively in laboratory experiments. It is readily available and relatively stable under the conditions employed. The process of hydrogen transfer to coal may be described by the reaction (Neavel, 1976)

$$\text{Tetralin} + \text{Coal} \rightarrow \text{Coal-derived products} + \text{Naphthalene}$$

Therefore, according to this model, 2 moles of hydrogen are transferred for every mole of naphthalene produced. However, naphthalene is not readily regenerated to tetralin. In addition, during the liquefaction process polymeric products produced from tetralin can not be separated from the substances formed from coal (Youtcheff and Given, 1983). It has been shown that the solubility characteristics of coal and solvent are defined not only by the donor properties of solvent but also by coal rank and solvent polarity (Derbyshire *et al.*, 1983). Tetralin was found to be a poor solvent for low-rank coal and its polar products. The liquefaction of low-rank coals can be considerably improved by using polar tetrahydroquinoline (THQ) as a hydrogen donor solvent. In the higher rank bituminous coals, both THQ and tetralin give similar conversion yields.

If hydrogen donor solvent is present in the system in adequate amount, mass transfer or diffusional effects are not rate controlling in laboratory batch-stirred autoclaves (Curran, 1967; Guin *et al.*, 1976). Particle size has been found to have no effect on the rate of solvation even at temperature as low as 350°C (Szladow and Given, 1979). This leads to the conclusion that coal contains its own source of donatable hydrogen and can stabilize the generated free radicals during the process, thus, simplifying the mass transfer problem. Benefits from the use of smaller particle size in liquefaction processes have been observed only at very short contact times and diminish as contact time is increased (Pollack *et al.*, 1991). At least in the case of Illinois No.6 coal, the diffusion of the hydrogen donor solvent into the coal has been shown to have no effect either on the amount of hydrogen transferred or on the amount of coal converted (Larsen and Amui, 1994).

1.3. Oxygen Functional Groups in Coal

O-functionalities play an important role in the coal conversion processes. Coal oxygen content ranges from 3% (maf) or less for anthracite to about 30-35% (maf) for lignite and brown coal. It appears in the organic matter, the mineral matter and in moisture. The organic oxygen takes a wide variety of forms, predominantly phenolic, carboxyl, methoxyl, and carbonyl. During liquefaction the concentration of carboxylic, carbonylic and etheric oxygen is greatly reduced (Cronauer and Ruberto, 1977). The loss of carbonyl functional groups was found to be associated with cross-linking reactions during coal pyrolysis (Solomon *et al.*, 1990). The evolution of CO_2 from carboxyl groups is related to retrogressive reactions in pyrolysis and liquefaction of low rank coals (Serio *et al.*, 1993).

According to Boudou *et al.* (1994), oxygen suppresses oil formation during coal pyrolysis. They found that selective decarboxylation and dehydroxylation of coal samples before pyrolysis resulted in a substantial increase of the oil yield.

Weathering of coal (exposure to air) increases the CO_2 yield and lowers fluidity and in extreme cases may result in the complete disappearance of coal coking properties. This is due to the formation of oxygen-containing functional groups which during heating are converted to cross-links within the coal macromolecule. Oxidized bituminous coal contains greater amounts of carboxyl and carbonyl groups and shows earlier cross-linking and lower tar evolution during the pyrolysis (Solomon *et al.*, 1990). Oxidation of steam pretreated coal 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 was in the form of diaryl ether or arylalkyl ether. The 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 ether cross-linking (benzylic or aryl-alkyl). Cross-linking 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 subsequent sections.

1.4. Non-Aqueous Pretreatment Methods to Enhance Coal Liquefaction

Various physical and chemical methods of coal treatment prior to low severity liquefaction can significantly improve the yield and quality of the product, even making them superior to those obtained at high severity conditions. There are many studies showing that the labile cross-linked coal structure can be weakened by alkylation, acylation, partial oxidation, alkali hydrolysis, solvent swelling, selective demineralization, water and steam treatments. As a result of such treatments, coal solubility in organic solvents, as tetrahydrofuran (THF) and toluene, is significantly increased. The low reactivity of many lignites and subbituminous coals may be an artifact caused by excessive retrogression and lack of available hydrogen at the initial stage of liquefaction. The reactivity, however, 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. The coal structure was partially disrupted by adding ethyl groups and cleaving the ether functionalities. 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).

Selective demineralization is another chemical method for modifying coal to enhance liquefaction reactivity. Ion exchange was used by Joseph *et al.* (1992) to remove different cations from low rank Wyodak subbituminous coal and North Dakota lignite. They found that the removal of magnesium, calcium, sodium and potassium from these coals improves high severity (400°C, 500 psig) liquefaction conversion and product quality. It has been proposed that the presence of alkaline and alkaline earth cations inhibit transfer of hydrogen. Mochida *et al.* (1983) reported that using a treatment with hydrochloric acid can remove the cations, thus, destroying cationic bridges found in low rank coals, allowing better contact between coal and solvent during the initial stage of dissolution. Shams *et al.* (1992) used the alcohol/hydrochloric acid system proposed by Sharma *et al.* (1985) for the removal of calcium from coal to enhance low severity liquefaction. A coal deashing method employing coal agglomeration with liquefaction recycle oil has been reported by Robbins *et al.* (1992).

The alteration of coal structure by solvent-swelling pretreatment is reported to improve liquefaction conversion. Baldwin *et al.* (1991) demonstrated that pre-swelling in THF very effectively promotes additional conversion, giving an 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 bonds, 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 removal of the swelling agent, significantly improves liquefaction yield and product quality. The greatest improvement in liquefaction yield was obtained for the bituminous coal. The explanation offered was 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 increasing 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.*, 1993a).

Generally, all of the above methods of enhancing coal reactivity somewhat improve liquefaction yield. However most of them involve complicated procedures, long pretreatment times and the use of exotic reagents, thus 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 relatively cheap and readily available.

1.5. Pretreatment in Aqueous Medium

1.5.1. Liquid Water Pretreatment

Steam has been considered inert to heavy complex hydrocarbon systems at relatively moderate temperatures. However, based on the work conducted 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. Since the properties and structure of shale oil are intermediate between crude oil and coal, aqueous medium came to be employed in treatment of coal at moderate conditions. 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). The participation of water in hydrothermal reactions was recognized and was then studied as a method to improve the yield of liquids from pyrolysis or liquefaction of coal.

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). During the pretreatment a sufficient amount of water was present to maintain a liquid phase at reaction temperature. Comparison of treated and untreated coal suggested that partial decarboxylation occurred during this pretreatment. The elemental analysis of water insoluble product indicated 36% oxygen reduction. For pretreated coal, the yields of CO and CO_2 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, CO_2 and H_2O. Pretreatment of Illinois No.6 bituminous coal resulted in more than doubling of pyridine extraction yield for freshly open sample. The concentration of hydroxyl groups in the bulk declined with the increase of pretreatment time. The yields of toluene and pyridine solubles in hydrogen donor solvent liquefaction of low rank coals were decreased at short pretreatment times and were improved at longer times, but never exceeded the yields from raw coal. Results for liquefaction of Illinois No. 6 coal were inconsistent because of their extreme sensitivity to sample "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 6-8% 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 at 350°C 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 a reaction was carried out at 400°C (Song *et al.*, 1993). The negative effect at higher temperature was attributed to the water/catalyst interactions. Analysis of oils obtained from liquefaction with added water showed more phenolic compounds as compared with liquefaction without water (Song and Saini, 1994).

1.5.2. Steam Pretreatment

Exposure of coal to subcritical steam leads to significant changes in coal structure and behavior in subsequent processing. The steam treatment of Illinois No.6 coal in the temperature range 300-370°C at 50 atm has been studied by Graff and Brandes (1987). These temperatures are considered to be very important, since in this region softening of plastic coal occurs, and aromatic hydrocarbons become highly soluble in water at about 100 atm. In this work two types of tests, pyridine extraction at room temperature and flash pyrolysis were conducted with raw and steam treated coal. It was observed that the pyridine extraction yields from steam treated coal gradually increases with pretreatment temperature reaching a maximum at 340-350°C. At temperatures above 370°C this effect is diminished. In coal pyrolysis, the yield of liquids 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 temperatures for steam pretreatment temperatures were established to be between 320 and 360°C. Treatment in helium, however, showed only slight changes in pyridine extraction yield but did not exceed the value for raw coal. As a result of steam treatment, 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 and on the evidence of coal reactivity from related model compound work, it was concluded that coal is partially depolymerized as a result of steam treatment. It was further suggested that a lighter product can be obtained in subsequent processes.

Analysis of pyrolysis liquids from raw and steam treated Illinois No.6 coal showed a decrease in molecular weight as large as 31% (Graff *et al.*, 1988). The oxygen content was considerably increased, although nitrogen content was 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 measure the level of the hydrogen bond cross-links in coal. The smaller the ratio, the fewer hydrogen bonds are present. Raw coal was found to have more hydrogen bond cross-links than steam treated and helium treated coal. Because the swelling ratio in water was doubled by the steam treatment, it was concluded that steam treated coal is more hydrophilic. DRIS spectra of raw and steam treated coal showed changes in OH group 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%. Combining results of swelling, DRIS and O-alkylation, it became evident that the absolute number of OH groups, especially phenols, was substantially increased by steam pretreatment. It was concluded that during the steam pretreatment new hydroxyl groups are introduced into the coal structure. As a result, the covalent cross-links in the coal structure have been greatly reduced yielding a partially depolymerized coal, potentially beneficial to the coal liquefaction process.

The 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 treatment coal compare to helium treated in the range 300-360°C with a maximum at 320°C. In this extraction experiment the distinction between the effect of steam and inert gas was clearly shown.

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%. 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 the 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 used.

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 argon. It was suggested that 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 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.

1.6. Temperature and Heating Rate in Coal Processing

The characteristics of products obtained from coal by pyrolysis or liquefaction are highly sensitive to the temperature and heating rate used in the process. To a large measure, this is because cross-linking reactions are strongly affected by temperature regime. These control tar yield and molecular weight distribution in pyrolysis, short contact time yields, and the distribution of oils, asphaltenes and preasphaltenes in liquefaction. When coal is heated, two distinct cross-linking events occur: for lignites these reactions begin at about 200°C; for higher rank coals, cross-linking starts at temperatures above 400°C (Solomon *et al.*, 1990). When low rank coal was heated very rapidly, the effect of low temperature cross-linking is reduced resulting in higher tar yield.

When steam pretreated coal is used in subsequent processing, temperature and heating regime must be carefully chosen. The pretreatment effect deteriorates if coal is heated above 360°C, as discussed in Section 1.5.2. Therefore, coal must reach the desired thermal conditions by quickly passing the upper limit of pretreatment temperature. If heating is slow, thermal effects destroy the benefits of pretreatment. Successful heating through this "critical" temperature region was demonstrated in flash pyrolysis (Graff and Brandes, 1987). Under pyrolysis conditions steam treated low rank coal (Khan *et al.*, 1989) showed an increase in tar yield when pyrolyzed at rapid heating rate. When steam treated coals were pyrolyzed at slow heating rate, no improvement in tar yields was observed for either a low or a high rank coal. When steam pretreated coal was subjected to slow heating slurry liquefaction (Ross and Hirschon, 1990), no increase in the yield of liquid products was observed.

1.7. Zeolites in Petroleum and Coal Processing

1.7.1. Zeolite Structure and Properties

Zeolites are typically crystalline, hydrated aluminosilicates of group I and II elements (sodium, potassium, magnesium, calcium, strontium, and barium) formed naturally or synthesized. Zeolites are tectosilicates whose framework structures are based on the infinitely extended three-dimensional network of $(AlO_4)^{5-}$ and $(SiO_4)^{4-}$ tetrahedra. The individual tetrahedra are linked to each other by sharing all of the oxygens. Because the shared oxygen linkage can accommodate T-O-T angles (T is a tetrahedral species, silicon or aluminum) from 130° to 180°, the tetrahedra can be combined into a variety of framework structures. The different framework topologies observed for aluminosilicate zeolites have pores that vary in shape, size and dimensions (Breck, 1974; Newsam, 1986).

A general formula for the aluminosilicate zeolites is

$M_{x/m}$	*	$Al_xSi_{2-x}O_4$	*	nH_2O
Nonframework Cations		Framework Components		Sorbed Water

The relative proportions of silicon and aluminum are variable within $0 \leq x \leq 1$. Since the framework is anionic, the structure contains mono- or divalent cations for charge compensation. These cations are usually mobile and can be replaced by ion exchange. The water in the system can be removed by heat and evacuation and can normally be re-sorbed by exposing the crystals to water vapor. A continuous channel system of uniform pores is formed upon dehydration, providing very high internal surface area (500-800 m^2/g). Approximately 99.5% of the available zeolite surface in particles with diameter above 0.5μ is in the interior. Therefore, the pore structure controls the approach of the reactant molecules to the active sites and the departure of the product (Venuto and Habib, 1979; Barrer, 1982; Newsam, 1986).

