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COAL CONVERSION CATALYSIS USING ZINC CHLORIDE IN ORGANIC MEDIA

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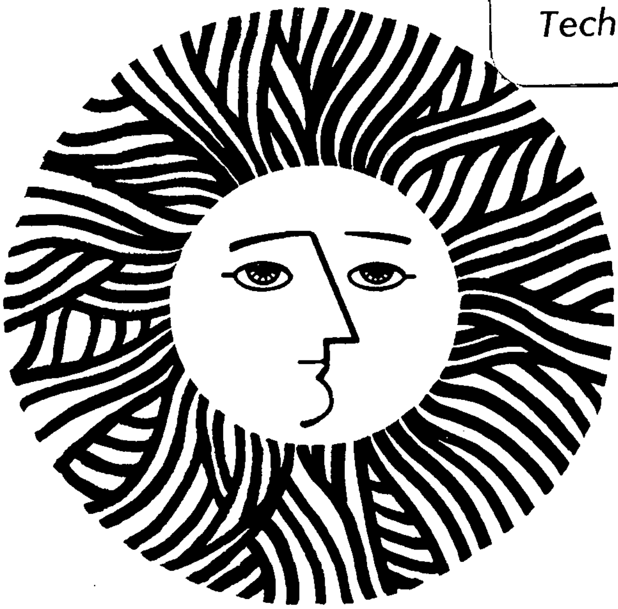
John H. Shinn and Theodore Vermeulen
(Ph.D. thesis)

September 1979



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COAL CONVERSION CATALYSIS USING ZINC CHLORIDE IN ORGANIC MEDIA

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ABSTRACT

The conversion of coal to soluble materials and liquids requires cleavage of chemical bonds. Because these bonds are inaccessible to contacting with conventional solid catalysts, current coal-processing technology uses high temperatures to initiate bond cleavage, with high hydrogen pressures and hydrogen-doner solvents in high concentration to "cap" the cleaved bonds. Undesirable side reactions of two types - repolymerization and fragmentation - accompany the conversion, wasting both coal and hydrogen.

This study examines the use of liquid-catalyst systems to penetrate the coal and carry out the cleavage reactions at temperatures well below where thermal cleavage occurs. In one hour runs at 250°C, solutions of $ZnCl_2$ in water proved quite ineffective at converting coal to pyridine-soluble components, giving only 25% solubility from coal originally 12% soluble. $ZnCl_2$-methanol solutions were considerably more effective yielding a product with 70% pyridine solubility. About 0.2 gm of methanol per gram of treated coal are chemically incorporated in the product during such treatment.

Numerous inorganic and organic additives were tested for their effects on solubilization activity in the $ZnCl_2$-water and $ZnCl_2$-methanol systems. Of the inorganic additives screened, only Zn metal gave positive results, improving the pyridine solubility of $ZnCl_2$-water treated coal by roughly 10%. Extractive solvents (n-decane, percloroethane, o-dichlorobenzene, cyclohexanol, p-xylene) tended to reduce conversion. Reactive solvents (tetralin, indoline, anthracene oil) increased both conversion and solvent incorporation.

In a detailed study of the $ZnCl_2$-methanol system, higher hydrogen pressures have been found to promote solubilization and reduce methanol incorporation. Increasing the temperature to $275^{\circ}C$ leads to total conversion to pyridine-soluble materials in roughly 30 minutes at 800 psig hydrogen pressure. Increasing amounts of methanol lead to a maximum conversion at a methanol/$ZnCl_2$ mole ratio of about 0.75 to 1.

Based on these results, a mechanism for catalytic solubilization is proposed. This involves penetration of the catalyst into the coal structure, activation of the crosslinks in the coal polymer by the catalyst, capping of cleaved bond fragments by hydrogen or solvents, and solvation of products so as to leave the unreacted coal accessible for further conversion. The action of the methanol appears to be multifunctional; it improves contacting, serves as a capping agent, facilitates product removal, and perhaps also promotes the catalyst activity.

A decrease in oxygen content of the coal accompanies the solubilization, suggesting that ether bonds are the important linkages for which cleavage leads to solubilization.

ACKNOWLEDGMENT

In a way, this thesis deserves to have a multitude of names as co-authors, for without the support of a host of others, I doubt that the job would ever have been done; certainly, it would have taken a lot longer. And so, I hope to at least register a meager form of thanks by mentioning these special people with these few words.

First, I would like to thank my friends for their support throughout this vigil. Roy and Gail Greenwald, Jim Wrathall, Jim Vislocky, David Bernstein, and my very special friend, Jean Owre, really helped me a great deal by hearing out my grumps and groans when things were bad, dealing with my obnoxious gloating when things went well, and in general helping me to keep my sanity. Thanks for those excursions to the backcountry which really helped to take the pressure off when the going got tough. Jean deserves a medal of honor for her patience with me and the many lonely hours she spent waiting for me to come home from the lab. I really needed all your support, Jean! Thank you!

Next, I would like to thank various members of the Coal Group for many stimulating and fruitful discussions which certainly helped me to formulate many of the ideas which went into this work. My talks with Newell Taylor, Dave Mobley, Frank Hershkowitz, and Tibor Derenscenyi were particularly fruitful. Manu Seth, Ron Holten, Jim Wrathall, Sadie Salim, Jon Maienschein, George Zieminski, Chris Onu, Peter Joyce, and Joe McLean also contributed.

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I would never have made it to Berkeley if it were not for the support of my family, especially my parents. My thanks to Professors Joseph Biesenberger, George Delancey, and Costos Gogos of Stevens Institute of Technology for convincing me to apply to graduate school and for all they taught me as an undergraduate. And to Bill Barnes, whereever you are, thank you for taking that 10-year-old kid and teaching him about chemistry and nature and instilling in him a love of science; you were the one who really started me on this path.

And finally I come to the person who deserves the most credit for this work reaching its completion: Dr. Vermeulen. My discussions with you were an immense stimulation, and I often found myself running out of your office to the lab, eager to try out some of our new ideas. Thank you for making this greenhorn graduate student feel like a respected colleague; you really gave me the chance to develop my potential to its fullest. I hope that I will be able to treat my subordinates as well as you treated me. It was a pleasure and a privilege to be able to work with you.

Last but not least, thanks to the U.S. Department of Energy for providing the funding for this work.

To the hope that more young people will receive the opportunity to use their talents to the fullest extent, and to all those who helped me use mine.

CHAPTER 1

INTRODUCTION

The Need for Coal Conversion

Rapidly dwindling supplies of petroleum and the need for independence from foreign energy sources have necessitated the investigation of alternate sources for the production of electric energy, petrochemical feedstocks, and liquid fuels. Alternatives to petroleum energy include nuclear, solar, geothermal, and coal. While perhaps nuclear energy through fission is technologically the most feasible at present, it suffers from (1) environmental risks through waste disposal, thermal pollution effects, and possible escape of radioactive materials, and (2) the threat of sabotage or terrorist activity. Fusion, geothermal, and solar power generation are not currently utilizable as major energy sources, due either to high cost of power generation (solar) or to major technological problems (fusion, geothermal). With the exception of coal, alternatives to petroleum do not offer a means of supplying liquid fuels and petrochemicals in the next 20 years. Thus, this country's energy independence, in terms of relatively continuous supplies of liquid fuels and petrochemical feedstocks seems to depend largely on the utilization of coal. The U.S. has abundant proven reserves of coal, and further reserves estimated to last several hundred years (compared to tens of years for petroleum supplies). (1). A synthetic crude oil produced from coal should be amenable to upgrading and subsequent conventional processing to products currently produced from petroleum. Generating such synthetic crude oil from coal would therefore be desirable.

Coal development is not without its difficulties. The first is mining of the coal which may involve significant environmental impact. Also, coal contains more nitrogen, sulfur, and trace metals than typical petroleum feedstocks. These may poison refining catalysts, and make the coal undesirable for combustion during which environmentally harmful gases (NO_x and SO_x) form. The inorganic material in coal must also be removed during its utilization. Finally, the organic material is deficient in hydrogen relative to oil or gasoline (see Figure 1-1), and is a solid which must be "depolymerized" to yield liquids. The problem of converting coal to a more usable form, therefore, involves reducing its molecular weight, removing heteroatoms and ash, and adding sufficient hydrogen.

A number of processes have been devised to accomplish this conversion of coal. Those developed beyond bench scale are shown in Table 1-1. All are characterized by fairly severe processing conditions - temperatures in excess of 400°C, and hydrogen pressures above 1500 psig. These high-temperature high-pressure processes not only consume large amounts of energy in converting coal to, at best, 75% liquid product, but also require expensive equipment to handle the severe operating conditions.

