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ABSTRACT

High conversions of subbituminous coal to liquid or soluble products were obtained by treatment with large amounts of zinc chloride together with tetralin at temperatures below those of coal pyrolysis. Treatments were carried out in a stirred batch reactor at 250 to 325°C for durations of 10 to 120 min with hydrogen at 3.5 MPa total pressure. The extent of conversion was determined by solvent extractions with cyclohexane, toluene, and pyridine, and products were characterized by elemental analysis, gel permeation chromatography, proton nuclear magnetic resonance, and oxygen functional group analysis. The conversions to soluble products reached 50% solubility in cyclohexane and 85% in pyridine for treatment at 300°C. This conversion increased with increasing temperature and duration of treatment, and was accompanied by progressive reductions in molecular weight as well as by elimination of oxygen (especially ether oxygen) in coal. This behavior, along with the increase in product

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aromaticity with increasing conversion, indicates a mechanism involving $ZnCl_2$-catalyzed cleavage of crosslinking bonds in the coal. Recombination of the resulting reactive species is prevented by $ZnCl_2$-catalyzed transfer of hydrogen from the tetralin, coal products, and reactor atmosphere, and by alkylation of the tetralin.

I. INTRODUCTION

There is little doubt that the United States' dependance on foreign oil could be reduced if her abundant domestic coal reserves were used as a major alternate energy source. Because much of our economy is based on liquid fuels, one desirable approach to increasing our utilization of coal is the conversion of coal to liquid fuels. This work concerns certain aspects of one approach to coal liquefaction; liquefaction by zinc chloride catalysis at temperatures below the coal pyrolysis temperature. The significance of this approach can be understood through examination of the currently well-developed approaches to coal liquefaction.

Conversion of Coal to Liquid Products

There are three general requirements of a coal liquefaction process. First, chemical bonds must be broken in the coal in order to convert it from a high molecular weight solid to a lower molecular weight liquid (1). Second, hydrogen must be added to the coal because most liquid fuels have a molecular hydrogen to carbon (H:C) ratio of from 1.2 to 2.2, while the ratio for bituminous or subbituminous coal is about 0.9. Although new liquid fuels might be developed with low H:C ratios, some hydrogen addition is still necessary (2). The third requirement of a coal liquefaction process is that there must be a means of processing the solid. Coal can be ground to a particle size of 0.1 mm or smaller, but a means must exist for transferring heat to the solid particles, and for removing products from them. This requirement is usually satisfied by slurrying the coal into an organic liquid vehicle, which is generated by recycle of a distillation cut of the coal liquefaction products.

Almost all of the processes that are now being developed for coal liquefaction operate at temperatures above 350°C (2), where thermal energy is sufficient to break chemical bonds in the coal (3). Called pyrolysis, this cleavage can be interpreted as the creation of intermediate coal products with reactive free radicals (4). These free radicals must be made unreactive, usually by saturation with hydrogen, to prevent recombination and condensation reactions that produce 'char', a high molecular weight byproduct of low hydrogen content (5).

The hydrogen that is required for free radical saturation can be introduced into the coal from high pressure gaseous hydrogen, from hydrogen rich portions of the recycle solvent, or from the coal itself (2). A solvent that has the capacity to lose hydrogen to the coal is called a hydrogen-donor solvent. If the H:C ratio of the coal is to be improved, then molecular hydrogen must be added at some point, either in a slurrying vehicle with hydrogen-donor capability, or by direct incorporation (catalyzed or uncatalyzed) of molecular hydrogen into the coal during pyrolysis.

There are several alternative approaches used to supply hydrogen to initial coal pyrolysis products in liquefaction processes presently under development. These different methods are represented by the Solvent Refined Coal (SRC I) process, the HCOAL process, and the Exxon Donor Solvent (EDS) process. SRC I and HCOAL both use high pressure hydrogen gas in the reactor to provide the needed hydrogen. The HCOAL process differs in its use of a heterogeneous catalyst in the coal conversion reactor to increase the rate of hydrogen transfer to the coal products and to the solvent. In the EDS process the recycle solvent is catalytically hydrogenated before being introduced into the uncatalyzed reactor. Hydrogen for EDS coal liquefaction is provided by the hydrogen-donor solvent and by gas phase hydrogen.

In the SRC I process, a slurry of coal and recycle solvent is heated to 440°C under 6.9 to 13.8 MPa of hydrogen pressure (6,7). Use of a solvent/coal slurry makes the coal solids handling and pumping easier, and the presence of solvent improves heat and mass transfer to and from the coal particles. The solvent also aids in the transfer of hydrogen from the gas phase, and from hydrogen rich portions of the coal, to the bonds cleaved by pyrolysis. The solvent 'shuttles' hydrogen by becoming hydrogenated and dehydrogenated in parts of its hydroaromatic structure (8). At a temperature of 440°C, hydroaromatics and aromatics are roughly in thermodynamic equilibrium at a hydrogen pressure of 6.9 MPa (9). At pressures above 6.9 MPa, gas phase hydrogen may combine with the solvent or the coal, and participate in hydrogenation and free radical saturation reactions (4,10).

The extent of conversion, in pyrolytic coal liquefaction, is primarily limited by the amount of hydrogen that is transferred to the coal and products (4,10,11). Also, the quality of the products can be improved if hydrogen is available for reactions such as hydrodesulfurization and hydrodenitrification (8,12). In the SRC I process, the amount of hydrogen available is limited by the rate of uncatalyzed hydrogen incorporation into the solvent and the coal from the gas phase. Although as much as 90% (by weight) of the moisture and ash free (MAF) coal is converted, less than 20% of the MAF coal is converted to liquids boiling below 427°C (13). The major product of the SRC I process is an ash-free, low sulfur solid which melts at a temperature of about 170°C.

The amount of hydrogen that is available for coal conversion can be increased by the use of a hydrogenation catalyst. In the HCOAL process, the coal/solvent slurry is reacted in the presence of a heterogeneous catalyst under process conditions similar to SRC I (14). The catalyst improves the rate of hydrogenation of the solvent and of the coal products, which can diffuse into the catalyst (12) resulting in a higher yield of distillable products (14). Total conversion is about 90%, with about 50% of the MAF coal going to liquids boiling below 427°C (14). In addition, the catalyst participates in hydrodesulfurization, hydrodenitrification, and hydrocracking reactions that result in improved product quality (12,15).

The disadvantage of a process like HCOAL lies is in the severity of the conditions that the catalyst must tolerate. Coal liquefaction conditions are severe because the high sulfur and metal content of the coal can lead to catalyst poisoning and regeneration problems (16). These problems parallel those for heavy petroleum and residuum desulfurization. For feedstocks with high sulfur and metal content, a residuum desulfurization catalyst has a life of about 30 days, and cannot be regenerated (16). Typical feed coal for liquefaction has a sulfur content that varies from zero to five percent, and has a variety of minerals and metals in the ash (13).

An alternative approach to increase the amount of hydrogen that is available for transfer into the coal is to catalytically hydrogenate the recycle solvent before it is combined with the coal. This is done in the Exxon Donor Solvent process, in which the hydrogenation catalyst is exposed only to a distillate liquid that is much lower in sulfur and ash than the original coal, so that catalyst poisoning, fouling, and regeneration problems are reduced (17).

In the EDS process, the slurry of coal and hydrogenated recycle solvent is heated to 450°C, with 6.9 to 20.7 MPa of H_2 pressure, as in the SRC I process (17,18). Hydrogen may still be shuttled from the gas phase, or from hydrogen rich portions of the coal, but the solvent itself has a large amount of hydrogen that can be donated to saturate the reactive free radicals and increase the H:C ratio of the products. The capacity of a solvent to donate hydrogen, as well as its effectiveness in shuttling hydrogen, is measures in terms of a "solvent quality index". When the solvent quality drops below a certain index (which varies for different coals) the yield of liquids, from EDS coal liquefaction, decreases sharply with decreasing solvent quality. When the solvent quality is high, the EDS process has a yield of about 40% of the MAF coal going to liquids boiling below 540°C (17).

None of the pyrolysis-based process cited above are fully effective at preventing the formation of char and light hydrocarbon gases (7,4,17). Char is undesirable because it is a refractory solid that is difficult to convert to lighter products. Gas creation uses much hydrogen because of high gas H:C ratios (example: methane, H:C = 4). Process improvements are important to minimize the utilization of costly hydrogen, and to maximize the liquid yield (19). The origin of gas production in pyrolytic coal liquefaction can be understood by examination of the chemistry of thermal reactions of coal.

Bituminous and subbituminous coal have been described as having a structure in which large (MW 200 to 1000) hydroaromatic clusters are crosslinked to each other by bonds including ether oxygen, aliphatic carbon chains, and hydrogen bonding (8,20-22). The cleavage of these crosslinks results in a liquid product. In their study of the thermal cleavage of chemical bonds in coal-related compounds, Benjamin and coworkers (3) found that, at 400°C, a wide variety of ether-oxygen and aliphatic-carbon bonds were cleaved. Thermal cleavage of chemical bonds in several compounds (example: butyl benzene) resulted in gas production (3). Any process that operates at temperatures above the coal pyrolysis temperature has to contend with thermal bond cleavage leading to gas formation (3,17,23,24). Typical gas yields for SRC I, HCOAL, and EDS are all in the range of 8 to 10% by weight of the MAF coal (13,14,17).

The implication of these observations is that if coal could be liquefied at temperatures below pyrolysis, it might be accomplished with less gas (and possibly char) formation. Unfortunately, the rate of cleavage of chemical bonds in coal at lower temperatures is not favorable. This has been demonstrated by Draemel, who treated Wyodak subbitiminous coal with tetralin, a hydrogen-donor solvent under suitable conditions and a good non-specific solvent for coal (25). At 350°C, the yield of dissolved material after 8-1/2 hours was only 30%. This yield decreased sharply at lower temperatures.

If coal is to be liquified at temperatures below pyrolysis, the rate of chemical bond cleavage must be increased. This could be accomplished by a catalyst that could selectively break crosslinking chemical bonds within the coal structure. However, heterogeneous catalysts, such as those used in the HCOAL process, cannot interact with the coal until thermal cleavage has created initial pyrolysis products that are dissolved in the liquid solvent and thus can diffuse into the catalyst (12). What is required is a dissolved (homogeneous) catalyst that can enter the coal particle to catalyze the required cleavage reactions.

Lewis Acid Catalyzed Coal Liquefaction

Since coal liquefaction below pyrolysis temperatures could be accomplished with homogeneous catalysts, the action of such catalysts on coal must be considered. To this point, the only class of catalysts that has been developed as homogeneous catalysts for coal liquefaction is Lewis acid catalysts (16). The Lewis acids that have received the most attention industrially are transition-metal halides such as zinc chloride and stannous chloride (26,27). These halides are frequently used as molten salts; in this form they have the additional abilities to remove heat because of their high thermal conductivity, to continuously expose fresh catalyst surface, and to increase catalyst activity and selectively by their high polarization forces (16,28). Research on the use of Lewis acid catalysts for coal liquefaction has been carried out at temperatures ranging from 200 to 500°C (26,29).

Experiments carried out in 1950 by researchers at the U.S. Bureau of Mines laboratories in Pittsburgh and Bruceton, Pennsylvania, showed zinc and stannous chloride to be effective for promoting subbituminous coal liquefaction (30,31). Since their experiments developed out of a program to test metal catalysts, the experiments were performed by mixing coal with several percent of a powdered metal, with or without ammonium chloride as a promoter. Reactions were carried out at 450°C, with 6.9 MPa of hydrogen gas pressure. Metals that were tested included tin, zinc, nickel, molybdenum, sodium, selenium, cadmium, antimony, and arsenic. Tin and zinc, when promoted by the chloride, were found to be the best catalysts. Initial states of the metal and halide were unimportant as long as both were present. Studies with stannous chloride showed that better coal liquefaction was obtained when more intimate catalyst-coal contacting was used.

In 1976, Ross and coworkers, at SRI International, screened a variety of homogeneous catalysts, including many metal halides, for their activity in promoting coal liquefaction under mild conditions (29). Halides of aluminum, antimony, zinc, and tantalum were used in a 1:1 weight ratio to coal to catalyze conversion at 210°C. The activity of the halides was ordered as follows:

$$AlCl_3 > AlBr_3 \gg SbCl_3 \approx SbF_3 \approx ZnCl_2 \approx TaF_2 \quad .$$

When experiments were performed with a constant molar amount of catalyst, the work revealed a dramatic effect of catalyst loading. The amount of tetrahydrofuran (THF) soluble material that was produced in five hours of reaction with antimony chloride rose from 1% for the 1:1 (by weight) loading to 100% for a 2.6:1 loading. Since all of the more active catalysts melted at temperatures below the reaction temperature, it was suggested that $ZnCl_2$ might be inactive at these conditions because of its high (315°C) melting point.

Two processes have been investigated for the conversion of coal to liquid fuels using Lewis acid catalysts. For both processes, zinc chloride has been selected as the catalyst of choice; the processes differ in the amount of catalyst loading. One process uses a small amount of $ZnCl_2$ impregnated into the coal, while the other uses a catalyst/coal ratio ranging from 1.0 to 2.5. Both processes operate at temperatures above pyrolysis.

The $ZnCl_2$ catalyzed coal conversion process developed at the University of Utah produces liquid fuels in a high temperature, short contact time reactor (26,32). The $ZnCl_2$ is solution impregnated into the coal to a concentration of about five percent by weight. Although early work showed that $ZnBr_2$, ZnI_2, $ZnCl_2$, and $SnCl_2$ were all effective as catalysts (26), zinc chloride was selected for economic reasons (33). The $ZnCl_2$ is cheaper and more easily recovered, and use of $ZnCl_2$ results in a better selectivity to liquids over gas and char.

In this process, powdered, impregnated coal is entrained in hydrogen, and passed through a heated 4.76 mm (I.D.) stainless steel tubular reactor (26,32). The conversion to products increases with increasing temperature, reaction time, and pressure. Conversion also increases with decreasing coal particle size. For subbituminous coal, liquefaction yields of about 40% soluble oil plus asphaltene, and about 13% gas (mostly methane), on a DAF basis are obtained for reaction conditions of: 500°C, 25 seconds, 13.8 MPa, 100 μm particle size. The $ZnCl_2$ can be recovered in amounts up to 99% by use of aqueous and acid washes of the products and char (26).

A chemical mechanism for conversion at these conditions has been proposed by the University of Utah researchers (32,34). In this mechanism, chemical bonds in the coal are thermally cleaved, yielding free radicals. These free radicals may be stabilized by hydrogen or they may condense to form char, as in other pyrolytic processes. The $ZnCl_2$ promotes an increase in the rate of hydrogen transfer to the free radicals. In addition, $ZnCl_2$ catalyzes the dehydrogenation of hydroaromatics in the coal, creating an additional, internal source of hydrogen. The role of the $ZnCl_2$ also includes promoting a decrease in the molecular size of the products. However, the researchers have not found $ZnCl_2$ to appreciably affect the structure of the products (34).

Conoco Coal Development Company has developed a zinc chloride catalyzed coal liquefaction process based on the use of massive amounts of the catalyst in a continous molten phase (27,35-40). Formerly the Consol Synthetic Fuel project, Conoco's process developed out of an attempt use zinc chloride to crack coal extracts (35).

In this process, coal is slurried with a recycle solvent and fed into a reactor with zinc chloride and hydrogen. Most of the product is taken off as vapor. Hydrogen is recycled, light gases are removed, and the liquid products are split between gasoline range liquids and recycle solvent. The spent catalyst melt is stripped of organics to a 5 to 7% carbon level and is regenerated in an adiabatic fluidized sand bed combuster (27).

Bench scale equipment has been used by Conoco to investigate the reaction system at temperatures of 350 to 450°C (mostly above 385°C), at hydrogen pressures of 10.3 to 34.5 MPa, $ZnCl_2$/coal weight ratios of

1.0 to 2.5, and residence times of 30 to 200 minutes (40). At 385°C, with 20.7 MPa of hydrogen and a $ZnCl_2$/coal ratio of 2.5, a variety of coals can be cracked to distillate fuels. For a 60 minute reaction with subbituminous coal at these conditions, typical yields are 55% of C_4 x 200°C distillate and a total of 75% C_4 x 400°C distillate plus MEK soluble products (on a DAF weight basis) (41).

The advantage of the Conoco process is the high yield of gasoline range products. Unfortunately, the process is very sensitive to zinc chloride loading (40). It is important to minimize the $ZnCl_2$/coal ratio because $ZnCl_2$ recovery is an expensive part of the process (27,39). However, the yield of C_4 x 200°C distillate drops to a 17% when a more reasonable $ZnCl_2$/coal ratio of 1.0 is used. At this catalyst loading, an increase of the temperature to 413°C increases the yield only to 25%. As the temperature is increased above 400°C, light (C_1 to C_3) gas production increases rapidly (38).

Conoco found $ZnCl_2$ also to be active at lower temperatures, catalyzing the conversion of coal to a low sulfur fuel oil (41). At a temperature of 358°C and a hydrogen pressure of 10.3 MPa, with a $ZnCl_2$/coal ratio of 2.5, bituminous coal is converted in 60 minutes to 56% C_4 x 400°C distillate plus 20% MEK soluble product. Subbitiminous coal could not be reacted without a solvent vehicle. When a non hydrogen-donor vehicle was used, the yield of distillate and solubles was very low. Use of tetralin, a hydrogen-donor solvent, gave a yield of 27.5% C_4 x 400°C distillate plus an additional 47% MEK soluble products. Use of tetralin did not increase the yield for bituminous coal, nor was tetralin necessary for use with any coal at higher temperatures.

All of the research on zinc chloride catalyzed coal liquefaction that has been performed by researchers at Conoco and at the University of Utah has concerned liquefaction at temperatures above the coal pyrolysis temperature. At Lawrence Berkeley Laboratory a program is underway to investigate coal liquefaction at temperatures below pyrolysis. Derencsenyi (42), Holton (43), Mobley (44), Salim (45), Maienschein (46), and others have studied various aspects of zinc chloride catalyzed coal liquefaction at temperatures of 200 to 325°C.

Derencsenyi and Holton both have studied $ZnCl_2$ catalyzed coal liquefaction at mild temperatures of 200 to 250°C. To avoid the effects of catalyst loading, both investigators used a $ZnCl_2$/coal weight ratio of 6:1. In addition, because $ZnCl_2$ melts at 315°C, they added 10% (by weight) water to the $ZnCl_2$. Yields were based on the DAF solubility of the melt treated coal in benzene and pyridine (benzene solubility is roughly equal to the 'soluble oil plus asphaltene' cited in the research at University of Utah (26)).

Derencsenyi investigated the activity of $ZnCl_2$ and the effect of inorganic additives on $ZnCl_2$ activity at 200°C and atmospheric hydrogen pressure (42). Treatment of Wyodak subbituminous coal under these conditions for 60 minutes resulted in benzene solubility being increased from an untreated-coal value of 0.5% to 2.3%. Additives, including other metal halides such as stannous chloride, and including metals such as Raney nickel and aluminum, were used in amounts of from 1 to 15% of the melt. These additives largely had no effect, except for $KI + I_2$, which increased the benzene solubility to 7%. Derencsenyi concluded that although $ZnCl_2$ has a strong mechanical effect of breaking up coal particles, very few chemical bonds were being broken at 200°C.

Holton studied the activity of $ZnCl_2$, and the effect of organic additives on $ZnCl_2$ activity, at 250°C with 3.5 MPa of hydrogen pressure (43). $ZnCl_2$ treatment of Wyodak coal for 60 minutes increased benzene solubility to 4.6%. Pyridine solubility was increased from an untreated-coal value of 12.8% to 21.4%. When a hydride donor, such as di-isopropyl-benzene, was added to the melt in amounts similar to the coal, the yield was increased to 7.8% benzene and 39.7% pyridine solubles. Use of tetralin together with the melt increased benzene solubility to 16.6%, and pyridine solubility to 77%. Although an unknown amount of solvent may have been incorporated in the melt treated coal and extracts, subbitiminous coal was converted into a pyridine-soluble material at temperatures well below coal pyrolysis temperatures by the use of $ZnCl_2$ with organic solvent additives.

Mechanisms of Lewis Acid Catalysis

In a coal liquefaction process that operates above pyrolysis temperatures, even with a homogenous catalyst, many of the bond cleavage reactions are thermally activated (32). At temperatures below pyrolysis the chemical reactions that are catalyzed become especially important (44). An understanding of these reactions can be gained by examination of Lewis acid catalysis of reactions in an environment that excludes coal.

Much of the catalytic activity of Lewis acids is attributed to their electrophylic interaction with organic substrates (44,47). The range of reactions that may be catalyzed is large (47-49). Aluminum chloride catalyzes Friedel-Crafts alkylation, in which an aromatic compound is alkylated with an alkyl halide (47). The same chemistry works with other Lewis acids, and can also use alcohols in the place of alkyl halides (47). Some other reactions that are catalyzed by metal halides include carbonylation of aromatics (49), isomerization of parafins (48), and dehydrochlorination (48). The importance of Lewis acid catalyzed reactions in coal liquefaction must be viewed in the light of the nature of chemical bonds in coal.

Subbituminous coal has been described as containing a variety of aromatic and hydroaromatic structures, with clusters in which the aromatic nuclei are usually condensed into groups of no more than four rings (8,50). These clusters, with molecular weights in the range of 200 to 1000, are crosslinked to each other primarily by ether oxygen and aliphatic bridges (20-22). Hydrogen bonding in and between the clusters is effected, in part, by the phenolic hydroxyl groups and the heterocylic nitrogen that is present (51). Oxygen, sulfur, and nitrogen are distributed throughout the organic structure of the coal, with most of the nitrogen, and some sulfur and oxygen, occupying positions within aromatic rings (2,52). The effect of zinc chloride and aluminum chloride on compounds that model the crosslinking between the aromatic and hydroaromatic structures in coal has been studied at Lawrence Berkeley Laboratory by Mobley, by Salim, and by Maienschein.

Mobley studied the reactions of oxygen and sulfur containing compounds (44). He found that at temperatures as low as 225°C, treatment of a variety of benzyl ethers with $ZnCl_2$ resulted in a total conversion of the ethers. The compounds were cleaved between the oxygen and the benzyl part of the molecule. The oxygen was removed, and both fragments alkylated any aromatic present (although not strictly an 'alkylation' reaction, this term is used for the chemical bonding of cleavage fragments to aromatics, because of the similarity of these reactions to Friedel-Crafts alkylation). For example, when dibenzyl ether was reacted in the presence of benzene solvent, diphenyl methane was the major product. If the oxygen was bound directly to an aromatic ring, that fragment remained phenolic. When the experiments were performed with cyclohexane solvent, the substrate itself was alkylated, and the reaction led to tar formation. Treatment of cyclic ethers, such as tetrahydrofuran, with $ZnCl_2$ in combination with benzene at 325°C resulted in cleavage of the ether-containing ring. The cracking products underwent rearrangement before alkylating the benzene, and several products were formed. Reactions of the oxygen-containing compounds were explained in terms of a carbonium ion mechanism. The zinc chloride-catalyzed reactions of several sulfide compounds were examined, and these compounds were found to behave similarly to their analogous oxygen compounds.

In her review of the literature, Salim found that most two and three ring aromatic compounds were reported to be susceptible to Lewis acid catalyzed cleavage reactions at temperatures of 350 to 450°C (49). Salim reacted two and three ring compounds in cyclohexane solvent at 325°C in the presence of zinc chloride or aluminum chloride. With both catalysts anthracene was more reactive than phenanthrene, which was more reactive than naphthalene. With zinc chloride, the compounds underwent ring hydrogenation, followed by cleavage of the saturated ring.

Hydrogenation was enhanced by the presence of a hydroxyl group on the substrate. All substrates were more reactive in the presence of aluminum chloride than zinc chloride; use of $AlCl_3$ resulted in substantial tar formation, as well as high yields of light products.

Both Mobley and Salim carried out their experiments with a large excess of solvent. Catalyst and substrate were both present in small (~5%) amounts. Maienschein reacted a variety of model compounds using large amounts of $ZnCl_2$ catalyst (46). A solution of 0.5% substrate and 2.5% alkylation medium (benzene or ethylbenzene) in an unreactive dodecane solvent, was contacted with four moles of zinc chloride per mole of solvent (approximately 1:1 solvent/$ZnCl_2$ on a volume basis). Water was added to the $ZnCl_2$ to insure a liquid phase. Maienschein studied the effect of $ZnCl_2$ treatment, at temperatures of 200 to 300°C, on compounds that model the aliphatic and ether bridges in coal.

In the series--diphenyl, diphenyl-methane, 1,2-diphenyl-ethane, 1,3-diphenyl-propane--only the diphenyl-methane reacted. Conversion was 70% after one hour at 250°C. The cleavage products were benzene and benzyl fragments, which then 'alkylated' onto the alkylation medium. The presence of a hydroxyl group on either of the rings increased the rate of cleavage by a factor of 100. Maienschein investigated a series of benzyl ethers and found them all to undergo rapid reaction. Reaction for 5 minutes at 200°C was sufficient to completely convert dibenzyl ether to alkylation products of benzyl fragments. Alkylation behavior was similar to that observed by Mobley. Maienschein also examined the reactions of methoxybenzene, methoxynaphthalene, and ethoxynaphthalene.

These compounds were found to cleave slowly, in the presence of zinc chloride at 250°C, to products including phenol or naphthol.

The studies with model compounds have shown that $ZnCl_2$ catalyzes the cleavage of a variety of bridging structures in coal. These studies have not explained why low temperature $ZnCl_2$ catalyzed subbituminous coal liquefaction yields are so improved by the presence of tetralin (41-44).

Tetralin can serve as an alkylation medium, as was the case when Mobley used tetralin as a solvent in his model compound studies (44). Tetralin may assume other roles in the coal liquefaction environment. At temperatures above the coal pyrolysis temperature, tetralin is considered a reactive solvent: a solvent with easily abstractable hydrogen, which provides hydrogen to the coal during pyrolysis (53). At temperatures below 320°C, and without a catalyst present, Draemel found no evidence of hydrogen donation from tetralin to bituminous coal (25). In the presence of $ZnCl_2$, however, Salim did see some naphthalene conversion to tetralin at lower temperatures (45), indicating that the usefulness of tetralin as a hydrogen-donor solvent may be extended to lower temperatures by the catalyst.

At temperatures below pyrolysis, tetralin is considered to be a non-specific solvent, a solvent that can extract only a relatively small amount of coal (53). In the coal liquefaction environment this type of solvent may still serve to dissolve and remove products from the coal particle, and thereby open up the particle for further reaction.

Scope

The subject of this investigation has been the conversion of subbituminous coal to soluble products by treatment with zinc chloride and tetralin at temperatures below the coal pyrolysis temperature. The roles of the tetralin and the $ZnCl_2$, in the conversion mechanism, were investigated. The effect of catalyst loading was specifically not investigated; a constant 6:1 $ZnCl_2$/coal weight ratio being used. The chemical mechanism of the reaction system, over the range of temperature from 250 to 325°C, was examined through an extensive characterization of the coal conversion products. This included an examination of the dependence of the yield of soluble products on the removal of oxygen from the coal during treatment.

Nature of Results

The reaction system was studied in batch treatments of the coal with zinc chloride, tetralin, and hydrogen gas, the extent of conversion being characterized by product solubility in cyclohexane, toluene, and pyridine. The yields of these fractions were found to increase rapidly with increasing treatment duration over the initial 30 minutes of treatment at 300°C, followed by a period in which the total yield was constant and there was a net conversion of pyridine solubles to cyclohexane solubles. The yields of 60 minute treatments were found to increase uniformly with temperature over the range from 250 to 325°C.

The extracts and melt treated coal have been characterized by a number of physical and chemical means. Elemental analyses for carbon, hydrogen, nitrogen, and ash were used to provide a firm basis for extraction calculations, as well as to examine the amount of hydrogen addition to, and oxygen and nitrogen removal from, the coal. While the amount of hydrogen addition was small over a wide range of conditions, the oxygen and nitrogen removals were found to be very nearly proportional to product yields. The extracts were also characterized for molecular weight distribution and for chemical structure by the use of gel-permeation chromatography and proton nuclear magnetic resonance, respectively.

II. EXPERIMENTAL EQUIPMENT AND PROCEDURES

The experimental program has been designed to investigate the effects of temperature, time, and solvent on the yield and character of soluble products from zinc-chloride catalyzed coal conversion at temperatures below pyrolysis. Most experiments consisted of combining subbituminous coal with $ZnCl_2$, heating under hydrogen to reaction temperature, addition of tetralin, reaction for a specified time, and finally transfer of the products into a quench tank containing water. A series of separations was used to remove $ZnCl_2$ and tetralin, and to separate the remaining melt treated coal (MTC) into product fractions.

Materials

The coal that has been used in most experiments was supplied by Wyodak Resources Development Company from the Roland seam of its mine in Gillette, Wyoming. The coal has an apparent rank of subbituminous-C; its proximate and elemental analyses are shown on Table II-1. The coal size as received was minus 3/4 inch, and it was subsequently crushed to minus 1/16 inch and stored in 20 lb quantities under nitrogen. In preparation for a series of experiments a quantity of coal was sieved in a nitrogen atmosphere to yield 36% of a minus-30, plus-60 mesh fraction which was split into 300 g portions, and stored under nitrogen in one pint cans. This coal was used in the later experiments on which most of this work has been based. Preliminary experiments were run using a minus-28, plus-100 mesh fraction that had been prepared by a previous investigator (43) (the minus-60, plus-100 mesh fraction of this coal represents 20% of the total fraction).

Table II-1: Analysis of Coals

Proximate Analysis

	Wyodak(1)		Rosebud(2)		Monarch(2)	
	AR(3)	Dry	AR(3)	Dry	AR(3)	Dry
Moisture	23.2		15		15	
Ash	10.8	14.1	7.8	9.2	6.0	7.0
Volatile Matter	35.6	46.3	33.2	39.0	34.8	40.9
Fixed Carbon	30.4	39.6	44.0	51.8	44.3	52.1

Elemental Analysis(4)

	Wyodak		Rosebud		Monarch	
	Dry	DAF	Dry	DAF	Dry	DAF
Carbon	62.5	72.3	64.6	75.4	64.4	70.2
Hydrogen	5.1	5.9	4.5	5.3	4.5	4.9
Nitrogen	0.93	1.08	0.93	1.09	1.27	1.38
Sulfur	0.56	0.65	1.48	1.73	0.26	0.28
Chlorine	0	0	-	-	-	-
Ash	13.6	-	14.4	-	8.2	-
Oxygen (by difference)	17.3	20.0	14.1	16.5	21.3	23.2

notes (1) Commercial Testing and Engineering Co. (Denver Co.)

(2) Penn. State Coal Data Base

(3) As Recieved, with moisture as used in experiments

(4) University of California Microchemical Analysis Laboratory

Other coals used were Rosebud seam coal, from near Colstrip, Montana, and Monarch seam coal, from near Sheridan, Wyoming. These coals were obtained from the Pennsylvania State University Coal Research Section. The Rosebud and Monarch coals are classified as subbituminous-B; they were received as minus-20 mesh under nitrogen and used as received. The proximate and elemental analyses for these coals are shown on Table II-1.

All inorganic reagents, analytical reagents, organic solvents, and cylinder gases used in this work, along with their source and purity, are listed in Table II-2. All water used for chemical and product washing purposes was distilled water. Solubility and vapor pressure data for the zinc chloride/water system is shown in Figure II-1 (see Holton (43)).

Apparatus

A few initial experimental runs were carried out in a top-stirred Parr autoclave, fitted with a 300-mL borosilicate glass liner. Details of this reactor can be found elsewhere (43).

The remaining experiments have been carried out in a reactor system designed to allow an accurate control of the temperature of treatment, duration of treatment, and presence or absence of tetralin. The overall reactor system includes a temperature controlled reactor vessel, a solvent preheat vessel, product quenching tanks, and a flow system for introduction of a metered amount of hydrogen to the reactor and for removal of gas from the reactor. The reactor system allowed a reproducible initiation of the treatment by tetralin addition to the reactor after sealing and heatup. A quick termination of the treatment was accomplished by transfer of the products into the quench tanks.

Table II-2: Sources and Purities of Reagents and Solvents Used.