Depending on the nonframework cation and Si/Al ratio, zeolites can have hydrophilic or organophilic micropores of desired dimensions and accessibility. The zeolites with lower Si/Al ratios have a strong polar anionic framework interacting with the nonframework cations and, therefore, such zeolites interact strongly with polar molecules. The siliceous zeolites have a framework which is close to neutral, thus, attracting organic molecules. The access of molecules to the interior of the zeolite is controlled by the dimension of the pore window. The characteristics of zeolite as a molecular sieve are determined by its framework topology and can be altered by ion exchange. For example, zeolite 4A, containing sodium cation will admit molecules with minimum cross section of up to about 4A. Partial calcium ion exchange, however, removes sodium ions which partially block the sites of the pore window, admitting species of up to 5A in minimum cross section (Newsam, 1986).

The acidic properties of zeolites have been intensively investigated and are attributed to Bronsted and Lewis acidity. Bronsted acidity is provided mainly by bridging hydroxyl groups. The stronger acidity is associated with isolated aluminum sites in an otherwise silica-rich environment for the material with high Si/Al ratio. The zeolite lattice, therefore, possesses the strongly acidic proton providing a catalytic sites for the reactions involving carbocation (Venuto and Habib, 1979; Newsam, 1986).

Due to their unique properties, including hydrothermal and thermal stability along with their chemical structure, zeolites are widely used as ion exchangers, sorbents, and in hydrocarbon conversion catalysis and separation.

1.7.2. Zeolites and Clays in Heterogeneous Acid Catalysis

The major area of zeolite application is heterogeneous acid catalysis. Clays were one of the first materials to be used for catalysis of fuel processing reactions. In the early 1960's zeolites were found to have an ability to promote cracking of crude oil superior to that of the traditional amorphous silica-alumina material. Cracking is the molecular weight reduction process by which the heavier components of crude oil are converted to lighter material such as those used in gasoline. The process is driven by the acidic sites within the zeolite, since the chemistry of catalytic cracking involves carbocation. Zeolites are also characterized by their outstanding selectivity, especially if crystalline alumosilicates exchanged to low sodium levels are used in the process. The increased ratio of gasoline/gas+coke reflects the direction of cleavage of heavier hydrocarbons to $C_5 \div C_{12}$ range by the zeolite catalysts. The activity of the currently employed zeolite catalysts has improved to the point where the almost complete conversion is reached in only 1 to 4 seconds of contact time. The use of zeolite catalysts for the cracking process results in the following improvements: about 20% reduction in coke; production of H_2, C_1 and C_2's are reduced by about 40% along with reduction of C_3 and C_4 olefins. Reflecting the superior hydrogen transfer ability of zeolites, the amount of saturated C_3 and C_4 is reduced and isobutane/butane ratio is increased. The yields of C_5+ gasoline and light fuel is increased by 6.5 and 1.9 vol% respectively, production of heavy fuel oil is reduced by 1.9 vol%. Zeolitic gasolines are usually lower in sulfur and nitrogen and have better storage stability (Venuto and Habib, 1979; Newsam, 1986).

The ZSM-5 zeolites have high activities for other conversions, such as xylene isomerization and production of gasoline from methanol and chloromethane (Newsam, 1986; White *et al.*, 1992). The shape selectivity of zeolites becomes the key factor for these processes.

The effect of H-mordenite zeolite as a component in Co-Mo-Al_2O_3 hydroprocessing catalysts on conversion of Boscan heavy oil was investigated by Minja and Ternan (1991). The results showed that catalyst with H-mordenite produces greater conversion than catalyst without H-mordenite. The catalyst, however, has to be prepared in such a way that its bulk density does not changes when H-mordenite is added. The improvement has been attributed to the increase in the number of acidic sites in the catalyst by addition of the H-mordenite zeolite.

The hydrocracking of coal volatile matter over zeolite catalyst has been studied by Chareonpanich and Tomita (1994). They reported that ultrastable Y-type zeolite catalyst shows a remarkable activity for the selective production of benzene and toluene in hydrocracking of volatile matter obtained from Millmerran coal (Australian subbituminous coal). The presence of catalyst significantly changed the product distribution increasing the yields of CH_4, C_2-C_4, and BTX (benzene, toluene, xylene).

Pillared clay catalysts (in which large cations are used to separate the silicate layers on the molecular level) allow very large molecules of heavy petroleum fraction to enter the pore (Quayle and Pennavaia, 1979; Gates, 1992). This clay catalyst, therefore, has potential for treatment of large coal-derived molecules such as preasphaltenes (Song *et al.*, 1989). Olson *et al.* (1992) achieved 90% conversion of Wyodak subbituminous coal using an alumina/iron-pillared montmorillonite catalyst. The application of montmorillonite with intercalated zero valent metal clusters for temperature-staged liquefaction has been investigated by Artok *et al.* (1993b). The liquefaction of Blind Canyon bituminous coal in the presence of a copper-intercalated montmorillonite resulted in enhanced conversion to tetrahydrofuran-solubles. Almost the whole increase in the conversion was due to an increase in yield of the asphaltene fraction. However, in the absence of a metal catalyst, no significant effect on liquefaction yield has been observed.

1.8. Reactions of Ether Model Compounds

Model compounds are used by many investigators as surrogates for the various functional groups found in coal so as 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, the studies of its structure most often requires disruption of its network. The character of liquids obtained during coal conversion provides information about product molecular structure and helps to understand the original coal pattern (Farcasiu, 1977). By examining the functional groups identified in a product, the type of 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 an 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).

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 temperatures from 250°C to 350°C for 30 minutes. The major products obtained were ArOH, $\mathrm{Ar'CH_3}$, and isomers of the starting ethers $\mathrm{Ar'CH_2ArOH}$. Minor amounts of $\mathrm{Ar'CH_3CH_2CH_2Ar'}$, ArCH=CHAr', $\mathrm{ArCH_2Ar}$ and "dehydrocompounds" were also produced. The relative rates of thermolysis were found to be:

α-BNE >> β-BNE > α-NMPE > β-NMPE
42 : 2 : 2 : 1

The products were formed by homolysis of the $\mathrm{CH_2\text{-}O}$ bond followed by recombination of the resulting radical. The observed differences in reaction rates was explained by the stability of the radicals produced from each ether. Replacement of glass ampoules by a stainless steel reactor reduced product isomerization. All of the four ethers studied showed up to 80% conversion at these relatively mild conditions.

An analysis of structural changes in the coal macromolecular network during 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 is no longer 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 were performed to better understand the cleavage mechanism of coal cross-links under aqueous and thermal conditions.

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 pathways for ethers and esters by comparing 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 in competition with radical reactions. The activated aryl ether 4-phenoxyphenol and ester 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, 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-phenoxynaphthalene 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 increases with increasing numbers of aromatic rings in the structure. The reactions are catalyzed by water, which is a stronger acid at the temperatures employed, and are inhibited by alkali halides, which at high temperature behave as salts of strong bases and weak acids in water.

2. OBJECTIVES AND TASKS OF THE STUDIES

2.1. Objectives

1. The first objective of this work is to establish the effect of steam pretreatment of coal on direct liquefaction.

2. The second objective is to investigate the chemistry of the steam pretreatment process using coal model compounds.

3. The third objective is to investigate the application of zeolite in model compounds studies and in coal liquefaction.

2.2. Tasks of the Studies

2.2.1. Development of the Coal Liquefaction Reaction System

Previous studies have demonstrated the effectiveness of exposing Illinois No.6 coal to subcritical steam in the temperature range 320-360°C at 50 atm as a pretreatment for room temperature pyridine extraction and for flash pyrolysis (Graff and Brandes, 1987). These studies established the existence of two factors critically detrimental to the successful application of the steam pretreatment process (Section 1.5.2.): (1)the exposure of steam treated coal to oxygen, and (2) the exposure of treated coal to temperatures above 360°C. Either of these can lead to the complete elimination of the pretreatment effect. The first can be rigorously avoided. The second can only be minimized.

Once the success of steam pretreatment had been established in pyrolysis, it was logical to test its application to direct liquefaction. Previous (unpublished) attempts by others to obtain an improvement in liquefaction yield by this method, however, had failed. (Some ambiguous results have appeared in the literature, Ross and Hirschon (1990), Serio *et al.* (1992).) Liquefaction was carried out either in an autoclave or in a tubing bomb. As noted above, temperatures above 360°C destroy the effect of pretreatment. On the other hand, previous pyrolysis studies (Graff and Brandes (1987)) were carried out at about 800°C, but preheating time was a second or less. It was, therefore, reasoned that the heating of pretreated coal to liquefaction temperatures must likewise be done rapidly to minimize deleterious retrogressive reactions. A tubing bomb (Maa *et al.*, 1984) or stirred autoclave (employed in the conventional way) would not be adequate to carry out liquefaction under sufficiently rapid heating conditions.

One way to achieve high heating rates is to use a method described by Whitehurst *et al.* (1976). In this method, the stirred autoclave is fitted with a feed injection system and a slurry of pretreated coal is injected into a hot liquefaction reaction vessel. A stirred autoclave containing only solvent was pressurized with hydrogen and heated to a 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 reaction temperature, the coal slurry was injected into the autoclave and rapidly dispersed by the stirrer. A system of this type, with some modifications, was designed, assembled, tested and used for the liquefaction tests.

Furthermore, since 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 was used for sample workup and the oxygen concentration of the bag monitored by mass-spectrometer. To verify successful pretreatment, the pyridine extraction yield was determined for each steam treated coal sample.

2.2.2. Liquefaction Tests

In this work liquefaction tests of raw and steam pretreated Illinois No. 6 coal were carried out to determine the effect of pretreatment on yield and 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 three different conditions of liquefaction severity.

2.2.3. Model Compound Studies

It is of interest of to investigate the chemistry of the steam pretreatment process using model compounds. An analysis of structural changes in the coal macromolecular network resulting from steam treatment showed that covalent bonds, particularly ether linkages, had been cleaved (Graff *et al.*, 1988; Brandes *et al.*, 1989).

To study ether linkage behavior during the steam pretreatment process the diaryl ethers α-benzylnaphthyl ether (α-BNE), α-naphthylmethyl phenyl ether (α-NMPE) and

9-phenoxyphenanthrene were chosen as model compounds. These model compounds were subjected to the steam treatment at the same conditions as coal. The ethers were reacted with steam and in inert atmosphere (nitrogen) to separate the effect of water from the thermal effect. The model compounds were also reacted under a high pressure when water is present in the liquid phase.

Model compound preparation and reaction product analyses were carried out by C.Brathwaite (Department of Chemistry, CCNY).

2.2.4. Studies of Zeolite Application

The third objective listed above was added to these studies after preliminary steam and inert gas treatment tests had been conducted with model compounds α-BNE and α-NMPE. These compounds produced mostly isomerized starting material as reaction product. At this point, zeolite (nonacidic) was introduced to immobilize the reactant, thereby suppressing isomerization and inducing the formation of cleavage product. Tests with α-BNE and α-NMPE mixed with 5Å zeolite were conducted in steam and in inert gas. following the same procedure as in the absence of zeolite.

The application of zeolite to coal liquefaction was also tested. Experiments were conducted using mixtures of Illinois No.6 coal and different types of zeolites (4Å, 5Å and 13X), added to coal before the steam pretreatment step or before the liquefaction (after pretreatment). Zeolites were tested at both high and low severity liquefaction conditions.

3. LIQUEFACTION OF STEAM PRETREATED COAL

3.1. 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 from the Pennsylvania State University Sample Bank are used in this work. These samples have been refrigerated and stored under inert atmosphere to avoid oxidation. The pretreatment and the liquefaction experiments are carried out with the 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 a coal sample before or after steam pretreatment is also examined. Three zeolite samples of different pore size are tested in this work: 5Å, 4Å, and 13X (Aldrich Chemical Company, Inc.). The zeolites 5Å, 4Å, and 13X are used in the experiments where zeolite is added to coal prior to steam pretreatment. When zeolite is added to pretreated coal, prior to liquefaction. only 5Å zeolite is employed. Zeolite powder is used "as received" (undried). The moisture content of the molecular sieve is determined separately from the coal sample before each run. Coal/zeolite tests are carried out the same way as the experiments with coal alone. When coal is mixed with zeolite before steam pretreatment, it is not separated after treatment, but carried over into the liquefaction step.

Steam pretreatments are conducted in a stainless steel tubular reactor which can be charged with up to 30 grams of sample. It is conducted in the continuous flow of steam at 50 atm and 340°C for 15 minutes while the reactor is submerged in the fluidized bath heater. The apparatus and procedure are as described in Graff and Brandes (1987) and Graff *et al.* (1988). These conditions were previously found to be an optimum for Illinois No.6 bituminous coal. After steam pretreatment is completed, the reactor is placed into 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 to be tested, the inert atmosphere is not used. A 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 (a loading reservoir and a rupture disc). After a portion of solvent is preheated in the autoclave to the desired temperature, coal slurry prepared from 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 for rapid heating of the coal sample.

After the liquefaction is complete and the reactor cooled down, coal conversion is determined as described by Joseph (1991). The liquid product distribution is defined 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.

3.2. Sample Preparation

3.2.1. Coal Sample Preparation

The work reported here is conducted with Illinois No.6 coal samples (DECS 2) from the Pennsylvania State University Sample Bank. After being received, samples are stored refrigerated in their unopened sealed foil containers. The coal batches are assigned numbers 27 (A, B, C) and 31 (A, B, C). The samples particle size is -20 mesh. Their elemental composition (weight percent on a dry coal basis) is given below (The Penn State Coal Sample Bank and Database, 1990) :

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. One container is ground at a time, the entire contents to pass 200 mesh. The 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.