This report describes efforts to use a catalytic inorganic medium at moderate temperature and pressure (below 300°C and 1000 psig H_2) to convert coal to liquids. To better understand the approach taken here and the chemistry of conversion, it will be necessary to review

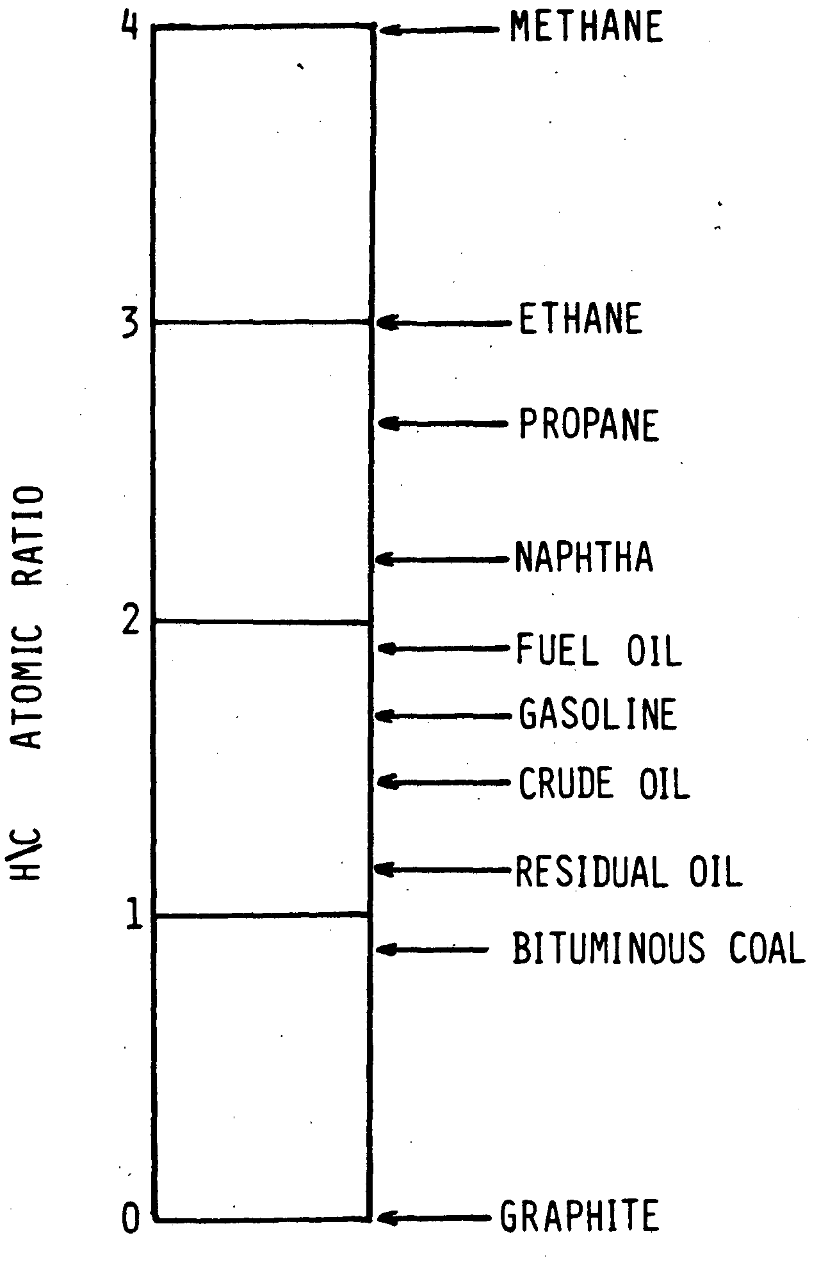


Figure 1-1. Representative Atomic H/C Ratios for Coal and Other Fuels (after Wiser, 2).

Table 1-1. Operating Conditions and Yields of Major Processes Being Developed for Conversion of Coal to Liquid or Clean-Burning Solid Fuels.

Process	Temperature (°C)	Pressure (psig)	Approximate Yields (%) Liquid	Gas	Char	Comments
COED	315-455-535-870	-	20	17	60	Multistage fluidized bed pyrolysis, with 4th stage gas and char recycle. Subsequent hydrogenation with catalysts at 2000 psig for product upgrading.
Occidental Pyrolysis	500	15	35	7	58	Pyrolysis at rapid heating rate. Ca. 30 sec. reactor residence time.
Solvent Refined Coal-I	440	2000-3000	75	5	20	Slurry of recycle solvent and coal. Product solid at room T. Coal minerals catalyze solvent hydrogenation.
Solvent Refined Coal-II	440	2000-3000	70	10	20	Liquid product by solid catalyst hydrogenation after SRC-I reaction.
Exxon Donor Solvent	400-480	1500-2500	50	15	35	External hydrogenation of recycle solvent. Liquid product.
H-Coal	450	2800	75	20	5	Ebulated bed reactor with Co-MoO catalyst.
Consol	380/450	400/3500	75	15	10	Low T, P extraction in donor solvent followed by high T, P hydrogenation over molten $ZnCl_2$.
U. Utah	500-550	2000	60	10	30	Rapid (t = 10-20 sec) hydrogenation of coal impregnated with ca. 5 wt% $ZnCl_2$.

the current knowledge of coal chemistry and structure, the nature of coal liquefaction processes, and the history of catalysts in coal conversion.

Coal Chemistry and Structure

General Coal Chemistry

There is a variety of structural and chemical makeup for coals of different rank (different carbon content) ranging from lignite, through sub-bituminous and bituminous, to anthracite. Much work has been done to characterize these differences and their effects on liquefaction.(3-6) As rank increases, aromaticity and average number of fused rings generally increase. Decreases in oxygen content occur; alkoxy and carboxyl groups diminish first, followed by hydroxyl and ethers. Volatile matter shows a maximum in mid-rank coals. Wyodak Roland-Seam coal (a Wyoming sub-bituminous coal, containing 73 wt-% carbon on a dry and ash-free basis), an example of low-rank western coals of which there are vast reserves, has been used in this study.

Several models of the chemical structure of coal have been proposed. These include: (1) macromolecules joined by hydrogen bonds or acid-base interactions(7); (2) entangled chains or sheets; or (3) highly cross-linked polymeric systems, possibly including smaller molecules lodged within the structure.(8) The best fit for the available data appears to be provided by a crosslinked model. Hill,(57) Wiser(9) and Given(58) have proposed schematic models of typical chemical structures in coal.

Coal is a relatively insoluble solid (typically with less than 15% pyridine solubility), with significant internal pore structure. The pore volume frequently is near 10% (0.16 cc/gm or less(11)). More than half of the pore volume occurs in pores less than 300 in diameter, making the interior of the coal particles relatively inaccessible for chemical conversion methods.(10)

Model of Sub-bituminous Coal Structure

Although earlier models of coal have shown some representative structures which may occur in the coal itself, lack of data on the specific chemical nature of the coal polymeric subunits has impeded efforts to construct a more accurate quantitative model. Recent improvements in wet-chemical, chromatographic, and spectroscopic methods have provided significant new data on coal chemistry which allow a more quantitative model to be constructed.

Most enlightening of the new developments has been solid state C^{13} - nuclear magnetic resonance (NMR) allowing direct measurement of the aromaticity of untreated coal (developed by Pines and others(12)). Earlier inability to measure the aromaticity of solids had generated a great deal of debate about the state of carbon in coal.(13-22) Direct measurement by the C^{13}-NMR technique of the coal used in this study (Whitehurst(118)) shows roughly 63% aromatic carbon.

A variety of oxidative degradation techniques have been employed by workers at Argonne National Laboratory to determine the nature and abundance of aromatic units in the coal structure.(20, 23-27) An interpolation of their data provides the structural types and abundances for sub-bituminous coal shown in Figure 1-2. The preponderance of

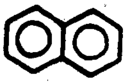
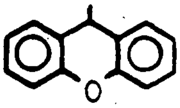
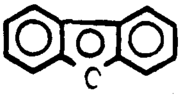
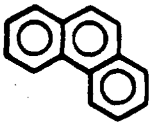
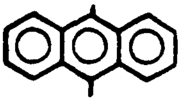
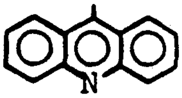
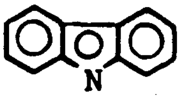
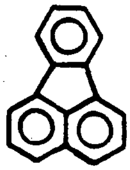
Structural Unit	Relative Abundance	Number of Aromatic C per Unit	Occurrence in 10000 MW Model
	100	6	20
	20	10	4
	15	13	3
	15	12	3
	12	14	2
	6	13	1
	4	14	1
	4	13	1
	3	5	2
	3	12	1
	3	16	1

Figure 1.2. Type and Abundance of Various Aromatic Centers in Sub-Bituminous Coal. (Interpolated from data by Hayatsu et al.(23))

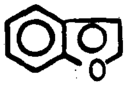
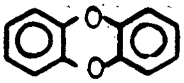
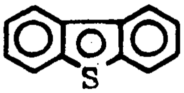
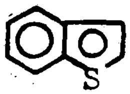
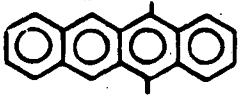
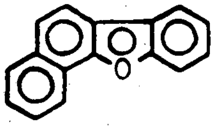
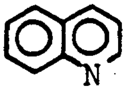
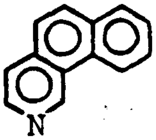
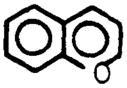
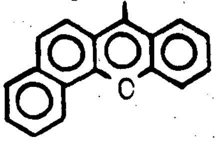
	3	8	1
	2	12	1
	2	12	1
	2	8	1
	2	18	-
	2	16	-
	2	9	-
	1	13	-
	1	9	-
	1	17	-

Figure 1-2 (continued)

single-ring units is notable (earlier studies had indicated many fused ring structures).