Chemical	Source	Grade	Purity
Acetone	Mallinckrodt	Reagent	
Acetic anhydride	Mallinckrodt	Reagent	97 %
Anthracene	Aldrich		98 %
t-Butanol	Aldrich		
Calcium acetate	Mallinckrodt	Reagent	
Cyclohexane	Eastman	Practical	
Distilled Water	(In-house supply)		
Ethanol	Publickers Chemical Corp.		95 %
Hexamethyldisiloxane	Eastman		
Hydrochloric acid	Mallinckrodt		36.5 - 38 %
Hydroxylamine hydrochloride	Mall.	Reagent	96 %
2-Methyl-1-tetralone	Aldrich	Reagent	
Naphthalene	J. T. Baker	Reagent	
1-Propanol	Mallinckrodt	Reagent	
Pyrene	Eastman		
Pyridine	Mallinckrodt	Reagent	
Pyridine-d_5	Merck + Co.		99 % atomic
Sodium hydroxide	Mallinckrodt	Reagent	98 %
Sulfuric acid	Mallinckrodt	Reagent	96 %
Tetrahydrofuran	Mallinckrodt	Reagent	
Tetralin	Aldrich	Reagent	99 %
Toluene	Mallinckrodt	Reagent	
Zinc chloride	M. C. B.	Reagent	97 %
Cylinder Gases			
Hydrogen	Liquid Carbonic		99.999 %
Nitrogen	Pacific Oxygen		99.999 %

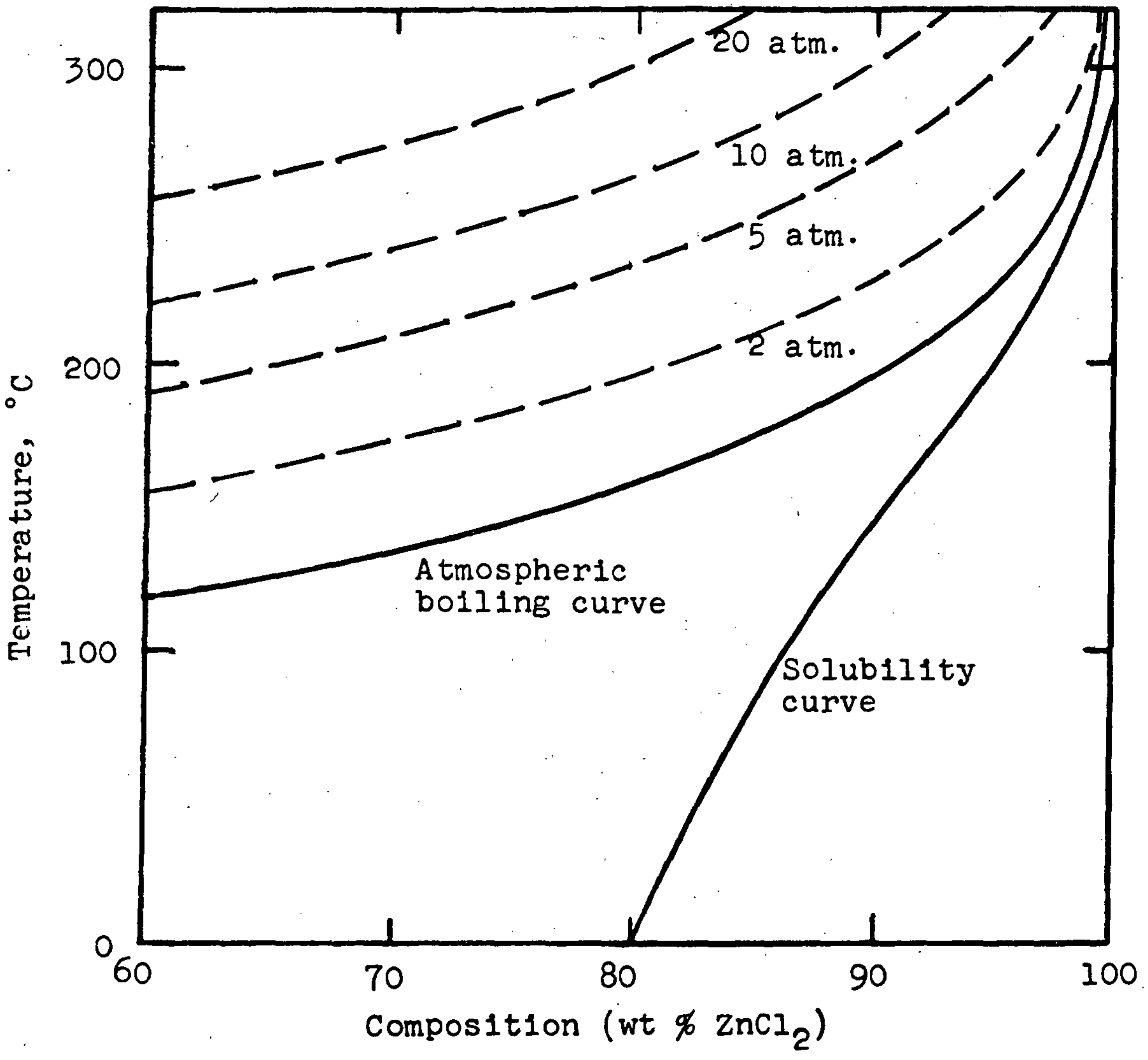
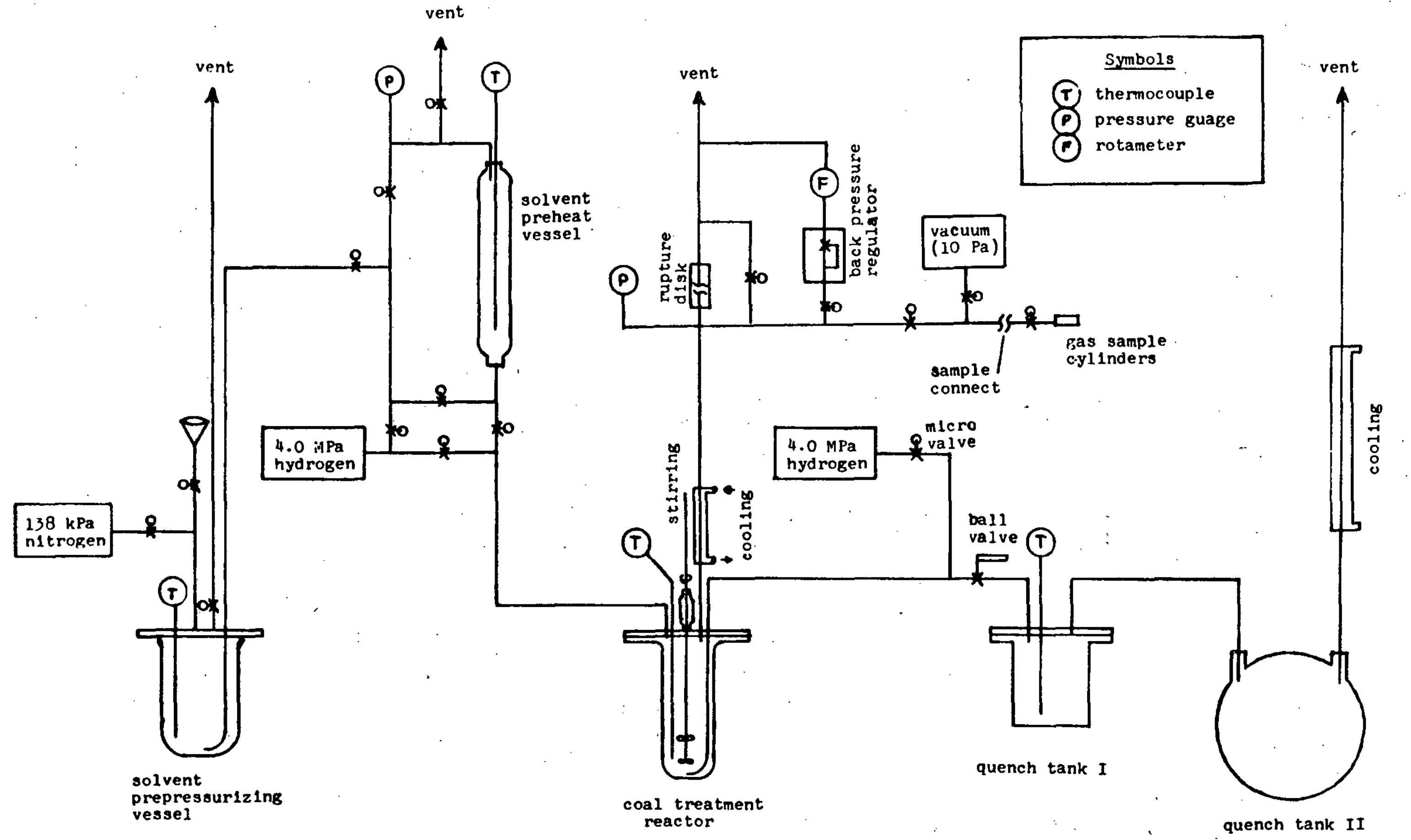


Figure II-1: Solubility and boiling curves for the $ZnCl_2/H_2O$ system (Holten (43)).

The overall flow system is shown in Figure II-2. The system includes (from left to right, following the direction of reactant and product transfer) a solvent prepressurization vessel, a solvent preheat vessel, the coal conversion reactor (with attached exit-gas manifold), and two sequential quench tanks. Low pressure nitrogen was used to direct solvent from the gravity-fed prepressurization vessel into the preheat vessel. High pressure hydrogen was used to drive the solvent into the reactor. Hydrogen gas flow was controlled by a micrometering valve, and introduced into the reactor through the same dip-tube that was used to transfer products to the quench tank. This arrangement served to keep the transfer line free of any reaction mixture until the end of the treatment, at which time the products were transferred through a high temperature and pressure ball valve into the quench tanks. During the run, the gas from the reactor exited via the exit-gas manifold, which includes a reflux condenser, a back pressure regulating check valve, an atmospheric-pressure gas rotameter, as well as a 5.0 MPa rupture disk and transfer lines for filling and evacuation of the 10 mL gas sample cylinders. All of the transfer lines are 1/4 inch O.D. stainless steel-316 tubing.

The reactor vessel, shown in Figure II-3, has a capacity of 500 mL, is top-stirred, and is constructed out of 316-stainless steel. It is sealed by a copper gasket that fits between knife-edges on the reactor flanges. Heating is provided with a 600 watt mantle that surrounds the reactor. Temperature was controlled by an Omega proportioning controller, actuated by a copper-constantan thermocouple, which monitored the temperature in the reactor.



<u>Figure II-2</u>: Schematic diagram for coal treatment reactor system

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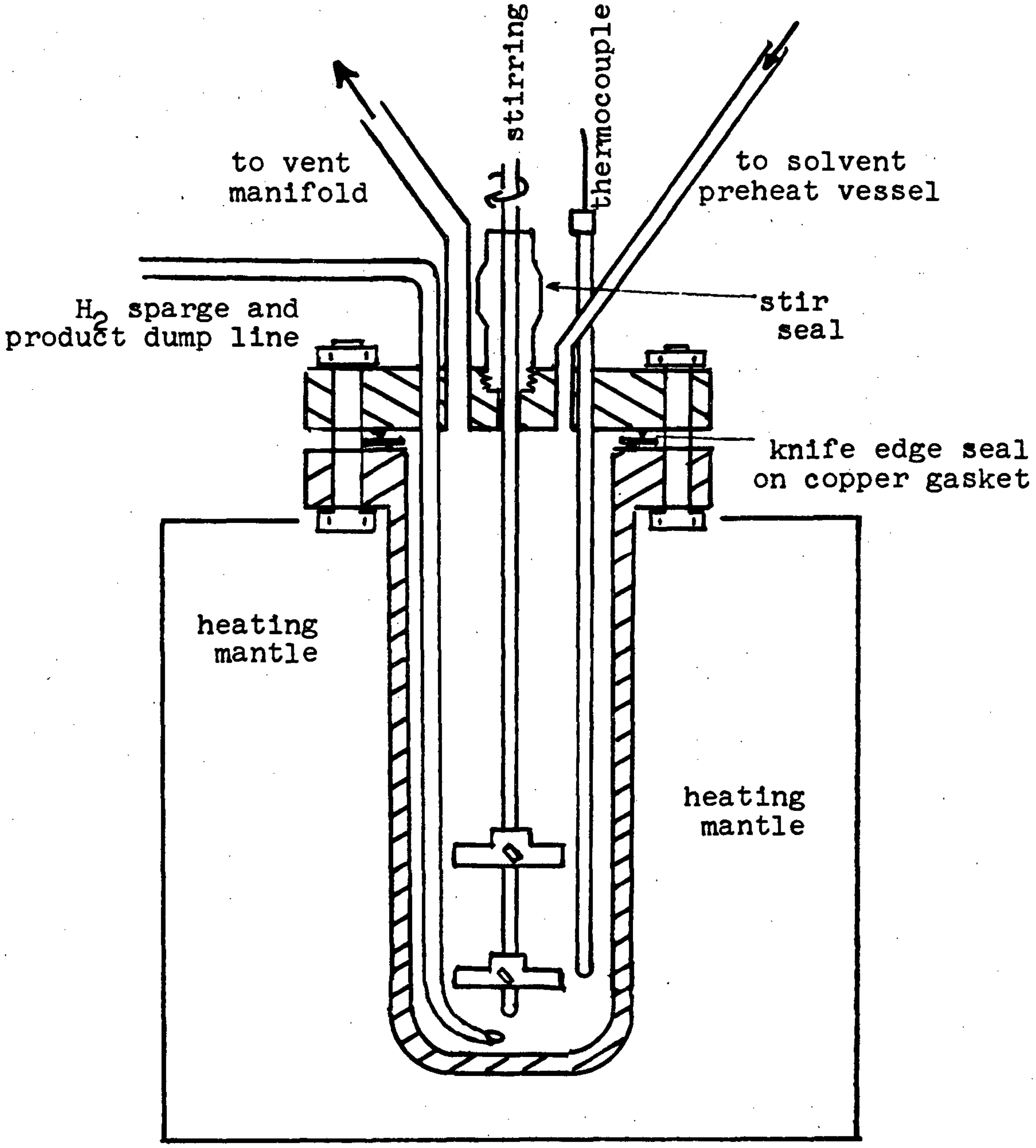

Figure II-3: Details, coal treatment reactor.

The solvent prepressurization vessel and the solvent preheat vessel have capacities of 500 mL, and are constructed of Corning Pyrex glass and 316-stainless steel, respectively. The quench tanks are constructed of stainless steel, for the first, and glass, for the second, and have capacities of 1000 mL and 3000 mL, respectively.

The preheat vessel, reactor flange, and transfer lines are heated with Briskeat high temperature heating tape, at a power of up to 12 watts per square inch. Power was controlled using variable AC transformers, and temperatures of these and other locations were monitored by means of iron-constantan thermocouples and an Omega digital thermocouple readout meter. Thermocouples were selected through a double-pole, twelve-throw rotary switch. Reactor temperature was read directly on the temperature controller and recorded on a Leeds and Northrup potentiometric recorder.

Procedures

The procedures of this work describe how the reactants and products of zinc chloride catalyzed coal liquefaction were handled in the course of the treatment and the separation that ensued. These procedures include the details of how reactants were combined, heated, reacted, and quenched, as well as the steps that were followed for removal of $ZnCl_2$, water, and tetralin from the products and the subsequent separation of those products into individual solubility fractions.

Conduct of Treatment

The procedure for the preliminary experiments conducted in the Parr reactor has been described elsewhere (43). In the vast majority of the remaining experiments a standardized procedure, developed for the equipment described in the previous section, was used, with slight variations.

In a typical treatment, 50 g of tetralin was heated to treatment temperature under nitrogen in the solvent preheat vessel. Simultaneously, 273 g of $ZnCl_2$ was combined with 27 g of water in the preheated reactor vessel. The mixture was heated to 175^oC, and 50 g of coal (containing moisture as received) was added. The contents of the reactor were stirred at about 60 rpm while the reactor was sealed, and H_2 flow was started through the dip-tube-sparger, with the vent open, to purge the reactor of air. After sealing, the vent was closed, and pressure quickly built up to the 3.65 MPa relief valve set point. Heating was started, and the temperature in the reactor rose at approximately $10^oC/min$ to the specified temperature. When the desired temperature was reached, stirring speed was increased to approximately 700 rpm and the preheated tetralin was added to the reactor; the reaction time was measured from this point. The hydrogen flow rate was adjusted to approximately 300 mL/min, and flow rate, pressure, and temperature monitored throughout the experiment.

After treatment for the desired period, the H_2 flow was reduced, heating stopped, stirring slowed to 60 rpm, and the ball valve opened slightly to transfer the reaction products into the quench tank, which contained 400 mL of cold water. Overflow from the first quench tank was caught in a second tank containing 1500 mL of water. After this transfer operation, 450 mL of cold water was transferred from the solvent preheat vessel to the reactor to cool any remaining contents. A small amount of this water was transferred into the quench tanks to insure that the transfer lines were empty. The total elapsed time from the start of the transfer to the reactor quenching was less than one minute.

Product Separation

After the reaction mixture was quenched, the contents of the quench tanks and reactor were vacuum filtered in an 11 cm Buchner funnel using filter paper. Any aqueous filtrate that was observed to contain oil was extracted with cyclohexane. The solid retained on the filter was transferred to a 1000 mL steel beaker, and 600 mL of boiling water was added. The mixture was then stirred vigorously while being boiled for 30 min, and was subsequently filtered as above. The (still moist) solids were next combined with 600 mL of boiling cyclohexane (plus any cyclohexane from filtrate extraction) and stirred vigorously while being boiled for 30 min. The mixture was then vacuum filtered in the Buchner funnel, and the filrate, which contained approximately 75% of the total cyclohexane soluble material, was devolatilized. The devolatilization was accomplished in three stages. First the liquid was boiled down to about 100 mL in an open 1000 mL boiling flask. The remaining material was then poured into a dried, weighed crystalizing dish, and the flask was rinsed into the dish with cyclohexane. The crystalizing dish was placed on a hot-plate at 120°C, and most of the remaining volatiles were removed in a 2 L/min stream of nitrogen that was directed at the sample. After about 60 min, the crystalizing dish, with oil and remaining volatiles, was transferred to a vacuum oven operated at 105°C with a 10 kPa atmosphere of nitrogen flowing at 200 mL/min (STP). The oil was dried to constant weight (approximately 48 h) and transferred to vials for storage. This cyclohexane soluble material is referred to as "wash oil" and was used for most oil analysis.

The solid that was retained on the filter paper after the cyclohexane wash was transferred to a crystalizing dish, dried in the vacuum oven for 18 h, and then cooled under vacuum, crushed with a mortar and pestle, washed in an 11 cm Buchner funnel (on filter paper) with 10 L of boiling water, and replaced in the vacuum oven to dry. The dried solids are referred to as "post-wash melt treated coal" (PWMTC). The total, non-volatile, organic product of the reaction, referred to as "melt treated coal" (MTC), was never actually recovered as a single product in this procedure; it is the calculated combination of the PWMTC and the wash-oil.

A 6 g sample of PWMTC was transferred to a dried, weighed, extraction thimble and sequentially extracted, in a standard Soxhlet apparatus, with cyclohexane (6 h), toluene (18 h), and pyridine (24 h) at their normal boiling points. These extracts are referred to as soxhlet-oil, asphaltene, and preasphaltene, respectively. The solutions of extracts were devolatilized using the same procedure that has been described for the wash-oil. The thimble with extraction residue was dried for 48 h in the vacuum oven then cooled and weighed. The dried and weighed extracts, residue, wash-oil, and remaining PWMTC were transferred to vials, placed in a second container with dessicant, and held for subsequent analysis.

Initial Product Recycle

Two experiments were performed using an isolated solubility fraction or residue as the substrate, in the place of coal. These experiments made use of several special procedures, mostly for the separations of the reactants and products.

The reaction substrates were generated using two standard treatments with the amounts of $ZnCl_2$, tetralin, and Wyodak coal increased by 10% in each. The product workup differed from normal in the following ways: the whole PWMTC from each reaction was extracted with cyclohexane (24 h) and then toluene (24 h) in a large Soxhlet apparatus. The extract solutions and the wash-oil solutions derived from each reaction were combined to form a single set of wash-oil and extract solutions before devolatilization. Product fractions of wash-oil, soxhlet-oil, asphaltene, and a "residual" fraction that included preasphaltenes and residue, were obtained in amounts that would have been generated by treatment with 220% of the standard amounts of feed materials.

A sufficient amount of residual fraction was generated by this procedure to allow re-reaction at 90% of standard stoichiometry; dry residual was used in an amount that had 90% of the carbon normally present in Wyodak coal, and the extra moisture that would have been in the Wyodak coal was added directly to the reactor.

For reaction of the asphaltene fraction, a special procedure had to be used for the separation of the reaction products; the mixture of oils, asphaltenes and insolubles was not porous like MTC, and could not be extracted in a Soxhlet apparatus. Instead, a procedure was used in which the asphaltenes, in solution, were poured into excess cyclohexane and precipitated.

The reaction was performed by dissolution of 5 g of asphaltene into 50 g of tetralin, combining the solution with 300 g of $ZnCl_2$ in the (specially cleaned) reactor vessel, and then heating and proceding as for any 60 min experiment. The first quench tank was filled with

200 mL of toluene and 200 mL of water, and was magnetically stirred during the transfer of products. The toluene phase, which contained toluene, tetralin, and reaction products, was filtered to remove any insolubles, and then boiled down to 100 mL and poured into 2000 mL of stirred, 50°C cyclohexane. The cyclohexane was then vacuum filtered in a Buchner funnel with paper to remove the asphaltenes, and was devolatilized by the usual procedure to recover the oil.

This separation procedure does not necessarily result in the same separation as does the Soxhlet extraction procedure. For this reason, the asphaltene recovered by Soxhlet extraction in the preparative experiments was subjected to the same solution-separation procedure before subsequent treatment.

Gas Sampling

For some experimental runs, three gas samples were taken at times during the treatment. The samples were taken of the cooled reactor-exit gas, into 10 mL, 316-stainless steel cylinders with valves attached. Before sampling, a cylinder was attached to the vent manifold, and heated while being evacuated to 10 Pa, to remove any material from previous use. Air was eliminated by filling the cylinder with 3.5 MPa of reactor-exit gas and then evacuation back to 10 Pa. The sample cylinder was then refilled to 3.5 MPa, closed, disconnected, and held for analysis. Condensation in the cylinders was not a problem because the reactor gas was already cooled to ambient temperature before sampling, and because samples are decompressed to sub-atmospheric pressures before analysis.

Recovery of Materials from Product Devolatilization

For several experiments, a special procedure was used to recover the organic volatiles that were normally lost during the devolatilization and drying of the melt-treated coal. These materials are in the boiling range of tetralin and, while not considered coal products, are of interest in that they may contain reaction products of the tetralin (and perhaps of the coal) in the reactor.

When the devolatilization products were to be recovered, two boiling cyclohexane washes were used instead of one. This raised the oil recovery to about 95% in the wash-oil fraction. The oil solutions were combined and boiled down to 100 mL in a 1000 mL boiling flask with attached standard Claisen head for condensation and collection of the distillate. The distillate was saved for analysis, and the wash-oil solution was transferred to the weighed, 250 mL, boiling flask of the devolatilization apparatus shown in Figure II-4. A steam bath maintained the oil-solution temperature at 100°C, while a 200 mL/min stream of nitrogen was used to transport the volatiles from the oil to the acetone/dry-ice trap, where they were collected at -78°C. The level of vacuum in the apparatus was increased gradually as the solution was dried, until a pressure of about 3.5 kPa was reached; the devolatilization was continued for about 4 h from this point. The oil, which by this time was within 1 g of its final weight, was transferred with cyclohexane to a weighed crystalizing dish and processed as usual. The distillate was melted and stored for analysis.

The distillates obtained by this procedure were analyzed by gas chromatography to distinguish between the cyclohexane and the treatment-

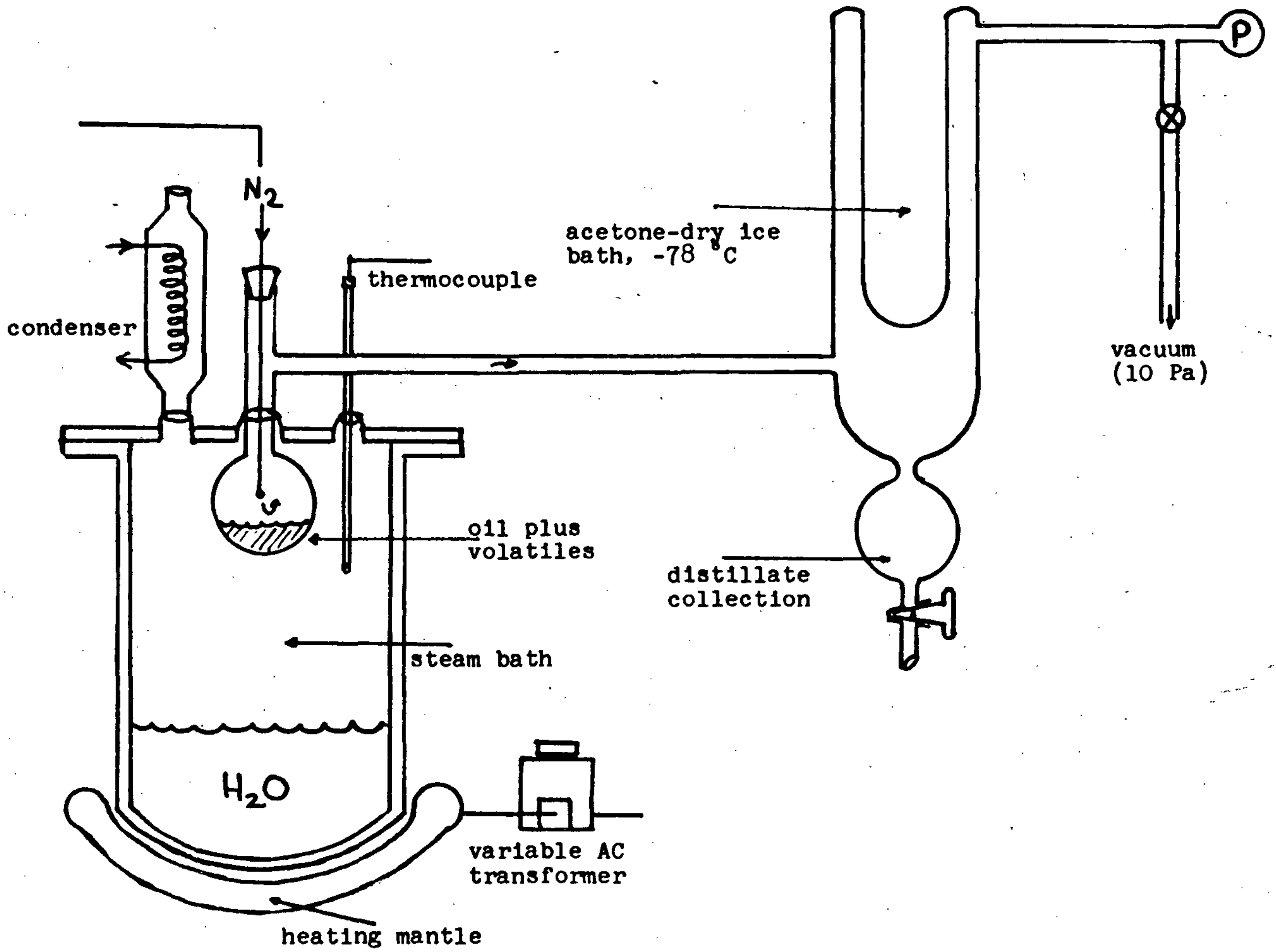

Figure II-4: Apparatus for product devolatilization originated volatiles. Although 50 g of tetralin was introduced into the reactor at the start of each experiment, only 15 to 30 g of volatiles were recovered. It is possible, with this procedure, that some volatiles were not extracted from the MTC during the cyclohexane washes.

Characterization of Products

The products of the treatments of coal with zinc chloride and tetralin, including wash oils, PWMTC's, Soxhlet oils, asphaltenes, pre-ashpaltenes, and residues, as well as the recovered volatiles and the gas samples, were all characterized using a variety of analyses that serve to elucidate the chemical and physical nature of the samples. These characterizations included elemental analysis, gel-permeation chromatography, proton nuclear magnetic resonance, chemical analysis for oxygen functional groups, gas chromatography, mass spectrometry, and gas chromatography mass spectrometry.

Elemental Analysis

Elemental analyses of the wash oil, PWMTC, extracts, and residue from each experiment were performed by V. T. Tashinian, Dorothy James, and Tom Morrison of the College of Chemistry, University of California, Micro-Analytical Laboratory. C, H, and N analyses were carried out using a Perkin-Elmer model 240 automated elemental analyzer. Metals were analyzed after sample digestion in H_2SO_4 and H_2O_2, with a Perkin-Elmer model 360 atomic absorption unit. S, Cl, and ash were measured by combustion in pure oxygen at 800^{0}C, followed by off-gas absorption in NaOH + H_2O_2, and precipitation of Cl with Ag, or SO_4 with Ba. The amount of non-ash oxygen in the sample was calculated by difference.

Gel-Permeation Chromatography

The extracts were characterized for molecular weight distribution by gel-permeation chromatography (GPC) on a Waters Associates ALC/GPC 201 Liquid Chromatograph, with 1x 100 A, 1x 500 A, and 1x 1000 A micro-Styragel columns. Tetrahydrofuran (THF) and pyridine were used as solvents for the chromatographic separations, and detection of the separated samples was by ultraviolet absorbance at 254, 313, or 365 nm. THF is a satisfactory solvent for oils and asphaltenes; its low viscosity allows fast chromatographic elution, and detection wavelengths as low as 254 nm can be used. The use of pyridine was necessary for preasphaltenes, which are not totally soluble in THF. Pyridine is more viscous than THF, and detection wavelengths below 313 nm cannot be used with pyridine because of its strong ultraviolet absorption at those wavelengths.

All wash-oils, as well as selected Soxhlet-oils, asphaltenes, and preasphaltenes were analyzed by GPC. Samples were prepared for injection into the GPC in one of two ways: some samples were prepared by retention of a 2 mL aliquot of extract solution from the Soxhlet or wash extraction before solvent evaporation. The other samples were prepared by dissolution of 0.05 g of dried extract in 2.5 mL of chromatography solvent, and then dilution to 2.0 g/L. All samples, whether redissolved or not, were filtered through a 0.5 µm Millipore Teflon filter before injection into the GPC. A recording was made of the UV absorbance versus elution volume: for all samples the 313 nm absorbance was recorded, along with either 254 nm for THF, or 365 nm for pyridine solvent.

Gel-permeation chromatography separates molecules based on their size in solution. The gel contains a network of pores into which the smaller molecules may diffuse. They are held up while the large molecules go past the gel more rapidly. One of the limitations of GPC is that the effective size of the molecule in solution is not a direct function of its molecular weight. If solvent molecules directly associate with the solute, the effective size may be larger. If two solute molecules are closely associated they may be eluted as one. This can lead to deceivingly large molecular sizes, especially with the preasphaltene fraction, which is considered to be polyfunctional (8). Another limitation of GPC, as it has been used in this research, lies in the detection system. The use of ultraviolet absorbance allows detection only of molecules that absorb at the detector wavelength; at 254 nm this includes all aromatics, but at 313 nm, aromatics must be as condensed as naphthalene (or more condensed) to absorb. Saturated compounds do not absorb at all these wavelengths, but even for the molecules that do absorb, some absorb much more strongly than others. The absorbance distributions are not distributions of mass or number of molecules.

Because of these limitations, the GPC information was not used as a true measure of the molecular weight distribution of the sample. Rather, it was used as a general indication of molecular weight distribution, and as a means for determination of the differences in sample character that were caused by different treatment conditions.

The GPC used in this work was calibrated for molecular weight versus elution volume in a number of ways. Tanner eluted a number of polystyrene standards and aromatic compounds through the columns in THF and pyridine (54). Davis collected elution fractions of a pyridine extract of Wyodak coal and determined the (number average) molecular weight of the fractions by vapor pressure osmometry (55). A graph of molecular weight versus elution volume for these calibrations is shown in Figure II-5. The high degree of scatter in this plot may be due to the lack of direct correlation between molecular weight and molecular size in solution, for different solvents and types of molecules. A similar degree of scatter has been observed by other researchers (56).

Proton Nuclear Magnetic Resonance

Proton nuclear magnetic resonance (NMR) provides a method for the study of the chemical character of the protons and, with a few assumptions, the carbons of the soluble products. The integrated NMR spectrum, along with elemental analysis, was used to calculate properties such as the aliphatic to aromatic proton ratio, the carbon aromaticity, and the degree of condensation of the aromatic nuclei. All wash oils from treated Wyodak coal have been analyzed in this manner, along with selected Soxhlet oils, asphaltenes, and preasphaltenes from treated and untreated Wyodak coal.