3.2.2. Zeolite Powder and Coal/Zeolite Mixture

Three different pore size zeolites are 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 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 then one (Breck, 1974). The zeolite 4Å has the unit cell content $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]*27H_2O$, when fully hydrated (oxide formula $Na_2O*Al_2O_3*2SiO_2*4.5H_2O$). 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 $Ca_{4.8}Na_{2.4}[(AlO_2)_{12}(SiO_2)_{12}]*28H_2O$ (oxide formula $0.8CaO*0.2Na_2O*Al_2O_3*2SiO_2*4.7H_2O$). The chemical formula of fully hydrated 13X zeolite is $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]*264H_2O$ (oxide formula $Na_2O*Al_2O_3*2.5SiO_2*6H_2O$). The molecular sieve of 13X zeolite has higher Si/Al ratio and, therefore is more organophilic then the A type zeolite.

The coal/zeolite mixture is prepared by mixing the undried zeolite powder with the coal sample (raw or steam pretreated) in a glass beaker. In all calculations the zeolite part of the mixture is considered "inert" and is treated as mineral matter (the amount of zeolite in the mixture is added to the amount of ash in coal).

3.3. Experimental Equipment

3.3.1. Steam Treatment Apparatus

The steam pretreatment apparatus (Graff *et al.*, 1988) consists of a steam generation section and a steam treatment section (Figure 3.1). The steam generation section includes a water reservoir, a pump, a furnace and a 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 opening and closing the boiler relief valve. The furnace is a three zone Lindberg furnace (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

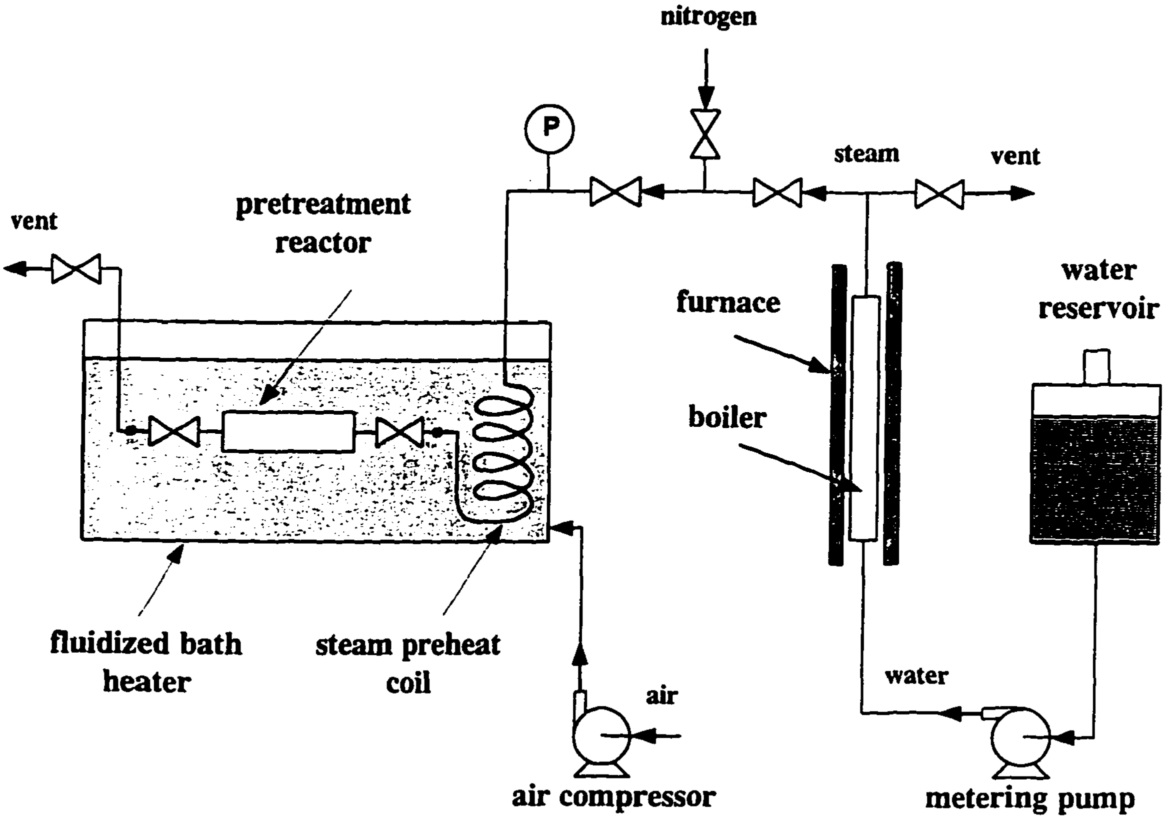


Figure 3.1. Steam Pretreatment Apparatus (Graff *et al.*, 1988).

line from a high pressure tank.

3.3.2. Liquefaction Apparatus

The rapid heating liquefaction apparatus consists of a 300 ml stirred autoclave and a coal slurry injection system (Figure 3.2). 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 (slurry vehicle) are loaded into reservoir through a valve from two syringes made of borosilicate glass. The slurry syringe is of 50 cc capacity and solvent syringe is of 30 cc capacity. The reservoir is separated from the autoclave by a 1000 psia rupture disc. The gas supply includes nitrogen and hydrogen high pressure tanks. Nitrogen is used for pressure testing of the system and hydrogen is used in the liquefaction process.

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 3.3). The gas transfer line down stream 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 flow meter. Hydrogen gas is used to sweep air from the transfer line before sampling of the reaction gas.

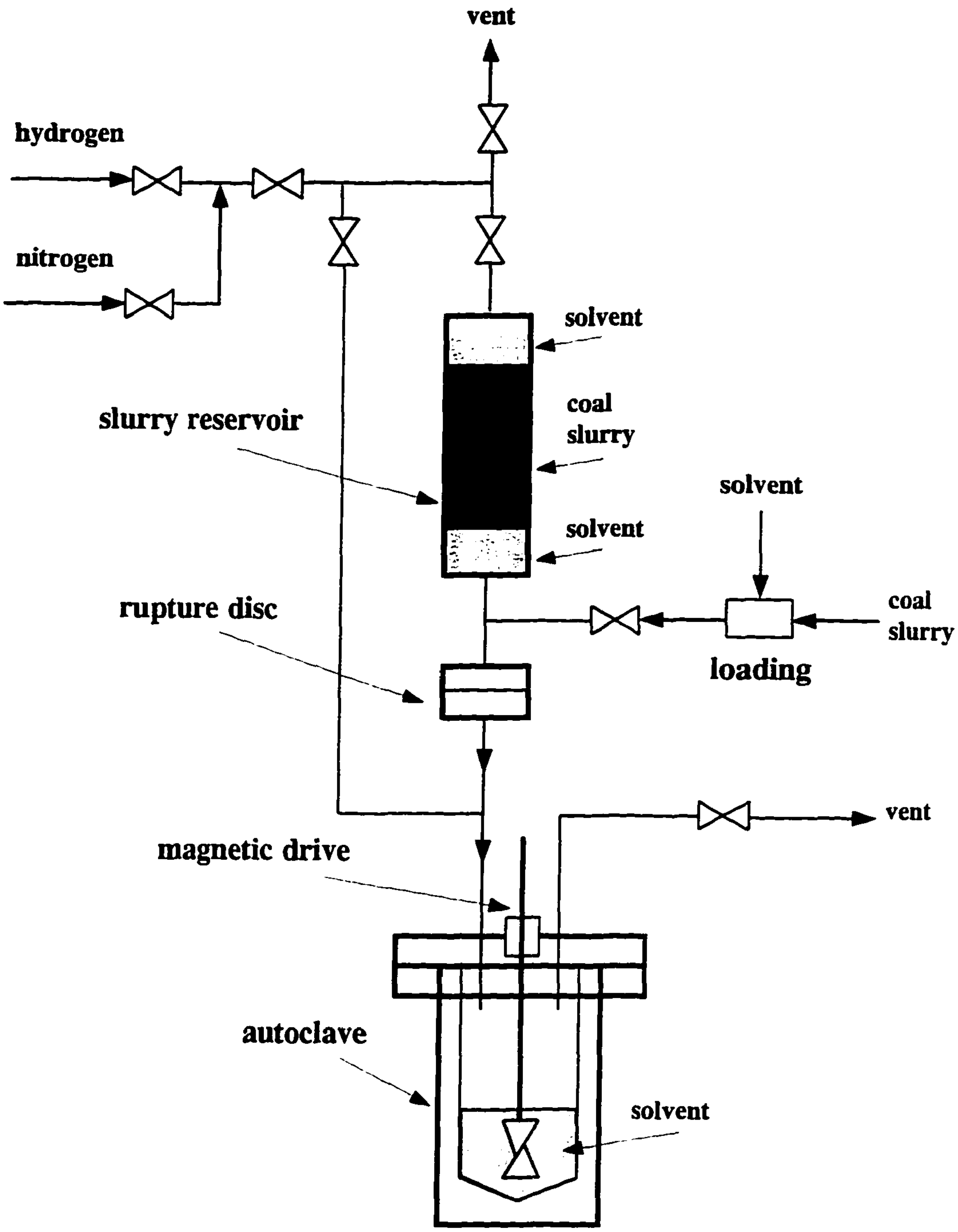


Figure 3.2. Stirred Autoclave with Coal Slurry Injection (Shown Prior to Coal Slurry Injection).

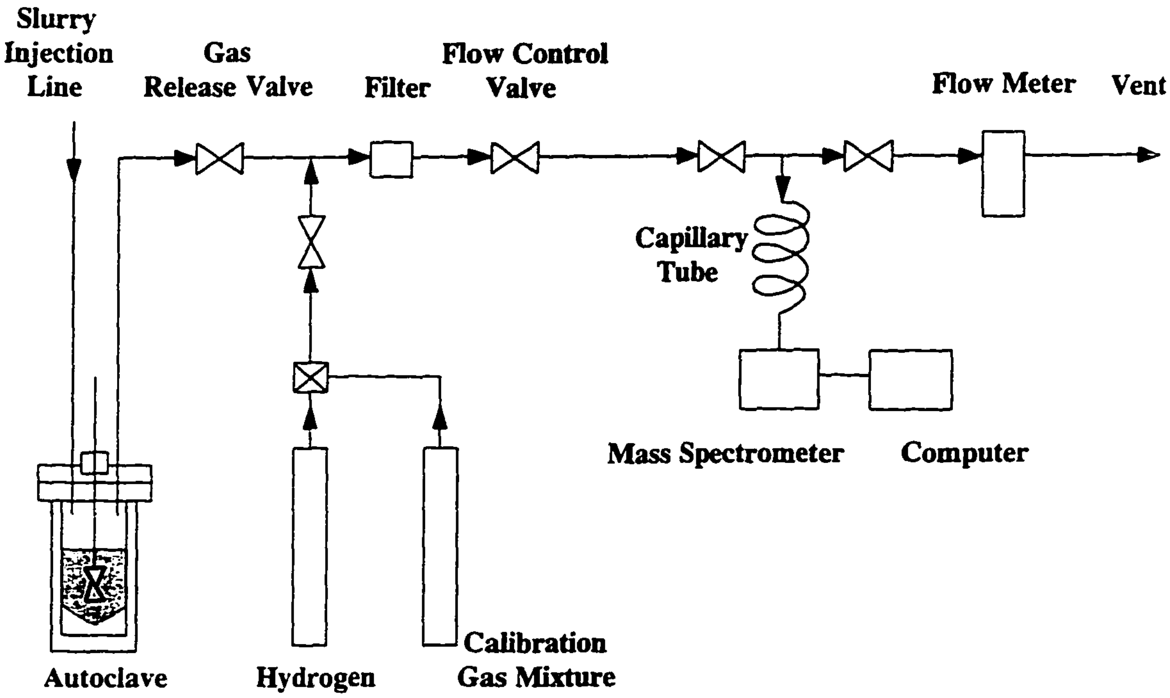


Figure 3.3. Gas Analysis Equipment.

3.4. Experimental Procedures

3.4.1. 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 the 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 the 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 reactor is submerged into the fluidized bath. Pretreatment in steam continues for 15 minutes. Then the 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 carefully weighed coal sample of known moisture content is loaded into a boat, 2 1/2 inch long and 1/4 inch wide. This boat is then placed in the 1/2 inch diameter reactor and the pretreatment is carried out the same way as described above. After the treatment the sample is weighted again and yield of the volatiles is determined.

In current 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 (Graff *et al.*, 1988). The dependance of the volatiles yield on steam flow rate has been established previously.

If coal is to be pretreated with a zeolite powder, the following procedure is employed: 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. The moisture contents of coal and molecular sieve are separately determined and used to calculated the moisture content of the mixture. 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.