Inverse oxidative degradation, which destroys aromatic units, has been employed to determine the nature of the aliphatic network in the coal.(28-30) Recent work using this technique on Wyodak coal indicates that about 23% of the hydrogen in sub-bituminous coal is found in aliphatic crosslinks of the types indicated in Table 1-2.(118) These structures also comprise roughly 10% of the carbon in the coal.

Table 1-2. Aliphatic Sturctures Present in Wyodak Coal. (after Whitehurst(118)).

Structure[1]	Percentage of Original Coal Hydrogen in Such Structures
$\mathrm{Ar\text{-}\underline{CH_3}}$	2.5
$\mathrm{Ar\text{-}O\text{-}\underline{CH_3}}$	1.3
$\mathrm{Ar\text{-}\underline{CH_2}\text{-}Ar}$	0.4
$\mathrm{Ar\text{-}\underline{C_2H_4}\text{-}Ar}$	1.7
$\mathrm{Ar\text{-}\underline{(CH_2)_x}\text{-}CH_3}$	10.0
$\mathrm{Ar\text{-}\underline{CH_2}\text{-}(CH_2)_x}$	4.4
$\mathrm{(CH_2)_x\text{-}\underline{CH_2}\text{-}(CH_2)_x}$	3.2
Total	23.5

1- Ar refers to an aromatic structure; $(CH_2)_x$ to an aliphatic structure. The underscored group is the aliphatic system of interest.

The nature of the oxygen groups in the coal has been examined with wet-chemical methods by Blom.(9) A wide range of coals of differing ranks were investigated. Estimates made from the data would indicate roughly 19.5% total oxygen for a 73% carbon coal (our analyses give 19.4%), with 3% carboxylic acids, 1.5% carbonyl, 5% acidic hydroxyl, 2.5% weakly- or non-acidic hydroxyl, and the remaining 7.5% as ether oxygen.

Organic sulfur and nitrogen groups for our coal are relatively sparse (ca. 10 atoms total per 1400), occurring predominantly in cyclic heteroatom structures. Some sulfide, disulfide, and amine bridges also exist, as well as mercaptans and amines in limited quantities.

The chemistry of the molecular sub-units of the coal polymer has been reported on in a study conducted by Mobil Research and Development Company and sponsored by the Electric Power Research Institute, utilizing solvent-refined Wyodak coal.(11,13) Successive elution of the solvent-refined coal (SRC) from a chromatographic column with solvents of varying chemical properties separated the daughter molecules into discrete fractions of varying polarity and aromaticity. Molecular-weight determinations by vapor-pressure osmometry and gel-permeation chromatography, together with elemental analyses, proton and carbon aromaticities, and other chemical tests, were performed on the fractions to characterize the types and abundances of molecular structures present in the SRC. Table 1-3 and Figure 1-3 give some of the characteristics and proposed structures for the product molecules from the Wyodak SRC.

Table 1-3. Characteristics of Solvent Refined Coal (SRC) from a Wyoming Sub-bituminous Coal.(31)

Fraction Number	Elution Solvent	Wt. % in SRC	Aromaticities (%)		Molecular Weight	Formula
			H	C		
Whole[1] SRC	Pyridine	100.0	52.0	62.0	-	$C_1H_{0.8}N_{0.012}\ O_{0.05}$
3	$CHCl_3$	20.8[2]	48.0	-	660	$C_{49}H_{42}O$ or $C_{49}H_{41}NO$
4	$CHCl_3$/10% Et_2O	20.0	47.0	-	630	$C_{45}H_{38}NO_2$
5	Et_2O/3% EtOH	10.7	47.0	-	580	$C_{40}H_{38}NO_4$
6	MeOH	4.4	-	-	-	-
7	$CHCl_3$/3% EtOH	4.7	-	-	ca.600	$C_{42}H_{33}NO_2$
8	THF/3% EtOH	16.3	-	-	740	$C_{50}H_{43}NO_5$
9-10	Pyridine/10% MeOH or Non-Eluted	23.1	-	-	-	-
Whole[2] SRC	Pyridine	100.0	30.0	60.0	600	-

1 - Whole SRC and extracts from run at ca. 450°C for ca. 90 minutes.
2 - Sum of fractions 1 through 3.
3 - Mild treatment - ca. 425°C, 1.3 minutes.

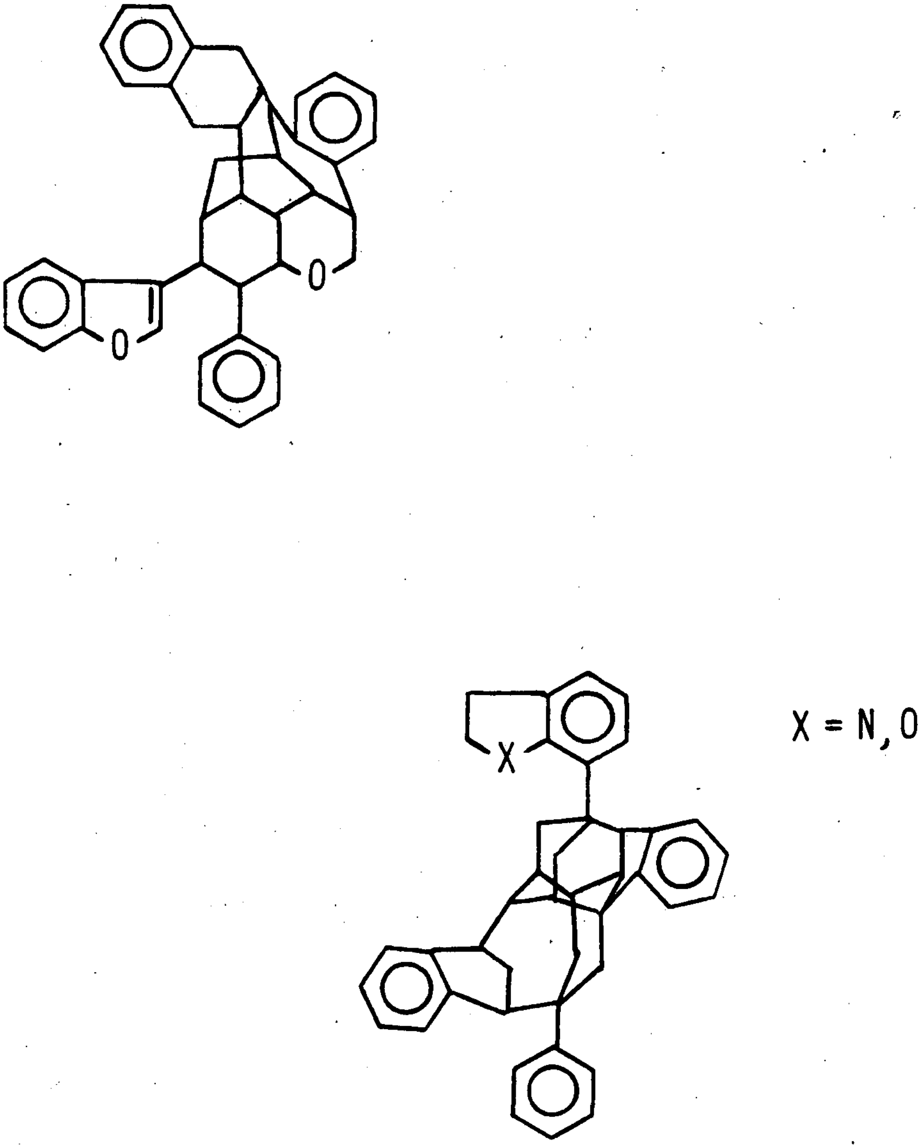


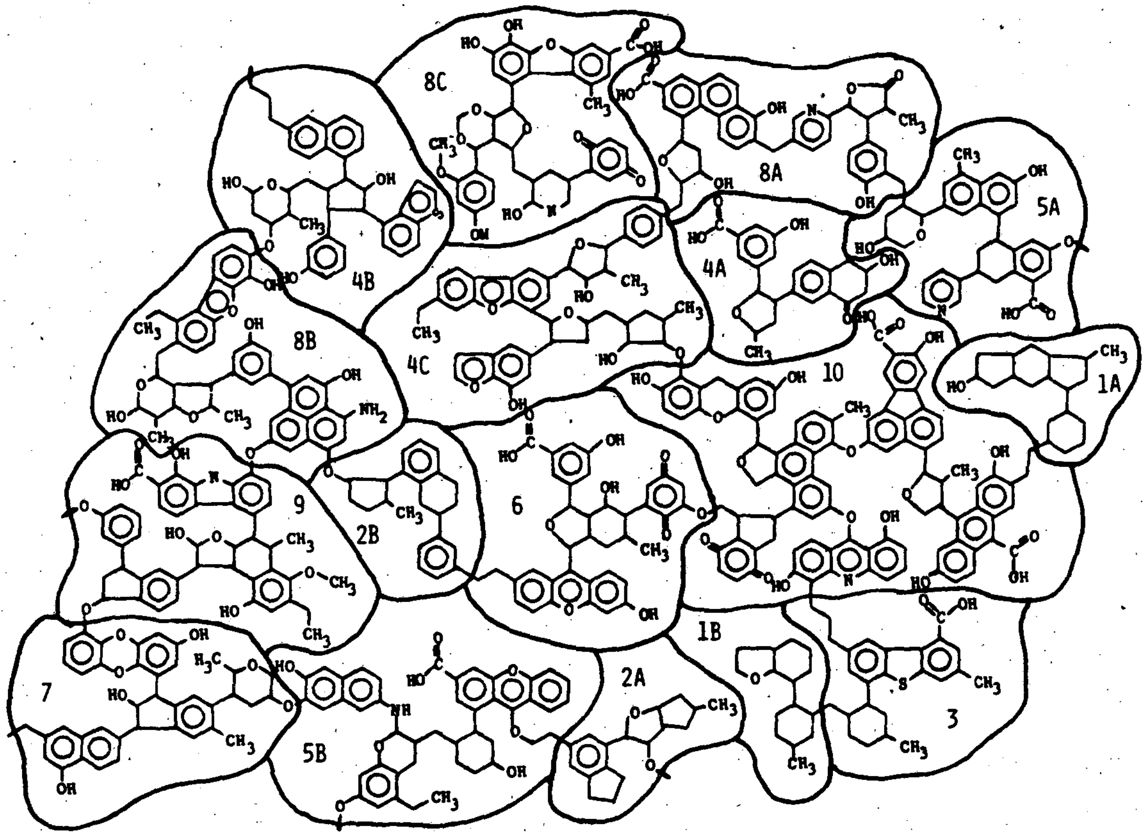
Figure 1-3. Proposed Structures for Solvent Refined Coal from a Wyoming Sub-bituminous Coal (Whitehurst, 31).