The samples for NMR analysis were prepared by weighing and dissolution of 0.1 g of dry extract in 1.0 mL of 99% atomic purity pyridine-d_5. Dissolution was accomplished by digestion at 100°C for a period of 90 min in a closed vial. The solution was then filtered through a dry, heated, 2 mL, medium-porosity fritted-glass filter, into a dry, weighed and heated vial. Exactly 5.0 μL of hexamethyldisiloxane (HMDS) was syringed into the vial, and the vial closed and shaken. HMDS is an NMR reference material, which, in basic solutions, absorbs very close to tetra-

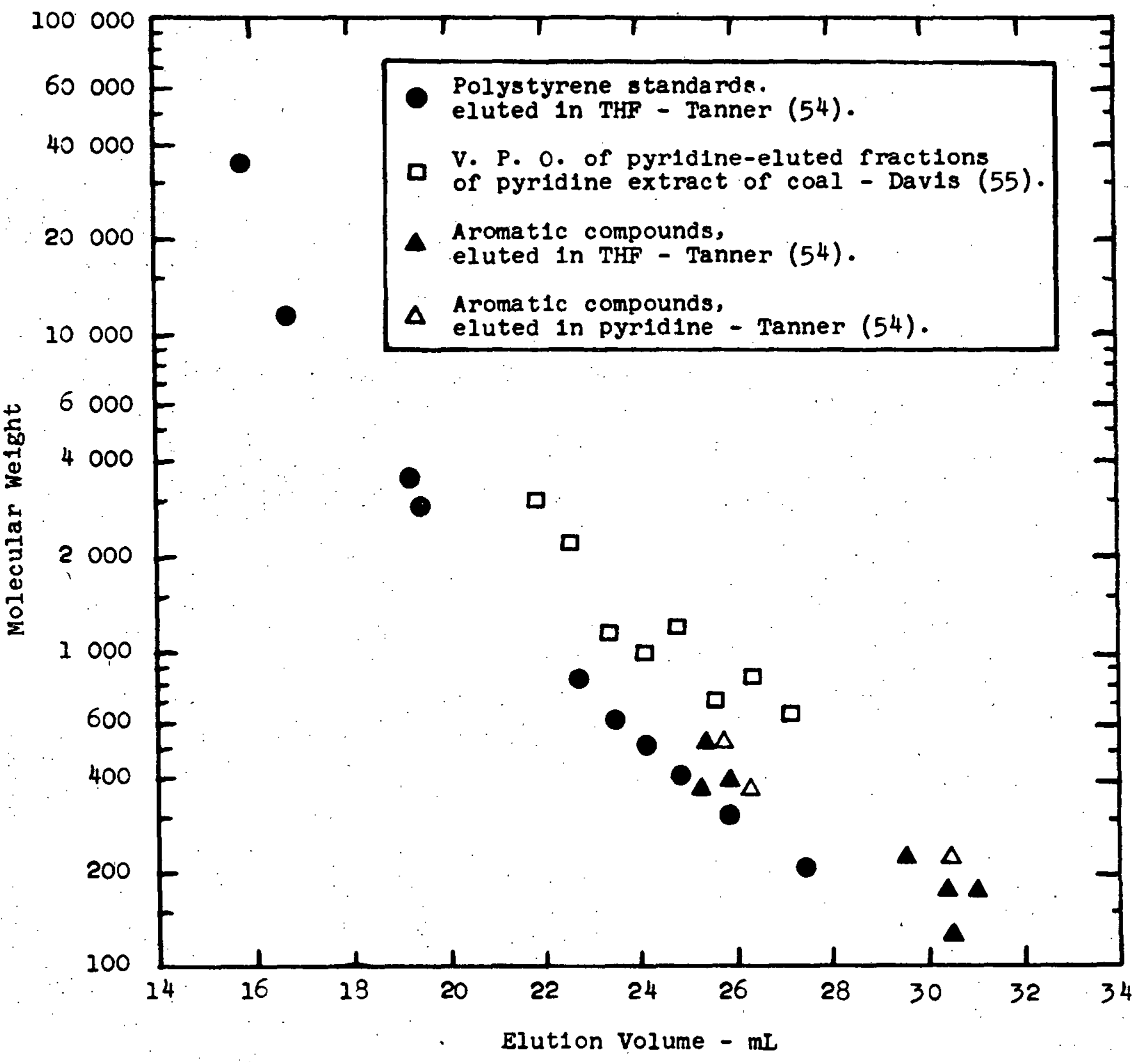

Figure II-5: Calibration of gel permeation chromatagraph.

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methysilane (TMS), but which can be added quantitatively to hot solutions because of its 98°C boiling point (TMS boils at 20°C). The NMR sample was transferred by pipette to a 5 mm tube, and analyzed on a 60 MHz Varian model T60 NMR spectrometer at a temperature of 35°C. The contents of the pipette and tube were then washed back into the weighed vial, and the vial dried in the vacuum oven, and reweighed to give the amount of sample to which the HMDS was added.

This NMR procedure is quantitative, in that the amount of protons in the sample can be calculated from the integrations of the sample spectrum and HMDS peak, and the known amount of HMDS. The weight percent of hydrogen is calcuated using the weight of sample to which the HMDS was added:

$$\%\mathrm{H} = \frac{(\text{integral of sample})}{(\text{integral of HMDS})}$$

$$\times \frac{(4.18\mathrm{x}10^{-4}\text{ moles of H in 5 }\mu\mathrm{L}\text{ of HMDS})\ (1\text{ g H/mole H})}{(\text{weight of sample to which 5 }\mu\mathrm{L}\text{ of HMDS was added})}$$

This percent hydrogen was used as a check, to insure that the protons that were detected in the NMR process were equal in amount to those that were known to be present by elemental analysis. The procedure is also quantitative in that it allows a check on the amount of material that was lost during filtration. This amount was small for wash oils (~10%), and the checks for sample loss were not made for many of these samples. With preasphaltene samples, about 20% of the sample was lost in filtration, and an additional 20% of the protons were not detected. This last effect has been found by researchers at Exxon to be caused by formation of an aromatic colloid that can pass through the filter, but which does not absorb in the NMR process (58). The asphaltene samples could be filtered about as well as the preasphaltenes, but once filtered, all of the protons were detected.

Structural information concerning the extracts was obtained by division of the NMR spectrum into regions that represent different chemical environments for the protons. The structural analysis follows that described by Brown and Ladner in 1960 (57), and more recently by Kanda and coworkers in 1978 (59). Location of regions in the NMR spectrum is expressed in terms of delta (δ), the parts per million of frequency shift, downfield from TMS absorption. Aromatics are located between 6.0 and 9.0 ppm, and aliphatics are between 0.4 and 4.0 ppm. The aliphatic region can be further divided based on the type of carbon to which the proton is attached. Aliphatic carbons are divided into three classes; alpha carbons are adjacent to an aromatic ring, and beta and gamma carbons are one, and two or more carbons removed from a ring, respectively. These carbons are referred to as primary, secondary, or tertiary (1^o, 2^o, or 3^o), when they are bound to 1, 2, or 3 other carbons. The aliphatic protons are thus divided into the following fractions (60). The alpha fraction (δ 2.1 to 4.0) contains protons on alpha carbons. The beta fraction (δ1.4 to 2.1) contains protons on 2^o and 3^o beta carbons. The del fraction (δ1.0 to 1.4) contains protons on 2^o and 3^o gamma gamma carbons and protons on 1^o beta carbons. The gamma fraction (δ0.4 to 1.0) contains protons on 1^o gamma carbons. There is a signficant amount of overlap between the spectra of beta, del, and gamma fractions, but the division between aromatic, aliphatic and alpha fractions is sharp.

In addition to these absorbances, there was an absorbance in the aromatic region that was due to the proton impurities in the pyridine-d_5. The amount of this absorbance was known (by ratio with the HMDS), and was subtracted during the spectrum interpretation calculations.

The aliphatic to aromatic proton ratio, the most basic expression for the aromatic nature of the sample, was calculated directly from the integrations of the respective regions. The fraction of carbon atoms that are aromatic, F_a, was calculated by assuming that aliphatic carbon atoms have an average of two protons, and by using the atomic carbon to hydrogen ratio (C/H, from elemental analysis):

$$F_a = \frac{(C/H) - (1/2)(\text{aliphaic H/total H})}{(C/H)}$$

The assumption that aliphatic carbons have an average of two protons each was suggested for use with coal materials by Brown and Ladner (57). It is central to most of the more complex structural analysis that follows. Although this assumption was verified by Retcofsky through the use of carbon-13 NMR analysis (61), many other assumptions cannot be verified at this time. The most important of these is the assumption that alpha carbons have an average of two protons. With this assumption, the values of $[H/C]_{nuclei}$, the H/C ratio of the hypothetical unsubstituted aromatic nucleus, and σ, the degree of substitution of the nucleus, can be calculated. The defining equations for these structural parameters can be found in Appendix B.

The protons in the del fraction, a major substituent in the NMR spectrum of Wyodak coal and products, include gamma $-CH_2-$ and beta $-CH_3$ protons. That beta $-CH_3$ groups are an important product of zinc chloride catalyzed reactions, was demonstrated by Maienschein, who found 1-methyl indan to be a product of the degradation of tetralin (46). The presence of beta $-CH_3$ groups of this kind may reduce the H/C ratio for the alpha position. The effect of this type of structure on calculated parameters has been investigated using computer-generated structural parameters, based on an iterated value of N, the number of beta $-CH_3$ groups per alpha carbon.

The other parameters that were calculated from NMR spectra include the average non-ring, unbranched aliphatic chain length (ACL), the average length of saturated-ring (naphthenic) side chains (NCL), and the fraction of napthenic side chains per total protons (NCF). These parameters, as well as values for the H/C ratio of the alpha position, $[H/C]_{nuclei}$, and σ, can be 'corrected' for the varying amount of beta $-CH_3$ groups. The defining equations for these parameters, and their values as a function of N, are listed in Appendix B.

There is no way to predict an exact value for the number of beta $-CH_3$ groups per alpha carbon (N). By varying the amount of beta $-CH_3$, it has been demonstrated that the calculated aliphatic chain length is particularly sensitive to this structural feature, while $[H/C]_{nuclei}$ and are not very sensitive. In this respect, the structural model should yield values for the latter two parameters that are not particularly sensitive to the assumptions of the model.

Chemical Oxygen Analysis

The amount of oxygen that is present in the coal and melt treated coal, in the form of phenolic hydroxyl, carbonyl, and carboxylic functionalities, was determined by 'wet' chemical analysis schemes. The procedures were essentially identical to those recommended by Blom for the analysis of chemical oxygen groups in coal (62). The hydroxyl groups were determined by acetylation with acetic anhydride, followed by titration of the unreacted acetic acid. The carbonyl oxygen was determined by reaction with hydroxylamine hydrochloride, and subsequent hydrolysis of the oxime which was formed. The carboxylic oxygen was determined by ion exchange with calcium acetate, followed by titration.

For all three procedures, the coal or MTC (usually, it was the PWMTC sample that was analyzed) was first treated by stirring with a 50:1 weight ratio of 1.0 N hydrochloric acid, in a closed flask, for about 18 h. The sample was subsequently washed with hot water until free of acid (~4000 mL), dried in the vacuum oven, and stored until use in a vacuum desicator.

In the hydroxyl determination, about 3/4 g of sample was weighed into a 50 mL boiling flask ("m" g), and 12 mL of pyridine and 500 μL of acetic anhydride were added. A condenser was attached, and the sample boiled for 24 h under reflux, after which time 10 mL of water was added and boiling continued for 5 min. The mixture was then washed into a 150 mL beaker with 40 mL of 50:50 (by weight) ethanol/water, and titrated to an endpoint of pH 9 with 0.25 N alcoholic NaOH ("a" mL, titer = t). A blank was run without coal ("b" mL), and a free acid blank run with coal but without acetic anhydride ("n" g, "c" mL). The hydroxyl is calculated as:

$$\frac{\text{milligram equivalents hydroxyl}}{\text{gram of sample}} = \frac{(b-a)t}{m} - \frac{c \cdot t}{n}$$

The reproducibility of this procedure was improved if the amount of acetic anhydride that was added to the coal sample was weighed, by weighing the boiling flask before and after addition. In this variation the blank, "b" mL, is replaced with the weight of acetic anhydride times a factor of K, which represents the amount of titrated NaOH that can be expected in a blank run, per g of acetic anhydride. The value of K was determined by a series of blank runs. A minimum of two replications were run for each acetylation reaction. The experimental error, expressed as the average standard deviation for all samples, was 6.5%. The free acid blank runs did not require replication. An unknown amount of hydroxyl was probably not detected because some of the hydroxyl is inhibited from reaction by stearic hindrance (62).

In the carbonyl analysis procedure, 800 mg of sample was weighed ("a" g) into a 250 mL flask. 1 g of hydroxylamine hydrochloride and 10 mL of pyridine were added, and the mixture boiled under reflux for 24 h. After being boiled, the mixture was cooled and diluted by addition of 50 mL of water. 12 mL of 36% hydrochloric acid were added and the mixture was washed into a weighed, 20 mL, medium-porosity sintered-glass crucible, filtered, and then washed with hot water. The crucible was dried overnight in the vacuum oven, and cooled and weighed ("b" g of sample). A small amount was subjected to elemental analysis ("q" =

% nitrogen), and the remaining material was weighed ("c" g) into a 250 mL flask. 20 mL of 2.0 N aqueous sulfuric acid and 20 mL of acetone were added to the flask, a condenser attached, and the mixture boiled under reflux for 24 h. After this time, the mixture was washed into a second weighed sintered-glass crucible, washed with hot water, and placed in the vacuum oven to dry. After 14 h, the sample was cooled, weighed ("d" g of sample), and analyzed for elemental composition ("r" = % nitrogen). The carbonyl is calculated as:

$$\frac{\underline{\text{meq carbonyl}}}{\text{g}} = (b \cdot q - d \cdot r \cdot b/c)/14 \cdot a$$

Because of the length of this analysis, only selected samples have been analyzed. Two replicate unreacted coal samples have been analyzed, giving a standard deviation of less than 1%.

The carboxylate and carboxylic acid groups were determined by ion exchange with calcium as calcium acetate. Any carboxylate is converted to carboxylic acid by the HCl·washing procedure. In the carboxyl procedure, 250 mg of sample was weighed into a 125 mL flask, and 10 mL of 1.0 N aqueous calcium acetate plus 50 mL of water were added. The flask was closed, and the contents stirred with a magnetic stirrer for 18 h. Then the mixture was filtered and washed with water to yield 100 mL of filtrate. The filtrate was transferred to a beaker and titrated to an endpoint of pH 9 with aqueous 0.02 N sodium hydroxide ("v" mL, titer = t). A blank was run without coal sample ("v_0" mL). The carboxyl groups are calculated as:

$$\frac{\underline{\text{meq carboxyl}}}{\text{g}} = (v - v_0) \cdot t/(\text{weight of sample})$$

Replicate measurements with untreated coal gave a standard deviation of 2.6%.

Only Wyodak coal and melt treated Wyodak coal samples were analyzed for chemical oxygen. The results are expressed as the percent of the whole sample that is oxygen in the form of the specific functional group.

The amount of total oxygen in the samples was calculated by difference, using the elemental analysis that was performed on each of the acid-washed samples. In the elemental analysis interpretation, chlorine was assumed to be stoichiometrically representative of the $ZnCl_2$ that was present and volatilized during ash analysis. The amount of total oxygen actually includes a small amount (~0.5%) of sulfur, and is calculated as follows:

$$\% \text{ Total Oxygen} = 100\ \% - (C + H + N + \text{Ash}) - 1.92(Cl)$$

This amount of total oxygen was checked against the (similarly calculated) total oxygen of the non-acid-washed samples by a comparison of the O/C ratios for the samples. If an O/C ratio discrepancy of more than 0.05 was discovered, a third analysis was performed.

The amount of oxygen present as ether functional groups was calculated as the difference between total oxygen and the other three functional-oxygen fractions. In this regard, the ether fraction contains the sulfur in the sample, as well as all of the error in the other functional group analyses and the elemental analysis.

Gas Chromatography

The distillates from wash oil and melt treated coal devolatilization were analyzed by gas chromatography (GC). The analysis was primarily for tetralin and naphthalene, although some other material in this molecular weight range was detected. Samples were prepared by filtering 2 mL of distillate through a 0.5 μm Millipore Teflon filter. All samples were first analyzed on a Chromalytics Multi Purpose Thermal Analyser, Model MP-3, with Dexsil-300 column and flame ionization detection (FID). Samples were vaporized in the injection port, and were carried by helium through the GC column, which was programmed to have a temperature that increased from 60 to 320°C at 12°C/min. Quantification with this GC was by integration of the recording of the FID signal. Most samples were also analyzed on a Hewlett Packard Model 5840 A Gas Chromatograph, with OV-225 column and FID. Helium was used as the carrier gas, and the column was temperature programmed to increase from 60 to 225°C by 10°C/min. Quantification on this GC is by a built-in digital integration, based on previously run calibration mixtures of cyclohexane, tetralin, naphthalene, and butyl-benzene. Materials for which FID constants or calibration are not available were quantified by direct area ratio to tetralin.

Gas Analysis

The gas samples, which were taken in selected runs, were analyzed by mass spectrometry (MS), and by gas chromatography/mass spectrometry (GCMS). The MS analysis, using a CEC Model 21103 spectrometer, and the GCMS analysis, using a Finnigan Model 4023 system, were carried out by Dr. Amos Newton and co-workers at Lawrence Berkeley Laboratory. A detailed description of this equipment is given by Taylor (63).

The mass spectrometry was used to determine the concentrations of CO, CO_2, and CH_4 in the hydrogen of the reactor-exit gas. Very small amounts (~500 ppm) of hydrocarbons such as isobutane, isopentane, methylcyclopentane, and benzene were detected using the GCMS, and are quantified by peak area ratio to CO_2. This GCMS procedure gives only a very crude measure of the relative amounts of hydrocarbons present.

Determination of Product Yields

In zinc chloride catalyzed coal liquefaction, as with any coal liquefaction process, the most important question is one of how much liquefaction has occured. The product yields from a coal conversion process must be described in terms of a basis that gives an understanding of how much coal is converted, and of what kinds of products it has been converted to. The basis for describing yields, in the coal liquefaction research at Lawrence Berkeley Laboratory, is coal product solubility in a series of solvents.

In this research, the coal conversion was measured in terms of solubility in cyclohexane, toluene, and pyridine (sequentially), which provide solubility data in terms of three extract fractions that contain progressively harder-to-extract material. This extraction procedure succeeds in describing the extent of conversion to different kinds of products, but to be really useful, the data must be accurately interpreted.

There were several problems that surfaced in the interpretation of extraction results: The MTC (or coal) contained some ash and $ZnCl_2$ that could be extracted into the product yield fractions, but which were not desired coal conversion products because they have no fuel or chemical product value. The interpretation of the pyridine extraction data was further complicated by the incorporation of pyridine into the extract and residue fractions. To circumvent these difficulties, a calculation procedure was developed that interprets extraction data in terms of the amount of carbon that is extracted into the product fractions, as a percent of the initial MTC carbon. Pyridine incorporation is corrected by nitrogen balance.

In this extraction calculation, all extract and residue samples were first analyzed for carbon, hydrogen, and nitrogen. The wash oil yield was calculated as the fraction of MTC carbon that is present in wash oil. The yields of Soxhlet extracts of the PWMTC were calculated as the fraction of PWMTC carbon that was extracted, multiplied by the fraction of MTC carbon that is present in PWMTC. The total oil yield is the sum of the wash oil yield and the Soxhlet oil yield. The sum of oil, asphaltene, and preasphaltene yields is referred to as "total" yield of soluble products.

The amount of carbon in the preasphaltene and residue that was originally from the PWMTC was calculated by subtraction of the incorporated-pyridine carbon from the total extract carbon. In this subtraction calculation, the total incorporated pyridine was calculated by nitrogen mass balance on the PWMTC extraction. This pyridine was divided between the preasphaltene and residue by using the assumption that the pyridine-free ratio of carbon to nitrogen in the extract is equal to the pyridine-free ratio of carbon to nitrogen in the residue. With this assumption, algebraic manipulation of the various mass balance and stoichiometric equations leads to the follow equation:

$$\text{(pyridine-free nitrogen in preasph.)} = \frac{E(A - C(60/14))}{B+A - (60/14)(C+D)}$$

where: A = total carbon in pyridine extract
B = total carbon in residue
C = total nitrogen in pyridine extract
D = total nitrogen in residue
E = pyridine-free nitrogen to be divided (from nitrogen balance on extraction)

The remaining distribution of carbon and nitrogen was calculated from the mass balance and stoichiometric equations. For example:

(Pyridine nitrogen in preasph.) = C - (Pyridine-free "N" in preasph.)

(Pyridine "C" in extract) = (60/14)(Pyridine "N" in preasph.)

(Pyridine-free "C" in preasph.) = A - (Pyridine "C" in preasph.)

A similar set of equations was used for the residue calculations.

III. RESULTS AND DISCUSSION

This investigation of the general mechanism of zinc chloride catalyzed coal liquefaction has comprised several series of experiments in which specific aspects of the coal-treatment conditions were examined. These aspects included the temperature of treatment, the duration of treatment, and the presence or absence of tetralin during treatment.

The first task of this investigation was to verify that the combination of $ZnCl_2$ and tetralin did provide a treatment system in which coal conversion to soluble products was enhanced. This verification included a series of preliminary experiments, carried out in the same apparatus and with the same procedures used by Holten (43), where several different combinations of the amounts of $ZnCl_2$ and tetralin used, and hydrogen pressure were examined. The results of these experiments, in which the treatment was carried out at 250°C for 60 min (plus heatup and cooldown time), are shown in Table III-1. The yields of soluble products are expressed as a percent of the MTC (DAF basis).

The yields of products obtained from coal treated with $ZnCl_2$ and hydrogen, both with and without tetralin, were similar to those obtained by Holten. The presence of hydrogen gas at pressures of about 3.0 MPa, in the absence of organic solvents, resulted in a small increase in conversion. The presence of tetralin resulted in an increased product H:C ratio, as well as greatly increased yields. Finally, high yields of soluble products were obtained when $ZnCl_2$ was used with other organic solvents, such as isopropyl alcohol.

Table III-1: Yield and character of products from preliminary experiments. Treatment of 50 g Wyodak coal with $ZnCl_2$ at 250°C for 1 hour.

Treatment Conditions			Yield of Soluble Materials (% DAF)		molar H:C ratio of MTC
$ZnCl_2$ (1)	H_2 (2)	Solvent	Benzene	Total (3)	
No reaction - extraction of untreated coal			1.7	10.1	0.98
300 g	none	none	3.0	11.5	0.85
300 g	3.5 MPa	none	3.9	16.3	0.87
300 g	none	50 g tetralin	24.0	60.4	0.94
300 g	3.5 MPa	50 g tetralin	34.5	70.9	0.93
25 g	3.5 MPa	150 g tetralin (4)	20.6	33.7	0.94
300 g	3.5 MPa	50 g 1-propanol	21.4	64.9	1.00
300 g	3.5 MPa	50 g t-butanol	4.3	27.7	0.89

(1) Grams of $ZnCl_2$ solution, containing 10% H_2O.

(2) Total Parr autoclave pressure is listed, includes hydrogen and vapor pressure.

(3) Total yield is cumulative yield from benzene and pyridine extractions.

(4) This experiment used only 25 g coal.

The study of zinc chloride-catalyzed coal liquefaction with solvents other than tetralin, including those miscible with $ZnCl_2$, such as methanol, has been pursued at Lawrence Berkeley Laboratory by Shinn (64) and Onu (67).

Experiments Performed

The main series of experiments were carried out in the apparatus described in Chapter II, with fixed procedures and amounts of materials. They are listed in Table III-2. With exceptions as noted, these experiments were all carried out with 273 g of $ZnCl_2$, 27 g of H_2O, 50 g of tetralin, 50 g of Wyodak coal (containing 24% moisture), and a total gas pressure of 3.5 MPa. For all experiments (except as noted), the $ZnCl_2$/coal mixture and the tetralin were combined at roughly the treatment temperature.

The primary results of these experiments are yields of soluble products. The yields (based on carbon content) of oil, asphaltene, and preasphaltene fractions are listed on Table III-2, along with the molar H:C ratio for the total melt treated coal.

Determination of Yields of Products

Many investigators, both at Lawrence Berkeley Laboratory and elsewhere, express their results on the same DAF basis that has been used in the preliminary experiments of this work. However, we have chosen to express our yields as the fraction of MTC carbon that is extracted into the products, because this basis provides a more accurate accounting for the ash, $ZnCl_2$, and pyridine that are present in the extracts.

The differences between alternative methods of yield calculation are illustrated by the example presented in Table III-3. The main

Table III-2: Experiments performed.

All experiments are with 50 g Wyodak coal, 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, 3.5 MPa total pressure, unless otherwise noted.

Treatment Conditions			Notes	% Yield of Products (C basis)			molar H:C ratio
Temp.	Time	(Run No.)		Oil	Asph.	Preasph.	of MTC
250°C	30 min	(30)		27.2	10.2	25.9	0.96
	60 min	(31)		31.4	9.3	26.8	0.97
	60 min	(45)	Tet. addn. at 200°C	32.5	9.9	27.9	0.97
	60 min	(40)	Rosebud coal	20.1	6.7	23.5	0.86
	60 min	(41)	Monarch coal	20.2	7.4	22.5	0.84
275°C	60 min	(39)		39.6	10.6	25.5	1.06
	60 min	(42)	Tet. addn. at 225°C	46.1	12.3	21.3	1.00
	60 min	(22)	Used only for MTC devolatilization - recovery				
300°C	10 min	(26)		28.5	13.1	27.9	0.92
	30 min	(25)		39.3	13.8	28.1	0.94
	60 min	(23)	(1)	46.5	13.0	21.8	0.96
	60 min	(47)		51.5	13.7	18.7	0.96
	120 min	(24)		55.8	15.3	17.2	0.96
	60 min	(28)	Tet. addn. at 250°C	53.2	15.9	16.8	0.92
	0 min	(27)	Heatup only, no tetralin	3.3	4.3	18.3	0.85
	20 min	(44)	No tetralin	2.8	7.9	16.9	0.88
	60 min	(38)	No tetralin	9.2	10.2	24.1	0.88
	30 min	(34)	Recycle preparation(2)	40.1	10.7		0.94
	90 min	(35)	Residual recycle(3)	30.6	15.8	27.6	0.91
	60 min	(36)	Asphaltene reaction		(not applicable)		
	60 min	(43)	Rosebud coal	33.1	18.1	22.9	0.81
325°C	60 min	(46)	Tet. addn. at 275°C	65.6	11.2	12.3	0.94

(1) Separate extractions were performed for the material found in the quench tanks and that which remained in the reactor after product transfer.

(2) Preparation of isolated solubility fractions for re-treatment by treatment and separation of 220% of normal amounts of reactants (treatment in two batches).

(3) Treatment of 35 g dry preasphaltene + residue in place of coal, with an additional 8 g of water added in place of the usual coal moisture.

Table III-3: Comparison of Yields from Different Calculation Approaches for Treatment of 50 g Wyodak Coal for 1 h, at 250°C in Parr Autoclave with 273 g $ZnCl_2$, 27 g H_2O, 50 g Tetralin, and 3.5 MPa Total Pressure (Vapor pressure plus hydrogen gas)

	Product Fraction (%)			
	Total MTC	Oil plus Asph.	Preasph.	Residue
Elemental Analysis (% MF)				
C	69.81	88.93	65.78	51.89
H	5.39	7.70	5.26	3.61
N	0.69	0.11	2.64	1.78
S	0.84	0.44	0.48	1.14
Cl	2.10	0.11	6.26	0.17
Zn	3.02	0.25	6.43	3.02
Ash	14.2	0.4	3.7	23.9
Extraction Sample Weight (MF):	8.415 g	2.490 g	2.629 g	3.791 g
Calculated Yield:	Total Soluble Plus Residue			
DAF Basis (1)	123.7	34.5	36.4	52.5
same, corrected for $ZnCl_2$ (2)	117.5	36.2	27.6	52.5
Carbon Basis (3)	94.7	37.7	26.3	30.8

(1) The "spirit" of a DAF calculation is that it requires no elemental analysis of the extracts. Therefore, yield is calculated as the extracted sample weight divided by the ash-free weight of initial MTC. Yields can be but are not, in this case, corrected for pyridine incorporation by assuming a distribution of pyridine between the preasphaltene and residue fractions.

(2) Calculated (without extract elemental analysis) using the assumption that all the $ZnCl_2$ in the MTC goes to $(pyridine)_2ZnCl_2$ in the preasphaltene, and that the remaining MTC zinc goes to the residue.

(3) Calculated (using MTC and extract C, H, and N analysis) by dividing the carbon content of the extract by the carbon content of the initial MTC. Preasphaltene and residue fractions are corrected for pyridine incorporation using a nitrogen balance, and by assuming that the pyridine-free ratio of carbon to nitrogen in the preasphaltene is equal to the pyridine-free ratio of carbon to nitrogen in the residue.

difference between DAF and carbon-based calculations is that DAF yield is based on the total weight of the extract, which may contain unknown amounts of ash, $ZnCl_2$, and pyridine, whereas the carbon-based yield is based on the pyridine-corrected weight of carbon in the extract, and so provides a precisely defined yield value. Moreover, the carbon-based yields are naturally normalized by mass balance constraints, so that the total yield of soluble products plus residue averages 99% for the experiments listed in Table III-2.

Both calculation procedures give extraction yields as a percent of the MTC. The amount of MTC is usually higher (by about 5 to 20%) than the amount of initial coal that is introduced to the reactor. The difference is solvent (tetralin) that has become incorporated, either chemically or physically, into the MTC (in runs without solvent, slightly less MTC is recovered than the amount of initial coal).

The incorporation of solvent into the coal during treatment has been investigated by balances on the carbon content of the materials that are introduced to, and recovered from, the coal treatment reactor; the details of the carbon balance can be found in Appendix A. Most of the non-MTC carbon recovered is in the form of tetralin-molecular weight materials that are normally volatilized. Volatile materials recovered for the treatment of Wyodak coal at $300^{\circ}C$ for 60 min (Run 47) are shown in Table III-4. The amount of recovered volatiles (29 g) is less than the amount of tetralin that is introduced to the reactor (50 g). The overall mass balance also shows a loss of carbon during treatment.

Table III-4: Recovery of compounds in the boiling range of tetralin. Treatment of 50 g Wyodak coal at 300°C for 60 min with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, 3.5 MPa total pressure.

Compound	Amount Recovered
Tetralin	17.73 g
Napthalene	6.73 g
Butylbenzene	trace
Methylindan	1.47 g
Higher boiling(1)	3.06 g

(1) Material that will volatilize at 100°C under 10 kPa of flowing nitrogen.

Although the lack of a closed mass balance on carbon does reveal a level of uncertainty in the results, the incorporation of solvent can be shown to have only a small effect on the total yield of soluble products: The total yield for run 47, as calculated by subtraction of all the incorporated solvent from the soluble products, is 81.4%, compared to 83.9% without correction.

Effect of Coal Used upon Conversion

In order to examine the influence of coal properties, for subbituminous coals, on the conversion obtained with $ZnCl_2$/tetralin treatment, a series of experiments were carried out using Rosebud and Monarch seam coals. These coals were selected to be quite different from the Wyodak coal, being subbituminous B rather than subbituminous C and having lower fractions of volatile matter on proximate analysis (about 40% as compared with 46%). A comparison of the yields of soluble products and the H:C ratio of the MTC for similar treatments of Wyodak, Rosebud, and Monarch coal is shown in Table III-5.

The Rosebud and Monarch coals were somewhat less reactive than the Wyodak, yielding approximately 20% oils for 250^{0}C, 60 min treatment as compared to 31%. However, the qualitative aspects of their response to treatment is very similar to that of the Wyodak coal, both in terms of the distribution of soluble product yields, and in the effect of treatment temperature on coal H:C ratio. Treatment at 300^{0}C for 60 min resulted in high total yields for both Wyodak (82.6%) and Rosebud (74%) coals. Moreover, as can be seen in Table III-5, the yields obtained with Monarch and Rosebud coals, which have very similar analyses but which derive from entirely different seams, are very nearly the same.

Table III-5: Comparison of soluble product yields for treatment of different coals. Treatment of 50 g coal with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

	Yield of Soluble Products(1) (and MTC molar H:C ratio)		
Coal	Wyodak	Rosebud	Monarch
Untreated Coal	(0.98)	(0.84)	(0.84)
Oil	1.0	1.0	0.1
Asphaltene	3.7	3.4	1.0
Preasphaltene	14.5	10.3	10.8
Total	19.2	14.7	11.9
250°C, 60 min treatment	(0.97)	(0.84)	(0.84)
Oil	31.4	20.1	20.2
Asphaltene	9.3	6.7	7.4
Preasphaltene	26.8	23.6	22.2
Total	67.5	50.4	49.8
300°C, 60 min treatment	(0.96)	(0.81)	
Oil	49.0	33.1	
Asphaltene	13.4	18.0	
Preasphaltene	20.2	22.9	
Total	82.6	74.0	

(1) Calculated with carbon basis.

This indicates that coal characteristics represented in the proximate and elemental analyses may be able to provide a crude guide to expected conversions for subbituminous coals.

Effect of Treatment Temperature on Conversion

The effect of treatment temperature on the conversion of Wyodak coal to soluble products was examined with treatments of 60 min duration at temperatures below coal pyrolysis, the onset of which is at a temperature of about 325°C (25). Two series of experiments were performed to study this effect. These series differed in the temperature at which tetralin was added to the reactor. For one series, which included experiments at treatment temperatures of 250, 275, and 300°C, the tetralin was added to the reactor after both the tetralin and the $ZnCl_2$/coal mixture were heated to treatment temperature. In the other series, which included experiments at treatment temperatures of 250, 275, 300, and 325°C, the tetralin was added during the $ZnCl_2$/coal heatup, at a melt temperature 50°C below treatment temperature. The melt temperature at which the tetralin was added is referred to as the "tetralin addition" temperature. The effect of tetralin presence during heatup was studied by comparison of the results of the two series of experiments.