3.4.2. Room Temperature Pyridine Extraction

The handling of the treated coal and pyridine extraction are conducted as described by Graff and Brandes (1987) and by Graff *et al.* (1988). After steam treatment is completed, the pretreatment reactor is placed in a nitrogen-filled glove bag. 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, and 100 ml of pyridine are added. If the coal sample is to be exposed to air the flask is removed from the glove bag, the contents stirred and then pyridine is added. Extraction of the raw coal is done under ambient air. The contents of the flask are continuously stirred. After 15 minutes of stirring, the particles are allowed to settle to the bottom of the flask. The solution is decanted into another flask through the weighed filter paper. An additional 100 ml of fresh pyridine is added to the residue in the flask and the solution is stirred for another 15 minutes. The decanting procedure is repeated, using the same filter paper. A final amount of fresh pyridine, 150 ml, is added and the solution is stirred again for 15 minutes. The flask is loosely covered and the sample is left in pyridine for 16 hours. The solution is then agitated and filtered through the same filter paper. The filter paper is left to dry and then placed into a vacuum oven at 90°C for 18 hours to assure complete removal of pyridine. The residue left on the filter paper is weighed and the extraction yield is calculated on the initial maf (moisture, ash free) weight of coal charged to the pretreatment reactor. The yield, therefore, includes the loss of volatiles during pretreatment.

3.4.3. 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 deoxygenate the solvent. Rapid heating liquefaction of the 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 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 slurry was made of equal amounts of coal and solvent.) When the autoclave has been preheated to operating temperature, two loading syringes are filled, one with about 40 ml of slurry and one with 20 ml of solvent. After 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, slurry is injected into the reactor and the system is pressurized. The valve above the reservoir is then closed. The reaction temperature is maintained with ±5°C accuracy. The run continues for 30 minutes (high severity liquefaction) or for 15 minutes (low severity liquefaction) 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 analyses are performed.

For the tests where exposure of pretreated coal to air is to be tested, 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.

For slow heating liquefaction tests, the above described 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. The test is then continued for the duration of the run.

The liquefaction tests are also conducted with coal/zeolite mixtures prepared just before liquefaction. In these cases equal amounts of steam pretreated coal and zeolite are mixed together under inert atmosphere. The mixture is then slurried with tetralin and liquefaction is carried out as described above.

3.4.4. Liquid Product Characterization

When the autoclave has cooled to room temperature and been vented to 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, placed in the vacuum oven at 90°C and dried to 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 maf raw coal 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 includes liquefaction gas and oils. According to Joseph (1991), the gas yield from raw Illinois No.6 coal in slow heating liquefaction is less then 5% (400°C, 1100 psia hydrogen, 30 minutes). The liquefaction conditions described by Joseph (1991) correspond to the high severity liquefaction (Section 5.1.1.1.) of the present work, except that 1500 psi pressure was employed. The gas make under this conditions was not determined.

3.4.5 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 3.3.2).

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, CO_2, H_2S, CH_4, C_2H_6, C_2H_4, C_3H_6, C_4H_{10}. 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 incorporated 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_2H_4	C_3H_8	C_2H_6	C_3H_6	C_4H_{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

$$N_i = \int F C_i dt \tag{3.1}$$

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 from the mass spectrometer for component i depends on the sensitivity of the instrument 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

$$I_i=C_i/k_i \tag{3.2}$$

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

Combining equations (3.1) and (3.2) at constant vent gas flow rate gives

$$N_i=k_iF\int I_i dt \tag{3.3}$$

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 (3.3) by the same equation written for neon

$$\frac{N_i}{N_{Ne}}=K_i\frac{\int I_i dt}{\int I_{Ne} dt} \tag{3.4}$$

where K_i is the ratio of the response constant k_i to that for neon. The use of Equation (3.4) 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 (3.4) 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 (3.4) to the calculation of liquefaction gas yields, N_{Ne} is determined from the autoclave charging pressure, temperature, and volume using the perfect gas law.

4. MODEL COMPOUND STUDIES

4.1. Choice of Model Compounds

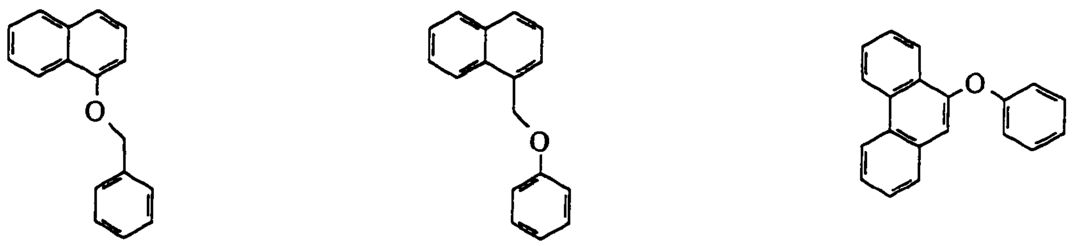
The thermolysis of four arylmethyl aryl ethers were studied by Chawla *et al.* (1990): α-benzylnaphthyl ether (α-BNE), α-naphthylmethyl phenyl ether (α-NMPE), β-benzylnaphthyl ether (β-BNE) and α-naphthylmethyl phenyl ether (β-NMPE). The α compounds were found to be more reactive at relatively mild temperatures then the β compounds,. Based on this observation, the steam treatment studies in this work were focused on the reactions of the two α compounds (α-BNE and α-NMPE) as most reactive.

The third ether selected for this work, 9-phenoxyphenanthrene, is thermally stable. However, as previously discovered by Siskin *et al.* (1993), 9-phenoxyphenanthrene, while unreactive at 315°C and 350°C in inert medium, can be cleaved at this temperatures in liquid water. The behavior in steam of this thermally stable compound can be compared with that of the thermally reactive α-BNE and α-NMPE.

4.2. Model Compound Preparation

The synthesis and preparation of all model compounds were carried out by C.Brathwaite (Department of Chemistry, CCNY). Three ether model compounds α-NMPE, α-BNE and 9-phenoxyphenanthrene were synthesized (Figure 4.1). The two ethers, α-NMPE and α-BNE, synthesized according to the procedures of Maslak and

Guthrie (1986) were found to be ca. 95% pure by high performance liquid chromatography (HPLC). 9-Phenoxyphenanthrene was prepared and purified using the method of Afzali *et al.* (1983). α-BNE was further purified by recrystallizations (>99.5% by HPLC), but high purity α-NMPE could not be obtained by recrystallizations, and flash column chromatography on silica gel led to its extensive decomposition due to acid-catalyzed rearrangement. However, recrystallizations from hexane/ether/ethanol (5/2/2) and final purification by flash column chromatography on basic alumina afforded >99.5% pure (HPLC) α-NMPE.



α-benzylnaphthyl ether α-naphthylmethyl phenyl ether 9-phenoxyphenanthrene

Figure 4.1. Ether Model Compounds.

4.3. Experimental Procedures

The chosen model compounds were reacted in steam, liquid water and inert gas; with or without zeolite.

Steam and inert gas treatment of model compounds were conducted using the same method as in coal pretreatment (Sections 3.3.1, 3.4.1). The experiments were carried out in a stainless steel tubular reactor of 2 inch length and 3/8 inch OD. The reactor was 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 was 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 the non-flow open reactor agreed with results obtained in continuous flow operation. Since the reactor walls may effect conversion, model compounds tests were carried out in both stainless steel and Pyrex-lined vessels. When the compound was treated under inert atmosphere. steam was replaced by a flow of nitrogen gas supplied from a high pressure tank.

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

The series of treatment experiments with α-NMPE and α-BNE were also conducted in the presence of 5Å zeolite to investigate its effect on the formation of isomeric starting material. The model compounds are mechanically mixed with zeolite using 1:5 weight ratio of compound to zeolite. The experiments were carried out following the above described procedure without zeolite. Only the stainless steel reaction vessel was used in these studies.

The model compounds were also reacted at a pressure high enough to maintain water in liquid phase. These tests were carried out according to the procedure described by Siskin *et al.* (1993) in an 11 ml stainless steal reaction bomb using from 100 mg to 1g of material. The desired amount of model compound and 7 ml of deoxygenated deionized water was placed in the reactor under inert atmosphere and the vessel was sealed. The reactor was 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).

4.4. Product Analysis

The products obtained in model compound studies were analyzed by C.Brathwaite (Department of Chemistry, CCNY).

The reaction products were 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 were carried out on a Hewlett-Packard 1090 chromatograph using a µ-Porasil column 4.5 x 250 mm (hexane:ether, 99:1). Gas chromatography-chemical ionization mass spectral analyses (GC-CI-MS) were conducted on a Finnigan SSQ-70 instrument using ammonia as reagent gas. Preparative GC experiments were carried out on a Hewlett-Packard 5890 gas chromatograph equipped with a thermal conductivity detector.

The condensable reaction products were washed from the reactor using 4 x 3 ml portions of methylene chloride (CH_2Cl_3) per 0.1 gram of sample pyrolyzed. The methylene chloride was then evaporated under a stream of nitrogen to establish recovery yield. The material obtained was then analyzed by GC-CI-MS using SPB-5 fused silica capillary column (30 m, Supelco). The ^1H nmr spectrum and GC-CI-MS of the mixture was also obtained to verify that no decomposition had occurred during the separation step. If decomposition of the product was detected the mixture was separated by preparative GC on a porous polymeric column Tenax-GC (Alltech) using a linear temperature gradient of 20°/min. The purity of the product was further verified by HPLC analysis. The peaks obtained from GC runs are collected and the pure compounds subjected to ^1H, ^{13}C nmr and CI-MS analyses to determine the structures of the products.

5. EXPERIMENTAL RESULTS

5.1. Liquefaction Studies

5.1.1. 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.

All yields presented in this work were calculated based on the dry, ash free (daf) raw coal charge. Pyridine extraction yields were determined for each batch of raw and steam pretreated coal. For the steam treated coal the value for pyridine extractables includes the volatiles generated during pretreatment. The yield of hexane solubles from the liquefaction experiments also includes gaseous products produced during liquefaction.

5.1.1.1. High Severity Liquefaction

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 5.1.1, classified according to the liquefaction conditions employed.

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

Table 5.1.1.

High Severity Liquefaction of Illinois No.6 coal (Sample 27 A, B).

(400°C, 1500 psia, 30 minutes)

		Conversion (%wt)			
Run No.	Conditions	Total (liquid + gas)	Hexane Solubles Oils+Gas	Toluene Solubles Asphaltenes	THF Solubles Preasphaltenes
1	raw coal slow heating	81.6	37.0	16.9	27.7
2	raw coal	73.8	42.2	10.0	21.6
8	rapid heating	80.0	48.7	16.7	14.6
10	steam treated coal slow heating	73.8	35.2	14.4	24.2

Table 5.1.1. (Continued)

High Severity Liquefaction of Illinois No.6 coal (Sample 27 A,B).

(400°C, 1500 psia, 30 minutes)

		Conversion (%wt)			
Run No.	Conditions	Total (liquid + gas)	Hexane Solubles Oils+Gas	Toluene Solubles Asphaltenes	THF Solubles Preasphaltenes
6	steam treated coal	85.7	60.1	17.2	8.4
12	rapid heating	79.3	55.8	14.7	8.8
7	steam treated coal rapid heating	91.9	56.0	14.2	21.7
9	tetralin contains dissolved oxygen	85.2	47.5	17.3	20.4
11	steam treated coal, exposure to air, rapid heating	66.3	38.6	19.8	7.9

slow (run 1) and rapid (runs 2 and 8) heating liquefaction conditions to establish baselines for these two different procedures. Then, a series of tests were conducted with steam pretreated coal: 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 had been previously opened and not protected against oxygen absorption. The deteriorating effects on the liquefaction yields of slow heating of treated coal (run10) and of the exposure of steam pretreated coal to air (run11) 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 hexane solubles, however, is increased and preasphaltene yield is decreased.

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.

However, under rapid heating liquefaction of steam pretreated coal with deoxygenated tetralin there is a definite improvement in the yields and in the quality of the products: hexane solubles are substantially increased, while preasphaltenes are reduced.

In the case where tetralin was not protected against oxygen absorption, an improved total yield is a results of the slight increase in the yields of all fractions, compared to rapid heating liquefaction of raw coal (runs 6 and 12). Evidently, when tetralin contains dissolved oxygen the liquefaction process becomes less selective to the formation of lighter product (hexane solubles).

When steam treated coal was deliberately exposed to ambient air for one hour before slurrying with deoxygenated tetralin, the pretreatment effect was destroyed. The yield of hexane solubles is 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 is 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 the average temperature drop was 62°C. In raw coal liquefaction, temperature dropped by 76°C on average. A temperature drop of 73°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 indicates the occurrence of some exothermic reaction(s) in pretreated coal under hydrogenation conditions which does not occur in raw coal. The possibilities for this exothermic effect are discussed in Section 5.1.2.

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 5.1.2) than

Table 5.1.2.

High Severity Liquefaction of Illinois No.6 coal (Sample 31 A).

(400°C, 1500 psia, 30 minutes)

		Conversion (%wt)			
Run No.	Conditions	Total (liquid + gas)	Hexane Solubles Oils+Gas	Toluene Solubles Asphaltenes	THF Solubles Preasphaltenes
22	raw coal rapid heating	72.3	39.2	13.2	19.9
24	steam treated coal slow heating	84.1	51.9	13.6	18.6
25		84.9	55.0	15.5	14.4
23	steam treated coal rapid heating	89.0	57.8	13.7	17.5
26	steam treated coal, rapid heating, exposure to air	85.7	48.4	12.0	25.3

the previous one (CFI No. 27, Table 5.1.1) In rapid heating liquefaction, steam pretreatment of sample 31A greatly enhanced the total yield and the yield of hexane solubles. These yields were only slightly diminished by slow heating. Exposure of steam treated coal to air also decreased the total yield and the yield of hexane solubles 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.