Information on the types of cleavable links joining these molecules in the coal has been generated in a study of model compound behavior under liquefaction conditions conducted at Oak Ridge National Laboratory.(32,33) It was found that aliphatic linkages between two aromatic units cleave easily, as do ethers with neighboring aliphatic hydrogens. Phenolic groups on an aromatic ring were found to promote cleavage of short aliphatic links attached to that ring.

Data from all these sources have been combined in the present study to formulate a structure for sub-bituminous coal. The basis chosen for the model was a molecular weight of 10,000. Elemental analyses determined that a coal unit of this size would have a molecular formula $C_{611}H_{568}O_{121}N_7S_2$ (mol. wt. = 9998). The determination of oxygen functionalities, carbon, and proton aromaticities, and the deduction of aromatic and aliphatic structures provide input data from which the model is constructed. The aromatic, aliphatic and heteroatom pieces were distributed among the molecules of various sizes and functionalities outlined in the Mobil study with additional oxygen reallocated to the fractions. Each molecule was then constructed from its fragments and a polymer of the fragments representing the original coal was built (see Fig. 1-4).

Considerations for the choice of molecular subunit structures included: (1) the major crosslinks are used to join aromatic units; (2) the degree of condensation of the aliphatic skeleton and extent of connection to aromatic species is forced by hydrogen content; (3) structures of plant precursors of the coal (lignins, resins, tannins, terpenes, and waxes) suggest the structures of the aliphatic skeleton.

Figure 1-4. Model of Sub-bituminous Coal Structure.



XBL 797-10469

Figure 1-4.

These individual structures should not be considered as accurate, as no detailed structural information is available. Rather, they provide a quantitative model of an average molecule of the original coal fragment which led to a particular SRC fraction.

Some words of caution are necessary in interpreting this model which merely reflects the quantitative proportions of chemical groups present in sub-bituminous coal and their distribution among various fractions produced by short-residence-time bond cleavage. Thus the linkages are consistent with the types that would be broken during the SRC process, and the fragments are consistent with the chemical nature of the SRC products. The figures are averages over groups of widely varying structures, and it is likely that the averages as such do not exist to any significant extent. It is conceivable that the SRC fragments may be considerably different from the original fragments, because considerable condensation and repolymerization may occur even in only a few minutes above 400°C during the formation of SRC.

Obviously, the model cannot show the three-dimensionality which would actually be present. Similarly, it does not show the higher-order structure in which various organic components of differing origins (known as macerals) are pressed together with each other, and the clay and silica which form the mineral matter of such coals. Some of the mineral matter (particularly calcium) is dispersed within the organic structure as ion-exchanged or chelated entities.

The accuracy of the quantitative data used in the model should also be considered. Carbon aromaticity data from the new NMR technique are accurate to within about 20%. Such variations in carbon aromaticity can force significant changes in the degree of condensation of the aliphatic skeleta. In addition, the oxidative degradation studies may suffer from significant side reactions, leading to possible misinterpretation of the data. Furthermore, the data on types and abundances of aromatic structures have been interpolated from data on lignite and bituminous coal, and are thus subject to interpolation errors.

Chemical methods for functional-group determination also suffer from side reactions or from the inability to drive a reaction to completion. These values are likely to be less than 15% inaccurate, although ether oxygen values (determined by difference from total oxygen) may be 20-25% inaccurate. Further uncertainties include the distribution of ether oxygen in aliphatic, alicyclic, aryl-alkyl, and aryl ethers, and the separate determination of ester and carboxylic acid groups.

Coal Conversion Processes

Thermolytic Coal Conversion

The conversion of coal to liquid materials or other clean-burning fuels has been pursued by many routes. All of these processes must deal with the same fundamental problems: to increase the hydrogen-to-carbon (H/C) ratio, remove nitrogen, sulfur, oxygen, and ash, and reduce the molecular weight.

As for petroleum processes, the effectiveness of coal conversion is usually monitored in general terms. A primary diagnostic is the product solubility in specific solvents. Compounds soluble in an aliphatic hydrocarbon solvent, such as pentane, hexane, or cyclohexane, are known as oils, and are characterized by low heteroatom content, low molecular weight (normal boiling point below 400°C), and high H/C ratio (1.5). Benzene-soluble compounds, known as asphaltenes, have more heteroatoms, higher aromaticity, higher molecular weight (between 200 and 1000), and lower H/C ratio. The benzene-insoluble pyridine-soluble fraction, known as preasphaltenes or asphaltols, has still higher heteroatom content, aromaticity, and molecular weight (400-3000). Finally, there is pyridine-insoluble material which is termed residue. Most processes strive to maximize the yields of oils and minimize the residue. Although volatile hydrocarbons ("gas") may be produced, these are to be avoided since their formation involves the expense of consuming large proportions of hydrogen.

The available conversion processes (34,35) as summarized in Table 1-1 are divided into several categories: indirect liquefaction, pyrolytic liquefaction, solvent-aided pyrolysis, and catalyst-aided pyrolysis.

Indirect liquefaction processes operate by first converting the coal to a mixture of CO and H_2 (synthesis gas), and then using Fischer-Tropsch synthesis to build higher hydrocarbons from the "syn-gas." The yield of the desired oil from Fischer-Tropsch may be limited by the synthesis mechanism which causes a wide distribution in carbon number of the product.

Mobil Research and Development Company has recently developed a process which avoids the wide product distribution of the typical Fischer-Tropsch synthesis. In the Mobil process, methanol produced from synthesis gas is reacted over a metal catalyst supported on a shape-selective zeolite, which limits the access of larger molecules to the metal. This avoids the production of heavier products, and results in a narrow molecular-weight distribution.

All of the indirect processes involve fairly severe conditions for coal conversion (gasification above 500°C), which tends to lower the thermal efficiencies.

Pyrolytic liquefaction of coal involves treatment at the temperatures necessary to produce free radicals thermally, 350°C or higher. These processes heat the coal in the absence of catalysts or solvents, and require hydrogen to achieve capping of the free radicals. The resulting decomposition reactions are fairly uncontrolled, and yields of desired liquids are generally low with undesirable gas and char formation dominating. The COED process is one example of pyrolysis; the Occidental Pyrolysis process improves upon it in yield by using high-speed heating to produce more liquids. Both operate near 500°C.

In an effort to maintain better control of thermal decomposition of the coal and enhance product hydrogenation, several processes employ solvents as pyrolytic media. One of these, the Solvent Refined Coal (or SRC) process, uses temperatures between 400 and 450°C. Two pilot plants are currently operating using the SRC process: the first, at Wilsonville, Alabama, produces a solid fuel with reduced heteroatom and ash content and H/C of about 0.9; the second, at Fort Lewis, Washington, uses a second-stage catalytic hydrogenation to produce liquid. Process solvent, taken from the product and recycled with the feed, enhances the breakup of coal particles,(36) dissolves the initial products, transfers hydrogen, and may aid bond cleavage.(31) In extensive work to characterize the solvent and its activity, the characteristic components found include aromatic and hydroaromatic hydrocarbons, phenols, and nitrogen bases.(11,31)

The Exxon Donor Solvent Process (EDS) represents an improvement over the SRC process by use of catalytic hydrogenation in the solvent-recycle loop, providing a hydrogen-rich solvent which more effectively hydrogenates the coal.(37) A pilot plant is currently in operation at Baytown, Texas, and engineering of a full-scale unit is under way with plant start-up anticipated for 1981.

In addition to using solvents to aid pyrolysis, several processes employ catalysts in liquefaction. The first group uses a cobalt molybdate catalyst to aid product hydrogenation and heteroatom removal. Both a fixed-bed (Synthoil) and a moving bed (H-Coal) design have been evaluated; The Department of Energy has slated the moving-bed version for full-scale development along with EDS and SRC.