The behavior of the cumulative oil, asphaltene, and preasphaltene yields with treatment temperature, for both series of experiments, is shown in Figure III-1. The oil yield increases uniformly from 31% to 65% over the temperature range of 250 to 325°C. The total yield of soluble products increases more slowly, from 70% at 250°C to 89% at 325°C. The yield of asphaltene is relatively constant, so that the

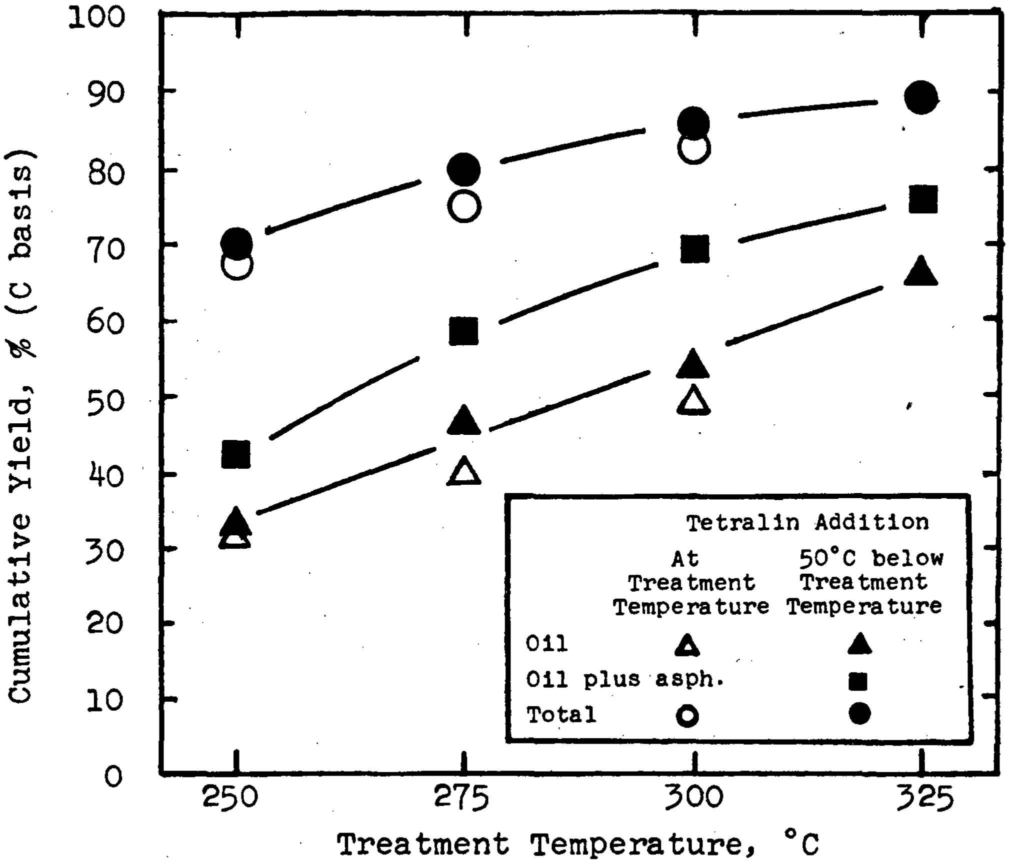

Figure III-1: Effect of treatment temperature on the conversion of coal to soluble products. Treatment of 50 g Wyodak coal for 60 min with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

large increase in oil yield is compensated by a decline in preasphaltene yield.

The oil and total yields for experiments in which tetralin was present during the last 50°C of heatup are higher than those with tetralin addition at treatment temperature. This increase could simply be due to an increase in treatment time: The presence of tetralin during heatup increased the treatmennt time during which tetralin was present by about 4 min. However, results that will be discussed later show that this increased reaction time cannot account for more than a 2% increase in yield. The roughly 5% increase in yield that was observed in treatments at 275 and 300°C is, therefore, an effect of the lower temperature at which the tetralin was added.

The other significant difference between the results of the two series of experiments lies in the levels of tetralin incorporation for these experiments. For experiments in which the tetralin was added at treatment temperature, the level of incorporation decreases as temperature increases, so that a 250°C, 60 min run has an incorporation level of 17% of the MTC, while the 300°C, 60 min treatment has an incorporation level of about 5%. For the series of experiments with tetralin addition during heatup, however, the incorporation level is similar to that of an experiment in which the treatment was at the temperature of addition. For example, a 300°C, 60 min treatment with tetralin addition at 250°C has an incorporation level of about 19%, a level similar to that for an experiment with tetralin addition and treatment both at 250°C.

The generally declining trend of solvent incorporation with increasing tetralin addition temperature is shown in Figure III-2. The high degree of scatter in this figure may be a result of the experimental variation of the mass balances that were used for solvent incorporation calculations. In any event, this scatter indicates that only a crude trend of incorporation can be identified. This incorporation trend may partially contribute to the higher yields for the series of experiments with tetralin addition at lower temperature, if the tetralin is incorporated perferentially into the soluble products, and the yield of those products is thereby artifically raised.

In the experiments with different treatment temperatures, the temperature of tetralin addition did not have a significant effect on the character of the soluble products. In the following examination of the effect of treatment temperature on the atomic composition (elemental analysis) of soluble products, the characteristics for the runs of different tetralin-addition temperature are averaged (for convenience of presentation).

Effect of Treatment Temperature on Character of Products

The yield fractions are materials that are soluble in different kinds of solvents, and as such, each of these solubility fractions can be expected to have a distinctive character that is not strongly affected by treatment conditions. This character is exemplified by the degree to which heteroatoms and ash (everything other than C + H) are present in the extracts. The hetroatom plus ash contents of the soluble products are constant with changing treatment temperature, as shown in Figure III-3. Each of the fractions has a distinct level of heteroatoms plus

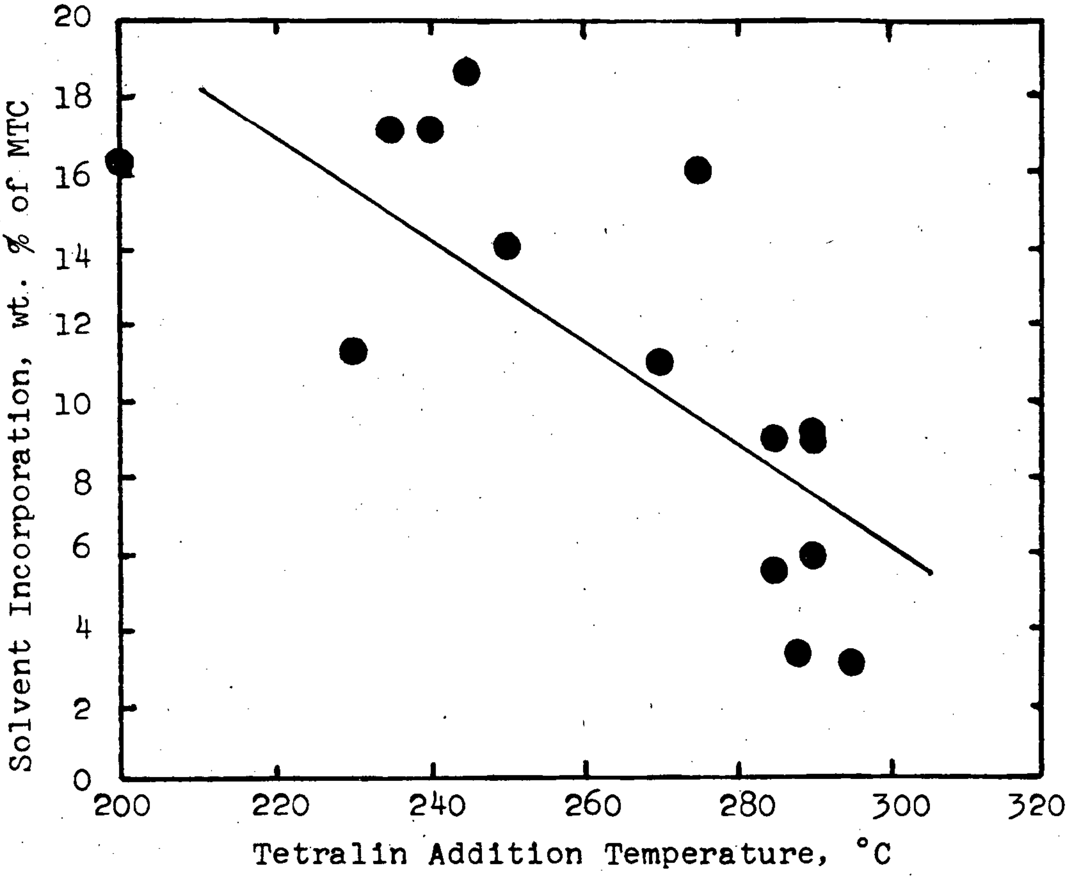

Figure III-2: Effect of tetralin addition temperature on the solvent incorporation during treatment. Treatments of 50 g Wyodak coal with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

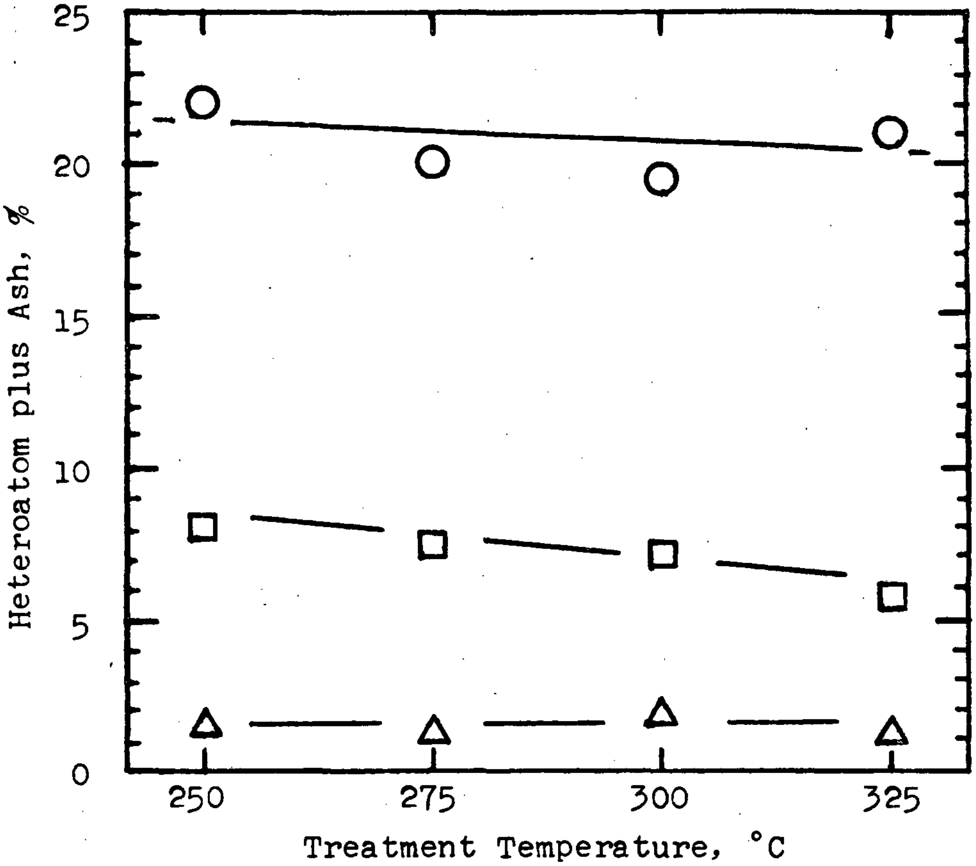

Figure III-3: Effect of treatment temperature on the heteroatom plus ash contents of the soluble products. Treatment of 50 g Wyodak coal for 60 min with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure. △- oil, □- asphaltene, ○ - preasphaltene (corrected for pyridine but not $ZnCl_2$).

ash. The oils are by far the lowest, only about 1.5% of the oil fraction being material other than C + H. The asphaltenes are higher (about 7%), and the preasphaltenes are higher still (about 21%). The heteroatom plus ash content of the preasphaltenes is not corrected for zinc chloride content because of a lack of chlorine analyses on most of these samples. For the two treatments at 300°C, however, this analysis has been performed, the corrected heteroatom plus ash content of the preashpaltenes from these experiments being 12%.

Although the total fraction of soluble products that is hydrogen plus carbon is more a function of solvent properties than coal-treatment conditions, the ratio of hydrogen to carbon in the soluble products is affected by treatment temperature, as shown in Figure III-4. All of the soluble product fractions have molar H:C ratios that decrease with increasing temperature. The H:C ratio of the asphaltenes decreases the most, followed by that of the preasphaltenes, and then oils.

Effect of Duration of Treatment on Conversion

The pathway of reaction, in zinc chloride catalyzed coal conversion with tetralin, can be, to some extent, characterized by the study of the conversion of coal to soluble product fractions, and by examination of the changes in conversion that occur with changing duration of treatment. Meaningful reaction-kinetic information, however, cannot be obtained because of the diversity of the molecules that make up the coal and products. In this context, the reaction pathway is generally defined as the bulk conversion of large amounts of molecules in one product fraction (or in coal) into molecules of another fraction.

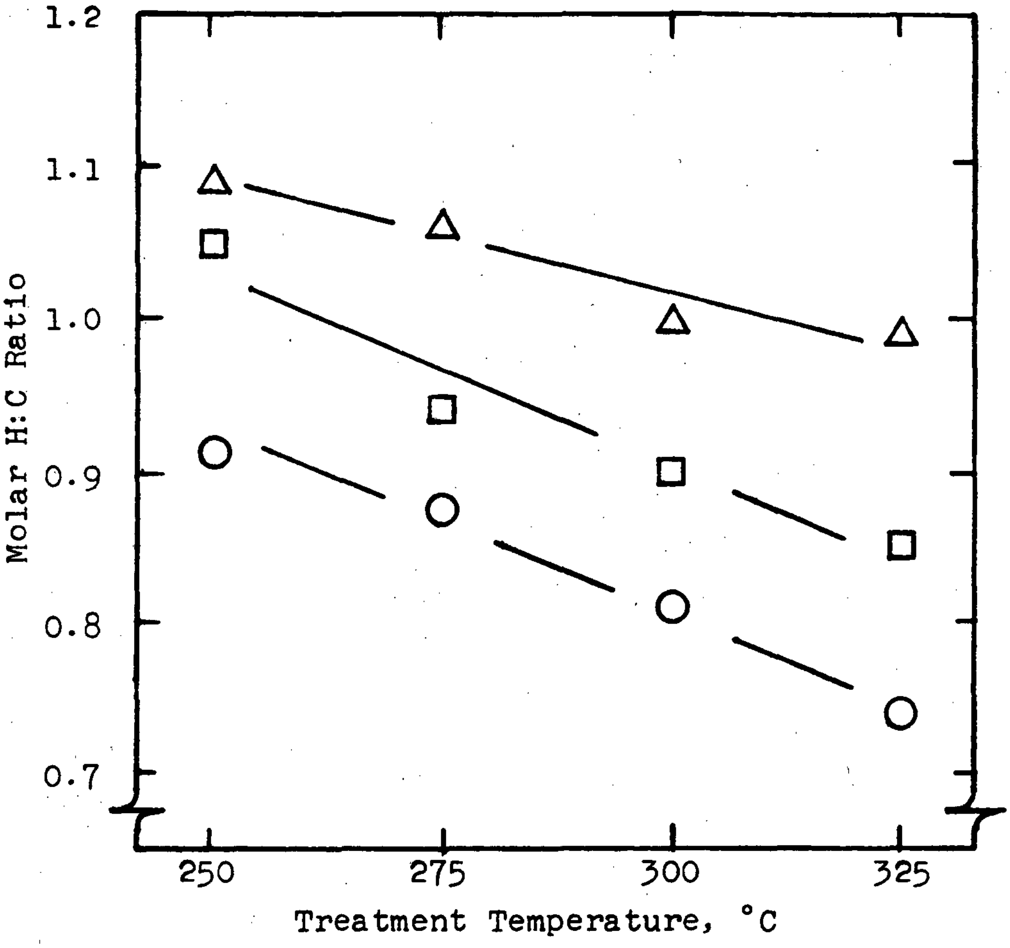

Figure III-4: Effect of treatment temperature on the molar H:C ratio of the soluble products. Treatment of 50 g Wyodak coal for 60 min with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure. △ - oil, □ - asphaltene, ○ - preasphaltene.

At a coal-treatment temperature of 300°C, a series of experiments were carried out with durations of treatment varying from zero to 120 min. The zero-time run represents an experiment in which the $ZnCl_2$/coal mixture was heated to treatment temperature and then transferred to the cold-water quench just at the point when tetralin would have been added. The addition of tetralin after heatup, and the product quenching after treatment, allow the use of treatment durations as short as 10 min, which are significantly shorter than the heatup and cooldown time that would be encountered without these procedures. The cumulative yields of oil, asphaltene, and preasphaltene fractions for these experiments are shown in Fig. III-5.

The conversion at 300°C starts very quickly. After 10 min there is a 70% total yeild and a 30% oil yield. The total and oil yields continue to increase for durations up to 30 min, but after this time the total yield increases very slowly, and there is a net conversion of preasphaltenes to oil. Despite this apparent net conversion of preasphaltenes to oil, the amount of asphaltene in the product remains nearly constant from durations of 10 to 120 min.

The pathway of reaction is difficult to deduce from these experments alone. It is possible that coal is converted to oil through the intermediate of preasphaltene. It is also possible that most of the oil is generated directly from a fraction of coal that, when treated with $ZnCl_2$ and tetralin, reacts directly to oil. Similar uncertainties exist with regard to the role of the asphaltene fraction, especially considering the constancy of the asphaltene yield with duration of treatment. These uncertainties of reaction pathway were investigated through

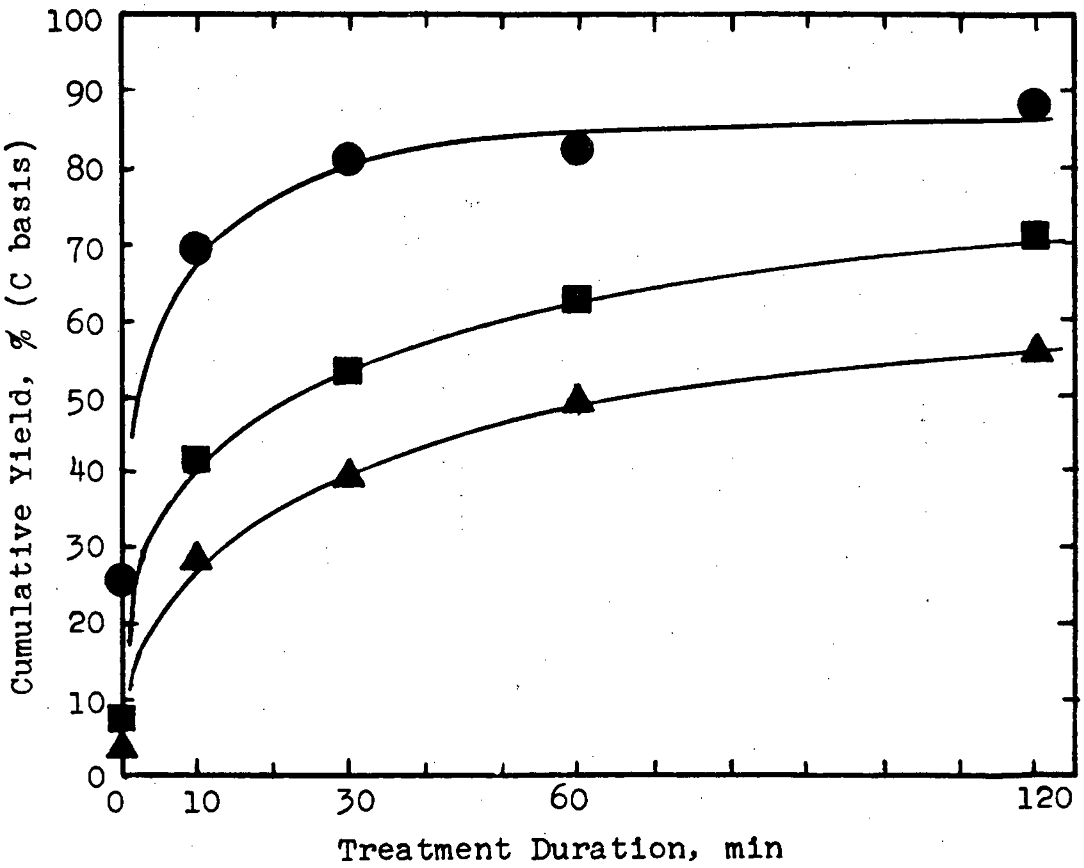

Figure III-5: Effect of treatment duration on the yields of soluble products. Treatment of 50 g Wyodak coal at 300°C with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure. ▲ - oil, ■ - oil plus asphaltene, ● - total.

several experiments in which product fractions from a 30 min, 300°C treatment were isolated and re-treated with zinc chloride and tetralin.

The initial reaction duration of 30 min was chosen for these "recycle" experiments because this was the duration after which the conversion of preasphaltenes to oil predominated. Two different recycle experiments were carried out. In one, an amount of the preasphaltene plus residue fraction, called "residual", that was equivalent in carbon content to 90% of the usual (50 g) amount of Wyodak coal, was treated at 300°C with 90% of the usual amounts of $ZnCl_2$, H_2O, and tetralin. In the other recycle experiment, 5 g of asphaltene was isolated, dissolved in 50 g of tetralin, and then treated with $ZnCl_2$.

For the residual recycle experiment, the residual was treated for 90 min, so that the combined yields could be compared to a 120 min treatment. The combined treatment yield of each soluble product was calculated as the yield from the preparative experiment (zero for preasphaltene and residue), plus the fractional yield from the recycle experiment times the yield of residual in the preparative experiment.

The yields for the initial 30 min experiment, the combined yield for the 120 min recycle experiment, and the yield for a non-recycle, 120 min treatment of coal are shown in Fig. III-6. The 120 min combined treatment has a similar oil and total yield to the non-recycle treatment.

The only noticeable difference between the results is the increased asphaltene yield for the combined treatment. The increased asphaltene yield suggests that asphaltenes do participate in the reaction pathway. These results are consistent with a reaction pathway in which preasphal-

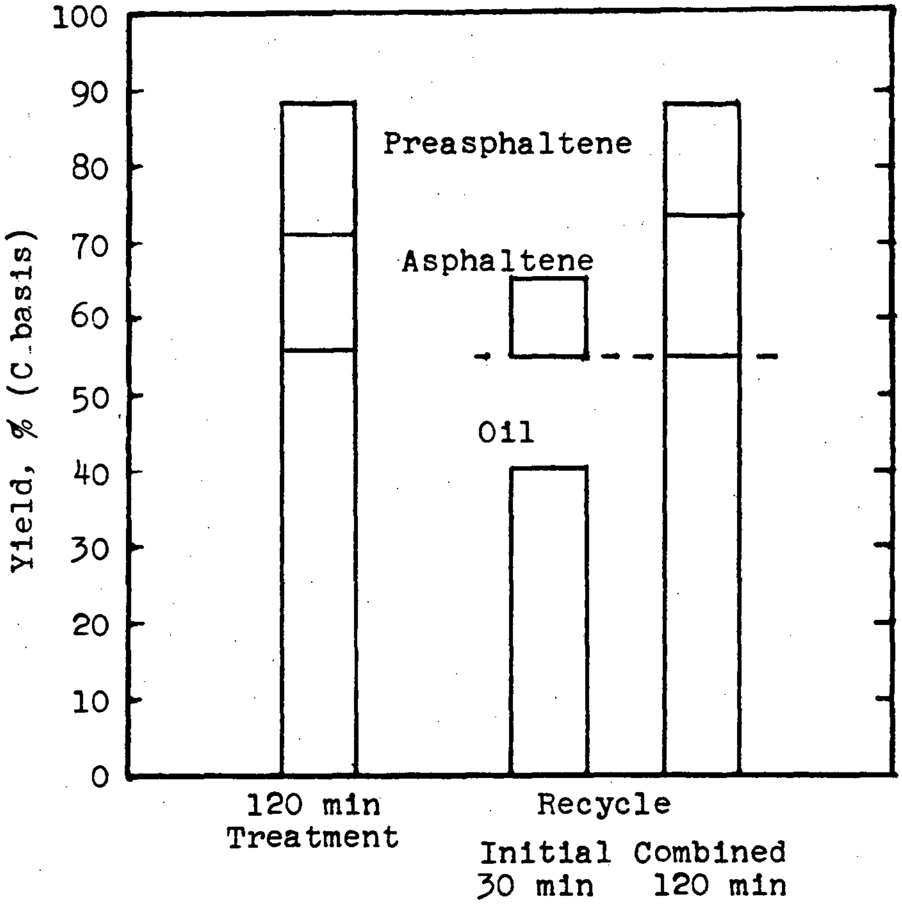

Figure III-6: Solubility fraction yields for the residual recycle experiment. Treatment of 50 g Wyodak coal at 300°C with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

tenes are first converted to asphaltenes and then to oil (with an undetermined amount of the parallel direct conversion of preasphaltenes to oil). The removal of asphaltenes and oil from the reactor, between the two stages of treatment, prevents the asphaltenes from reacting to oil and results in the increased asphaltene yield for the combined treatment. Unfortunately, the small differences in yield beetween recycle and non-recycle experiments make it difficult to base firm conclusions on these results.

A more direct method to study the reaction pathway is to isolate and re-treat the individual solubility fractions. This approach is actually limited to the treatment of asphaltene*, and even an asphaltene recycle reaction is subject to the limitation that product separations cannot be made by Soxhlet extraction.

In the asphaltene experiment 5 g of asphaltene, roughly the amount that would be recovered in a 300°C treatment of coal, was dissolved in 50 g of tetralin and treated with 273 g $ZnCl_2$ and 27 g H_2O, under 3.5 MPa hydrogen pressure for 60 min at 300°C. The product separation was accomplished by pouring the solution of asphaltene plus the oil product in tetralin (and toluene) into an excess of cyclohexane, and collecting the asphaltene as precipitate.

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* Reaction of oil is not interesting because it is unlikely that a reverse reaction (involving heteroatom and ash addition) will occur to any great extent. The preasphaltenes can not be extracted from the MTC without incorporation of pyridine and $ZnCl_2$.

The distribution of final products (in terms of fractional carbon recovery) is shown in Fig. III-7. The treatment of asphaltene results in a high level of conversion to oil and a high incorporation of tetralin into the products, with more oil being recovered than the amount of initial asphaltene. If the conversion is evaluated based on the level of remaining asphaltene, the conversion is 67%. The amount of reverse reaction to toluene-insolubles is so small as to preclude separation of these insolubles into preasphaltene and residue fractions.

The conversion of asphaltene to oil confirms that the asphaltene fraction is a part of the reaction pathway from coal to oil, and the high levels of conversion are an indication that this pathway via asphaltene is a major one. The high level of conversion is also an indication that the asphaltenes may be converted more quickly in isolation than in the presence of coal and preasphaltenes. From examination of Fig. III-5 we see that for treatment durations between 60 and 120 min, at 300°C, the oil yield increases by only 6%, despite the presence of about 14% asphaltene. This represents a maximum asphaltene conversion of about 43%, if all the oil is produced by this pathway, compared to a 67% conversion in isolation. Conversely, the oil yield obtained in the first 10 min of coal treatment at 300°C is very large (28.5%) compared to the yield of asphaltene (13.1%), indicating that if all this oil was produced through the intermediate of asphaltene, then the conversion of asphaltene to oil is faster in this initial period of coal treatment than is the conversion in isolation or in the later stages of coal treatment. The apparent variation in the rate of asphaltene conversion indicates that the reaction pathway is sufficiently complex to

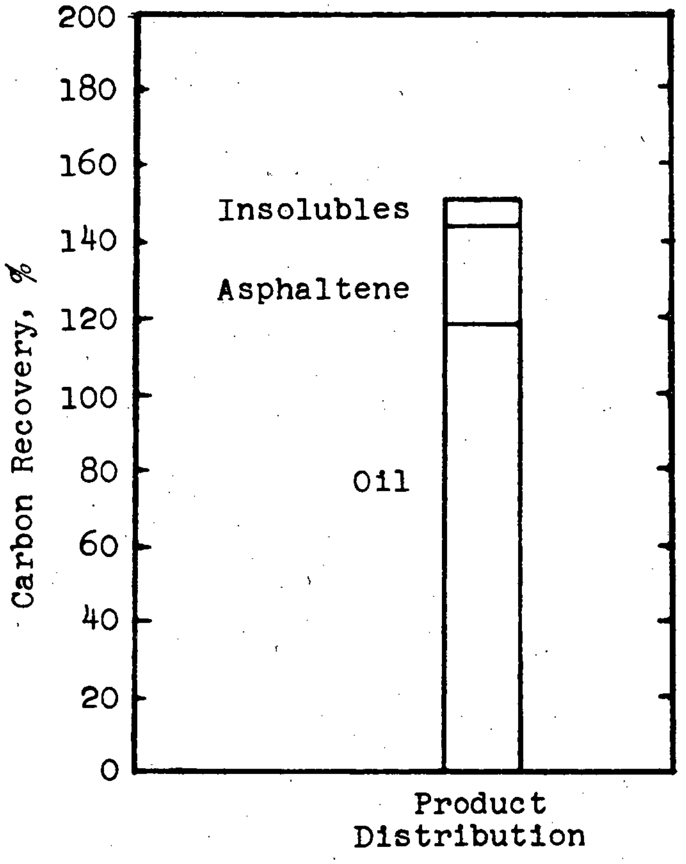


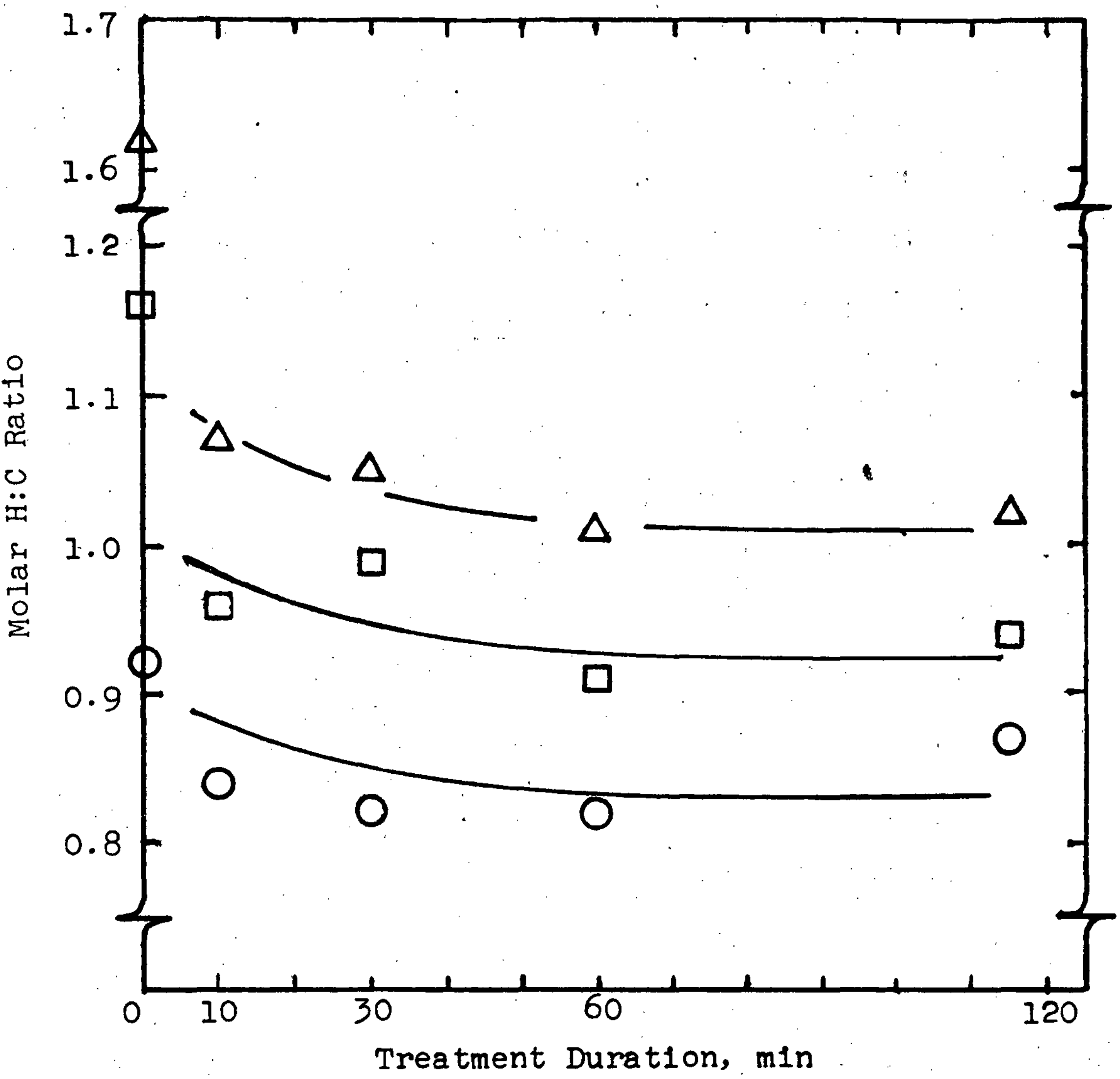
Figure III-7: Fractional recovery of carbon in the asphaltene recycle experiment. Treatment of 5 g asphaltene with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

involve product fractions with changing activities, and may be better described as the combination of several conversion pathways between coal and products.

Effect of Treatment Duration on H:C Ratio of Products

The results of the reaction-pathway investigation serve to indicate the interconversion of the solubility fractions. Thus it is important to examine the influence of this interconversion on the character of the soluble products, and to study any effect on molar H:C ratios of the soluble products that might arise in the conversion of one soluble product into another.