5.1.1.2. Low Severity (a) Liquefaction

The liquefaction tests with Illinois No.6 coal (Sample 31 B,C) were also conducted under conditions of reduced severity. In the first series of tests (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). In this case, liquefaction of raw and steam pretreated coal was conducted only 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 5.1.3. and the gas composition in Table 5.1.4.

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 a difference between the weight of the starting daf coal sample and the weight of the residual dry solid after Soxhlet extraction by hexane. This weight loss, therefore, includes the oils extractable by hexane, the volatiles lost in steam pretreatment (8 wt% at the

Table 5.1.3.

Low Severity (a) Rapid Heating Liquefaction of Illinois No.6 Coal (Sample 31 B,C).

(350°C, 1500 psia, 30 min)

		Conversion (%wt)					
		Total	Hexane Solubles			Toluene Solubles	THF Solubles
Run No.	Conditions	(liquid + gas)	Total	Gas	Oils	Asphaltenes	Preasphaltenes
28	raw coal	73.9	47.4	5.5	41.9	10.9	15.6
29	steam treated	71.3	47.1	13.5	33.6	9.5	14.7
30	coal	70.6	42.6	12.0	30.6	11.0	17.0

Table 5.1.4.

Low Severity (a) Rapid Heating Liquefaction Gas Composition (Sample 31 B.C).

(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_2H_4	C_2H_6	C_3H_6	$C_3H_8+C_4H_{10}$
28	raw coal	5.5	5.5	1.8	74.1	8.3	3.0	0.8	2.8	9.2
29	steam	13.5	5.5	1.4	63.4	6.9	3.8	0.8	6.0	17.7
30	treated coal	12.0	4.0	1.4	63.1	10.0	4.1	1.2	3.4	16.8

conditions used (Graff *et al.*, 1988)), and gas formed in the liquefaction process (determined by mass spectrometry). This breakdown of the hexane solubles is given in Table 5.1.3. and gas composition in Table 5.1.4.

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.

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, the sample had passed too slowly through a region around 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.

5.1.1.3.Low Severity (b) Liquefaction

To keep the reaction temperature higher after slurry injection and during reaction, the low severity liquefaction conditions were modified. 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. This is referred to as low severity liquefaction (b). The procedure was also slightly modified: the autoclave was initially preheated to 400°C. After the temperature drop caused by slurry injection, the temperature was raised to 385°C.

A third series of liquefaction tests were conducted under these low severity (b) conditions (Coal sample 31 B,C). The results are shown in Table 5.1.5. (yield of liquid product) and 5.1.6. (gas composition). In none of these rapid heating liquefaction tests did the reaction temperature drop below 320°C. Recovery time was between 1.5 minute for raw coal and 1 minute for steam treated coal.

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 increased with a slight reduction in the total gas make. Remarkably, the oil yields doubled while preasphaltenes were 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 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

Table 5.1.5.

Low Severity (b) Liquefaction of Illinois No.6 Coal (Sample 31 B,C).

(385°C, 1500 psia, 15 min)

		Conversion (%wt)					
		Total	Hexane Solubles			Toluene Solubles	THF Solubles
Run No.	Conditions	(liquid + gas)	Total	Gas	Oils	Asphaltenes	Preasphaltenes
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	77.5	41.8	11.9	29.9	16.4	19.3
34	rapid heating	76.2	38.9	10.3	28.6	15.8	21.5
35	steam treated coal,	72.7	30.5	14.9	15.6	18.9	23.3
36	exposure to air,	71.4	31.2	13.8	17.4	17.1	23.1
	rapid heating						
37	steam treated coal	74.9	35.2	16.4	18.8	20.0	19.7
38	slow heating	73.9	34.1	19.2	14.9	18.6	21.2

Table 5.1.6.

Low Severity (b) Liquefaction Gas Composition.

(385°C, 1500 psia, 15 min)

Run		Gas Yield,%wt		Liquefaction Gas Composition (%wt)						
No.	Conditions	Total	Liq.Gas	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	$C_3H_8+C_4H_{10}$
32	raw coal	13.7	13.7	2.3	51.9	14.9	5.2	1.3	3.1	21.3
33	rapid heating	15.5	15.5	1.8	54.5	17.2	5.9	1.4	4.0	15.2
31	steam treatment	11.9	3.9	1.5	40.6	15.4	6.5	2.4	9.1	24.5
34	rapid heating	10.3	2.3	1.4	39.5	19.6	7.8	2.3	5.4	24.0
35	steam treatment	14.9	6.9	1.4	48.1	21.0	6.8	2.3	5.1	15.3
36	exposure to air	13.8	5.8	1.0	46.2	19.2	5.6	2.0	4.7	21.3
	rapid heating									
37	steam treatment	16.4	8.4	1.1	40.3	24.1	6.2	2.3	5.0	21.0
38	slow heating	19.2	11.2	1.0	40.2	23.1	6.7	2.5	4.8	21.7

of hexane solubles and oils alone have intermediate values 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 the autoclave to 385°C), since the liquefaction process starts before the reactor temperature reaches 385°C, even under low pressure.

Regarding the yields of liquefaction gas (Table 5.1.6), 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. Steam treatment and heating rate also affect the composition of liquefaction gas. More C_3-C_4 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 CO_2. The heating rate does not show any effect on the production of CO_2. More methane was produced under slow heating conditions, compared to rapid heating, contributing to the highest overall gas yield. Increased production of CO_2 as well as CH_4 may indicate the occurrence of retrogressive reactions (Solomon *et al.* 1990).

Comparison of the gas composition at the two low severity liquefaction conditions (Tables 5.1.4. and 5.1.6.) 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 CO_2 are reduced.

In summary, the behavior of Illinois No.6 coal in low severity liquefaction (385°C, 15 min, 1500 psia) follows the same trends as at higher temperature and longer reaction time are (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). A further improvement in yields of desirable products is to be expected if experimental conditions are arranged so that the temperature minimum reached after coal injection is kept above the region of retrogressive reactions. 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.

5.1.2. Thermal Effects in Liquefaction Initiation.

When coal slurry at room temperature is injected into the hot autoclave, the temperature in the autoclave rapidly drops and then, more slowly, recovers. However, as previously noted (Section 5.1.1.1), this initial thermal history is different for pretreated coal as compared to raw coal. When steam pretreated coal is injected into the autoclave the temperature drop is smaller than for raw coal. Evidently, the initial reaction stage of steam treated coal liquefaction is exothermic relative to raw coal.

In this section an attempt is made to explain the exothermicity of steam treated coal at its injection into the autoclave. The possibility of the rupture of the covalent bonds with further capping of the radical by hydrogen as well as the possibility of hydrogen bond formation are explored. The behavior and properties of raw coal are discussed only in comparison to a steam treated coal.

5.1.2.1. Evaluation of the Heat Effect at the Time of Coal Slurry Injection.

The heat generated at the time of injection of the coal slurry into the liquefaction reactor containing a hot solvent can be evaluated from the heat balance for the autoclave

$$c_p^t m_{atc1}^t T_{atc1} + c_p^t m_{inj}^t T_{room} + c_p^c m_{inj}^c T_{room} + Q_f + Q_r = c_p^c m_{inj}^c T_{atc2} + c_p^t m_{atc2}^t T_{atc2} \tag{5.1}$$

where c_p^t = solvent (tetralin) specific heat (cal/g°C),

c_p^c = coal specific heat (cal/g°C),

T_{atc1} = reactor temperature before the injection (°C),

T_{atc2} = reactor temperature after the injection (°C),

T_{room} = temperature of the material to be injected (°C),

m^t_{atc1} = amount of solvent in the autoclave before the injection (g),

m^t_{inj} = amount of solvent injected into the autoclave (g),

m^t_{atc2} = amount of solvent in the autoclave after the injection (g),

m^c_{inj} = amount of coal injected into the autoclave (g),

Q_f = heat supplied by the furnace (cal),

Q_r = heat of reaction at the time of injection (cal).

The calculation is performed with the following assumptions: (a) all heat capacities are constant in the temperature range employed (c_p^t = 0.464 cal/g°C (Mellan, 1950), c_p^c = 0.316 cal/g°C (Van Krevelen, 1993)); (b) heat capacities of raw and steam treated coal are equal (c_p^c); (c) heat supplied by the furnace at the time of injection (Q_f) is constant for all runs. The value of Q_f is evaluated from a separate run ("blank") where only solvent is injected into the liquefaction reactor

$$c_p^t m_{atc1}^t T_{atc1} + c_p^t m_{inj}^t T_{room} + Q_f = c_p^t m_{atc2}^t T_{atc2} \tag{5.2}$$

The experimental data for evaluation of the heat effects for raw and steam treated coal is shown in Table 5.1.7.

The injected masses (m^t_{inj} and m^c_{inj}) and temperatures of the autoclave after the injection (T_{atc2}) from Table 5.1.7 are used in Equations (5.1) and (5.2). The initial temperature of the solvent prior to the slurry injection (T_{atc1}) and the initial amount of solvent in the autoclave (m^t_{atc1}) were the same in all runs. The amount of solvent in the autoclave after the injection (m^t_{atc2}) is obtained by adding amounts of solvent present in the reactor initially (m^t_{atc1}) and the amount injected (m^t_{inj}). The injected solvent (m^t_{inj}) includes washing solvent and solvent contained in the slurry (Section 3.4.3). The amount of solvent in the slurry was not directly measured. It was estimated from the total amount of coal and the solvent injected into the autoclave and from the coal content of the slurry.

Table 5.1.7.

Experimental Data for the Heat Effect Evaluation.

	blank (average of 2 runs)	raw coal (average of 2 runs)	treated coal (average of 3 runs)
temperature, °C			
T_{atc1}	400	400	400
T_{atc2}	327	324	337.67
T_{room}	23	23	23
mass, g			
m^t_{atc1}	60	60	60
m^t_{inj}	60	53.21	49.74
m^t_{atc2}	120	113.21	109.47
m^c_{inj}	---	14.29	13.26

Using Equations (5.1) and (5.2) the heat effects at the time of injection (based on the ash free raw coal charge) for raw (Q_r^{raw}) and steam treated (Q_r^{tr}) coal were determined to be:

$Q_r^{raw} = 20.31$ cal/g; $Q_r^{tr} = 31.18$ cal/g.

(The exothermic heat effect of the steam treated coal is well below the value of heat of combustion, 6,610.63 cal/g (The Penn State Coal Sample Bank and Database, 1990), for Illinois No.6 coal.)

5.1.2.2. Coal Model

An evaluation of the coal reactivity at the time of slurry injection is based on the molecular model of bituminous coal structure developed by Shinn (1984) (Figure 5.1).

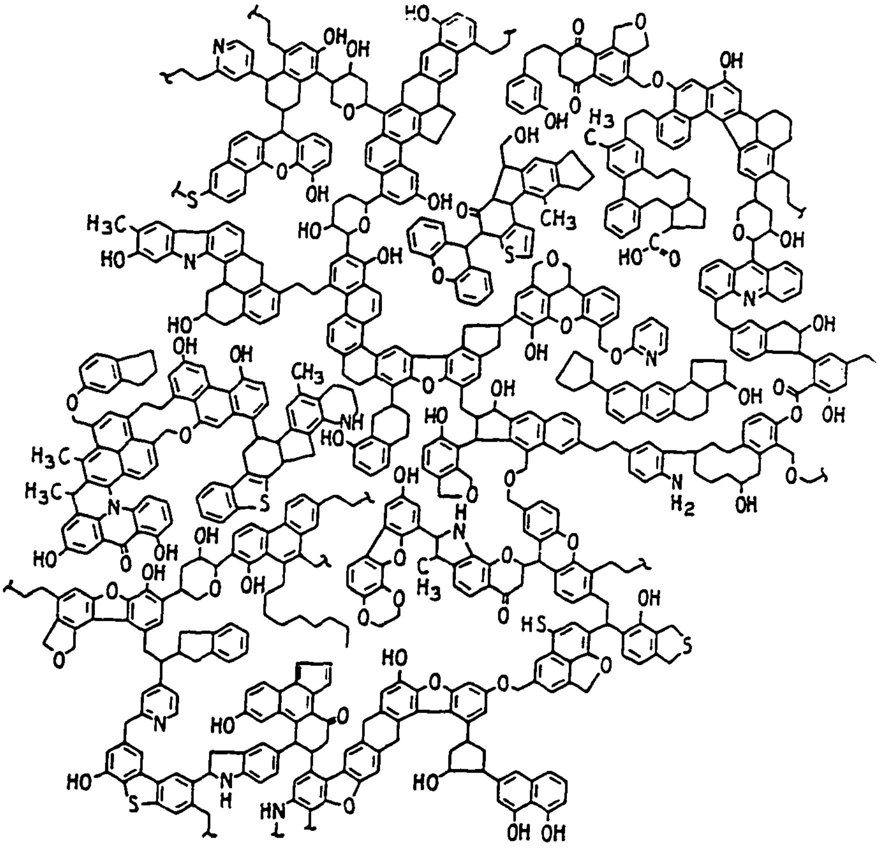


Figure 5.1. Model of Bituminous Coal Structure (Shinn, 1984).