A wide range of other ctalysts has been investigated for use in high temperature coal conversion.(97,98) Extensive screening was carried out at the Bureau of Mines involving metals and metal chlorides (especially $SnCl_2$,$AlCl_3$, and $ZnCl_2$).(88-94)

Molten salts, especially the chlorides just mentioned, have been particularly attractive as coal-conversion catalysts.(95,96) Although $AlCl_3$ and $SnCl_2$ appear more active than $ZnCl_2$, both are more expensive than $ZnCl_2$, more difficult to recover, and more corrosive. Excessive gas and char formation have also been reported when $AlCl_3$ is used, and small amounts of water destroy its activity.

For these reasons, zinc halides have been the focus of activity in molten salt catalysis. Shell Oil Company holds patents on zinc halide hydrocracking of coal.(99,100) Workers at Montana State University have found an equimolar $ZnCl_2$/KCl mixture to be an active hydrocracking medium which may be more readily separated from products than the $ZnCl_2$ alone.(101)

Further, two processes are currently being developed which utilize zinc halide catalysis. Conoco Coal Development Company (formerly Consolidation Coal) uses massive quantities of molten $ZnCl_2$ to produce high yields (60%) of gasoline from a coal extract.(38-44) This process is currently under demonstration at Library, Pennsylvania. It is likely that the primary mechanism for coal breakup in this process is thermal; the $ZnCl_2$ appears to stabilize and promote low-molecular-weight products. The University of Utah process uses short contact times, and only small amounts of $ZnCl_2$ (5 wt-%) with which the coal is impregnated.(45-47) Holten(48) and Derenscenyi(49) have reviewed both $ZnCl_2$ processes in detail.

All of the coal-conversion methods reviewed so far have used high temperatures (over 400^{o}C) and high pressures (over 1500 psig) to accomplish the desired bond cleavages. None of the process variations is fully effective for preventing char and gas formation. Furthermore, these high-temperature high-pressure processes consume considerable energy and require expensive equipment because of the severe processing conditions.

Low-Temperature Low-Pressure Conversion

Conversion of coal under milder conditions will require selective chemical activation of the crosslinking bonds, and may thus offer the opportunity to limit gas and char formation. As this study has the goal of investigating lower-temperature and lower-pressure routes to coal conversion, previous studies of catalytic coal conversion will now be briefly reviewed.

Several investigators have developed chemical methods to "depolymerize" coal at temperatures below the onset of thermal decomposition. Although most of this work was done to gain structural information on coal through mild decomposition, the techniques used may give an insight into the methods effective for mild-condition processing.

One group of low-temperature processes involves oxidative degradation of the coal. Many techniques have been developed for oxidizing aliphatic carbon, using alkali-oxygen oxidation,(50) ozonation,(51) aqueous sodium hypochlorite(13-16,52-54) aqueous sodium dichromate,(23-27) hydrogen peroxide-acetic acid,(23) and fluorine,(20) as well as photochemical oxidation.(23) Deno has recently developed a "reverse oxidation" which oxidizes aromatic groups using concentrated aqueous hydrogen peroxide with trifluoroacetic acid.(28-30)

Other techniques have been developed to disassemble coal without the destructive effects of oxidation. Sternberg and others have reductively alkylated coal using potassium, tetrahydrofuran, and naphthalene to produce a coal anion, which is subsequently alkylated with an alkyl halide.(60-63,81)

Numerous acid-catalyzed depolymerizations have been investigated following the lead of Heredy and Neuworth, who used BF_3 and phenol in 24-hour reactions at 100°C to solubilize coal.(64-66) Darlage achieved similar results with a preliminary nitric acid wash, or substituting sulfuric acid for the BF_3.(67,68) Other workers have found several other catalysts which are effective for coal solubilization with phenol, including p-toluenesulfonic acid, phosphorus pentoxide, picric acid, and $ZnCl_2$ with trichloroacetic acid.(69-73)

While the phenol-acid catalyst combination is effective in producing nearly totally soluble coal, incorporation of phenol in the product lessens its process potential. The mechanism of solubilization apparently involves cleavage of aliphatic bridges with insertion of phenol,(75) and condensation reactions of the phenol itself further contribute to its retention in the products.(73)

Acid-catalyzed alkylations have been investigated using solvents other than phenol. Kroger has alkylated coals using isopropyl chloride with $AlCl_3$ in CS_2 at 45°C, or using olefins with $AlCl_3$/NaCl between 160°C.(76) Increases in pyridine solubility occurred from 20% untreated to between 40 and 60% after treatment, accompanied by a 20 to 30% weight increase in the coal due to alkylation. Larsen and Kuemmerle used sulfuric acid catalyst with isobutylene at temperatures between 20 and 100°C to improve the solubility of a variety of coals.(75, 78) Denson and Burkhouse alkylated coal using various olefins and alcohols with anhydrous HF at 135°C, with similar results.(79)

Acylation with acyl chlorides and $AlCl_3$ is another route to increased coal solubility.(80) The action of this medium may be predominantly physical, however, with high-molecular-weight (10^5 to 10^6) products being solubilized by interaction of the acyl chains with the dissolving solvents.(75)

Ross and co-workers at Stanford Research Institute (SRI Inc.) have investigated a variety of prospective catalysts for low-temperature coal conversion.(84) Combinations of Lewis and Bronsted acids (such as $AlCl_3$/HCl or $SbBr_3$/HBr) were used at temperatures between 190° and 210°C for periods of 5 to 15 hours on dried Illinois No. 6 coal. Hydrogen pressures in excess of 800 psi were used, as earlier experiments had indicated that diminished pyridine solubility resulted if no hydrogen were present. When 1:1 weight ratios of catalyst:coal were used, catalyst effectiveness was found to be in the order: $AlCl_3$ $AlBr_3$ $SbCl_3 = SbBr_3 = SbF_5 = ZnCl_2 = TaF_5 = NiSO_4 = CoSO_4$. When a constant molar quantity of catalyst was used, catalyst effectiveness was found to be: $SbBr_3 = SbCl_3$ $AlBr_3$ $AlCl_3$ $Ni(acetylacetonate)_2$ TaF_5 $SbF_5 = MoCl_5 = WCl_6$. Virtually total pyridine solubility was achieved with the most active systems ($SbCl_3/HCl/H_2$). It is notable that several of the catalysts ($ZnCl_2$, SbF_5, and WCl_6) were below their melting points during reaction, and may have had their effectiveness limited by contacting problems.

Continued work at SRI, performed at 335°C for 90 minutes, used alcohols with basic catalysts, such as aluminum isopropoxide, potassium isopropoxide, or potassium tert-butoxide. The combination of potassium isopropoxide and isopropanol was found to be highly effective in producing a totally pyridine-soluble product, but the process was found to be uneconomical due to the cost of incorporated isopropanol in the product.(85)

More recently, Makabe and Ouchi have used sodium hydroxide in ethanol at temperatures between 200° and 400°C and reaction times of 1 to 20 hours to produce pyridine-soluble material from a variety of coals.(87) Again, hydrolysis of ether bonds has been assumed as the mechanism of solubilization.

Catalytic Coal Conversion Using $ZnCl_2$ Under Mild Conditions

The process potential of $ZnCl_2$ at 400-500°C and the promising activity of acid catalysts under mild conditions led Derenscenyi to begin investigation of $ZnCl_2$ for low-temperature coal conversion.(49) Operating at 200°C, the effectiveness of various inorganic additives to a $ZnCl_2$-water solution in promoting benzene solubility of the treated coal was studied. The best results were obtained by the addition of small quantities of KI and I_2, improving benzene solubility from 1% (untreated) to 7% (treated).

Holten, extending this study to 250°C and 600 psig hydrogen pressure, found little effect on product pyridine solubility from additions of tetradecene, diisopropylbenzene, or various inorganic additives to the $ZnCl_2$-water melt.(48) A breakthrough came using tetralin as an additive, improving product pyridine solubility from about 20% without tetralin to nearly 70% with tetralin.(128)

Scope and Objectives of the Present Study

As the foregoing survey indicates, high-temperature high-pressure processes have major drawbacks, wasting input coal and hydrogen producing undesired products, and requiring high capital expenditures for equipment to handle the severe conditions. These limitations emphasize the need for advanced process concepts which would be more selective (producing less gas and char), and would utilize less severe operating conditions. Liquid-catalyzed conversion offers the potential for meeting these requirements.

Previous studies have shown that various catalyst-solvent combinations may be effective in solubilizing coal at temperatures below the onset of thermal degradation (about 350°C), albeit with significant incorporation of solvent in the product. $ZnCl_2$ has been shown to be one of the most promising catalysts for coal conversion at 400-500°C, but very little work has been done with this catalyst at lower temperatures. Preliminary work with $ZnCl_2$ at milder conditions in these laboratories with use of solvent additives has shown the most promise.

The current study investigates in depth the action of $ZnCl_2$ for catalyzing coal conversion in the presence of organic and inorganic additives. Emphasis has been placed on solvent additives, particularly those miscible with the catalyst. Reaction temperatures between 200 and 300°C and hydrogen pressures up to 800 psig have been used in one-hour batch autoclave experiments.