The H:C ratios for the soluble products of the 300°C treatments remain approximately constant over the range of treatment duration from 10 to 120 min, as shown in Fig. III-8. The large difference between the H:C ratios of the products for the zero-time treatment and those of products for the longer duration treatments is an indication that the initial oils and asphaltenes, which are recovered in amounts similar to the soluble yields from untreated coal, reflect the properties of soluble materials originally present in the coal and do not represent material that is formed by the treatment with $ZnCl_2$ and tetralin. The constancy of the H:C ratios that are observed after this initial decrease from the zero-time ratios is an indication that, as one soluble product is converted into another, the new product does not necessarily retain the H:C character of the original material. This observation is supported by the asphaltene reaction, in which an initial asphaltene with H:C = 0.88 is converted to an oil with H:C = 1.01 and an asphaltene with H:C =



<u>Figure III-8</u>: Effect of treatment duration on the molar H:C ratio of the soluble products. Treatment of 50 g Wyodak coal at 300°C with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure. △ - oil, □ - asphaltene, ○ - preasphaltene.

0.92. Both products have H:C ratios that are similar to those of their respective solubility fractions on Fig. III-8.

This H:C constancy over different treatment durations contrasts with the changes in H:C noted for 60 min runs at different treatment temperatures. The increase in temperature from 250 to 300°C results in an increase in yields that is similar to that obtained by a change in duration from 10 to 120 min at 300°C. Thus the H:C decrease that is observed with increasing temperature can not be simply explained as a progressive conversion of more hydrogen deficient material.

H:C ratio is just one indication of the character of the soluble product. Other product characterizations can be made, in particular for the oil product, with the use of proton nuclear magnetic resonance.

Products Characterization by Proton Nuclear Magnetic Resonance

Proton nuclear magnetic resonance (NMR) was used to determine the chemical character of the protons and with a few assumptions, of the carbon atoms of the soluble products obtained in this work. The information obtained by NMR can be used to calculate estimates of the structural character of the coal-derived materials. Besides its general value in revealing product chracter, structural information is an important tool in the study of the effects of zinc chloride catalysis.

As with all of the analytical procedures, proton NMR has limitations; in this application important limitations arise in heteroatom content and solubility. The presence of heteroatoms in the NMR sample can shift the proton absorbances out of their standard locations. Solubility of samples can be a problem for asphaltenes and particularly for preasphaltenes. Even in such NMR solvents as pyridine-d_5, asphaltenes and preasphaltenes can form colloids that pass through a filter, and for which the aromatic protons do not absorb strongly$^{(58)}$. Because of these limitations, the product oils have been studied more extensively than the asphaltenes or preasphaltenes. The oils have few heteroatoms and are completely soluble in the pyridine-d_5 solvent.

The proton NMR spectrum of the oil derived directly by hexane extraction of Wyodak coal (called here "natural" oil), shown in Fig. III-9, is quite different from the spectrum of the oil produced by 300°C treatment with $ZnCl_2$/tetralin (Run 47), shown in Fig. III-10. The natural oil spectrum is similar to that for the oil from a 300°C, zero-time treatment (Run 27), while the spectrum of the oil from Run 47 is typical of that obtained for the oils from all of the other treatments with $ZnCl_2$ and tetralin, although there are measureable differences in the relative contributions of each region in the spectra. The region from 6 to 9 ppm (frequency shift downfield from TMS absorption) represents aromatic protons, with the three largest peaks containing some proton absorbance from the pyridine-d_5 (all the spectra are corrected for pyridine-d_5 absorbance before analysis). The region from 0 to 4 ppm includes the alpha, beta, del, and gamma portions of the aliphatic proton spectrum, as well as the reference absorption (at 0.03 ppm). Example proton NMR spectra for asphaltenes and preasphaltenes derived from untreated coal and from coal treated at 250°C for 60 min with $ZnCl_2$ and tetralin can be found in Appendix B.

The natural oil from Wyodak coal has an aliphatic to aromatic proton ratio (H_{ali}/H_{aro}) of about 20 (this ratio becomes numerically unreliable for values above about five because of the small amount of

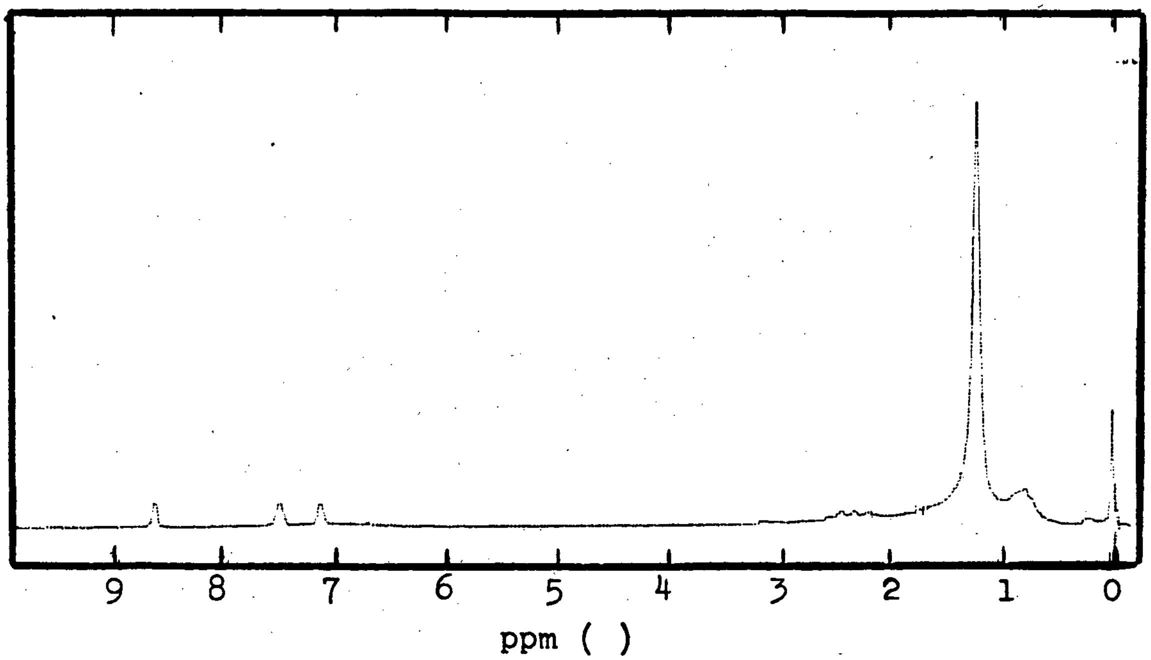


Figure III-9: Proton-NMR spectrum of oil extracted from untreated Wyodak coal.

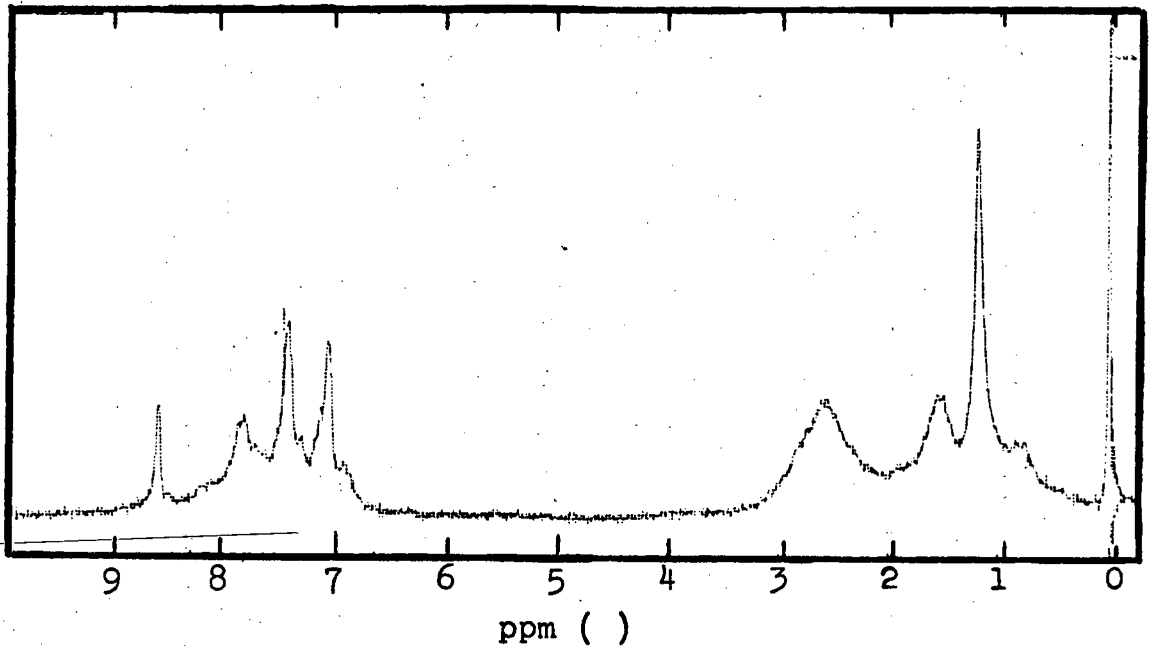


Figure III-10: Proton-NMR spectrum of product oil. Treatment of 50 g Wyodak coal at 300°C for 60 min with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, 3.5 MPa total pressure.

absorbance for integration in the aromatic region). Nearly 60% of the protons are represented by the single peak at 1.2 ppm, indicating that the structure of this oil is that of saturated (aliphatic) carbon chains, either simple or cyclic. These aliphatics are expected to be resistant to zinc chloride catalysis, as shown by Maienschein, who found n-dodecane to be unaffected by $ZnCl_2$ treatment at temperatures up to 300°C(46). It is, therefore, not surprising that all of the spectra of oils from $ZnCl_2$ treatment of Wyodak coal should have large peaks at 1.2 ppm (del fraction).

Since the actual reaction products of the treatment of Wyodak coal with $ZnCl_2$ and tetralin may bear no resemblance to the natural oil, the reaction product spectra have been corrected by subtraction of the natural oil in an amount equal to the natural oil yield determined by extraction of untreated coal. The effect of this correction on the fraction of protons in the del region of the spectrum is shown in Table III-6. The del-region protons of the natural oil, and those of Run 27, represent nearly 60% of the total protons. The two recycle experiments, in which a material expected to be devoid of natural oil is reacted, result in oils that have only about 10% del-region protons. For the treatments with $ZnCl_2$ and tetralin at 300°C, the natural-oil correction reduces the amounts of del-region protons from about 18% to values of 6 to 13%. Although some variation is introduced into the results by this correction all of the regions in the NMR spectra should have proton absorbances that more closely resemble the values for the actual reaction products after being corrected in this manner.

Table III-6: Effect of "natural" oil on the fraction of protons absorbing at 1.0 to 1.4 ppm (del fraction) in the proton-NMR spectra. Treatment of 50 g Wyodak coal with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

Oil Sample Origin		Fraction of Del Protons	
Natural Oil		55.6 %	
300°C, 0 min treatment (Run 27)		59.6	
Re-treatment of initial products(1)			
Residual treatment (Run 35)		9.0	
Asphaltene treatment (Run 36)		9.5	
Runs of Different Duration		Uncorrected	Corrected
300°C	10 min	17.3 %	5.9 %
	30 min	18.9	11.3
	60 min	17.2	10.7
	120 min	18.2	12.7
300°C, 60 min treatment with no tetralin		45.3	30.7

(1) Retreatment at 300°C of products from 300°C, 30 min treatment of coal.

For the oils, enough NMR spectra have been determined so that more precise sturctural information can be obtained by averaging the results for oils obtained under similar treatment conditions. The oil produced by long treatment (≥60 min) at 300°C is represented by five experiments; three 60 min treatments, a 120 min treatment, and the residual recycle experiment. The averaged experimental structural parameters for the oils obtained in these experiments are shown in Fig. III-11, along with an example molecule that is characteristic of these parameters. The product oils are actually the combination of a large variety of different molecules, so that the molecule shown can only be considered an example of the type of molecule that may be present in the oils.

The most important aspects of this molecular model are: that the aromatic nuclei are condensed to about three rings, that there are roughly three substituents per nucleus, that the ratio of aliphatic to aromatic hydrogens is about 1.7, and that the carbon aromaticity is 0.7 (the last two aspects force the H:C ratio to also correspond between model and experimental). The large amount of alpha- and beta-region protons relative to the del- and gamma-region protons results in an aliphatic structure that is composed mostly of saturated side chains on the aromatic nuclei. The sizes and shapes of the aliphatic substituents are subject to quite wide choice because of the overlap of the beta, del, and gamma regions of the spectra. The locations of these substituents are totally arbitrary.

The structural characteristics of the oils from experiments representative of the treatment temperatures and durations used in this work are shown in Table III-7. Structural characteristics for the remainder

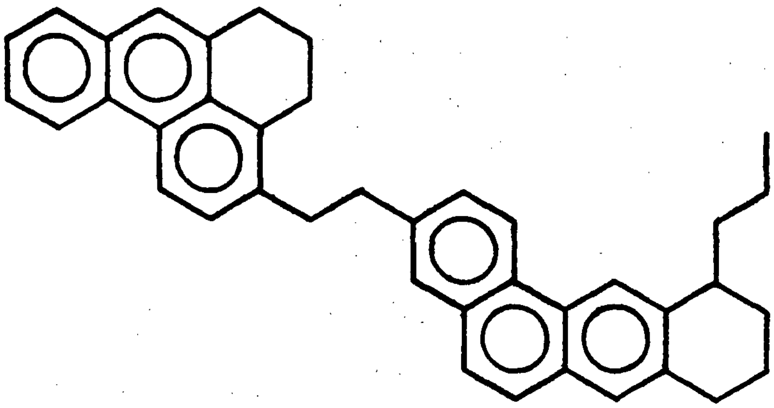


Figure III-11: Example structure of product oil. Treatment of 50 g Wyodak coal at 300°C, for durations 60 min or greater, with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

Structural Property	Experimental Average	Example Molecule
Molecular Weight (by GPC)	500	518
H:C (by elemental analysis)	0.96	0.95
NMR		
H_{ali}/H_{aro}	1.70	1.71
F_a	0.705	0.70
$[H:C]_{nuclei}$	0.712	0.714
(aromatic substitution)	0.291	0.30
Aliphatic Proton Fractions:		
alpha	0.292	0.289
beta	0.177	0.211
del	0.108	0.053
gamma	0.044	0.079
Aliphatic chain length	5.76	4.0
Napthenic chain length	3.32	3.0

Table III-7: Structural characteristics of selected oils, produced in treatments of 50 g Wyodak coal with 273 g $ZnCl_2$, 27 g H_2O, 3.5 MPa total pressure.

Parameters are calculated from proton-NMR spectra, and are corrected for natural oil.

Treatment	(Run No.(1))	H_{ali}/H_{aro}	F_a	$[H:C]_{nuclii}$	Substitutions per nucleus	Aliphatic chain length	Aromatic chain length
300°C :							
10 min	(26)	1.58	0.70	0.78	0.30	3.9	3.3
30 min	(25. 34)	1.70	0.69	0.74	0.29	6.0	3.3
60 min	(23, 28, 47)	1.58	0.72	0.71	0.28	5.7	3.3
120 min	(24)	1.96	0.68	0.72	0.30	6.6	3.3
60 min :							
250°C	(31, 45)	2.11	0.66	0.75	0.33	4.7	3.7
275°C	(39, 42)	1.67	0.69	0.78	0.30	7.1	3.3
300°C	(23, 28, 47)	1.58	0.72	0.71	0.28	5.7	3.3
325°C	(46)	1.42	0.73	0.71	0.26	6.1	3.0

note (1) Multiple run numbers indicate averaged parameters.

of the oils may be found in Appendix B. Such structural parameters as the aliphatic or naphthenic chain length, and the degree of the aromatic substitution, are not strongly affected by treatment temperature or duration. For these parameters, the variation observed between the individual runs (instead of the averaged parameters on Table III-7) shows that there is not much significance to the level of difference observed with changing treatment conditions.

The aromaticity of the oils, as expressed in the ratio of aliphatic to aromatic protons, is affected by treatment temperature and duration in a manner similar to that observed for the H:C ratio. The H_{ali}/H_{aro} ratio is roughly constant with treatment duration, as shown in Fig. III-12, and decreases with increasing temperature, as shown in Fig. III-13. The similarity in the changes of the H:C ratio and the H_{ali}/H_{aro} ratio is not surprising, as the aliphatic structures have a much higher H:C ratio ($\sim$2.0) than do the aromatic structures ($\sim$0.5).

In contrast to H_{ali}/H_{aro}, the degree of aromatic condensation can be totally independent of the sample H:C ratio. The degree of aromatic condensation is represented, in this work, by the H:C ratio for the hypothetical unsubstituted aromatic nucleus ($[H:C]_{nuclei}$). This H:C ratio decreases as the nucleus becomes more condensed, and is unrelated to the overall sample H:C ratio. For the oils resulting from treatment of coal with $ZnCl_2$ and tetralin at 300°C, the value of $[H:C]_{nuclei}$ decreases from 0.78 to 0.7 as the duration of treatment increases from 10 to 60 min, as shown in Fig. III-14. This change in $[H:C]_{nuclei}$ is representative of a change in degree of condensation from roughly that of naphthlene ($[H:C]_{nuclei} = 0.8$) to that of anthracene ($[H:C]_{nuclei} =$

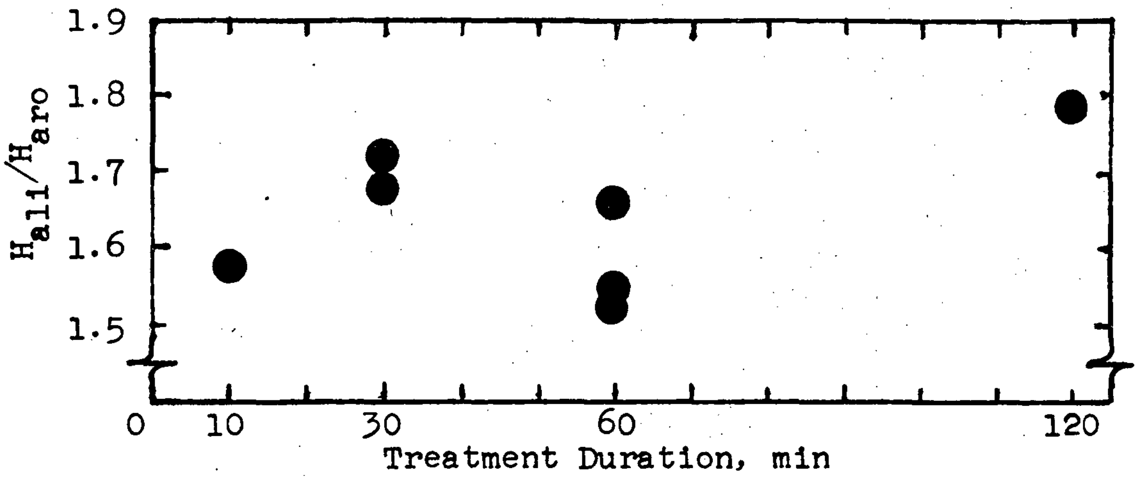


Figure III-12: Effect of treatment duration on the H_{ali}/H_{aro} ratio of the oil product. Treatment of 50 g Wyodak coal at 300°C with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

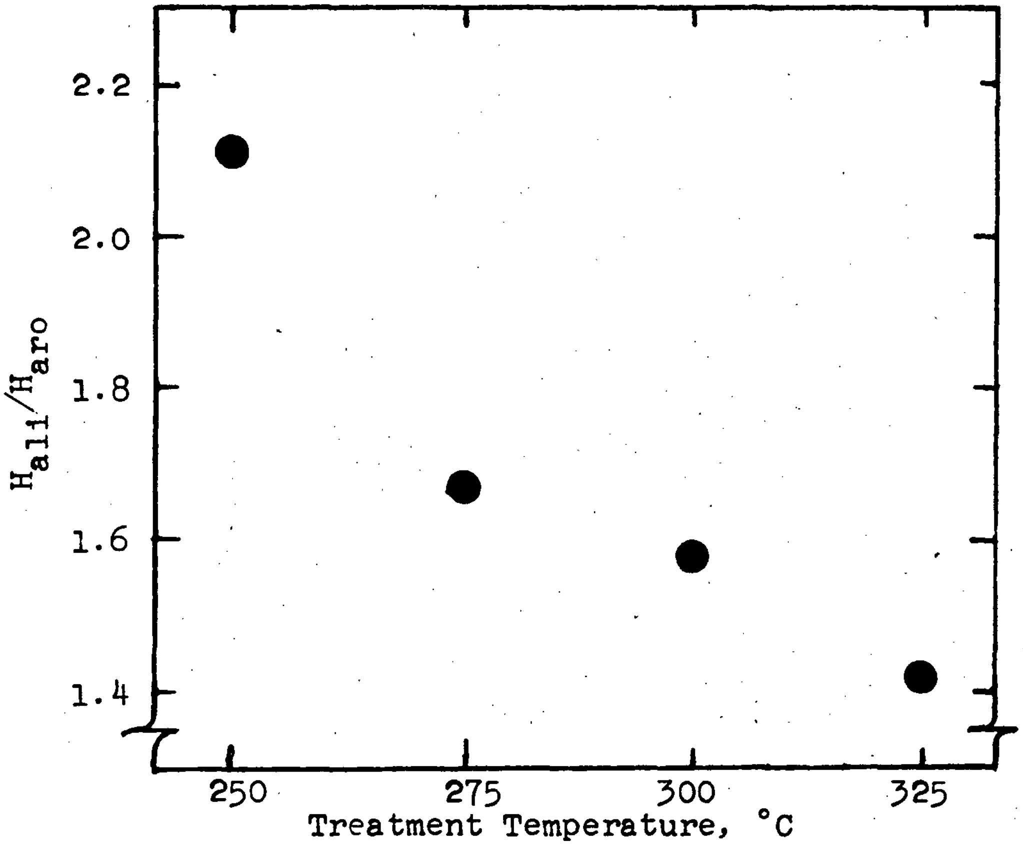


Figure III-13: Effect of treatment temperature on the H_{ali}/H_{aro} ratio of the oil product. Treatment of 50 g Wyodak coal for 60 min with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

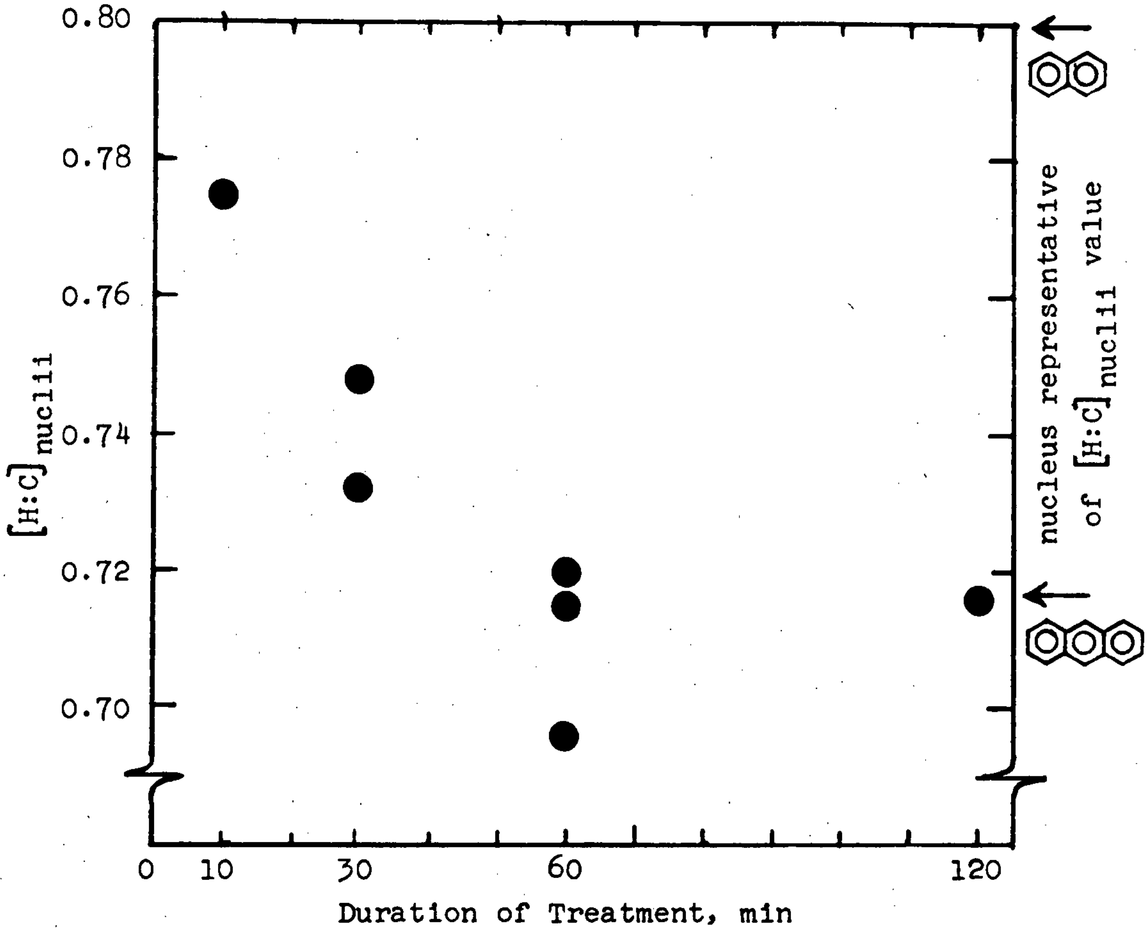


Figure III-14: Effect of treatment duration on $[H:C]_{nuclii}$. Treatment of 50 g Wyodak coal at 300°C with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

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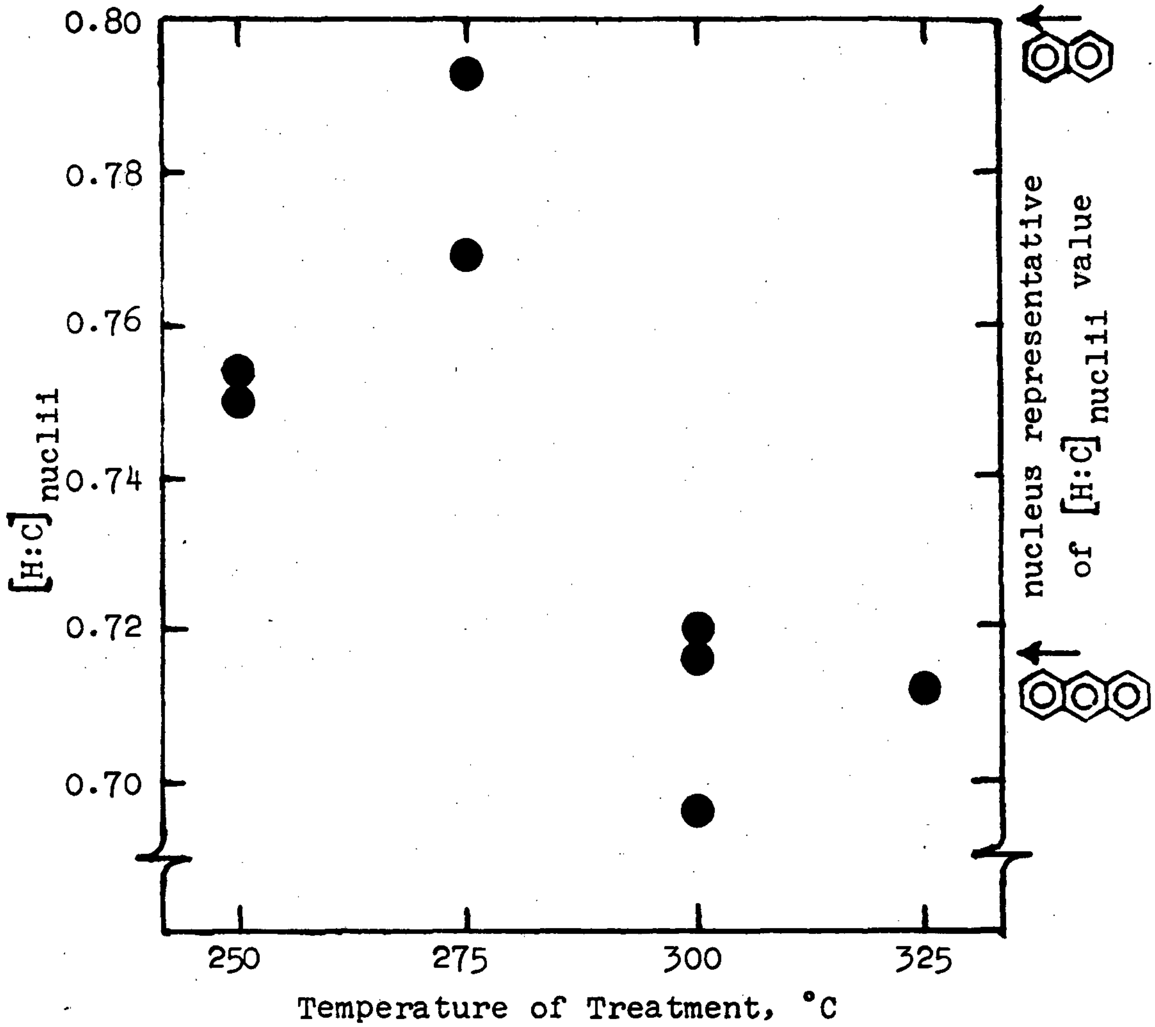
0.716). This result can only be interpreted as meaning that the material that is converted to oil at later stages of treatment is more condensed than that which is converted earlier.

The variation of $[H:C]_{nuclei}$ for oil products as a function of treatment temperature, shown in Fig. III-15, is somewhat bewildering, especially in the behavior at 250 and 275°C. For these 60 min treatments, the $[H:C]_{nuclei}$ apparently increases from about 0.75 to about 0.78 as the temperature increases from 250 to 275°C, and then drops to a value of 0.71 for 300 and 325°C treatments. These results may serve to indicate that the calculated values of $[H:C]_{nuclei}$ are affected by structural characteristics other than the degree of condensation. In any event, the results show that the increased yield at higher temperature is accompanied by very significant changes in the character of the oil.

The proton-NMR spectra provide structural characteristics of the soluble oil products, show that the change in H:C ratio with reaction conditions is closely related to the ratio of aliphatic to aromatic protons, and indicate that the degree of condensation of the soluble oil product increases as the treatment progresses at 300°C. But NMR analysis can not, as of yet, be used to study the non-oil fractions of the MTC with sufficiently high resolution to allow observation of the structural changes that accompany coal conversion. For example, in model compound studies the cleavage of the alkyl bridge in diphenyl methane results in a quantitative NMR change, but to try to observe alkyl bond cleavage in coal structure, using solid-phase NMR, would be impossible. However, some of the effects of the structural changes



<u>Figure III-15</u>: Effect of treatment temperature on $[H:C]_{nuclii}$.
Treatment of 50 g Wyodak coal for 60 min with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, 3.5 MPa total pressure.

that accompany conversions of coal to soluble products can be observed in the molecular weight distributions of the soluble products.

Product Characterization by Gel Permeation Chromatography

In this work, gel permeation chromatography (GPC) has been used to study the molecular weight distributions of molecules in the oil, asphaltene, and preasphaltene fractions of melt treated coal. GPC analysis is subject to several limitations, the most important being that the chromatographic separation correlates more with molecular size and shape than with molecular weight, and that detection by ultraviolet (UV) absorbance does not directly correlate with solute concentration. These limitations notwithstanding, GPC does provide some valuable information about the molecular weight ranges of the different products and of the changes that occur in the product's molecular weight distribution with changing coal-treatment conditions.

The chromatograms of oils, asphaltenes, and preasphaltenes from a treatment of Wyodak coal at 300°C for 60 min, shown in Fig. III-16, are typical of soluble products from zinc chloride-catalyzed subbituminous coal conversion in tetralin. The preasphaltenes have the highest molecular weight, ranging from approximately 500 to 10,000. The asphaltenes have a molecular weight range of about 200 to 5000, and the oils have the lowest molecular weight range, about 200 to 1000. From the molecular weight distributions, it is apparent that the conversions of preasphaltenes to asphaltenes, and of asphaltenes to oils are accompanied by large reductions in the molecular weight of the molecules being converted.