The model is consistent with data on coal properties, liquefaction product compositions. and displays the various structural units in coal. The units are connected in a way that is consistent with the observed behavior of coal under liquefaction conditions. In addition to the immobile phase, where fragments are connected by covalent bonds, a mobile phase is incorporated into the macromolecular network, connected by hydrogen bonds. The model is representative of such bituminous coals as Illinois No.6, Illinois No.2, Indiana V, and Kentucky 9 and 11.

The model unit has a molecular weight of 10,023, large enough to construct a liquefaction product distribution. The atom distribution in the molecule, determined from the elemental composition of Illinois No.6 coal, is $C_{661}H_{561}O_{74}N_{11}S_6$. For comparison, the elemental compositions of raw and steam treated Illinois No.6 coal (Brandes *et al.*, 1989) are shown in Table 5.1.8 along with values for the Shinn model.

Table 5.1.8.

Elemental Composition (% wt) of the Model for Bituminous Coal (Shinn, 1984) in Comparison with Raw and Steam Treated Illinois No.6 Coal (Brandes *et al.*, 1989).

Element	Model (Shinn, 1984)	Raw Illinois No.6 (Brandes *et al.*, 1989)	Steam Treated Illinois No.6 (Brandes *et al.*, 1989)
C	79.14	76.98	80.56
H	5.59	5.92	5.76
O (org)	11.81	14.56	10.78
N	1.54	1.39	1.55
S (pyr)	1.92	1.15	1.35

5.1.2.3. Exothermicity Due to Rupture of Covalent Bonds

To explain the exothermic effect occurring at the injection of steam pretreated coal, the possibility of covalent bond scission was first considered. Based on the molecular model prediction of the products for the short contact time liquefaction of bituminous coal (Figure 5.2), the simplified chemical reactions involving the most reactive cross-links were derived.

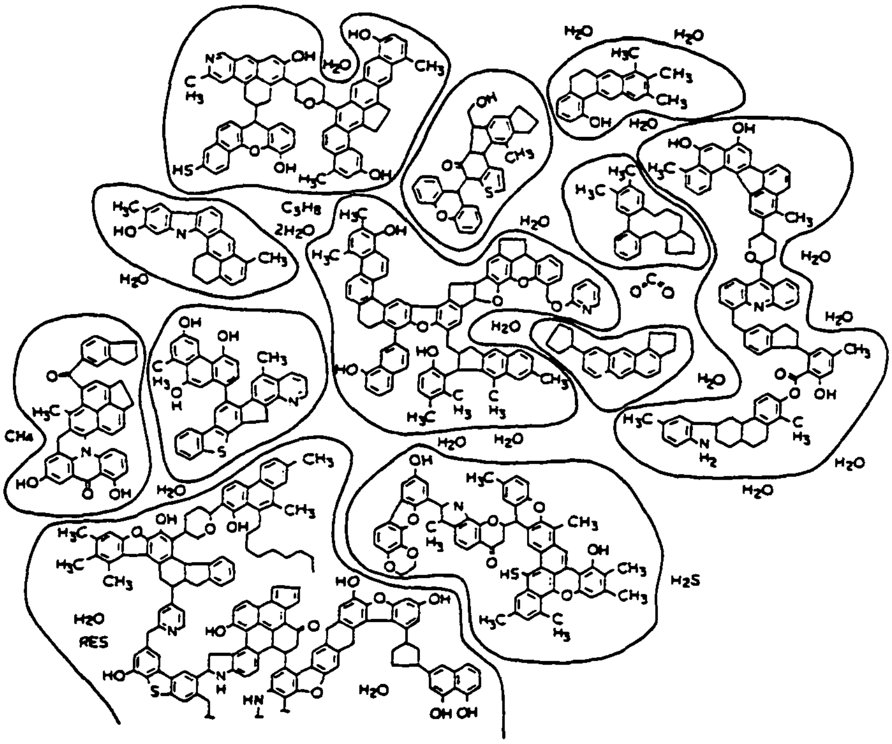


Figure 5.2. Short - Contact Time Liquefaction Product from Bituminous Coal (Shinn. 1984).

For steam treated coal. the model of raw coal was modified (Figure 5.3).

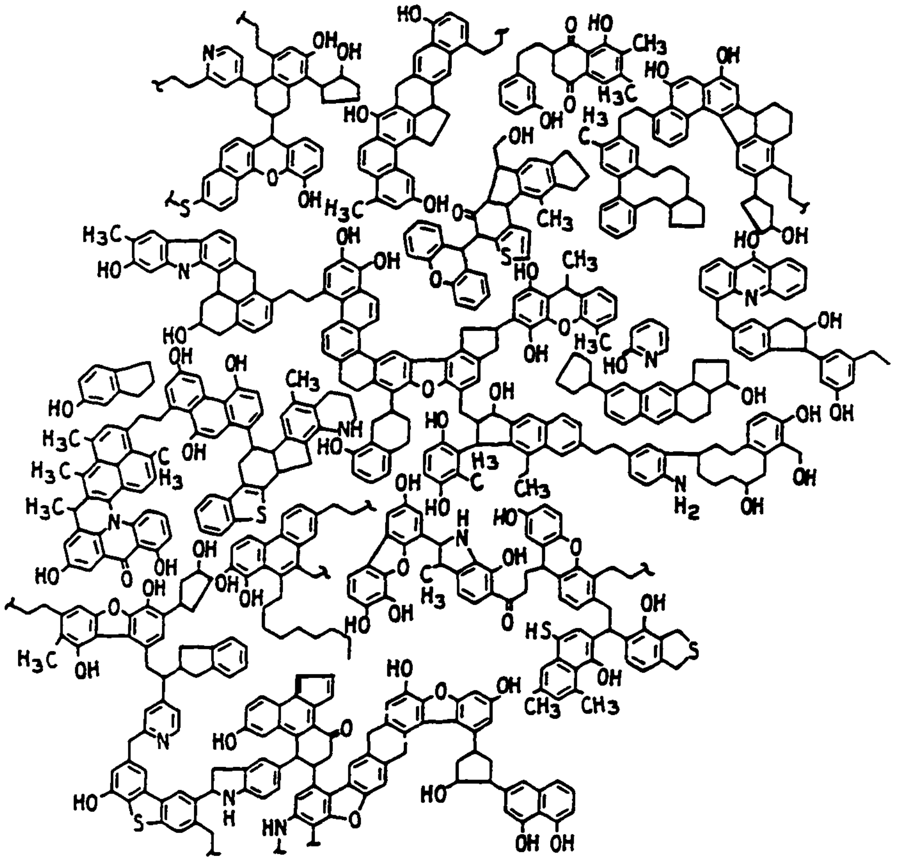


Figure 5.3. Model of Steam Treated Bituminous Coal Structure.

According to previous findings (Brandes et al., 1989) treated coal contains fewer ether cross-links because these have been ruptured by steam pretreatment and replaced by hydroxyl groups. To reflect this structural change, the ether linkages involved in product formation as modeled by Shinn were replaced by hydroxyl groups. In this modification, the mobile phase is, therefore, increased at the expense of the immobile phase, but the molecular weight remains the same as for the raw coal (volatiles loss is neglected). The short-contact time liquefaction product for steam treated coal was derived by analogy with raw coal using the steam treated coal model (Figure 5.4).

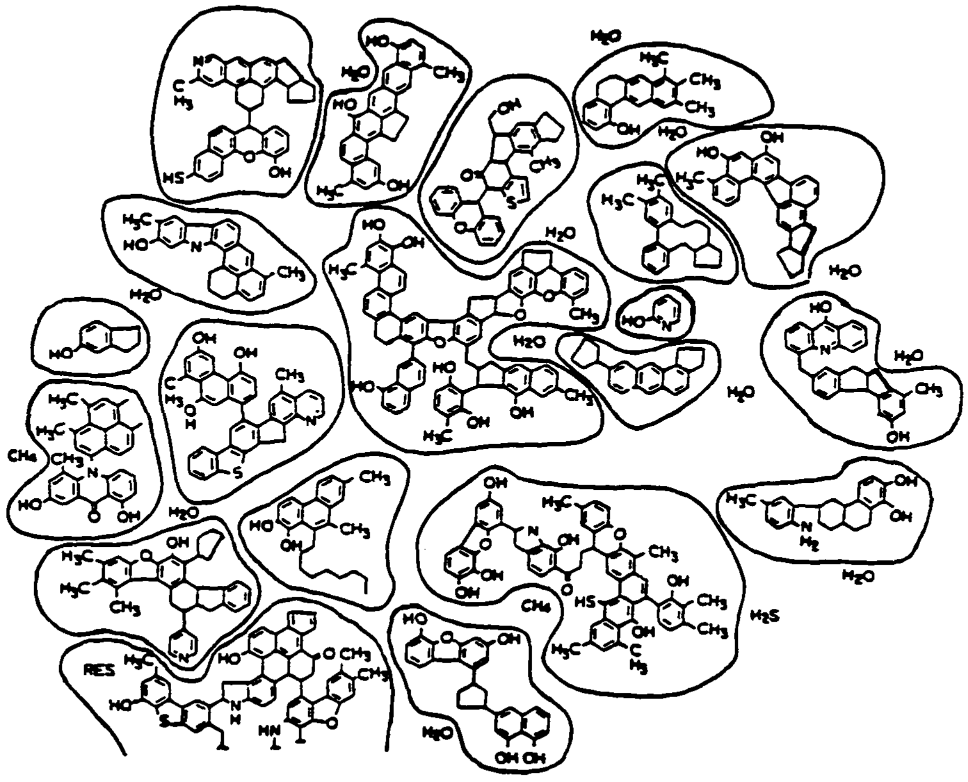


Figure 5.4. Short - Contact Time Liquefaction Product from Steam Treated Bituminous Coal.

The heat effects of reactions involved in the short-contact time liquefaction product formation were then evaluated for raw and steam treated coal. Where necessary, thermodynamic data were estimated using additivity of group properties (Benson, 1976). The results are given in Table 5.1.9.

The overall enthalpy change for raw coal (the sum total enthalpy change of reactions from 1 to 12) is equal to -635,561 cal/mol, and 43 moles of hydrogen are consumed in the process. Conversion of the steam treated coal requires 26 moles of hydrogen, and overall enthalpy change is -417,668 cal/mol (the sum total enthalpy change

Table 5.1.9.

Heat Effect of Reactions for Raw and Steam Treated Coal.

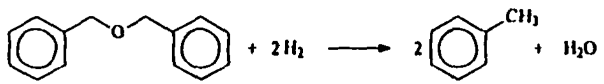
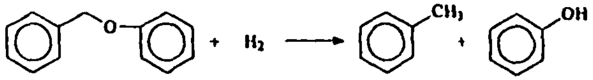
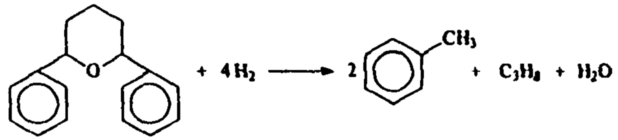
#	reaction	ΔH (cal/mol)	reactions/mol		ΔH tot. (cal/mol)	
			raw	treated	raw	treated
1		-35710.56	2	0	-71421.12	0
2		-14948.14	2	0	-29896.28	0
3		-32371.18	1	0	-32371.18	0

Table 5.1.9. (Continued)

Heat Effect of Reactions for Raw and Steam Treated Coal.

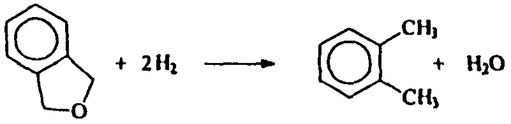
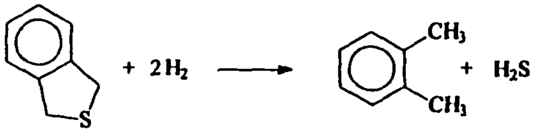
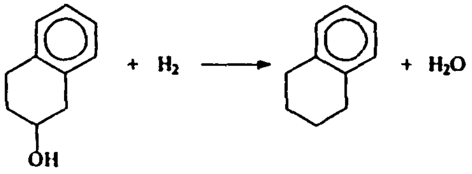
#	reaction	ΔH (cal/mol)	reactions/mol		ΔH tot. (cal/mol)	
			raw	treated	raw	treated
4		-40147.75	4	0	-160591.00	0
5		-24890.75	1	1	-24890.75	-24890.75
6		-15728.80	2	2	-31457.60	-31457.60

Table 5.1.9. (Continued)

Heat Effect of Reactions for Raw and Steam Treated Coal.

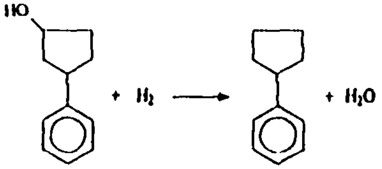
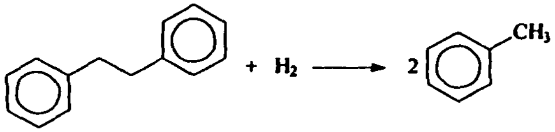
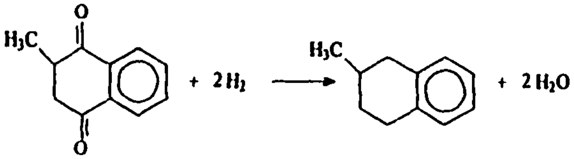
#	reaction	ΔH (cal/mol)	reactions/mol		ΔH tot. (cal/mol)	
			raw	treated	raw	treated
7		-15728.80	5	1	-78644.00	-15728.80
8		-10153.59	11	12	-111689.50	-121843.00
9		-55262.87	1	1	-55262.87	-55262.87

Table 5.1.9. (Continued)

Heat Effect of Reactions for Raw and Steam Treated Coal.