Due to the high melting point of the $ZnCl_2$ (315°C), solvents have been added to render the catalyst liquid under reaction conditions. Previous work in this laboratory led to the choice of 10 wt-% water as the melting-point depressant based on its low reactivity with $ZnCl_2$ and its low cost relative to other solvents. The current study reveals that other solvents may yield better results.

The choice of catalyst loading was based on previous work which had indicated that conversion was not dependent on $ZnCl_2$ loading above

3/1 melt:coal weight ratio. To eliminate this variable, and to be consistent with Holten's work,(48) a ratio of 6/1 was used in most of these experiments.

The autoclave experiments performed may be divided into three major categories according to the agent used to solubilize the $ZnCl_2$: (1) $ZnCl_2$-water runs; (2) $ZnCl_2$-solvent runs (other than water or methanol), and; (3) $ZnCl_2$-methanol runs. For selected runs, the off-gases were analyzed by mass spectrometry, gas chromatography and combined gas chromatography and mass spectrometry. Selected extracts were analyzed by gel-permeation chromatography to determine relative molecular weight distributions. Several samples of the treated coal were examined using a scanning electron microscope to help determine the effects of physical factors such as catalyst-coal contacting and product extraction on conversion.

CHAPTER 2

EXPERIMENTAL STUDIES

Table 2-1 provides a list of the autoclave experiments performed in this study. Numerous inorganic and organic additives were screened for their effect on catalytic activity with $ZnCl_2$ at temperatures between 200 and 300°C and hydrogen pressures between 0 and 800 psig.

Materials

Coal

The coal utilized for the experiments was a sub-bituminous coal supplied by the Wyodak Resources Development Corporation from the Roland top seam of its Gillette, Wyoming mine. In one experiment, Illinois No. 6 bituminous coal was used, supplied by the Illinois Geological Survey.

The coal was received ground to minus 3/4 inch in 55-gallon drums. This material was passed through jaw and roller crushers, reducing the particle size to minus 1/6 inch, and was stored in polyethylene bags. Subsequently, it was milled and screened, with the -28+100 Tyler mesh fraction split into ca. 500-gm portions and stored under nitrogen in 1-quart paint cans.

Proximate and ultimate analyses of the two coals are shown in Table 2-2. Replicate samples of the Wyodak coal taken from the 55-gallon supply drum over a two-year period revealed no consistent change in oxygen content (by difference), indicating negligible oxidation had occurred. The data listed in the table are averaged from replicate analyses of -28+100 mesh samples.

Table 2-1. Autoclave Experiments.

					Solvents			
Run	T (^oC)	PH_2 (psig)	t (min)	Substrate (gm)	$ZnCl_2$ (gm)	Primary (gm)	Additional (gm)	Additives (gm)
2	250	500	60	Wyodak-50	273	Water-27-2727	Piperidine-50	
3	250	500	60	Wyodak-50	147	Water-27		KBr-45.3;NaI-57.1
4	250	500	60	Wyodak-50	273	Water-27	Dihydroanthracene-50	
5	250	500	60	Wyodak-50	206	Water-27		KCl-37.6; NaCl-29.4
7	250	500	60	Wyodak-50	273	Water-27	Mesitol-50	
9	250	500	60	Wyodak-50	273	Water-27	t-Butanol-50	p-Toluene Sulfonic acid-50
10	250	500	60	Wyodak-50	273	Water-27	Methyl-Naphthalene-50	Tetralin-10
11	275	500	60	Wyodak-50	273	Water-27		
12	250	500	60	Wyodak-50	273	Water-27	Anthracene Oil-50	
13	300	500	60	Wyodak-50	273	Water-27		
14	255	500	60	Wyodak-50	273	Water-27	p-xylene-50	$CaCl_2$-24.7
15	250	200	60	Wyodak-50	273	MeOH-50		
16	280	500	60	Wyodak-50	273	Water-27		$CaCl_2$-24.7
17	255	0	60	Wyodak-50	273	MeOH-100		
18	250/300	250	60	Wyodak-50	273	Water-27		NO-250 psig
19	275	650	20	Wyodak-50	273	MeOH-50		
20	320	400	60	Wyodak-50	273	MeOH-25	n-Decane-100	
21	250	250	60	Wyodak-25	137	MeOH-25	n-Decane-25	

Table 2-1. Autoclave Experiments (continued).

					Solvents			
Run	T (^oC)	PH_2 (psig)	t (min)	Substrate (gm)	$ZnCl_2$ (gm)	Primary (gm)	Additional (gm)	Additives (gm)
22	250	500	60	Wyodak-50	273	Water-27		
23	250	500	60	Wyodak-50	273	Water-27		$CaCl_2$-24.7
24	250	200	60	Wyodak-50	273	MeOH-50		Zn-25
25	250	250	60	Wyodak-50	273	N,N-Dimethyl Formamide-100		
26	250	250	60	Wyodak-50	273	MeOH-50	Anthracene Oil-10	
27	250	200	60	Wyodak-50	273	MeOH-50		$CdCl_2$-38.5
28	250	200	60	Wyodak-50	273	MeOH-50		$SnCl_2$-42.1
29	250	200	60	Wyodak-50	273	MeOH-50	Tetralin-10	
30	275	200	60	Wyodak-50	273	MeOH-50		
31	200	200	60	Wyodak-50	273	MeOH-50	Anthracene Oil-10	
32	250	200	60	Wyodak-50	273	MeOH-50	Cyclohexanol-10	
33	250	200	60	Wyodak-50	273	i-PrOH-50		
34	250	200	60	Wyodak-50	273	t-BuOH-50		
35	250	200	60	Wyodak-50	273	MeOH-50	C_2Cl_6-50	
36	250	200	60	Wyodak-50	273	Acetone-50		
37	250	200	60	Wyodak-50	273	MeOH-50		
38	250	200	60	Wyodak-50	273	CH_3COOH-50		
39	250	500	60	Wyodak-50	273	MeOH-50		
40	250	200	60	Wyodak-50	273	MeOH-25		
41	250	200	60	Wyodak-50	273	MeOH-75		
42	300	500	60	Wyodak-50	273	Water-27	Tetralin-50	

Table 2-1. Autoclave Experiments (continued).

						Solvents		
Run	T (^{o}C)	PH_2 (psig)	t (min)	Substrate (gm)	$ZnCl_2$ (gm)	Primary (gm)	Additional (gm)	Additives (gm)
43	250	800	60	Wyodak-50	273	MeOH-50		
44	250	200	60	Wyodak-50	273	Water-10	MeOH-10	
45	250	0	60	Wyodak-50	273	MeOH-50		
46	250	200	60	Wyodak-50	273	Water-27		
47	250	800	60	Wyodak-50	273	MeOH-25		
48	275	800	60	Wyodak-50	273	MeOH-50		
49	225	800	60	Wyodak-50	273	MeOH-50		
50	250	0	60	Wyodak-50	273	MeOH-50		N_2-800 psig
51	250	800	60	Wyodak-50	273	MeOH-35		
52	225	200	60	Wyodak-50	273	MeOH-50		
53	250	200	60	Wyodak-25	137	MeOH-25	o-$C_6H_4Cl_2$-60	
54	250	200	60	Wyodak-50	273	EtOH-50		
55	250	500	60	Wyodak-50	273	MeOH-50		ZnO-18.8
56	250	800	60	Wyodak-50	273	Water-27		
57	250	500	60	Wyodak-50	273	MeOH-50		ZnO-9.0
58	250	500	60	Wyodak-50	273	MeOH-50		HCl- 100 psig
59	250	500	60	Wyodak-50	273	MeOH-50	Indoline-10	
60	250	500	60	Wyodak-50	0	n-Decane-200	Tetralin-50	HCl- 100 psig
61	250	0	0	Wyodak-50	273	MeOH-50		ZnO- 18.8
62	200	0	60	Wyodak-50	273	Water-27		
63	250	500	60	Wyodak-50	273	Water-27		
64	250	0	60	Wyodak-50	273	Water-27		

Table 2-1. Autoclave Experiments (continued).