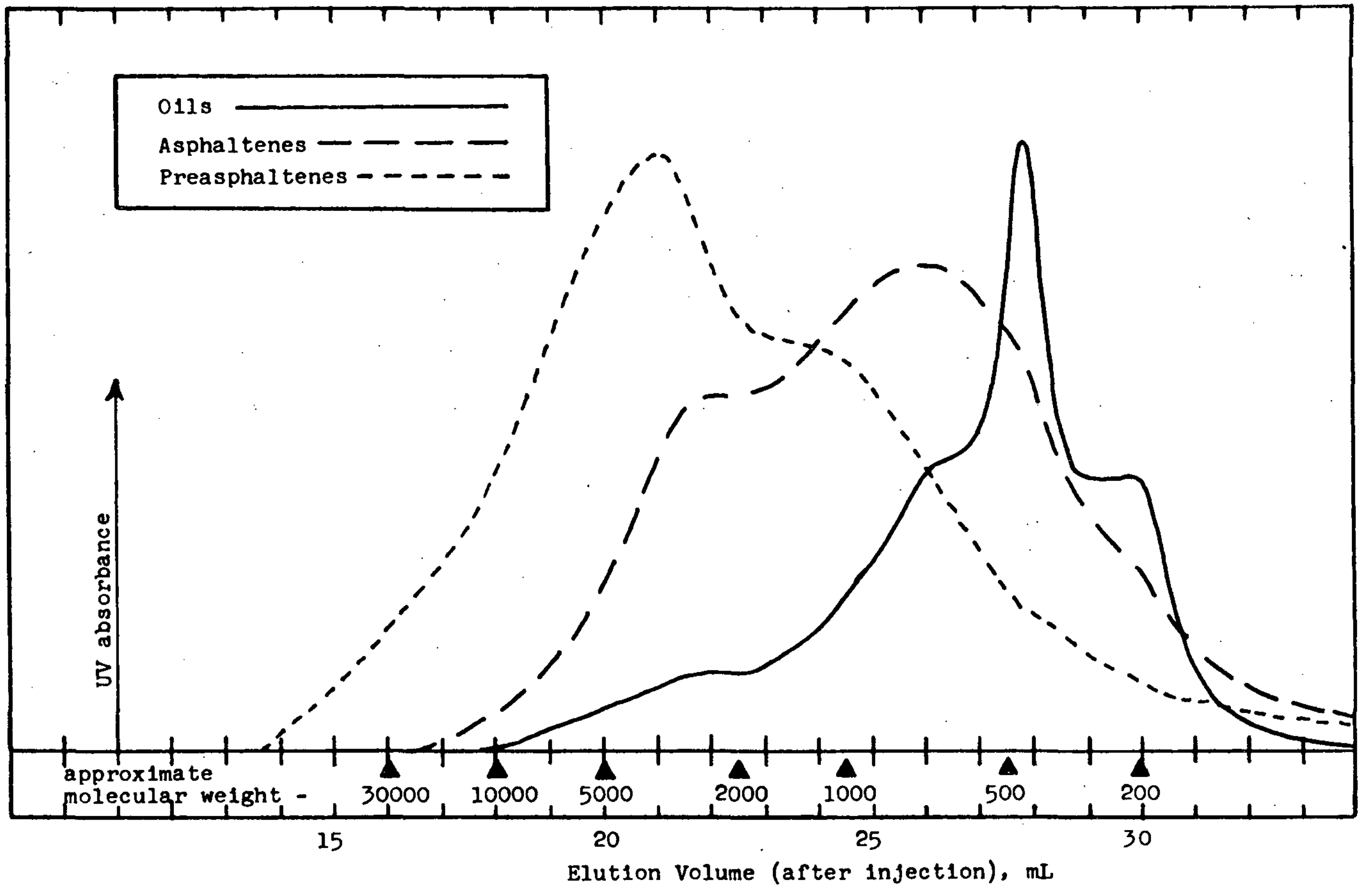


Figure III-16: Gel permeation chromatograms of soluble products.

Treatment of 50 g Wyodak coal at 300°C for 60 min with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, 3.5 MPa total pressure. Chromatography was conducted with THF carrier (pyridine for preasphaltenes) using 100 A + 500 A + 1000 A micro styragel columns and 313 nm UV detection

The chromatograms of the asphaltene and preasphaltene fractions change little over a wise range of treatment conditions (e.g. temperature and duration). In fact, the chromatograms of asphaltene and preasphaltene extracts of untreated coal and of coal treated in the absence of tetralin are virtutally identical to those for the fractions from the treatments with the highest conversions. It thus appears that molecular weight is one of the important determinants of solubility in the asphaltene and preasphaltene fractions.

For the oils, however, significant differences in molecular weight distribution are observed with changing treatment conditions. The greatest difference is that between the natural oil and the oil product of higher conversion experiments. The chromatograms of oil fractions for untreated coal, for Run 27 (the 300°C, zero-time experiment), for a 300°C, 60 min experiment without tetralin (Run 38), and for the 300°C, 60 min run with tetralin (Run 47) are compared in Fig. III-17. The oils that derive from treatments without tetralin all have higher molecular weight distributions than does the oil from the treatment in which tetralin is present. The yields of oil from untreated coal (1.9%) and from Run 27 (3.3%) are close enough to suggest that the same material is observed in each chromatogram. For Run 38, the yield is higher (9.2%), as is the amount of material (or, more correctly, absorbance) in the lower molecular weight end of the chromatogram. It appears from these chromatograms that the "natural" oil present in Wyodak coal has a different molecular weight distribution from that of the reaction product oil, and is not much affected by treatment with zinc chloride and tetralin. This natural oil has a molecular weight range of 200 to 5000 and, because

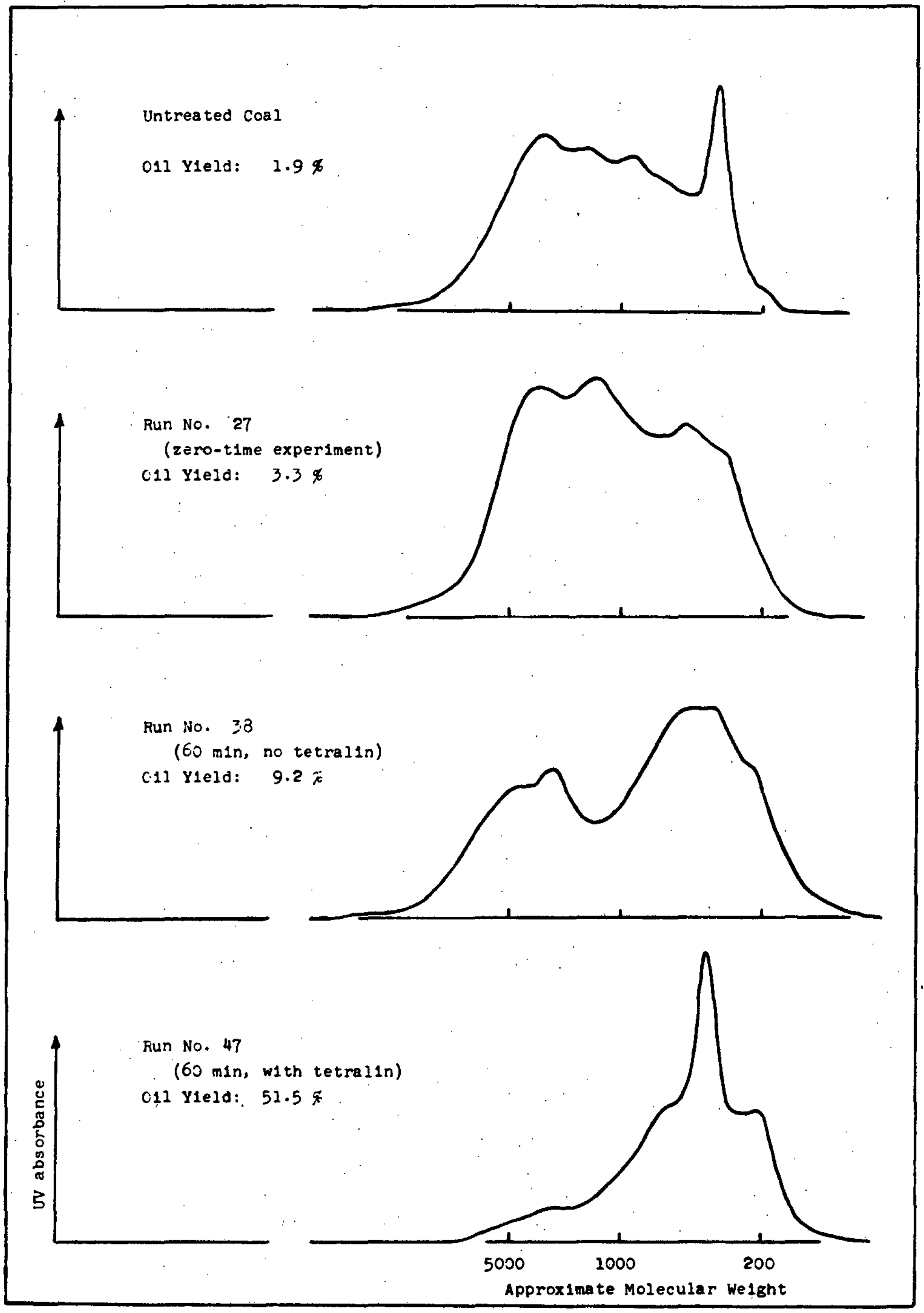


Figure III-17: Comparison of gel permeation chromatograms of oil from treated and untreated coal. Treatments are of 50 g Wyodak coal at 300°C with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

Chromatography is conducted with THF or pyridine carrier using 100 A + 500 A + 1000 A micro styragel columns and 313 nm UV detection.

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it is present in small amounts, is not noticeable in the products from $ZnCl_2$/tetralin treatments in which the oil yields are 30% and higher.

A more subtle change in the molecular weight (MW) distribution of the oil is observed with changes in treatment temperature, as shown in Fig. III-18. By comparison of an oil from a 60 min, 250°C treatment to that of a 10 min, 300°C treatment, the influence of oil yield is eliminated (both are about 30%). Both of these chromatograms have the same basic molecular weight range shown for oils on Fig. III-16, but, for the lower temperature treatment, the curve has a larger peak at MW $\approx$ 200, and a smaller amount of absorbance in the higher MW region. The difference in the 200 MW peak is observed in comparison of 300°C and 250°C treatments in general, with the treatment at 275°C resulting in an oil chromatogram with a 200-MW peak that is intermediate in size. It must be noted that these narrow peaks may be caused by relatively small amounts of highly UV-absorbing species.

To this point, all of the chromatograms that have been discussed have been made using ultraviolet detection at 313 nm. The effect of detection wavelength on apparent molecular weight distribution is small, but significant, as shown in Fig. III-19. The use of a 254 nm wavelength allows detection of materials that are less condensed than those detected at 313 nm, but the net effect of the detection change is a peak at approximately MW = 500 that dominates the remainder of the chromatogram. As before, it must be noted that these narrow peaks may be caused by relatively small amounts of highly UV-absorbing species.

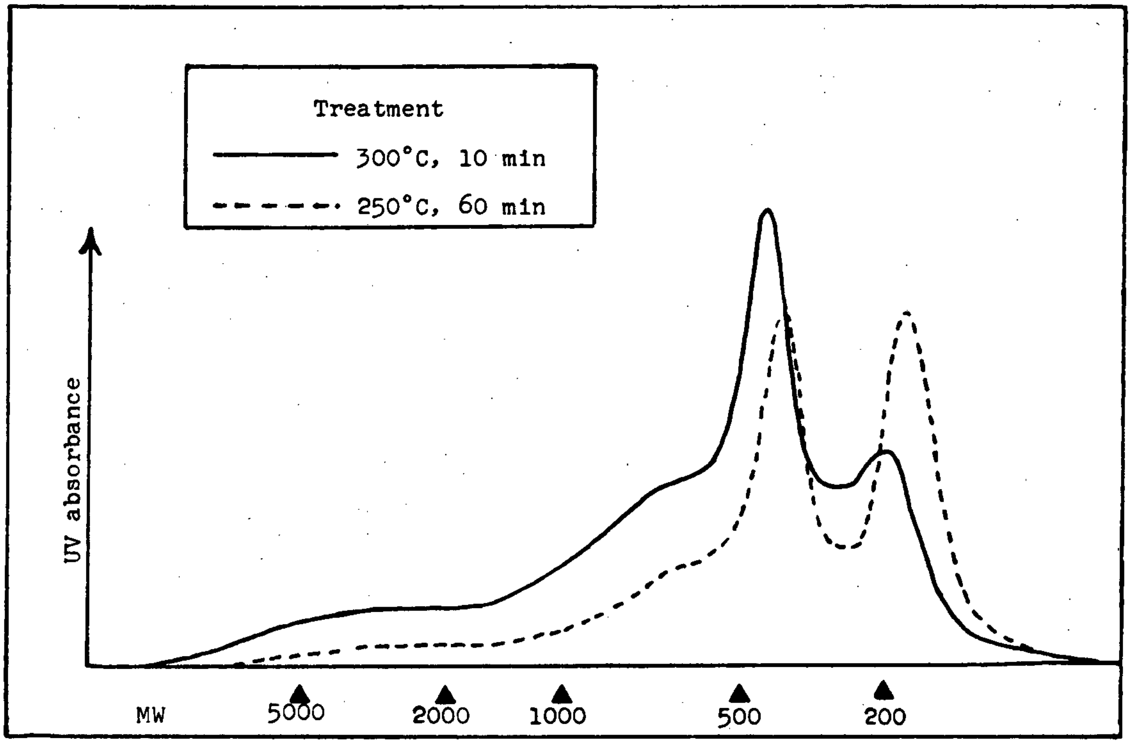

Figure III-18: Effect of treatment temperature on the molecular weight distribution of the oil product. Treatment of 50 g Wyodak coal with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

Chromatography was conducted with THF carrier using 100 A + 500 A + 1000 A micro styragel columns and 313 nm UV detection (chromatograms are scaled to provide equal integrated absorbance).

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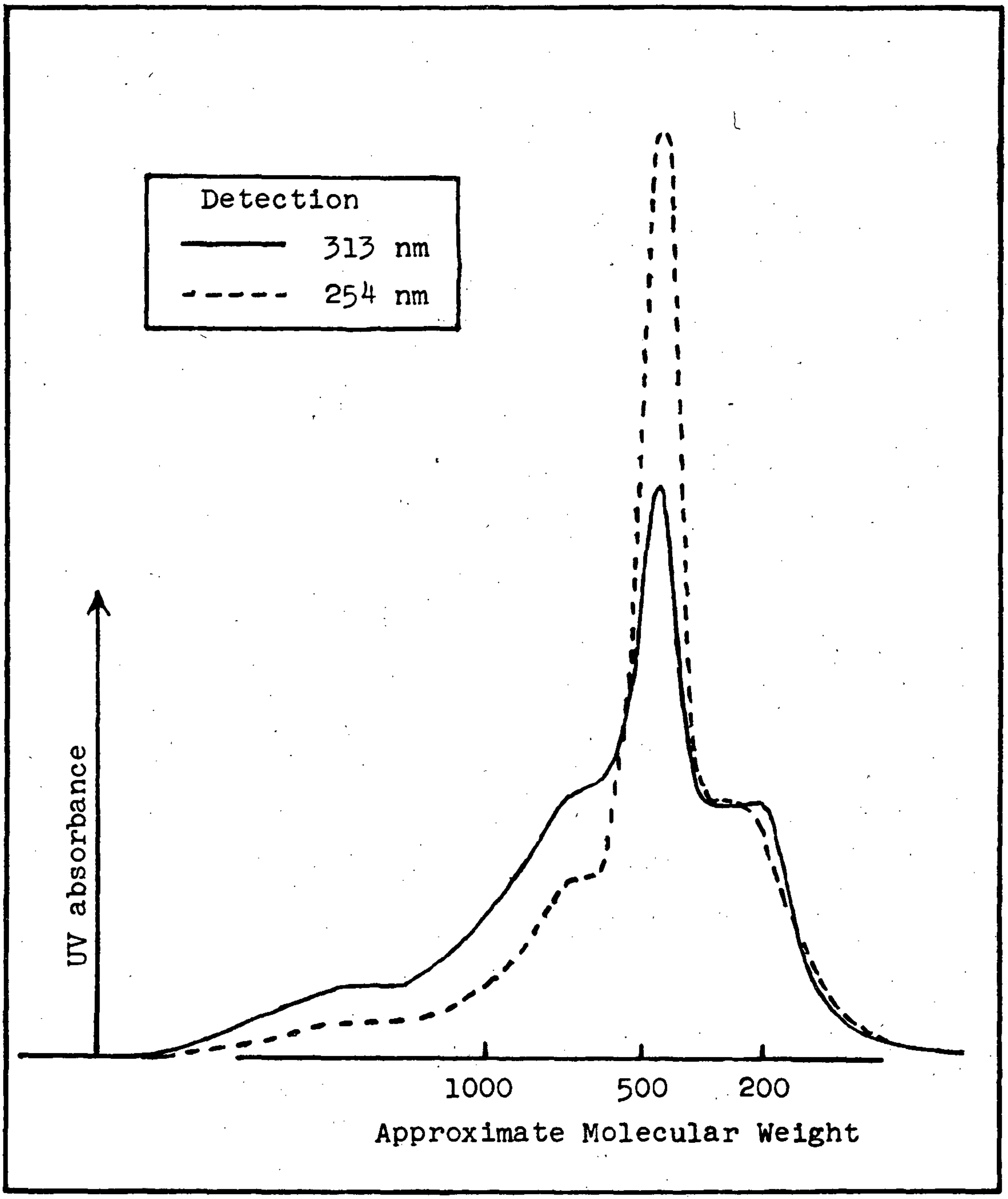

Figure III-19: Effect of gel permeation chromatography detection wavelength on the apparent molecular weight distribution of the oil product. Treatment of 50 g Wyodak coal at 300°C for 60 min with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, 3.5 MPa total pressure. Chromatography was conducted using THF carrier and 100 A + 500 A + 1000 A micro styragel columns (chromatograms are scaled to provide equal integrated absorbance).

The GPC analysis confirms that the natural oil of the Wyodak coal is significantly different from the oil produced by zinc chloride treatment. The analysis also shows that there is some effect of treatment temperature on the molecular weight distribution of the oil product. But the most important result of the GPC analysis is the most obvious: that conversion of one soluble product into the next is accompanied by a significant decrease in molecular weight.

Mechanism of Molecular Weight Reduction

The reduction in molecular weight that accompanies soluble product conversion can be understood in terms of the discussion of subbituminous coal structure that was presented in the introduction. There it was proposed that subbituminous coal can be described as containing a variety of aromatic and hydroaromatic structures in which the aromatic nuclei are condensed into groups of no more than four rings. These structures are grouped into clusters that have molecular weights in the range of 200 to 1000. The clusters are crosslinked to each other by ether oxygen and aliphatic bridges, as well as acid-base and hydrogen bonds. It was proposed that coal could be converted to low molecular weight products by cleavage of these crosslinking bonds, and it was suggested that $ZnCl_2$ is a catalyst that can accomplish this cleavage.

In fact, the NMR and GPC analysis of the soluble oil product, from treatments of Wyodak coal with zinc chloride and tetralin, describe a material that can be identified with the clusters of the coal model. This oil must have been produced by the cleavage of crosslinking bonds, and the high yields of oil are evidence of the effectiveness of $ZnCl_2$ at cleaving these bonds. The NMR characterizations of the soluble oil now take on added significance, as the structure in Fig. III-11 can be considered to represent a basic "cluster" subunit of Wyodak subbituminous coal.

In order to support this proposed mechanism of molecular weight reduction, it is desireable to demonstrate that crosslinking bonds are broken in coal conversion reactions. These bonds, both aliphatic and ether-oxygen, are very difficult to identify by chemical analysis. Fortunately, the ether oxygen can be estimated if other oxygen functional groups are determined.

Relationship between Oxygen Functional Groups and the Yields of Products

The importance of coal oxygen in zinc chloride catalyzed coal liquefaction with tetralin was noted at an early stage of this research. The relationship between total yield of soluble products and the degree of oxygen removal for treatments at 250°C in the Parr autoclave is shown in Fig. III-20. There is a nearly perfect correlation between yield and oxygen removal for experiments using a variety of solvents and treatment conditions. It appears that oxygen removal is directly involved in the conversion mechanism, and is not just the result of a side reaction.

This relationship between total yield and total oxygen removal is not particularly useful in discerning the mechanism of conversion, because the coal oxygen may be present in a number of different oxygen functional groups, including ether, hydroxyl, carboxylic acid, and carbonyl. However, the individual functional groups can be determined, and the relationships between yield and specific functional groups can thus be observed.

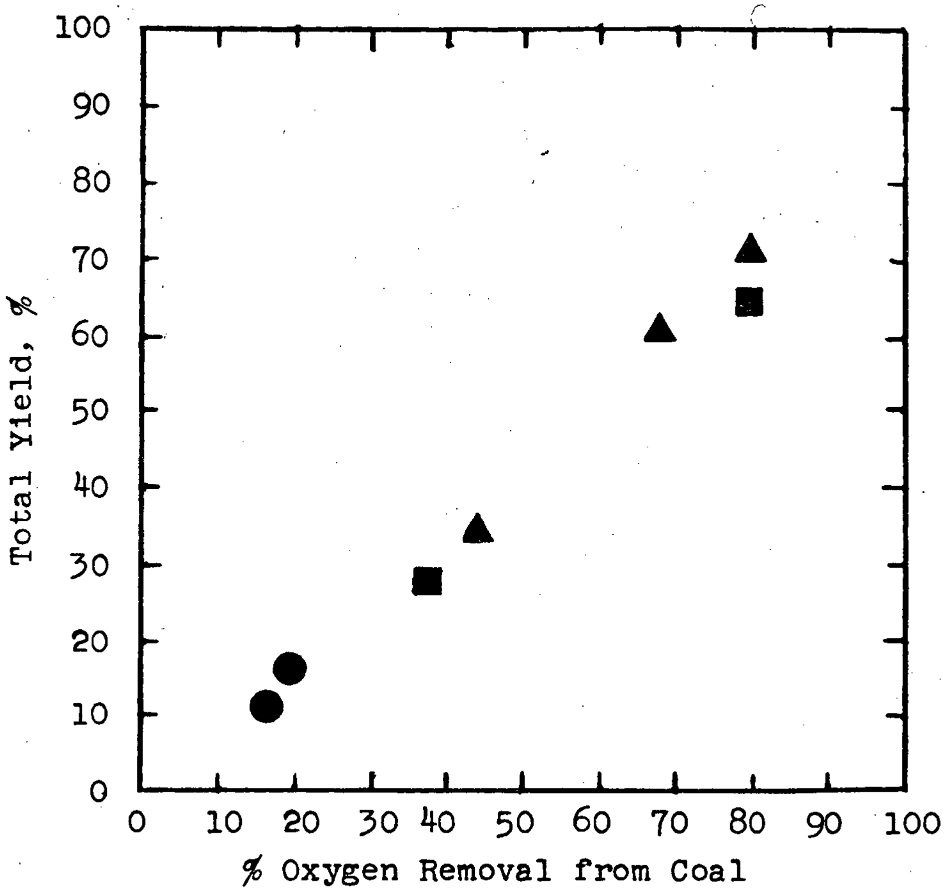

Figure III-20: Relationship between total yield of soluble products (DAF basis) and the removal of oxygen during treatment. Treatment of 50 g Wyodak coal at 250°C for 60 min in Parr autoclave with 273 g $ZnCl_2$, 27 g H_2O, 50 g solvent, 3.5 MPa total pressure (when H_2 is used). ● - $ZnCl_2$ alone, ▲ - $ZnCl_2$ + tetralin, ■ - $ZnCl_2$ + alcohol.

The concentrations of hydroxyl, carboxylic acid, and carbonyl oxygen were determined following the procedures outlined by Blom (62) in 1957. These oxygen concentrations, as well as the concentration of total oxygen, and the amount of oxygen, by difference, taken to be ether bonds are shown in Table III-8 for Wyodak coal and the products of treatments of Wyodak coal with $ZnCl_2$ and tetralin. The majority of samples that have been analyzed are materials that represent the MTC after most of the cyclohexane soluble (oil) material has been removed. Two analyses of the removed oil material are included on Table III-8.

In his analysis of a variety of coals, Blom found that, for a coal with a carbon concentration similar to that for Wyodak, the oxygen concentrations (in the units of Table III-8) were 18.5% total, 7% hydroxyl, 1% carbonyl, 3.5% carboxylic acid, and 7% ether. Compared to this, the Wyodak coal used in our experimental program is similar, with a higher ether and lower hydroxyl oxygen content.

Oxygen concentrations for all functional groups are reduced by treatment with $ZnCl_2$ and tetralin. The carbonyl concentration is reduced during heatup to 300°C with $ZnCl_2$ alone to a level that remains constant after further treatment with $ZnCl_2$ and tetralin. Carboxylic acids are quickly eliminated at 250 and 300°C. The hydroxyl oxygen concentration decreases gradually, and the ether oxygen concentration decreases at a rate similar to that of the total oxygen concentration. The oxygen contents for the 30 min, 300°C residual can be compared to those for the 30 min, 300°C, oil-free MTC. The residual, containing only preasphaltene and residue fractions, is 75% (carbon basis) of the oil free MTC. The residual contains a much higher level of total

Table III-8: Concentration of oxygen functional groups in samples of Wyodak coal and products of the treatment of 50 g Wyodak coal with 273 g ZnCl$_2$, 27 g H$_2$O, 50 g tetralin, and 3.5 MPa hydrogen.

Origin of Sample			Percent by weight of sample that is oxygen as:				
Treatment Conditions			Elemental	Functional Groups			Difference
Temp.	Time	Run Number	Total	Hydroxyl	Carbonyl	Carboxyl	(Ether)
Untreated Coal			17.3	3.34	1.00	3.52	9.44
Samples of Oil-free MTC							
250°C	30 min	30	10.1	2.78	0.65		
	60 min	31	9.6	2.80		0.26	6.0(1)
300°C	0 min	27	14.0	3.22	0.31	0.84	9.6
	10 min	26	8.0	2.71	0.25		4.7(2)
	30 min	25	4.9	2.48	0.24	0.05	2.1
	60 min	28	4.7	1.95	0.25		2.5(2)
	120 min	24	4.1	2.12			1.7(3)
Samples from Recycle Experiment (Runs 34 + 35)							
300°C	30 min preperative Experiment;						
	Analysis of Residual Fraction:		9.9	2.45			
	90 min treatment of residual;						
	Analysis of Oil-free MTC:		4.4	2.17			
Samples of Soluble Oil Product							
300°C	30 min	25	1.6	0.52			
	90 min (residual recycle)	35	1.0	0.42			

(1) Calculated assuming a carbonyl concentration of 0.55 %.

(2) Calculated by assuming that the carboxyl concentration decreases exponentially with reaction duration after the tetralin is added to the reactor.

(3) Calculated as above, with the additional assumption that carbonyl concentration is constant at 0.25 %.

oxygen, but a similar hydroxyl oxygen content to the MTC, indicating that the ether oxygen is partitioned into the preasphaltene and residue fractions. The soluble oil products, on the other hand, have very low levels of total and hydroxyl oxygen.

The treatments of different durations at 300°C can be used to show the relationship between oxygen removal and soluble product yield. The relationship between total soluble product yield and the removal of total oxygen is shown in Fig. III-21. The relationship between total soluble product yield and the removal of ether oxygen is shown in Fig. III-22. Both figures are similar, because the hydroxyl, carbonyl, and carboxylic acid oxygen fractions are removed by $ZnCl_2$ treatment at a combined rate that resembles the rate of ether oxygen removal. Both figures show a good correlation between oxygen removal and yield of soluble products, but the figure for ether oxygen represents directly the conversion of coal to soluble products by the cleavage of crosslinking bonds (in this case ether bonds) in the coal structure. The relationship for total oxygen happens to follow closely because of the already mentioned correlations with the rates of removal of the other functional groups

By calculation of an approximate number of ether bonds broken per product molecule, the removal of ether oxygen can be shown to represent sufficient cleavage of crosslinking bonds in the coal to account for the large reduction in molecular weight that accompanies coal conversion with $ZnCl_2$ and tetralin. For the treatment at 300°C for 60 min, assuming a total soluble product number-average molecular weight of 400, the removal of ether oxygen amounts to the removal of 3.4 ether

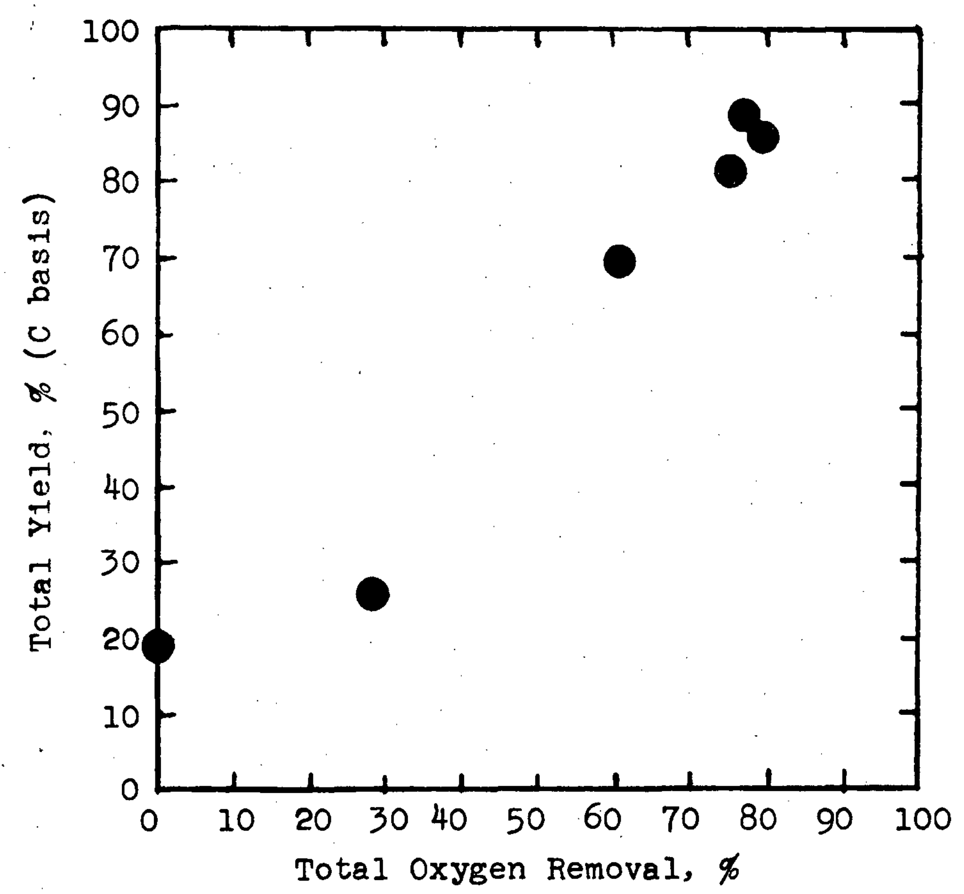

Figure III-21: Relationship between total yield of Soluble products and the removal of total oxygen during treatment. Treatment of 50 g Wyodak coal at 300°C with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

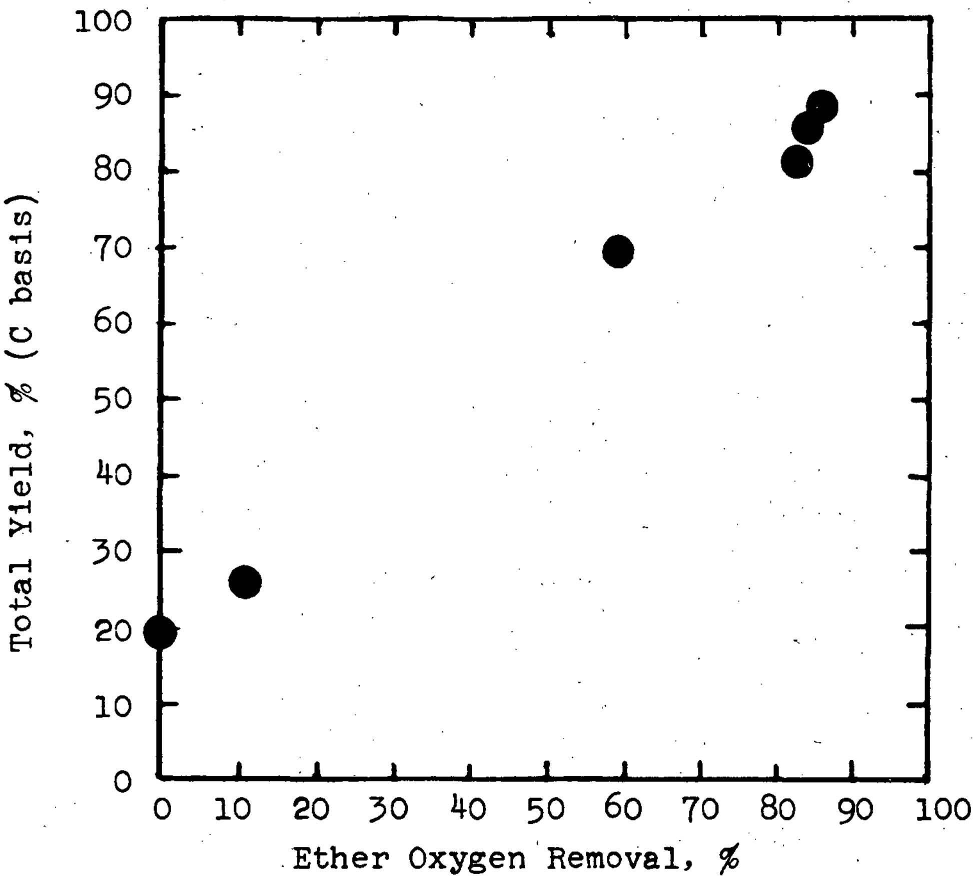

Figure III-22: Relationship between the total yield of soluble products and the removal of ether oxygen during treatment. Treatment of 50 g Wyodak coal at 300°C with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

oxygen atoms per product molecule. Even if over half of these atoms represent such functionalities as furans or methoxys (whose cleavage does not directly contribute to significant molecular weight reduction), the removal of ether still represents the cleavage of over 3 links to each product molecule.