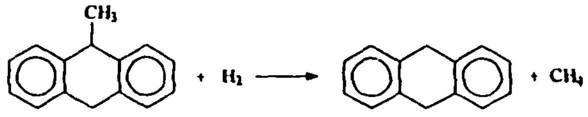
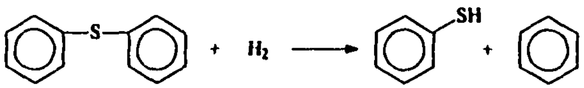
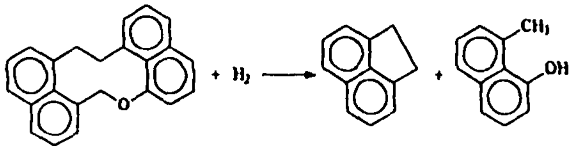
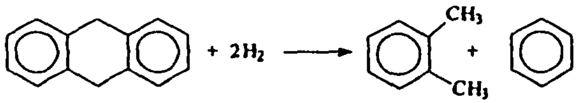
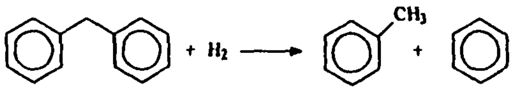
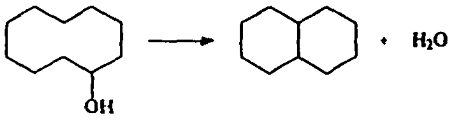
#	reaction	ΔH (cal/mol)	reactions/mol		ΔH tot. (cal/mol)	
			raw	treated	raw	treated
10		-8228.36	1	2	-8228.36	-16456.72
11		-8989.77	1	1	-8989.77	-8989.77
12		-22118.35	1	0	-22118.35	0

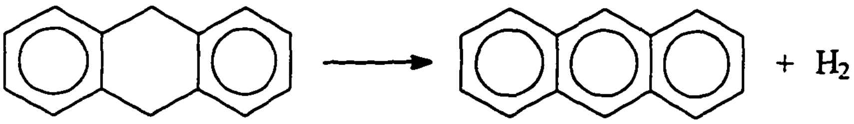
Table 5.1.9. (Continued)

Heat Effect of Reactions for Raw and Steam Treated Coal.

#	reaction	ΔH (cal/mol)	reactions/mol		ΔH tot. (cal/mol)	
			raw	treated	raw	treated
13		-11845.59	0	1	0	-11845.59
14		-6506.29	0	2	0	-13012.58
15		-23636.58	0	5	0	-118180.00

of reactions from 5 to 15).

In the early stages of liquefaction, the hydrogen consumption from the gas or donor solvent remains low. Protons to cap the cross-links are supplied internally giving rise to the aromaticity of short contact time liquefaction product (Shinn, 1984; Provine *et al.*, 1991). At residence times greater than 2 minutes, the aromaticity begins to decrease (Provine *et al.*, 1991). Internal hydrogen transfer can be described by the endothermic reaction (ΔH= 14,617.45 cal/mol):



Therefore, to provide 43 moles of hydrogen to form the products of the short contact time liquefaction of the raw coal, 628,550 cal/mol of heat are consumed. The overall heat effect of the process for raw coal then is:

$$-635{,}561+628{,}550=-7{,}011 \text{ cal/mol.}$$

For the conversion of the steam treated coal, 26 moles of hydrogen are required (380,054 cal/mol). The overall heat effect of the process for steam pretreated coal then is:

$$-417{,}668+380{,}054=-37{,}614 \text{ cal/mol.}$$

(It is also possible that some of the hydrogen is provided by tetralin. Since the average amount of heat released by dehydrogenation of tetralin is 14,536 cal/mole H_2, the difference in the overall heat effect is not significant.)

According to this reaction scheme, the net heat effects for raw and steam treated coal are both exothermic, but the effect is more pronounced for steam treated coal. Calculated on a relative basis, the short time liquefaction of steam treated coal is more exothermic than that of raw coal by

(37,614-7,011)(cal/mol)/(10,023g/gmol)=3.1 cal/g raw coal

This, however, is inadequate to explain the measured value (Section 5.1.2.1),

31.18-20.31=10.47cal/g ash free raw coal

which is about four times the model value. A disadvantage of this liquefaction model is its dependence on the degree of conversion of starting coal (how many reactions take place). There is also a problem with time scale. Short contact time liquefaction products are considered to be formed over a time period of two minutes, whereas the slurry injection temperature drop occurs in one to two seconds. Consequently, it is concluded that the higher exothermicity for steam treated coal may partially explain the more rapid temperature recovery after injection of pretreated coal, but not its initial exothermicity.

5.1.2.4. Exothermicity Due to Formation of Hydrogen Bonds

Evidently, the rupture of covalent bonds during short contact time liquefaction does not fully explain the behavior of coal at the time of slurry injection. However, since the time usually reckoned for short contact time liquefaction is about two minutes, the possibility exists for some other energy releasing reactions of shorter duration to occur immediately after injection.

It is well established that besides covalent bonds, non-covalent interactions, such as hydrogen bonds, contribute to the cross linking of different macromolecular coal segments (Larsen *et al.*, 1985; Larsen and Mohammadi, 1990). Hydroxyl groups (mainly phenolic) can participate in the formation of hydrogen bonds with oxygen, nitrogen, and sulfur atoms. The strength of these bonds vary from ~2 to ~10 kcal/mol depending on the functional groups involved (Pimentel and McClellan, 1960).

Here we postulate that hydrogen bond formation immediately following the injection of steam treated coal generates the observed exothermicity. The reduction in covalent cross-links during steam treatment not only increases the mobility of the structural units, it also increases the number of hydrogen donor hydroxyl groups. The new structure, however may not be totally relaxed. It is possible that at the time of injection, before the covalent bonds are broken, the mobility of the structural components is sufficiently raised by the higher temperature and the presence of solvent to allow molecular folding into more favorable conformation. This would involve the formation of hydrogen bonds, not formed in raw coal, which is accompanied by energy release.

The number of hydroxyl groups present in raw and steam treated coal were previously evaluated using O-alkylation (Brandes *et al.*, 1989). The number of derivatized OH sites in the pretreated coal was determined to be 7.38 groups / 100 carbon atoms, and for raw coal 3.85 groups / 100 carbon atoms. The number of new OH groups formed by the steam is then

$$7.38-3.85=3.53 \text{ groups / 100 carbon atoms,}$$

or on a molar basis (using molecular formula $C_{661}H_{561}O_{74}N_4S_6$ suggested by Shinn)

$$3.53x6.61=23.3 \text{ groups / mole.}$$

If the average hydrogen bond energy is -4.1 kcal / bond (this value was evaluated by

Carlson (1992) using energy minimization of the model proposed by Shinn) and all the new OH groups participate in the formation of hydrogen bonds at the time of injection, the heat effect is

$$-4.1x23.3/10{,}023=-9.5 \text{ cal/g}.$$

This theoretical result is not far from the experimental value of 10.47 cal/g.

This calculation shows that the number of new hydroxyl groups introduced into coal by steam pretreatment is almost sufficient to explain the increased exothermicity observed in the early stages of its liquefaction.

5.1.3. Coal/Zeolite Mixtures

Liquefaction experiments under high and low severity conditions were also conducted with steam pretreated Illinois No.6 coal (Sample 27 A,B) mixed with zeolite powder. All tests were carried out under rapid heating. At high severity conditions, coal was mixed with zeolite prior to steam pretreatment. The treated mixture was then used in liquefaction tests. Under low severity (b) conditions, two cases were examined. The first one was conducted the same way as high severity tests. In the second case, raw coal without zeolite was steam treated and then mixed with zeolite before the liquefaction step. To verify successful pretreatment pyridine extraction yield was determined for the steam treated mixtures as well as for treated coal alone. For all steam treated coal/zeolite samples there was no significant difference in the value of pyridine extraction yield (unless noted) compared to coal treated without zeolite.

5.1.3.1. High Severity Liquefaction

The high severity liquefaction was carried out at 400°C, 1500 psia for 15 min using three types of zeolite, 5Å, 4Å, and 13X. Results are listed in Table 5.1.10. 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 hexane solubles (51-63.8%) were obtained in the presence of zeolite, they are not higher then 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.

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 application of zeolite 13X was less successful (run 20). The yield of hexane

Table 5.1.10.

Rapid Heating High Severity Liquefaction of Steam Treated Illinois No.6 Coal (Sample 27 A,B) and Zeolite Mixtures. (400°C, 1500 psia, 30 min)

		Conversion (%wt)			
Run No.	Conditions	Total (liquid + gas)	Hexane Solubles Oils+Gas	Toluene Solubles Asphaltenes	THF Solubles Preasphaltenes
	No Zeolite				
6	steam treated	85.7	60.1	17.2	8.4
12	coal	79.3	55.8	14.7	8.8
	5Å Zeolite				
13	coal:zeolite=1:1	95.5	51.2	25.0	19.3
14	"	96.2	53.5	17.3	25.4
16	"	98.1	63.8	18.8	15.5
17	coal:zeolite=10:1	88.0	51.4	19.4	17.2

Table 5.1.10. (Continued)

Rapid Heating High Severity Liquefaction of Steam Treated Illinois No.6 Coal (Sample 27 A,B) and Zeolite Mixtures. (400°C, 1500 psia, 30 min)

		Conversion (%wt)			
Run No.	Conditions	Total (liquid + gas)	Hexane Solubles Oils+Gas	Toluene Solubles Asphaltenes	THF Solubles Preasphaltenes
	<u>13X Zeolite</u>				
20	coal:zeolite=10:1	84.7	45.8	22.7	16.2
	<u>4Å Zeolite</u>				
21	coal:zeolite=10:1	89.4	53.9	15.8	19.7

solubles is at the raw coal (no zeolite) level. The pyridine extraction yield is also the same as for raw coal. To verify this result "blank" extraction experiments were carried out. Pyridine extraction and Soxhlet extraction with hexane were carried out using 13X zeolite alone. The sample showed a weight increase of about 17% after extraction and drying were complete. This different behavior of zeolite 13X from 5Å and 4Å can be attributed to structural differences giving the former greater moisture and solvent absorption and retention. Zeolite 13X has Si/Al ratio greater then one, and it is more organophilic. The pore size of this zeolite is two times larger than that of 5Å molecular sieve giving it the ability to absorb up to 264 molecules of water. The zeolite pores can retain extraction solvent and moisture (absorbed from ambient air) resulting in an artificial decrease of pyridine extraction and liquefaction yields.

The results obtained with 4Å and 5Å zeolites suggest that these zeolites assist in the breakdown of 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.

5.1.3.2. Low Severity (b) Liquefaction

After the effectiveness of the application of 5Å zeolite was demonstrated for high severity liquefaction, tests were conducted under conditions of low severity (b): T=385°C. P=1500 psia, 15 min. In addition to liquid product characterization, the gas formed in the process was also analyzed as previously described. Liquefaction yields are given in

Table 5.1.11 and the gas composition in Table 5.1.12. First, a set of experiments were carried out using coal mixed with zeolite (raw coal:zeolite=1:1 by wt%) in the steam pretreatment stage (runs 39, 43). The second set of tests were conducted with a coal sample which was first steam treated, then mixed with zeolite (treated coal:zeolite=1:1 by wt%) in the liquefaction stage (runs 41, 42).

The total liquid yield obtained from coal treated with zeolite (runs 39, 43) is increased compared to the yield obtained without zeolite (run 31 and 34, Table 5.1.11.). The improvement is achieved by an increase in the asphaltene fraction, yields of hexane solubles and preasphaltenes are not distinctly affected. The results obtained with steam treated coal mixed with zeolite at the liquefaction stage (runs 41, 42) are similar to those obtained from steam treated coal/zeolite mixture.

The amount of liquefaction gas produced with zeolite added at the pretreatment stage is slightly lower then with zeolite added at the liquefaction stage and is in the same range as when no zeolite was present. There is, however a significant difference in the gas compositions between the results obtained with and without zeolite. Addition of zeolite has reduced the formation of CO_2 by the order of magnitude, and the yields of CH_4 and C_2H_4 are almost doubled. An increase in the yield of the propane plus butane fraction is also observed.

The results obtained under low severity conditions show the effectiveness of zeolite addition for increasing the total yield of liquids. It appears to be unimportant at which stage, pretreatment or liquefaction, zeolite is added: in both cases similar yields of liquids and of gaseous product were obtained. Also, pyridine extraction yield is not

Table 5.1.11.