						Solvents		
Run	T (^{o}C)	PH_2 (psig)	t (min)	Substrate (gm)	$ZnCl_2$ (gm)	Primary (gm)	Additional (gm)	Additives (gm)
65	250	500	60	Wyodak-50	273	Water-27		
66	250	510	60	Wyodak-50	273	MeOH-50	Pyrrollidine-50	ZnO-9.0
67	40	0	7200	Wyodak-50	63	Et_2O-306		
68	235	0	60	Wyodak-50	0	MeOH-240		
69	250	500	60	Wyodak-50	273	MeOH-50		ZnO-9.0
70	275	800	30	Wyodak-50	273	MeOH-50		
71	250	500	60	Ill.No.6-50	273	MeOH-50		
72	250	800	60	Wyodak-50	273	MeOH-50		
73	250	800	60	Wyodak-50	273	MeOH-50		
74	250	800	0	Wyodak-50	273	MeOH-50		
75	250	500	60	Wyodak-50	273	MeOH-50		
76	250	800	30	Wyodak-50	273	MeOH-50		
77	275	800	0	Wyodak-50	273	MeOH-50		
78	250	500	60	Wyodak-100	137	MeOH-25		
79	250	500	60	Wyodak-50	273	MeOH-50		Zn-1.0
80	250	800	60	Wyodak-50	273	Water-27		Zn-10.0
81	250	500	60	Petrol. Resid.-50	273	MeOH-50		
82	225/275	1000	60	Wyodak-50	273	Water-27		Zn-10.1
83	150	0	30	Filter Paper-21	273	MeOH-50		

Footnotes to Runs

FN	Run	Note
1	2	Reactor leaking, pressure refilled after 100 psi leak.
2	3	T overshoot to 275°C; down to 250°C within 5 minutes.
3	4	T overshoot to 290°C; down to 215°C 9 minutes later; Stabilized at 250°C at t = 30 min.
4	5	Approx. 55 min at 250°C with drop to 220°C during run.
5	7	Max. T of 264°C (less than 10 min. above 255°).
6	9	T = 260°C 10°C.
7	10	25 gm each of 1-methyl and 2-methyl naphthalene.
8	12	Max. T of 264°C (less than 5 min above 255°C); T dropped to 236° (less than 4 min below 255°C).
9	14	T = 255 10°C.
10	15	Max. T of 265°C (less than 5 min above 255°).
12	18	1 hour at 250°C then 1 hour at 300°C.
13	19	Seal failed during run; ca. 20 min residence time.
14	20	T = 315 15°C.
15	22	Pressure leaks - refilled to original pressure after 120 psig drop.
16	23	Max T of 270°C (ca. 5 min above 255°); Pressure leaks - allowed hydrogen to flow in to maintain pressure.
17	24	Liner broken during run - no mass balance on run. Max. T of 270°C (less than 5 min above 250°C). Large pressure rise during run.
18	25	Very large pressure rise during run - cracked outlet valve to retain pressure at 1500 psig.

Footnotes to Runs

FN	Run	Note
1	2	Reactor leaking, pressure refilled after 100 psi leak.
2	3	T overshoot to 275°C; down to 250°C within 5 minutes.
3	4	T overshoot to 290°C; down to 215°C 9 minutes later; Stabilized at 250°C at t = 30 min.
4	5	Approx. 55 min at 250°C with drop to 220°C during run.
5	7	Max. T of 264°C (less than 10 min. above 255°).
6	9	T = 260°C 10°C.
7	10	25 gm each of 1-methyl and 2-methyl naphthalene.
8	12	Max. T of 264°C (less than 5 min above 255°C); T dropped to 236° (less than 4 min below 255°C).
9	14	T = 255 10°C.
10	15	Max. T of 265°C (less than 5 min above 255°).
12	18	1 hour at 250°C then 1 hour at 300°C.
13	19	Seal failed during run; ca. 20 min residence time.
14	20	T = 315 15°C.
15	22	Pressure leaks - refilled to original pressure after 120 psig drop.
16	23	Max T of 270°C (ca. 5 min above 255°); Pressure leaks - allowed hydrogen to flow in to maintain pressure.
17	24	Liner broken during run - no mass balance on run. Max. T of 270°C (less than 5 min above 250°C). Large pressure rise during run.
18	25	Very large pressure rise during run - cracked outlet valve to retain pressure at 1500 psig.

Footnotes to Runs (continued)

FN	Run	Note
19	26	Repressurized with hydrogen if P dropped 100 psig (twice).
20	27	Repressurized with hydrogen if P dropped 50 psig (thrice).
21	28	Cooling system malfunction - T = 260 25°C.
22	29	Repressurized with hydrogen if P dropped 50 psig (thrice).
23	30	Repressurized with hydrogen if P dropped 100 psig (thrice).
24	31	T = 215 7°C. Methanol wash.
25	32	Repressurized once. Filtering took full day.
26	34	Pressure rose 300 psig during run.
27	38	Cooling system malfunction; Max. T of 270°C, less than 3 min above 255°C.
28	51	Max. T of 258°C, less than 1 minute above 255°C.
29	57	Controller malfunction: T = 250°C for ca. 45 min; T = 235 10°C for ca. 15 min.
30	60	Suspected leak - 100 psig HCl dropped to 15 psig in 7 min - could have been dissolved in $ZnCl_2$.
31	61	Run aborted - copious leak in cooling loop.
32	62	Heater malfunction. T = 195 20°C.
33	63	Hydrogen leak - P allowed to run down to 200 psig by end of run.
34	67	Run made in glassware - severe "bumping" problem encountered.
35	68	T held at 235°C to avoid excessive pressure buildup.
36	74	Heatup only.
37	77	Heatup only.
38	79	Max T of 261°C, less than 1/2 min above 255°C; Min T of 235°C, less than 2 min below 245°C.
39	80	Max T of 260°C, less than 1/2 min above 255°C.
40	82	50 min at 225°C, 6 min heatup then 15 min at 275°C.

Table 2-2. Coal Analyses. Ultimate Analyses Performed by University of California Microchemical Analysis Laboratory (replicate analyses). Proximate Analyses Performed by Commercial Testing and Engineering, Inc. (Denver, CO).

Proximate Analysis	Wyodak	Illinois No. 6
% Moisture	22.50	12.64
% Ash	10.92	14.57
% Volatile	37.14	32.96
% Fixed Carbon	29.44	39.83
Ultimate Analysis	**% Moisture-Free Coal**	
Carbon	62.49	64.30
Hydrogen	5.10	4.47
Nitrogen	00.86	1.33
Sulfur	00.50	4.35
Ash	14.40	16.68
Oxygen (Difference)	16.65	8.87
	100.00	100.00
H/C (atomic)	0.98	0.83

Reagents and Solvents

All inorganic reagents (including cylinder gases) and organic solvents used in the study, along with their sources and purities, are listed in Table 2-3.

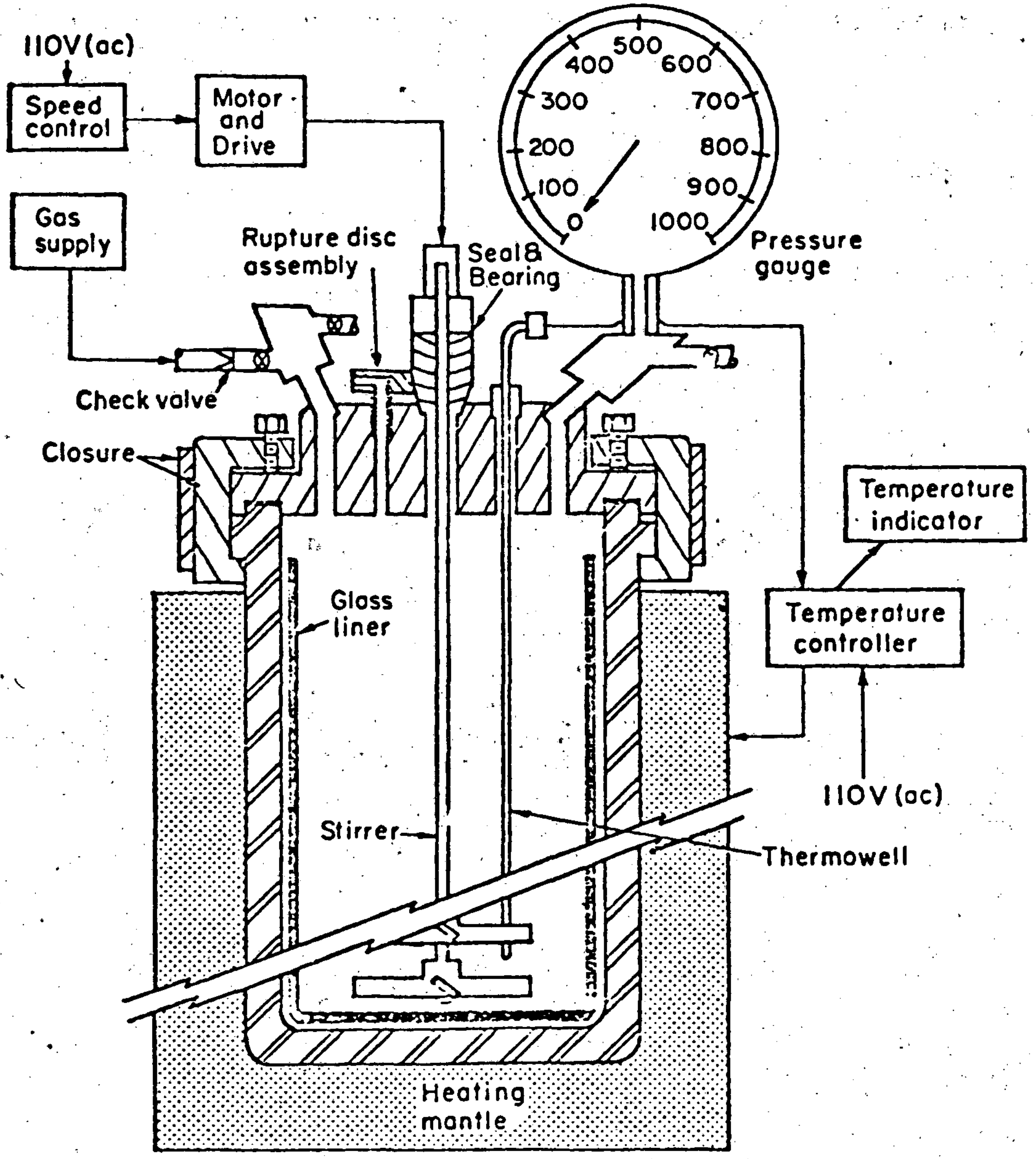
Equipment

The reactor consisted of a 600-ml stirred autoclave acquired from Parr Instrument Company, Moline, Illinois. The autoclave and associated apparatus are shown in Fig. 2-1. The initial twenty-two experiments were performed in a monel autoclave used by a previous investigator,(48) with no direct cooling inside the reactor. The remainder of the experiments were performed in a Hastelloy B autoclave, identical to the original monel reactor, but with the addition of an internal cooling loop connected to an external pump actuated by the temperature controller.