The oxygen analysis of the residual (residue plus preasphaltene) from a 30 min, 300°C treatment allows calculation of approximate functional group concentrations for some of the other fractions. Assuming that after 30 min of treatment there remains only ether and hydroxyl functional groups, then the combined preasphaltene/residue contains 2.5% hydroxyl and 7.5% ether; the asphaltene contains 2.5% hydroxyl and 4.5% ether (total 7% oxygen); and the oil contains 0.5% hydroxyl and perhaps 1% ether; all compared to 3.3% hydroxyl and 9.4% ether in the original coal. The conversion of one soluble product into the next, which is accompanied by a reduction in molecular weight, is also accompanied by a decrease in ether oxygen concentration. It follows, then, that the ether removal reactions participate in the conversion between soluble products as well as in the production of total yield. It is also apparent that the production of oil involves the elimination of the hydroxyl oxygen.

The removal of hydroxyl oxygen that accompanies oil production parallels the removal of nitrogen atoms, as shown in Fig. III-23. For the products of coal treatment at 300°C for 60 min, the nitrogen is partitioned in such a way that the oil-free MTC contains 0.84% nitrogen, the asphaltene contains 0.87% nitrogen, and the oil contains only 0.10% nitrogen, all compared to 0.93% in the coal. Thus, as with the

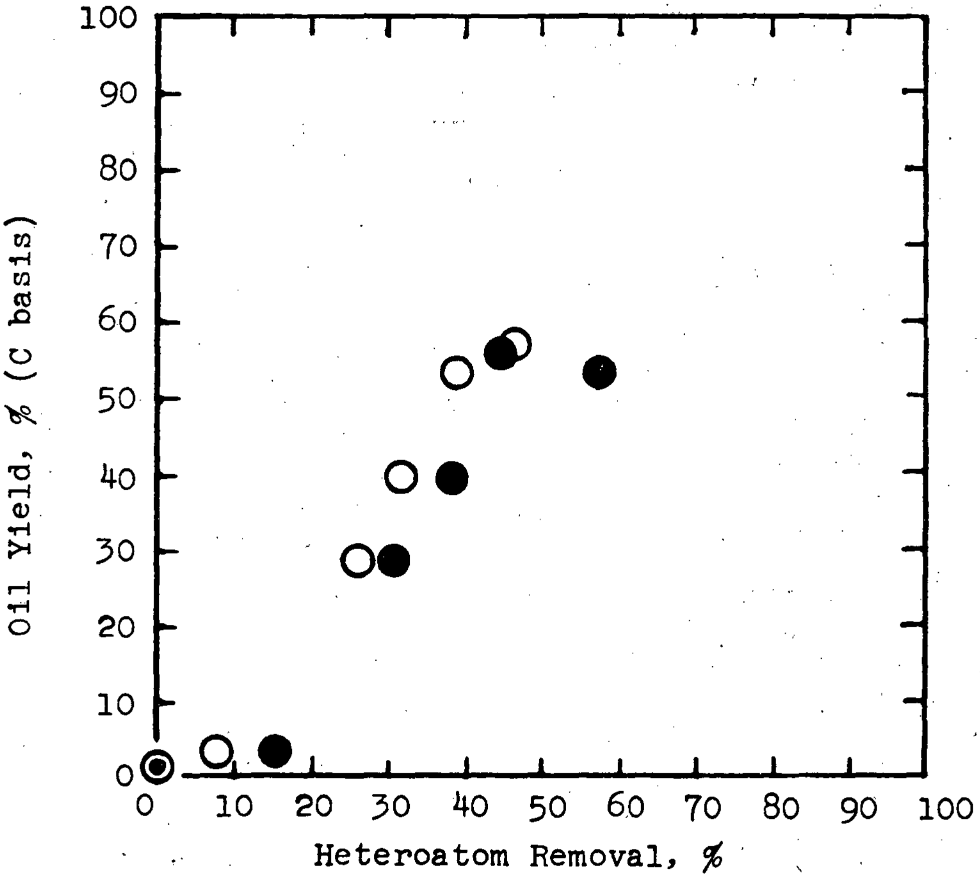

Figure III-23: Relationship between oil yield and the removal of heteroatom functionalities during treatment. Treatments of 50 g Wyodak coal at 300°C with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure. ○ - nitrogen, ● - hydroxyl oxygen.

hydroxyl oxygen, much of the nitrogen removal is associated with the high yield of an oil having a low nitrogen concentration.

The relationship between oil yield and the removal of nitrogen and hydroxyl oxygen from the coal can be interpreted in terms of the structure of asphaltene that was proposed by Sternberg and coworkers in 1975 (65). In their work, asphaltenes were found to consist of hydrogen bonded complexes of acidic and basic components, with the acidic components including functional groups such as phenolic-hydroxyl oxygen and pyrrolic nitrogen, and the basic components including functional groups such as ring or ether oxygen, and ring nitrogen such as pyridine. In moderately polar solvents, such as toluene, the asphaltenes are soluble because the acidic and basic components are separately solvated. In a non-polar solvent, such as cyclohexane, a large complex is formed, and the asphaltenes precipitate. In our work, the effectiveness of the zinc chloride catalyst at removing the acidic and basic functional groups in the asphaltene intermediate results in reduced hydrogen bonding and high conversions of asphaltenes to oils.

A mechanism of coal liquefaction that includes ether and aliphatic bond cleavage for total soluble yield, and includes hydroxyl removal as an additional mechanism in the production of asphaltenes and oils, was suggested by Szladow and Given in 1978 for conversion of bituminous coal by reaction with tetralin at pyrolytic temperatures (340 to 400°C) (66). This present research indicates that similar mechanisms may be applicable at lower temperatures for conversion of subbituminous coals by treatment with $ZnCl_2$ and tetralin.

As might be expected, the rate of heteroatom removal is affected by treatment temperature. The total oxygen removal after 60 min at 250^{o}C is 49%, compared to 80% at 300^{o}C. However, the yields are lower at 250^{o}C, so a better comparison, shown in Table III-9, is that of the 250^{o}C, 60 min treatment, and the 300^{o}C, 10 min treatment. It is seen that the lower temperature of treatment results in a reduction in the amount of heteroatom removal that accompanies a similar yield. This effect is largest with the ether and hydroxyl fractions. It may be that the lower ether removals are compensated for by other bond cleavage, such as aliphatic links, or that a certain amount of ether oxygen removal at higher temperatures is from locations that do not contribute to increased yield, such as furan structures.

Hydrogen Donation Effects

The oxygen functional group analyses provide a basis on which one can show that the amount of solvent incorporation that accompanies zinc chloride-catalyzed coal conversion is far less than might be expected. In the conversion mechanisms of $ZnCl_2$ catalysis that have been described in the model compound research of Mobley (44) and of Maienschein (46), an aromatic solvent molecule is alkylated by each of the two reactive fragments that are produced by ether bond cleavage. Although the conditions of treatment of the model compounds were quite different from those of the coal, in that the model compound experiments were usually performed without hydrogen-donor solvents, an estimate can be made of the amount of tetralin that would be incorporated into the coal if the tetralin was acting as a substrate for reactive fragment alkylation. For a 300^{o}C, 60 min treatment in which 85% of the ether

Table III-9: Effect of treatment temperature on the relationship between soluble product yield and heteroatom removal. Treatment of 50 g Wyodak coal with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

Treatment Conditions	250°C 60 min (Run 31)	300°C 10 min (Run 26)
Total Yield, % (C basis)	67.5	69.8
Total Oxygen Removal, %	49	61
Ether Oxygen Removal, %	43	59
Oil Yield, % (C basis)	31.4	28.5
Hydroxyl Oxygen Removal, %	22	31
Nitrogen Removal, %	25	26

oxygen is removed, approximately 50 g of tetralin would be incorporated. This level of incorporation is about ten times higher than that which is actually observed in treatments of coal with zinc chloride and tetralin.

The solvent incorporation results, together with the low conversions of coal achieved with zinc chloride and aromatics such as xylene by Shinn (64), show that the primary role of the tetralin, in zinc chloride catalyzed coal liquefaction with is not that of an alkylation substrate. The role of tetralin can be examined by recovery of the tetralin-molecular weight products that are lost during devolatilization, by study of the soluble oil products, and by examination, in more detail, of the results of treatments that were carried out without tetralin.

Three treatments were run at 300°C for different durations without tetralin present (Runs 27, 44, 38). The yields of soluble products from these experiments increase slowly with treatment duration, as shown in Fig. III-24. The total yield after 60 min (Run 38) is 43%, compared to 84% for treatment at 300°C for 60 min with tetralin (Run 47). The oil yield from Run 38 was less than one fifth the yield obtained in Run 47. But despite this low yield, the oxygen removals in the treatments without tetralin were almost as high as those with tetralin. In Run 38, 74% of the total oxygen was removed, compared to 80% for Run 47. Of the oxygen in Wyodak coal, the ether represents such a large fraction of the total that much of the oxygen removal, in Run 38, must have been from cleaved ether bonds. It is apparent that $ZnCl_2$ is effective at catalyzing the cleavage of ether bonds during the treatment of coal, with or without the presence of tetralin. The tetralin, then, apparently participates in the conversion process in a manner that allows the bond

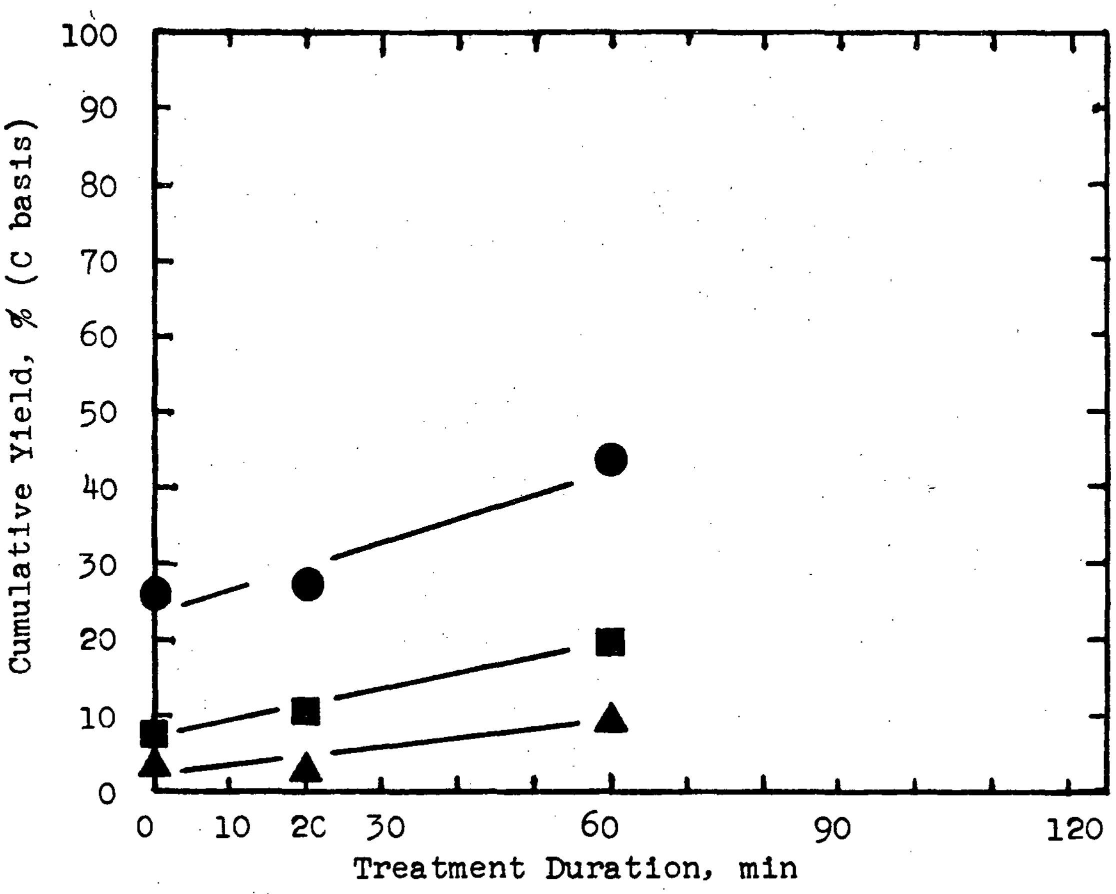

Figure III-24: Effect of treatment duration on the yields of soluble products. Treatments of 50 g Wyodak coal at 300°C with 273 g $ZnCl_2$, 27 g H_2O, and 3.5 MPa total pressure. ▲ - oil, ■ - oil + asphaltene, ● - total.

cleavage reactions to lead to molecular weight reduction and conversion to soluble products.

This can be explained as follows: The model compound work of Mobley (44) and of Maienschein (46) shows that ether bond cleavage results in two reactive products that, in the model compound studies (usually in the absence of hydrogen-donor solvent), alkylate aromatics that are present. When coal treatments are run in the absence of alkylation substrates, these products can alkylate each other, or other parts of the coal. This recombination reaction has been observed for pyrolytic coal liquefaction and results in a material that is more refractory than the initial uncleaved coal (5). In our work, the high yields of soluble products that are obtained indicate that the presence of tetralin prevents this recombination, and the relatively low solvent incorporation suggests that this prevention is accomplished with only little alkylation of the tetralin itself. In the absence of tetralin, then, the recombination reactions can lead to low product yields despite the effective bond cleavage by the $ZnCl_2$ catalyst.

The manner in which tetralin prevents the product recombination reaction can be studied by examination of the products of tetralin that are recovered from the treatments of coal with $ZnCl_2$ and tetralin. If the tetralin prevents the recombination by donating hydrogen to the reactive products, and thereby rendering them unreactive, then unusually high ratios of naphthalene to tetralin should be detected, reflecting this hydrogen donation. The ratio of recovered naphthalene to recovered tetralin for various treatment temperatures is shown in Fig. III-25, along with the equilibrium ratio that is expected. This

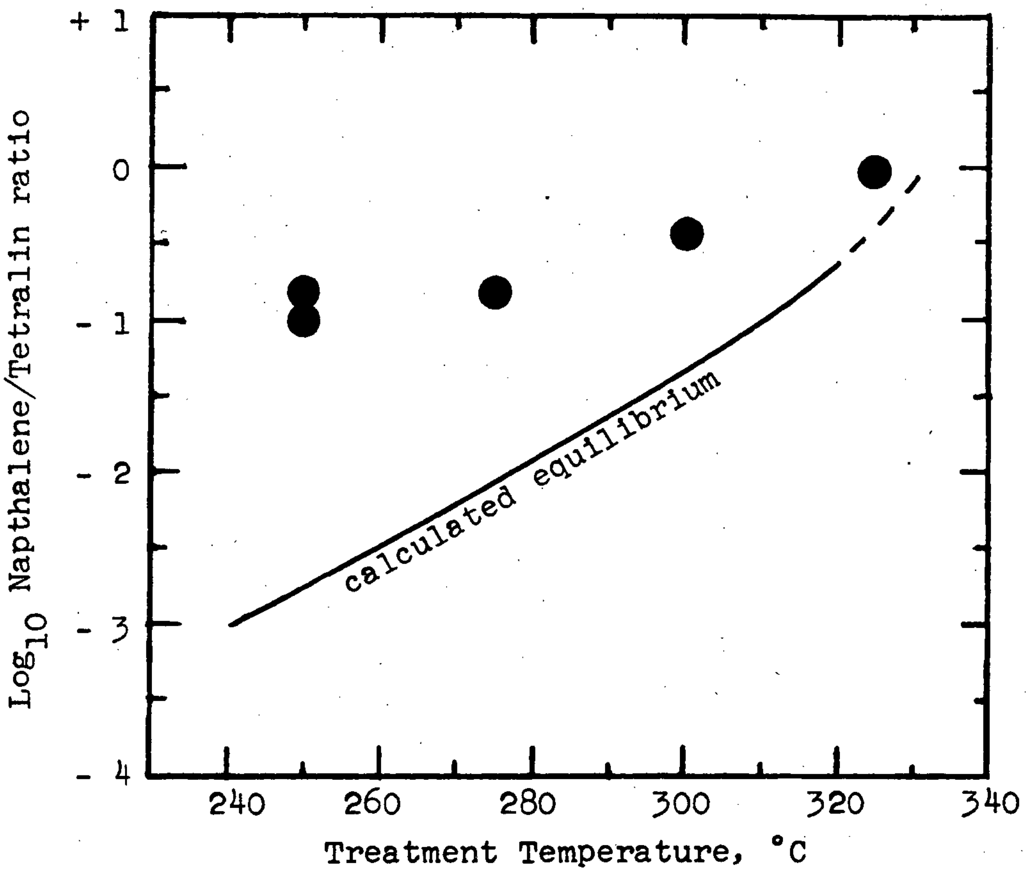

Figure III-25: Effect of treatment temperature on the ratio of recovered napthalene to recovered tetralin. Treatments of 50 g Wyodak coal for 60 min with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure (hydrogen plus vapor).

equilibrium increases with temperature rapidly because, as treatment temperature increases, the increased solvent vapor pressures displace hydrogen at constant total pressure, the resulting lower hydrogen pressures favoring naphthalene. The ratios of naphthalene to tetralin found for the treatments were higher than equilibrium for every case. Moreover, the ratio of naphthalene to tetralin increases from 0.1 at 250°C to nearly 1.0 at 325°C. There is a higher conversion of tetralin to naphthalene at the higher temperatures, at which the coal conversion levels are higher, and the amount of oxygen removal from the coal is higher.

The amount of hydrogen that is needed to completely saturate the oxygen and products of a cleaved ether bond is four hydrogen atoms per oxygen atom. If all of this hydrogen is provided by tetralin conversion to naphthalene, then one molecule of tetralin is required per ether oxygen atom removed. At a treatment temperature of 325°C, the approximate reactor hydrogen pressure is 0.5 MPa, so the rate of naphthalene hydrogenation to tetralin should be slow, and the detected ratio of naphthalene to tetralin may reflect the degree to which tetralin has donated hydrogen to the coal conversion reactions. For the 325°C treatment, assuming an 85% removal of ether oxygen, about half of the 50 g of tetralin would be converted to naphthalene for ether cleavage reactions. This level of conversion compares well with the 1:1 ratio of naphthalene to tetralin that was observed. In contrast to this, the low (0:1) ratio of naphthalene to tetralin that was observed for the 250°C treatment represents a net amount of tetralin conversion that can not account for the levels of ether oxygen removal that are observed for this treatment.

There are several implications of these results: There must be hydrogen donation from the tetralin in order for naphthalene to be produced in these above-equilibrium amounts. Although the naphthalene levels are much higher at higher temperatures, there is not necessarily that much more hydrogen donation at the higher temperatures, because the $ZnCl_2$ can catalyze a rehydrogenation of the naphthalene (45). It is possible that all of the hydrogen required for cleaved-product stabilization at lower temperatures is provided by the tetralin, and that the low naphthalene equilibrium ratio provides an adequate driving force for naphthalene rehydrogenation. If this is the case, then the high naphthalene ratio that is observed at higher treatment temperatures is a result of the low rehydrogenation driving force that results from the low pressure of hydrogen in the reactor.

The use of tetralin as a hydrogen donor is well known under pyrolytic conditions (53), but this work shows that in the presence of $ZnCl_2$, the hydrogen donation abilities of tetralin are extended to temperatures below pyrolysis. It is, therefore, possible that other hydrogen transfer reactions that have been identified for pyrolytic coal liquefaction also apply to liquefaction by zinc chloride-catalysis below pyrolysis temperatures. The range of possible reactions include direct transfer of hydrogen from the gas phase to the cleaved bonds; transfer from the gas phase to the solvent, coal, and product molecules; transfer of hydrogen from the solvent, coal, and product molecules to the cleaved bonds; and transfer of hydrogen between the solvent, coal, and product molecules. In pyrolytic coal liquefaction, these hydrogen transfer reactions combine to a net effect represented by a solvent that "shuttles" hydrogen from the gas phase and hydrogen rich portions of the coal to the cleaved bonds and hydrogen deficient portions of the coal (8).

If zinc chloride does catalyze the fuller range of hydrogen shuttling reactions, as well as the hydrogen donation reaction, then the level of hydrogenation of the treatment products should show the same effects of hydrogen pressure that have been observed for the ratio of naphthalene to tetralin. A comparison of the H_{ali}/H_{aro} ratio for the soluble oil product and a calculated H_{ali}/H_{aro} for the tetralin-naphthalene product mixture is shown in Fig. III-26. Although the soluble oils are more aliphatic, both products are affected in the same manner by treatment temperature. Both soluble oils and the tetralin/naphthalene mixture have a decreasing H_{ali}/H_{aro} ratio at the higher temperatures for which hydrogen pressure is lower, and the demand for hydrogen, from the high conversion to products, is higher. Thus, it appears that the broader range of hydrogen transfer reactions are catalyzed by the zinc chloride.

The chemical mechanism of $ZnCl_2$ catalyzed coal conversion with tetralin can be summarized as follows. The role of the tetralin is primarily that of a hydrogen donor and a hydrogen shuttler, providing hydrogen to the cleaved bonds from its own hydrogen rich structure, from hydrogen rich portions of the coal, and from the gas phase hydrogen. The $ZnCl_2$ performs two functions, that of catalyzing the cleavage of chemical bonds and that of catalyzing the hydrogen shuttling reactions.

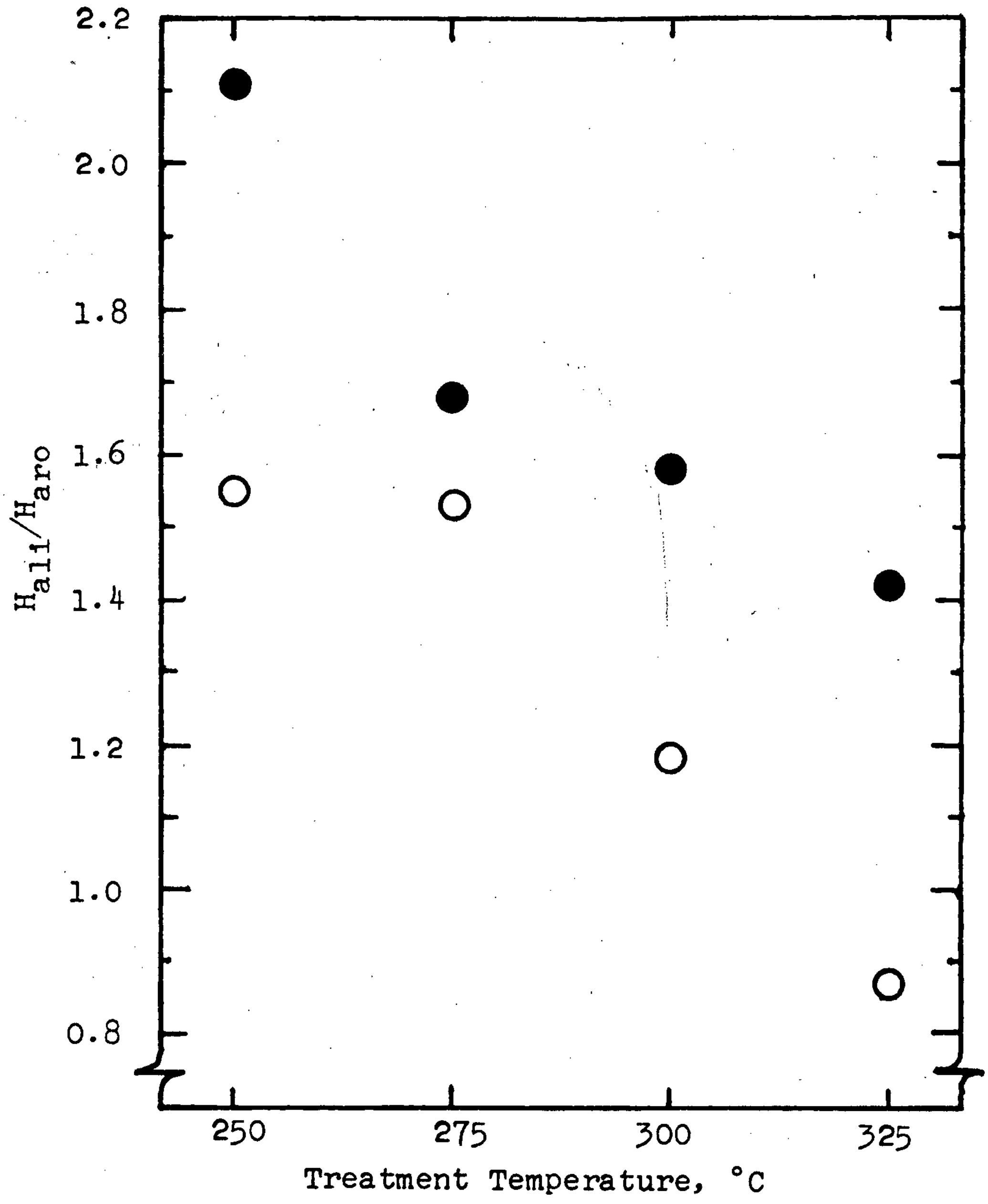

Figure III-26: Effect of treatment temperature on the H_{ali}/H_{aro} ratios of the oil product and the recovered tetralin and napthalene. Treatment of 50 g Wyodak coal for 60 min with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure. ● - oil product, ○ - tetralin/napthalene products (calculated).

In addition, it is likely that some of the low molecular weight oil product molecules may serve in the same shuttling manner as the tetralin.

IV. CONCLUSIONS

This investigation has shown that the conversion of subbituminous coal to high yields of soluble products, and especially to oils, can be achieved by treatment with zinc chloride in combination with tetralin at temperatures below the coal pyrolysis temperature. Treatment at 300°C for 1 hour results in yields (85% total; 50% oil) that are similar to those for commercially-developed, heterogeneously-catalyzed processes operating at 450°C and high pressures of hydrogen (e.g., the HCOAL process).

Soluble product characterizations by gel permeation chromatography indicate that the progression of coal conversion is accompanied by large reductions in the molecular weight of the product molecules, attributable to the cleavage of crosslinkings bonds in the coal. The reduction in oxygen contents that are observed during treatment, both overall and of the different oxygen functional groups in the products are strong evidence that this bond cleavage is accomplished, to a great extent, by the removal of ether linkages in the coal. Moreover, the ultimate production of the oil fraction is accompanied by the removal of acidic and basic functional groups, specifically phenolic-hydroxyl and ring-nitrogen, from the asphaltene intermediate.

Examination of the effects of tetralin presence during treatment, as well as of product aromatic character and naphthalene formation, demonstrate that the tetralin acts as a hydrogen donor and a hydrogen transfer agent. In this role, it serves to prevent recombination reactions of coal fragments by providing hydrogen to the catalytically cleaved bonds from its own hydrogen rich structure, as well as from the hydrogen atmosphere and the hydrogen rich portions of the coal. The zinc chloride serves to catalyze these hydrogen transfer reactions, as well as the cleavage of crosslinking bonds in the coal and products.

In view of the degree to which $ZnCl_2$ has been found to catalyze hydrogen transfer reactions at temperatures below pyrolysis, an important extension of this work would be an investigation into the degree to which a more hydrogen-rich product can be obtained using moderate (4 to 10 MPa) pressures of hydrogen during treatment. A consideration that will be important in terms of the potential process applications of zinc chloride-catalyzed coal liquefaction, is the extent to which the soluble oil product can be used as a substitute for the tetralin. Finally, the research described here has been carried out with high catalyst loadings (6:1 $ZnCl_2$/coal) in order to examine other reaction parameters; the economical application of this coal liquefaction technique will be dependent on the investigation of treatments with lower catalyst loading.

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Appendix A: Mass Balances for Coal Treatment

The mass balance between amount of initial reactants and final products is important in any process. In this work, the balance over the carbon content of the reactants and products is of interest, because it is on carbon content that the product yields are based.

The amount of initial carbon is well known from the measured amounts of coal (about 24.2 g carbon) and tetralin (about 45.5 g carbon) that are introduced into the reactor. The carbon content of the non-volatile MTC that is recovered from an experiment is always determined, although this differs from one experiment to the next. The other products that have been recovered in selected experiments are the gas that are swept out of the reactor by hydrogen flow during treatment, and the volatile organics that are recovered from the oil during solvent-removal operations. These latter products have not been included in yield or solvent incorporation calculations.

For one experiment at 300^{o}C for 1 hour (Run 47), both gas analysis and recovery of volatiles have been performed. The results for this experiment are typical of recoveries that have been obtained for other experiments. The amounts of recovered volatile products are shown in Table III-4, and the results of the gas analysis are shown in Table A-1. The major product product compounds recovered from the devolatilization were tetralin, naphthalene, and methylindan. In addition, an amount of material boiling higher than these components was recovered but not identified. The higher sensitivities of the procedures used in gas analysis result in a greater number of compounds being identified.

Table A-1: Recovery of products in the exiting reactor gas flow. Treatment of 50 g Wyodak coal at 300°C for 60 min (Run 47) with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

Compound	Avg. Conc.(1) (molar)	Amt. Recovered(2)
By Mass Spectrometry		
Carbon Monoxide	0.315 %	0.04 g
Carbon Dioxide	0.368 %	0.07 g
By GCMS; very crude concentrations		
Isobutane	1000 ppm	0.13 g
Isopentane 60	600 ppm	
Iso-C_6	200 ppm	
Methylcyclopentane	1000 ppm	
Benzene	600 ppm	
Dimethylcyclopentane	200 ppm	
Methylcyclohexane	200 ppm	
Toluene	150 ppm	
Ethylbenzene + Xylene	50 ppm	

(1) Average of three gas samples.

(2) Concentration multiplied by total gas flow of 10.8 L.

These compounds may be interesting from a qualitative point of view, but they represent a very small amount of carbon.

For Run 47, the carbon content of the reactants was 69.7 g. In this experiment, 25.2 g of carbon was recovered as non-volatile MTC, 26.4 g as volatiles, and 0.1 g as gas, for a total of 51.7 g. The amount of carbon recovered was 18 g less than the initial carbon. That the "lost" carbon was due mostly to incomplete volatiles recovery can be seen in a comparison of the recovery for the volatile products and that for the non-volatile. The roughly 25.2 g of non-volatile carbon recovered from the treatment compares well with the 24.2 g of (coal) carbon introduced. However, out of 50 g of tetralin introduced to the reactor, only 29 g of volatile products were recovered.

There are several places where this carbon may have been lost. These include: losses that occur during the transferring and preheating of the tetralin before treatment, the retention of volatiles in the cyclohexane-washed MTC (which is not devolatilized with recovery), the loss of water soluble organics into the $ZnCl_2$ phase or into the wash water, and the general loss of solids during filtration and handling of the MTC.

Appendix B: Nuclear Magnetic Resonance Spectra, Calculations, and Results

Proton nuclear magnetic resonance (NMR) has been used to provide information about the aromatic structure of the soluble products. For reasons explained in the body of this dissertation, only the spectra of the oil samples are suitable for this structural analysis. Typical oil spectra for treated and untreated coal are shown in Figures III-9 and III-10. For purpose of completeness, the spectra of asphaltene and preasphaltene fractions of coal treated at 250^{0}C for 1 hour, and the spectrum of a whole pyridine extract of untreated coal are presented in Figures B-1 through B-3.

The oil characterization has been accomplished by calculation of a series of parameters, based on the fractional amounts of protons absorbing in the various regions of the NMR spectra. The parameters are calculated twice; once for the oil spectrum as recorded (but corrected for pyridine-d_5 absorbance) and once for the spectrum as corrected to subtract the absorbance of the natural oil that would be extracted from untreated coal. The calculated parameters for sample structure are listed in tables at the end of this section. An understanding of the calculations, themselves, is best obtained by review of the assumptions involved for each parameter.

Parameter Correction for Beta -CH_3 Functionalities. For each spectrum, corrected or uncorrected for natural oil, the structural parameters are calculated for four different values of the number of beta -CH_3 groups per alpha carbon (N). For a value of N=0, the structural parameters are those for the case where average alpha carbons are 2^{0} gamma carbons.