Rapid Heating Low Severity (b) Liquefaction of Illinois No.6 Coal (Sample 31 B,C) and 5Å Zeolite Mixture (1:1 wt%). (385°C, 1500 psia, 15 min)

		Conversion (%wt)					
		Total	Hexane Solubles			Toluene Solubles	THF Solubles
Run No.	Conditions	(liquid + gas)	Total	Gas	Oils	Asphaltenes	Preasphaltenes
31	steam treated coal	77.5	41.8	11.9	29.9	16.4	19.3
34	rapid heating	76.2	38.9	10.3	28.6	15.8	21.5
39	liquefaction of	83.6	42.2	11.1	31.1	25.8	15.6
43	coal treated with zeolite	78.1	38.8	10.4	28.4	22.5	16.8
41	steam treated coal	80.7	43.0	11.9	31.1	21.0	16.7
42	liquefaction with zeolite	------	------	12.5	------	------	------

Table 5.1.12.

Rapid Heating Low Severity (b) Liquefaction of Illinois No.6 Coal (Sample 31 B,C) and 5Å Zeolite Mixture (1:1 wt%). Liquefaction Gas Composition.

(385°C, 1500 psia, 15 min)

Run		Gas Yield, %wt		Liquefaction Gas Composition (%wt)						
No.	Conditions	Total	Liq.Gas	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8+C_4H_{10}
32	raw coal	13.7	13.7	2.3	51.9	14.9	5.2	1.3	3.1	21.3
33	rapid heating	15.5	15.5	1.8	54.5	17.2	5.9	1.4	4.0	15.2
39	liquefaction of coal treated with zeolite	11.1	3.1	1.3	5.4	34.0	10.3	2.5	10.0	36.5
43		10.4	2.4	1.6	5.0	36.3	11.7	2.6	8.6	34.2
41	steam treated coal, liquefaction with zeolite	11.9	3.9	2.2	5.1	34.5	13.7	2.9	9.5	32.1
42		12.5	4.5	1.3	4.7	37.3	11.5	2.6	8.9	33.7

affected by zeolite addition. In the gaseous fraction zeolite suppresses release of carbon dioxide and promotes formation of hydrocarbon gases.

Most likely, zeolite assists in the breaking down of coal molecules at the liquefaction stage. It is also likely that some acidic functionality is introduced into the molecular sieve by ion exchange with coal during the liquefaction step. The induced acidity could explain the improved liquefaction yields.

5.2. Model Compounds Studies

5.2.1. Steam, Inert Gas and Liquid Water Treatments

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 ±3°C as in coal pretreatment. The condensed reaction product was separated by preparative GC and the structures of its constituents determined by a combination of ^{1}H and ^{13}C nmr, and CI-MS analysis.

The major reaction products of α-benzylnaphthyl ether were identified as 1-naphthol, isomeric starting material 2-benzyl-1-naphthol and 4-benzyl-1-naphthol, and minor products (Figure 5.5). The presence of toluene (a volatile compound) in the reaction product was detected by mass spectrometer prior to workup.

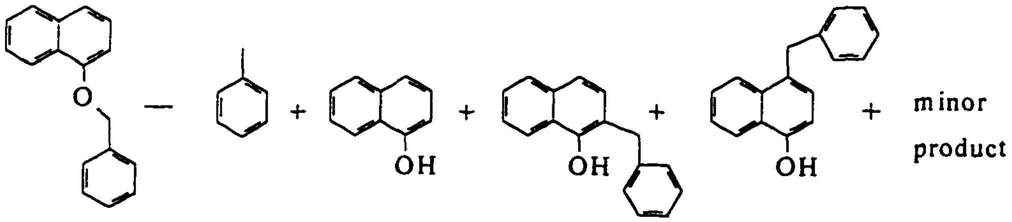


Figure 5.5. Products Obtained from the Pretreatment of α-Benzylnaphthyl Ether.

The reaction products of α-naphthylmethyl phenyl ether were determined to be phenol, 1-methylnaphthalene, 1-naphthaldehyde, and isomeric starting material *o*-naphthylmethyl phenol and *p*-naphthylmethyl phenol (Figure 5.6).

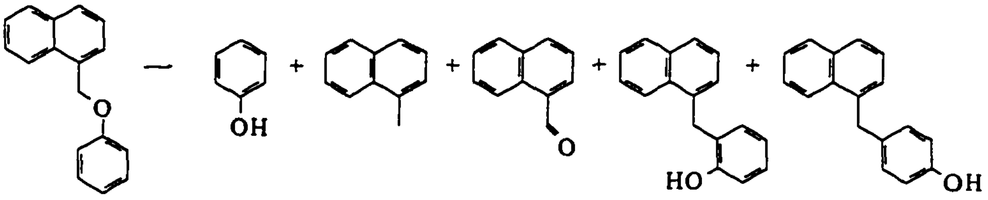


Figure 5.6. Products Obtained from the Pretreatment of α-Naphthylmethyl Phenyl Ether.

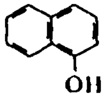
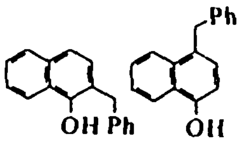
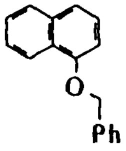
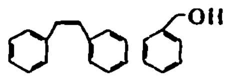
Treatment runs in the stainless steel vessel were conducted using 200 mg of model compound; when the reaction vessel was glass-lined the amount of material was reduced to 100 mg. The reaction product distribution was determined based on the amount of condensed material recovered after treatment. The results are shown in Table 5.2.1 for α-BNE and in Table 5.2.2 for α-NMPE.

About 40% of the product obtained from α-BNE, and about 30% of the product obtained 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 was obtained from α-BNE in the glass-lined reactor. In case of α-NMPE, the difference was 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

Table 5.2.1

Pretreatment of α-Benzylnaphthyl Ether.

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

PRODUCT CONDITIONS		1-naphthol 	isomeric starting material 	recovered starting material 	minor product* 
STEAM	metal	51.8	42.6	0	5.6
	glass	48.1	46.3	0	5.6
INERT	metal	51.8	37.5	0	10.7
	glass	50.0	39.3	0	10.7

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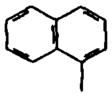
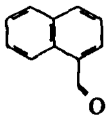
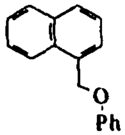
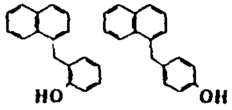
* Since the relative amounts of two constituents in minor product were not available, the average value for there molecular weight was used to determine mole %.

Table 5.2.2

Pretreatment of α-Naphthylmethyl Phenyl Ether.

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

CONDITIONS	PRODUCT	phenol  	1-methyl naphthalene 	1-naphth aldehyde  	recovered starting material  	isomeric starting material 
STEAM	metal	37.9	24.2	4.5	6.1	27.3
	glass	13.2	22.6	7.5	11.3	45.4
INERT	metal	36.3	27.3	9.1	0	27.3
	glass	40.0	18.5	7.7	0	33.8

model compound treatment because it appears to promote undesired isomerization.

Isomeric starting material is produced by recombination of benzyl radicals formed by homolysis. The radical recombination reaction, therefore, competes with the formation of cleavage products and must be controlled. It is possible that the model compound has far more freedom to isomerize than similar structures in a coal matrix.

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. Accordingly, tests under aquathermolysis in liquid water were carried out using α-NMPE as well as 9-phenoxyphenanthrene. The reaction products obtained from cleavage of 9-phenoxyphenanthrene are shown on Figure 5.7.

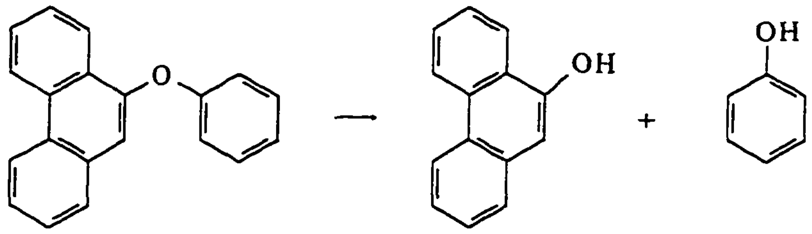
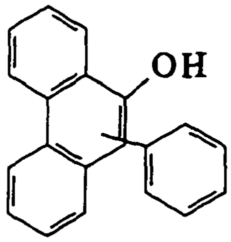


Figure 5.7. Aquathermolysis of 9-Phenoxyphenanthrene.

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 72% mole of the material recovered (recovery was close to 100%).

Under coal pretreatment conditions (325°C, 750 psia, 15 minutes) 9-phenoxyphenanthrene was unreactive. The product was approximately 80% mole 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 in liquid water. Clearly, the ether linkages in coal are more reactive than 9-phenoxyphenanthrene even at the lower water density of steam pretreatment.

The studies were then conducted with α-NMPE under conditions of aquathermolysis in liquid water. The results are shown in Table 5.2.3. along with values

Table 5.2.3.

Conversion of α-Naphthylmethyl Phenyl Ether (% mol).

PRODUCT CONDITIONS	phenol	methyl naphthalene	naphth-aldehyde	isomeric starting material	starting material
Inert	36.3	27.3	9.1	27.3	0.0
Steam	37.9	24.2	4.5	27.3	6.1
Liquid Water	35.5	10.2	6.8	47.5	0.0

obtained under steam treatment conditions and under inert atmosphere.

In all cases there is a substantial amount of isomeric starting material present. The major difference between results obtained at high pressure in the liquid phase 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.

5.2.2. Treatments in the Presence of Zeolite

The use of zeolite was tested as a way to control the reaction pathway by reducing molecular rearrangement. Zeolite in the form of neutral molecular sieves was used in this part of the study. Steric and transport effects can modulate the product distribution and, therefore, may inhibit pathways to isomerized starting material.

The model compounds α-BNE and α-NMPE mixed with 5Å zeolite were reacted in steam and in a flow of nitrogen at 322±3°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 the same way as when no zeolite was present. The reaction products are shown in Table 5.2.4 for α-BNE and in Table 5.2.5 for α-NMPE.

In case of α-BNE the isomerization and recombination of radicals was successfully suppressed by zeolites. Only 4.5% mole of the isomerization product was formed under inert atmosphere and none under steam pretreatment conditions.

The effect of zeolite addition to α-NMPE was less dramatic. It has to be noted, however, that α-NMPE was found to be thermally less reactive by Chawla *et al.* (1990). In the presence of zeolite the yield of methyl naphthalene was reduced, the yield of isomeric starting material increased; the amount of phenol was increased in steam and decreased in inert atmosphere.

For both α-BNE and α-NMPE the difference between steam and inert treatment became more pronounced in the presence of zeolite.

9-Phenoxyphenanthrene was also reacted in the presence of 5Å zeolite under coal pretreatment conditions (325 C, 750 psia, 15 min). However, as in the absence of zeolite, 9-phenoxyphenanthrene was unreactive. The reaction product contained about 80% of isomerized starting material.

Comparing these results with the results obtained in the studies of coal/zeolite mixtures (Section 5.1.3.2), it appears that the way zeolite influences model compound product distribution is different from its effect on coal. Most likely, in the case of coal, zeolite works in the liquefaction stage, even when the coal/zeolite mixture is first exposed to steam. For model compounds, on the contrary, the effect of zeolite is seen during

Table 5.2.4.

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

Product Distribution in Steam and in Inert Atmosphere (% mol)

PRODUCT CONDITIONS	1-naphthol	isomeric starting material
STEAM	91.4	0
INERT	79.1	4.5

Table 5.2.5.

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

Product Distribution in Steam and in Inert Atmosphere (% mol)

PRODUCT CONDITIONS	phenol	methyl naphthalene	naphthaldehyde	isomeric starting material
STEAM	45.6	19.1	5.9	27.9
INERT	35.5	21.0	6.5	35.5

thermal and hydrothermal treatments. However, a dramatic improvement resulting from zeolite addition was observed only for one compound, α-BNE. For α-NMPE, application of zeolite affected product distribution only slightly.

It appears that water assisted reactions do not play a major role in the treatment of α-BNE and α-NMPE, even in the presence of zeolite. In case of α-BNE, zeolite induces the formation of cleavage products in both steam and inert atmospheres. Zeolite, from the other hand, does not have any effect on the cleavage of 9-phenoxyphenanthrene. This thermally stable compound can be cleaved only in liquid water under high pressure, where the reaction mechanism becomes ionic. For two other ethers (α-BNE and α-NMPE) the reaction pathway, probably, remains mostly radical, independent of the presence of water. (α-BNE, however, was not reacted in liquid water.)

6. CONCLUSIONS

1. Steam pretreatment substantially improves the yield and the quality of 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 a 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 350°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. A more pronounced exothermic effect is observed in the initial stages of liquefaction of steam pretreated coal compared to the liquefaction of raw coal. The number of new hydroxyl groups introduced into coal by steam pretreatment is sufficient

to explain this increased exothermicity.

5. The compounds α-benzylnaphthyl 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.

6. 5Å Zeolite (neutral) is effective in suppressing the formation of isomerized starting material in the thermolysis of α-benzylnaphthyl ether but not α-naphthylmethyl phenyl ether and 9-phenoxyphenanthrene, when treated in steam and in inert atmosphere.

The presence of 4Å and 5Å zeolites during pretreatment and liquefaction increases yields of asphaltenes and preasphaltenes. Zeolites, most likely, work at the liquefaction stage and do not have to be present during steam pretreatment.

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