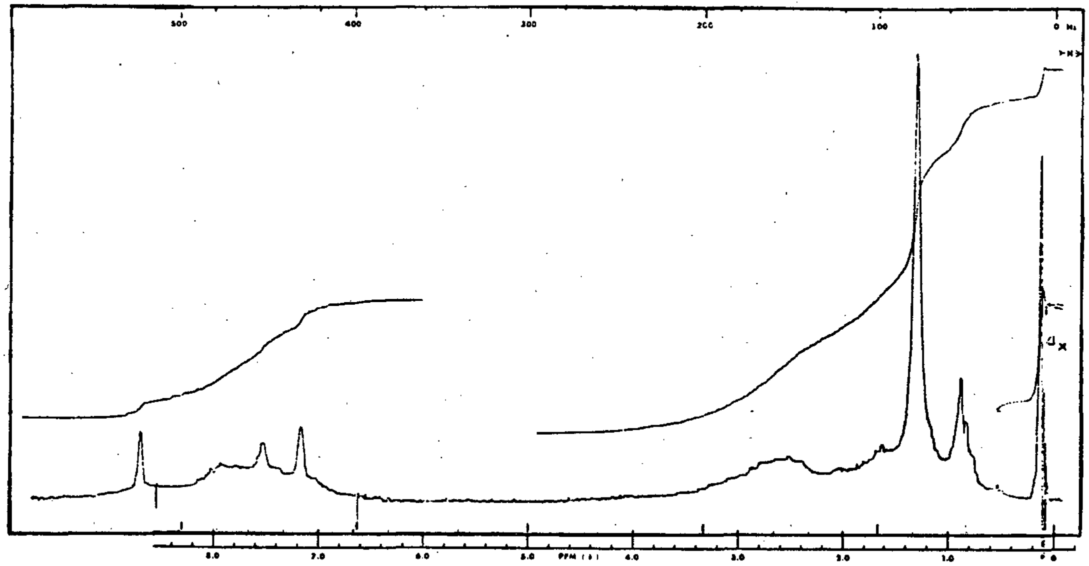

Figure B-1: Proton nuclear magnetic resonance spectrum of asphaltene product. Treatment of 50 g Wyodak coal for 1 h at 250°C with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

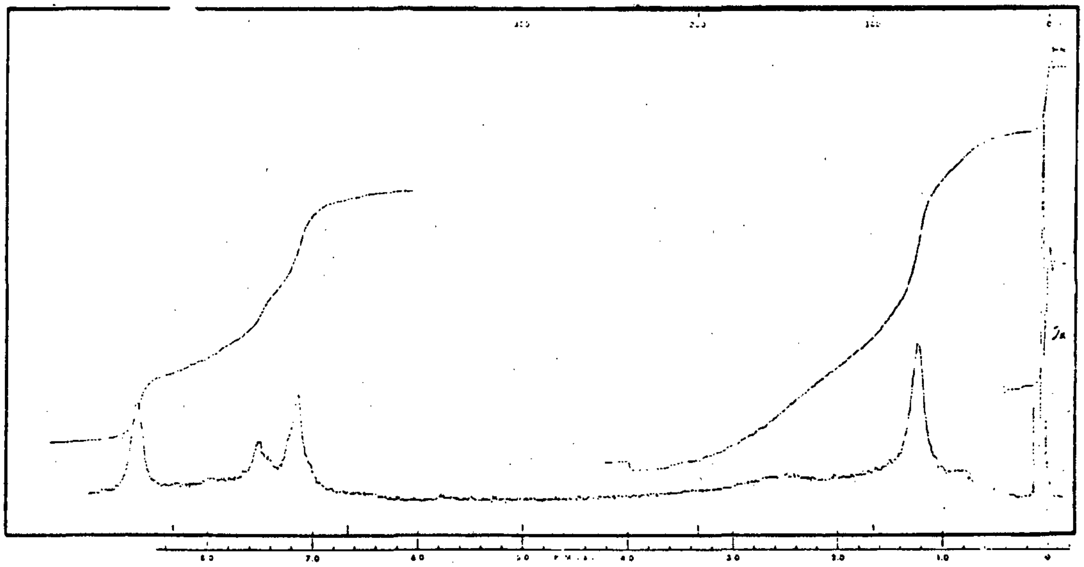

Figure B-2: Proton nuclear magnetic resonance spectrum of preasphaltene product. Treatment of 50 g Wyodak coal for 1 h at 250°C with 273 g $ZnCl_2$, 27 g H_2O, 50 g tetralin, and 3.5 MPa total pressure.

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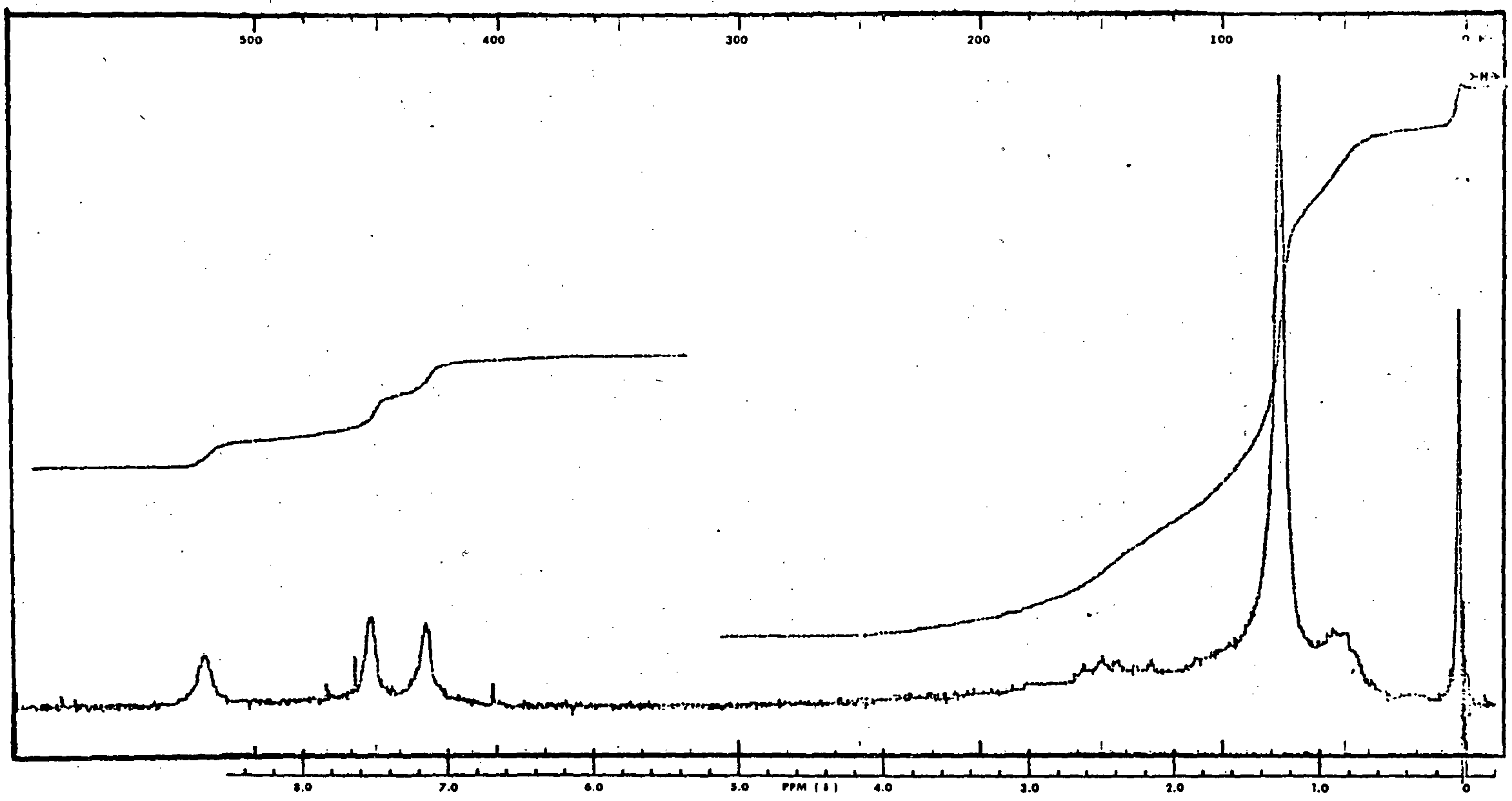

Figure B-3: Proton Nuclear Magnetic Resonance Spectrum of a Pyridine Extract of Wyodak Coal.

Increasing values of N reduce the number of protons per alpha carbon (by N, exactly) and reduce the calculated amount of del fraction protons that are on 2^{o} gamma carbons (this represents a loss of the long-chain $-CH_2-$ groups).

Pyridine-d_5 Correction. The pyridine-d_5 that is used as a solvent for the NMR analysis has an atomic purity of 99%. The remaining 1% protons absorb in the aromatic region of the spectrum. The integration of this region is corrected for pyridine-d_5 absorbance by ratio with the HMDS standard. For the oil samples, for which no filtration step was used and for which the HMDS and pyridine-d_5 were always combined in the same ratio, the absorbance ratio of pyridine-d_5 to HMDS, as determined by NMR analysis of a mixture of these compounds alone, is 1.72. The integration of the aromatic region is reduced by 1.72 times the HMDS integration, and then the integrations from all the proton regions (except the HMDS) are summed and normalized to a total proton concentration of 1.0. The normalized concentrations, referred to as "proton fractions", and designated as "H" suscripted by region, are used to calculate the remainder of the parameters.

Correction for Natural Oil. Parameter calculation, using both the normalized proton fractions and the molar H:C ratio of the samples, is performed twice, once with correction for natural oil. The correction is calculated by the assumption that each of the natural oil proton fractions are present in the same concentration in the MTC as they are in the untreated coal. For example, the aromatic region correction is:

$$\text{corrected } H_{aro} = \frac{(\text{old } H_{aro})(\text{oil yield})}{[C/H]_{oil}} - \frac{\begin{pmatrix}\text{natural}\\ \text{oil } H_{aro}\end{pmatrix}\begin{pmatrix}\text{natural}\\ \text{oil yield}\end{pmatrix}}{[C/H]_{\text{natural oil}}}$$

The other proton fractions are corrected in this manner, and then fractions are re-normalized. The elemental compositions and atomic ratios are also corrected, by a similar formula.

Aliphatic to Aromatic Proton Ratio. The ratio of aliphatic to aromatic protons, H_{ali}/H_{aro}, is simply the ratio of the proton fractions for these respective regions:

$$H_{ali}/H_{aro} = \frac{H_{alpha} + H_{beta} + H_{del} + H_{gamma}}{H_{aro}}$$

Carbon Aromaticity. The fraction of carbons that are aromatic, F_a, is calculated by use of a variation of the assumptions of Brown and Ladner (57). In this calculation, alpha, beta, and del protons are assumed to be attached to 1/2 carbons each, while gamma protons are attached to 1/3 carbon:

$$F_a = \frac{C/H - 1/2(H_{alpha} + H_{beta} + H_{del}) - H_{gamma}/3}{C/H}$$

The values of F_a and H_{ali}/H_{aro} are not affected by variation of N. The following parameters, however, are affected, and so each parameter is listed as a function of N.

H:C Ratio for the Hypothetical Unsubstituted Nucleus. The H:C ratio for the Hypothetical unsubstituted nucleus, $[H:C]_{nuclei}$, provides a measure of the degree of ring condensation of the aromatic nuclei.

It is calculated by summation of the aromatic protons and substituents and division by the aromatic carbons. The aromatic substituents included are alpha carbons and a phenolic hydroxyl concentration that is assumed to be constant at 0.0042 substituents per total protons (approximately 0.5% of total sample) and whose protons absorb in the aromatic region. The non-phenolic oxygen in the sample is assumed to be present as aromatic-ether oxygen (represented as O_{aro}, and calculated as a weight fraction of the NMR sample) that should be represented both as a nuclear carbon and as a hypothetical substituent location. Actually, the atomic C:O ratio is so high (~100) that these model details have practically no effect on parameter values. $[H:C]_{nuclei}$ is calculated as follows:

$$[H:C]_{nuclei}(N) = \frac{H_{alpha}/N + H_{aro} + O_{aro}/H}{(C/H)F_a + O_{aro}/H}$$

Fraction of Available Edge Atoms Occupied by Substituents. The fraction of available aromatic-nuclear edge atoms that are occupied by substituents, σ, is the sum of the substituents divided by the total available edge sites. The edge sites are equal to the hypothetical unsubstituted protons of the $[H:C]_{nuclei}$ calculation. The substituents are alpha carbons and hydroxyls:

$$\sigma(N) = \frac{H_{alpha}/(2-N) + 0.0042}{H_{alpha}/(2-N) + H_{aro} + O_{aro}/H}$$

Aliphatic Chain Length. The aliphatic chain length, ACL, is calculated with the assumption that all del protons that are not in beta $-CH_3$ groups are present as 2^o gamma groups (straight, $-CH_2-$ groups). It is further assumed that the straight chains that these groups comprise are initiated at an alpha carbon and terminated with a gamma $-CH_3$ group. Some assumptions are necessary to allow calculation of an aliphatic chain length. Although these assumptions may not be the best or the only assumptions possible, they do allow comparsions of the ACL values for oil products of different coal-treatment conditions. ACL is calculated as:

$$\mathrm{ACL(N)} = \frac{H_{\mathrm{del}} - 3N(H_{\mathrm{alpha}})/(2-N)}{(2/3)H_{\mathrm{gamma}}}$$

Naphthenic Chain Fraction. The naphthenic chain fraction, NCF, is the fraction of saturated side-ring structures per total number of protons. It is calculated with the assumption that each gamma $-CH_3$ group represents one alpha substituent, and that the remaining alpha substituents are in naphthenic side-rings on the aromatic nuclei. There will be one side ring per two alpha substituents:

$$\mathrm{NCF(N)} = \frac{H_{\mathrm{alpha}}/(2-N) - H_{\mathrm{gamma}}/3}{2}$$

Naphthenic Chain Length. The naphthenic chain length, NCL, is the calculated length of the naphthenic sub-rings identified in the previous section. It is calculated from the assumption that any carbon that is not aromatic, aliphatic-chain, or beta $-CH_3$, must be part of the naphthenic ring structure. This amount of carbons is divided by NCF:

$$\mathrm{NCL(N)} = \frac{(C/H)(1-F_a) - (H_{\mathrm{gamma}}/3)\mathrm{ACL(N)} - N(H_{\mathrm{alpha}})/(2-N)}{\mathrm{NCF(N)}}$$

Tables of NMR Parameters. The calculated structural parameters for the soluble oils obtained by treatment of Wyodak coal with $ZnCl_2$ and tetralin are presented in Tables B-1 through B-5. The NMR samples are identified by experimental run number; the conditions and details of each run may be found both in Appendix C (Table C-1) and in Table III-2. The structural parameters for spectra as uncorrected for natural oil are shown in Tables B-1 and B-2. Only parameters for a value of N=0 are reported for the uncorrected spectra. The structural parameters for the natural oil-corrected spectra are shown in Table B-3 for N-independent parameters, in Table B-4 for N=0, and in Table B-5 for values N=0.10 and 0.20. The data on these last two tables demonstrates the strong effect of beta $-CH_3$ groups on calculated aliphatic chain length, and the relative insensitivity of most of the other parameters.

Table B-1: NMR Structural Parameters for Oils from Treatments of Wyodak Coal with $ZnCl_2$.
For Run Number Identification, and Run Details, see Table C-1.
Parameters are not corrected for natural oil.

Run Number	H_{ali}/H_{aro}	F_a	H_{aro}	H_{alpha}	H_{beta}	H_{del}	H_{gamma}	C/H
1	18.92	0.205	0.050	0.102	0.163	0.556	0.128	0.571
23	1.91	0.675	0.344	0.245	0.180	0.166	0.066	0.976
24	2.13	0.660	0.319	0.274	0.172	0.182	0.052	0.975
25	2.15	0.646	0.318	0.261	0.177	0.186	0.058	0.936
26	2.22	0.634	0.310	0.267	0.185	0.173	0.065	0.913
27	24.74	0.226	0.039	0.128	0.135	0.596	0.102	0.599
28	1.89	0.686	0.345	0.272	0.151	0.175	0.056	1.014
30	2.78	0.612	0.264	0.264	0.231	0.176	0.064	0.922
31	2.95	0.594	0.253	0.282	0.236	0.165	0.063	0.893
34	2.18	0.644	0.314	0.250	0.189	0.191	0.056	0.938
35	1.96	0.682	0.337	0.313	0.215	0.090	0.045	1.018
36	1.91	0.679	0.344	0.299	0.207	0.095	0.056	0.994
38	5.87	0.453	0.146	0.183	0.117	0.453	0.101	0.750
39	2.17	0.633	0.315	0.280	0.199	0.168	0.038	0.915
42	2.01	0.654	0.333	0.271	0.175	0.165	0.056	0.938
45	2.54	0.611	0.283	0.254	0.212	0.190	0.061	0.897
46	1.68	0.700	0.373	0.257	0.130	0.183	0.058	1.012
47	2.02	0.670	0.331	0.283	0.164	0.173	0.048	0.988

Table B-2: NMR structural parameters for oils, not corrected for natural Oil, from treatment of Wyodak coal with $ZnCl_2$. Values are for N=0. For run number identification, and run details, see Table C-1.

Run Number	NCF	ACL	NCL	σ	$[H:C]_{nuclii}$
1	0.004	8.49	21.07	0.413	0.896
23	0.050	5.79	3.79	0.264	0.714
24	0.060	7.21	3.44	0.301	0.715
25	0.056	6,79	3.59	0.296	0.745
26	0.056	6.01	3.66	0.306	0.768
27	0.015	10.75	6.53	0.513	0.804
28	0.059	6.66	3.29	0.287	0.695
30	0.055	6.11	4.08	0.339	0.706
31	0.060	5.94	3.97	0.365	0.745
34	0.053	7.15	3.78	0.289	0.730
35	0.071	5.00	3.52	0.323	0.713
36	0.065	4.54	3.58	0.312	0.731
38	0.029	8.72	4.02	0.381	0.711
39	0.064	8.67	3.56	0.313	0.788
42	0.058	6.42	3.50	0.295	0.765
45	0.053	6.66	3.99	0.313	0.751
46	0.055	6.73	3.19	0.262	0.710
47	0.063	7.34	3.31	0.302	0.718

Table B-3: NMR structural parameters for oils, corrected for natural oil, from treatments of Wyodak coal with $ZnCl_2$
For run number identification, and run details, see Table C-1

Run Number	H_{ali}/H_{aro}	F_a	H_{aro}	H_{alpha}	H_{beta}	H_{del}	H_{gamma}	C/H
23	1.53	0.718	0.396	0.270	0.183	0.096	0.054	1.039
24	1.79	0.694	0.358	0.298	0.174	0.128	0.041	1.027
25	1.68	0.694	0.373	0.294	0.180	0.109	0.044	1.002
26	1.58	0.702	0.388	0.316	0.192	0.059	0.046	1.003
27	Natural oil yield exceeds experimental oil yield; no further listing for this run.							
28	1.55	0.724	0.392	0.299	0.148	0.115	0.045	1.076
30	2.00	0.680	0.333	0.316	0.252	0.543	0.044	1.019
31	2.28	0.648	0.305	0.328	0.256	0.065	0.046	0.965
34	1.72	0.692	0.368	0.280	0.194	0.117	0.041	1.004
35(1)	1.96	0.682	0.337	0.313	0.215	0.090	0.045	1.018
36(1)	1.91	0.679	0.344	0.299	0.207	0.095	0.056	0.994
38	2.56	0.638	0.280	0.298	0.052	0.307	0.062	0.965
39	1.72	0.680	0.368	0.315	0.206	0.091	0.020	0.976
42	1.62	0.696	0.381	0.300	0.177	0.098	0.044	0.994
45	1.94	0.667	0.340	0.292	0.224	0.099	0.044	0.968
46	1.42	0.731	0.413	0.276	0.125	0.136	0.049	1.060
47	1.66	0.708	0.376	0.312	0.164	0.111	0.036	1.047

(1) Oil product of Recycle Reaction; listed without correction for natural oil.

Table B-4: NMR structural parameters for oils, corrected for natural oil, from treatment of Wyodak coal with $ZnCl_2$.
For run number identification, and run details, see Table C-1.

Parameter values on this table are for N=0.

Run Number	NCF	ACL	NCL	σ	$[H:C]_{nuclii}$
23	0.058	4.65	3.56	0.258	0.715
24	0.068	6.64	3.28	0.297	0.716
25	0.066	5.76	3.36	0.289	0.748
26	0.071	3.93	3.34	0.297	0.775
28	0.067	5.83	3.11	0.281	0.696
30	0.072	3.86	3.76	0.331	0.709
31	0.074	4.12	3.72	0.359	0.750
34	0.063	6.30	3.54	0.282	0.732
35(1)	0.071	5.00	3.52	0.323	0.713
36(1)	0.065	4.54	3.58	0.312	0.731
38	0.064	9.38	2.41	0.357	0.698
39	0.075	8.91	3.37	0.307	0.793
42	0.068	5.38	3.31	0.389	0.769
45	0.066	5.36	3.71	0.306	0.754
46	0.061	6.15	3.03	0.257	0.712
47	0.072	6.68	3.14	0.293	0.720

(1) Oil Product of Recycle Reaction; <u>not</u> corrected for natural oil.

Table B-5: NMR structural parameters for oils, corrected for natural oil, from treatment of Wyodak coal with $ZnCl_2$. For run number identification, and run details, see Table C-1.

Run Number	NCF	ACL	NCL	σ	$[H:C]_{nuclii}$
Parameters calculated for N = 0.10					
1(1)	0.006	8.30	16.49	0.424	0.914
23	0.062	3.48	3.47	0.267	0.725
24	0.072	4.94	3.21	0.307	0.727
25	0.070	4.16	3.28	0.300	0.759
26	0.075	2.29	3.27	0.307	0.787
28	0.071	4.26	3.04	0.292	0.707
30	0.076	2.15	3.66	0.342	0.721
31	0.079	2.43	3.62	0.370	0.764
34	0.067	4.68	3.45	0.292	0.743
35(1)	0.075	3.35	3.43	0.334	0.725
36(1)	0.069	3.27	3.49	0.322	0.742
38	0.068	8.25	2.38	0.368	0.710
39	0.080	5.12	3.30	0.318	0.806
42	0.072	3.75	3.24	0.306	0.780
45	0.069	3.80	3.62	0.317	0.766
46	0.065	4.82	2.97	0.267	0.721
47	0.076	4.61	3.08	0.308	0.731
Parameters Calculated for N = 0.20					
1(1)	0.007	8.09	13.44	0.436	0.934
23	0.066	2.17	3.39	0.278	0.735
24	0.076	3.04	3.14	0.318	0.739
25	0.074	2.39	3.21	0.311	0.771
26	0.080	0.47	3.20	0.319	0.800
28	0.075	2.52	2.98	0.303	0.718
30	0.081	0.25	3.56	0.354	0.734
31	0.083	0.55	3.53	0.383	0.779
34	0.071	2.88	3.37	0.303	0.755
35(1)	0.079	1.52	3.35	0.345	0.736
36(1)	0.074	1.86	3.40	0.334	0.755
38	0.072	6.99	2.36	0.380	0.724
39	0.084	0.91	3.22	0.330	0.820
42	0.076	1.95	3.17	0.311	0.793
45	0.074	2.07	3.53	0.328	0.779
46	0.069	3.34	2.91	0.277	0.732
47	0.081	2.31	3.02	0.320	0.744

(1) not corrected for natural oil; these parameters are for natural oil, or for oil products of recycle reactions.

Appendix C: Detailed Experimental Results

This appendix contains several tables with the specific conditions, treatment details, carbon balances, and elemental analyses for the experiments that were carried out as a part of this research. This data is divided into tables as follows: Table C-1 includes the temperatures and durations of treatments, as well as the amounts of reactants used and the amounts of wash oil and post-wash MTC that were recovered, and the level of solvent incorporation into the products. Table C-2 includes the elemental analyses of the wash oil and PWMTC, as well as the weights of MTC and extracts from the Soxhlet product separation. Table C-3 includes the elemental analyses of the soxhlet extracts and residue. Table C-4 includes the elemental analyses for MTC samples that were washed with HCl in preparation for oxygen functional groups analysis.

Table C-1: Treatment conditions and material balance for experiments.

Run	Treatment		Tetralin Addition Temp.	Weights of Reactants, g				Products, g		Solvent[1] Incorp. % of MTC
	Temp. °C	Duration min		$ZnCl_2$	H_2O	Tetralin	Coal	Wash Oil	PWMTC	
1	Run number designation for untreated coal.									
19	250	60	250	Reaction termination by filtration; used only for gas analysis.						
22	275	60	275	Experimental problems; used only for MTC devolatilization-recovery.						
23	300	60	290	273	27	50	49.734 Wyodak	10.322	25.868	5.9
24	300	120	290	273	27	50	49.994 Wyodak	13.691	22.442	8.9
25	300	30	290	273	27	50	50.187 Wyodak	8.177	30.015	9.2
26	300	10	285	273	27	50	49.942 Wyodak	6.129	31.27	9.0
27	300	0	-	273	27	0	50.010 Wyodak	0.766	33.343	-10.1
28	300	60	245	273	27	50	50.705 Wyodak	16.293	23.385	18.7
30	250	30	235	273	27	50	50.276 Wyodak	4.573	36.541	17.2
31	250	60	240	273	27	50	50.143 Wyodak	6.816	34.114	5.4
34(2)	300	30	288	600	60	110	110.031 Wyodak	20.523	56.424	3.3
35	300	90	300	245	35	45	34.977 Dry Residual	6.490	28.284	12.6
36	300	60	-	273	27	50	4.917 Asphaltene	7.363(3)		33.7
38	300	60	-	273	27	0	50.402 Wyodak	1.656	29.111	-21.2
39	275	60	270	273	27	50	50.144 Wyodak	8.713	28.718	11.0
40	250	60	245	273	27	50	50.359 Rosebud	6.450	38.123	17.6
41	250	60	245	273	32	50	44.773 Monarch	5.864	34.608	22.8
42	275	60	225	273	27	50	49.904 Wyodak	12.030	26.221	11.3
43	300	60	285	273	32	50	45.309 Rosebud	8.439	27.703	10.1
44	300	20	-	273	27	0	50.359 Wyodak	0.186	30.968	-18.3
45	250	60	200	273	27	50	50.173 Wyodak	8.301	32.184	16.3
46	325	60	275	273	27	50	50.125 Wyodak	19.762	18.776	16.0
47	300	60	295	273	27	50	50.402 Wyodak	13.564	22.215	4.0

(1) Solvent incorporation is calculated on a carbon basis.

(2) This recycle-preparation experiment was performed in two batches.

(3) Total product of asphaltene treatment, product separation is listed as Soxhlet extraction on Table C-2 + C-3.

Table C-2: Elemental analyses of PWMTC and wash oil, and soxhlet extraction sample weights

	MTC Analysis						Wash Oil Analysis				Soxhlet Sample Weights				
Run	C	H	N	Cl	Zn	Ash	C	H	N	Ash	MTC	Oil	Asph.	P.A.	Res.
1	62.5	5.1	0.93	-	-	13.6					6.468	0.050	0.245	0.748	5.912
23a(1)	65.03	5.21	0.92	3.44	12.1	19.2	90.15	7.70	0.05	-	4.604	0.793	1.115	1.502	1.403
23b(1)	61.43	4.33	0.64	2.83	3.63	25.1					4.685	0.270	0.357	1.287	2.318
24	61.02	4.64	0.75	2.33	12.3	24.8	90.11	7.70	-	-	4.993	0.515	0.911	1.652	2.082
25	63.77	4.73	0.78	2.45	6.72	20.7	90.32	8.04	0.11	-	3.038	0.532	0.678	1.841	1.982
26	66.48	4.86	0.82	1.07	3.96	18.2	90.44	8.25	0.09	-	5.122	0.351	0.658	1.703	2.621
27	63.48	4.41	0.98	0.59	6.59	16.6	82.26	11.45	0.03	-	5.523	0.017	0.197	0.983	4.778
28	64.54	4.62	0.88	1.06	12.1	19.5	91.04	7.48	0.07	0.1	5.239	0.267	1.226	1.565	2.444
30	68.39	5.34	0.75	0.80	3.11	14.9	90.46	8.18	0.04	0.0	4.899	0.557	0.487	1.480	2.599
31	67.09	5.22	0.80	1.08	3.35	15.6	90.46	8.44	0.07	0.3	5.460	0.519	0.510	1.840	2.887
34	63.95	4.63	0.80	1.77	3.86	19.9	90.31	8.02	0.11	0.0	55.492	3.668	5.771	45.039	
35	59.40	4.37	0.77	2.35	4.78	27.4	91.41	7.48	0.13	0.0	5.212	0.207	0.761	1.769	2.653
36(2)	85.69	6.26	0.64			0.0					7.363	5.352	1.380	0.631	
38	63.59	4.48	0.81	1.94		21.6	87.15	9.68	0.26	-	6.708	0.102	0.545	1.823	4.662
39	66.77	5.87	0.87	1.47		17.9	90.40	8.23	0.12	-	5.655	0.609	0.656	1.964	2.526
40	72.44	4.93	0.93	2.25		9.5	91.63	8.04	0.07	-	6.111	0.158	0.415	1.821	4.094
41	76.30	5.08	1.35	1.37		7.2	91.60	7.96	0.06	-	5.761	0.188	0.450	1.752	3.716
42	61.46	4.91	0.83	1.57		19.7	90.53	8.04	0.11	-	5.983	0.395	0.879	2.029	2.965
43	71.75	4.45	0.86	2.66		12.8	92.10	7.60	0.13	-	6.710	0.315	1.192	2.569	3.061
44	65.48	4.50	0.81	0.58		18.8	85.15	9.96	0.24	-	6.573	0.099	0.413	1.041	5.416
45	66.22	5.06	0.84	1.29		15.9	89.78	8.34	0.06	-	6.899	0.444	0.724	2.559	3.497
46	56.57	4.06	0.88	3.86		27.5	91.21	7.51	0.17	-	6.544	0.297	1.272	1.808	3.427
47	58.37	4.39	0.81	1.82		25.9	90.25	7.61	0.48	-	6.204	0.238	1.121	2.048	3.057

(1) For Run 23, separate extractions were performed on the MTC from the quench tank, and that remaining in the reactor. Quench Tank MTC (23a) amounted to 10.375 g, while Reactor-MTC (23b) amounted to 15.494 g. Soxhlet extract analysis was performed only for the quench tank MTC extraction samples, but was applied to both sets of extraction samples (extract analyses are listed in Table C-3).

(2) Run 36 is the treatment of Asphaltene; the elemental analysis listed for MTC is actually that of the untreated asphaltene. Soxhlet sample weights are actually the total product weight distribution.

Table C-3: Elemental analyses of the soxhlet extract samples.

Run	Soxhlet Oil			Asphaltene			Preasphaltene			Residue		
	C	H	N	C	H	N	C	H	N	C	H	N
1				78.16	10.79	0.07	73.78	6.70	1.82	61.63	4.66	2.41
23(1)	87.61	7.01	0.45	85.72	6.96	0.82	73.43	5.60	3.28	28.32	2.70	1.70
24	90.61	7.16	0.21	86.99	6.78	0.62	65.55	4.85	3.39	33.88	2.72	0.95
25	90.61	7.55	0.22	85.68	7.06	0.35	73.49	5.15	3.28	41.97	3.11	1.29
26	91.00	7.77	0.08	86.13	6.89	0.50	76.32	5.44	2.47	48.99	3.37	1.62
27	assume same as wash oil			78.85	7.65	0.53	72.9	5.61	2.39	62.23	3.98	2.33
28	90.33	6.79	0.55	87.17	6.48	0.74	78.58	5.34	2.72	38.09	2.95	0.63
30	91.29	7.98	0.04	81.54	7.34	0.48	74.16	5.61	2.34	56.57	3.83	1.99
31	90.96	7.93	0.05	84.73	7.77	0.34	74.16	5.72	2.58	53.45	3.70	1.89
34	90.56	7.32	0.16	85.43	6.60	0.58	combined with residue			56.78	4.06	0.91
35	91.21	6.95	0.18	86.87	6.23	0.79	74.81	5.02	3.26	37.56	2.76	1.00
36(2)	91.23	7.65	0.59	78.96	6.06	0.63	combined with residue			44.88	3.52	0.60
38	assume same as wash oil			86.10	6.80	0.52	72.15	5.15	3.50	58.46	3.65	1.42
39	91.18	7.79	0.17	85.73	6.79	0.58	75.22	5.58	2.71	42.05	3.37	1.48
40	assume same as wash oil			86.35	6.72	0.34	77.01	5.33	2.75	68.26	4.04	2.10
41	assume same as wash oil			87.31	6.75	0.41	73.81	5.22	2.99	71.44	4.18	2.35
42	90.58	7.53	0.14	86.12	6.68	0.53	74.12	5.46	3.27	48.50	3.43	1.44
43	91.58	7.09	0.14	88.19	6.33	0.44	72.65	4.93	3.91	63.68	3.76	1.43
44	86.87	9.73	0.20	82.86	7.68	0.50	75.16	5.52	2.42	60.62	3.75	1.83
45	90.92	7.79	0.09	84.28	7.04	0.36	73.78	5.61	2.58	54.53	3.85	1.76
46	90.83	6.80	0.34	87.96	6.21	0.75	75.62	4.83	3.21	36.36	2.57	0.85
47	88.89	6.80	0.32	85.87	6.48	0.87	74.89	5.27	3.48	40.90	3.10	1.05

(1) Analysis of extracts from Soxhlet extraction of MTC recovered from quench tank

(2) Analyses of total products from asphaltene experiment, as described in chapter II.

Table C-4: Elemental analyses of acid-washed PWMTC samples used for oxygen functional group analysis.

Run	Elemental Analysis (Dry basis) C	H	N	Cl	Ash
24	66.42	4.85	0.74	2.05	20.0
25	69.48	5.04	0.81	1.95	15.9
26	69.08	4.98	0.87	1.52	14.2
27	67.79	4.49	0.94	0.12	12.6
28	68.03	4.75	0.93	1.42	18.8
30	69.91	5.42	0.84	0.91	12.5
31	69.54	5.23	0.86	0.74	13.4
34(1)	63.05	4.25	1.02	0.80	20.2
35	61.29	4.41	0.86	2.32	24.6

(1) Elemental and oxygen functional group analysis was carried out on sample of "residual", the combined preasphaltene plus residue.

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