Agitation of the reactor contents was provided by a direct-drive stirrer using a self-sealing packing gland. Automatic temperature control was provided by a solid-state potentiometric system operating from an iron-constantan thermocouple; temperature was read from a deviation meter mounted on the controller. Heating was supplied by a 780-watt mantle which surrounds the reactor. The autoclave was operable to 350°C, and was equipped with a gold-coated Inconel rupture disc rated at 2000 psig.

Table 2-3. Sources and Purities of Reagents and Solvents Used.

Material	Source	Grade	Min. Purity (%)
Acridine	Student prep.		
Acetic acid	Mallinckrodt	Reagent	
Acetone	Mallinckrodt	Reagent	
Anthracene oil	Cooper Ck. Chem.		
Benzene	Mallinckrodt	Reagent	
t-Butanol	Aldrich		99.5
$CaCl_2 \cdot 2H_2O$	Mallinckrodt	Reagent	
$CdCl_2 \cdot 2.5H_2O$	Mallinckrodt	Reagent	
Cyclohexanol	Mallinckrodt	Reagent	
n-Decane	Aldrich	Technical	
o-Dichlorobenzene	Student prep.		
Dihydroanthracene	Aldrich		95.0
N,N-Dimethylformamide	Matheson/C/B	Reagent	
Ethanol	Mallinckrodt	Absolute	
Ethyl ether			
Hydrochloric acid	Mallinckrodt		36.5-38.0
Indoline	Aldrich		99.0
Methanol	Mallinckrodt	Reagent	
Mesitol	Aldrich		99.0
Perchloroethane	Aldrich	"Analyzed"	98.0
Piperidine	Aldrich		98.0
Potassium bromide	Mallinckrodt	Reagent	
Potassium chloride	Mallinckrodt	Reagent	
i-propanol	Mallinckrodt	Reagent	
Pyridine	Mallinckrodt	Reagent	
Pyrrolidine	Aldrich		99.0
Sodium chloride	Mallinckrodt	Reagent	
Sodium iodide	Allied Chem.	Reagent	
Tin Chloride$\cdot 2H_2O$	Mallinckrodt	Reagent	
p-Tol. sulfonic acid	Eastman	Reagent	
p-Xylene	Matheson/C/B		
Zn metal	Mallinckrodt		
Zinc chloride	Matheson/C/B		95.0
Zinc oxide	Matheson/C/B		
Cylinder gases			
HCl	Matheson	Technical	99.0
Hydrogen	Liquid Carbonic		99.999
Nitrogen	Pacific Oxygen		99.999
NO	Matheson	CP	99.0



XBL7711-4006

Figure 2-1. Parr Autoclave

Procedures

In a typical reaction, 273 gm (2 moles) of $ZnCl_2$ were introduced into a borosilicate-glass liner vessel for the autoclave, along with the liquefying agent for the $ZnCl_2$ (either water or an alcohol). This mixture was heated to 150°C and reweighed, and any solvent which evaporated during heatup was replaced. At this time, 50 gm of undried coal was added to the liner along with any additional solvent or reagent, and the liner was inserted into the autoclave.

The autoclave was then sealed, purged with hydrogen to remove air, and pressurized with hydrogen so as to achieve the desired pressure at the reaction temperature. The contents were heated at a rate of approximately 10°C/minute, with stirring, until the desired temperature was reached. Throughout the course of heatup and reaction, the temperature and pressure gauges were monitored and periodically recorded. After reaction for the desired period, the autoclave was immersed in a cold water bath, depressurized, and opened.

The reactor contents were dumped into 2 l. of cold distilled water, filtered in a Buchner funnel, washed with 6 l. of distilled water at 90°C, and dried to a constant weight in a vacuum oven at 110°C under 50 millibars of nitrogen.

In some of the experiments, variations in the wash procedure were used. For a few runs, the product was excessively hydrophobic, which interfered with easy removal of the $ZnCl_2$ by water washing. In these runs, the coal was initially washed with benzene to reduce the hydrophobic components, and was then washed with water as described above. The benzene-soluble material removed by such a wash was collected, dried, and weighed. For certain other runs, the product was split after water-quenching, half being washed with dilute HCl (15-20 ml concentrated HCl in 1 l. water) before the hot-water rinse.

After oven-drying, a sample of the product (referred to as melt-treated coal, or MTC) was immediately collected, pulverized with a spatula in a glass sample vial (which was inserted into a second vial containing dissicant), and submitted to the Microlab for analysis. Another sample of the MTC (approximately 2 gm) was weighed into a predried single-weight Whatman 25 x 100 mm cellulose extraction thimble. The remainder of the MTC was bottled and stored in a vacuum dessicator for later use.

A standard Soxhlet apparatus was used to extract sequentially the MTC with benzene and pyridine at their normal boiling points. The extractions were run to completion, as indicated by a colorless solution in the soxhlet siphon arm. Extraction times were typically 5 hours for benzene and 18 hours for pyridine extraction. A fine screen (200 mesh) was inserted into the top of the Soxhlet thimble to inhibit the overflow of insolubles, and whenever any material was found in the screens, the extractions were rerun with a smaller quantity of MTC.

The liquid extracts were dried in predried weighed Petri dishes. The samples were allowed to evaporate to near-dryness in the fume hood (sometimes with the aid of a hot plate at a low setting), and then placed with the thimbles and residue in a vacuum oven at 110^{o}C under 50 millibars of nitrogen. After removal from the vacuum oven, all samples were cooled in a vacuum dessicator prior to weighing.

Chemical Analysis:
Material Balance and Solubility Calculations

Elemental analyses were performed by V. T. Tashinian, Dorothy James and Tom Morrison of the 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°C, followed by off-gas absorption in NaOH + H_2O_2, and precipation of Cl with Ag or SO_4 with Ba.

In experiments in which an organic solvent was used in conjunction with $ZnCl_2$, some solvent was usually retained by the MTC and could not be removed by simple vacuum oven drying. It was of interest to estimate the amount of solvent so retained, and to correct the hydrogen-to-carbon ratio and solubility of the MTC for this amount of incorporated material. The analyses needed and calculations method developed to accomplish this will now be described.

First, the washed and dried MTC was analyzed for C, H, N, Zn, Cl and ash. The elemental analyses were combined with the weight of dried MTC recovered, to give the elemental ratios of the product (H/C, N/C, etc), and the weight of each element recovered.

Because the Zn content of water-washed MTC generally showed a stoichio metric excess relative to Cl, the Cl was assumed to be present entirely as $ZnCl_2$ (this amount of Zn was assumed to volatilize during ashing). The "excess" Zn, above that needed for $ZnCl_2$, was assumed to appear as ZnO in the ash. Thus, to count only the coal-derived mineral, this amount of ZnO was subtracted from the ash value to give a corrected ash value.

With the ash value corrected, the oxygen content (including sulfur, insignificant because of its low initial level) was then calculated by difference.

$$O + S = \text{Total MTC} - C - H - N - Zn - Cl - \text{corrected ash.} \qquad (1)$$

By comparison to the analysis of the oven-dried raw coal, the % recovery of each element was calculated.

Early runs at 250°C with no solvent additives consistently yielded 90-95% recovery of input carbon. Assuming that the low values were due to material loss in handling, it was decided to use 95% as an approximation of the amount of coal-derived carbon that could be recovered in the MTC under these conditions. With this baseline, an estimate of the amount of retained solvent could be made. This quantity was expressed as the incorporation ration R, gm incorporated C/gm coal-derived C.

$$R = (\%\ C\ \text{recovery} - 95)/95 \qquad (2)$$

Using the data from the extractions, it was then possible to calculate the solubilities. First, the total organic material extracted was determined from the amount of MTC extracted and the percentage C,H,N and O+S in the sample. A mass balance on the extraction then provided a figure for the retention of pyridine during extraction.

$$\text{Retained pyridine} = \text{benzene extract} + \text{pyridine extract} + \text{residue} - \text{MTC extracted} \qquad (3)$$

A nitrogen analysis on the pyridine extract and residue yielded an estimate of the pyridine retained in the pyridine extract.

$$\text{Fraction pyridine in extract} = \frac{\text{gm N in pyridine extract}}{\text{gm N in pyridine extract + residue}} \tag{4}$$

The amount of $ZnCl_2$ in the pyridine extract (equal to all the $ZnCl_2$ in the MTC extracted) was then calculated, knowing the $ZnCl_2$ in the MTC.

$$ZnCl_2 \text{ in pyridine extract} = \frac{\text{MTC extracted}}{\text{MTC recovered}} \times ZnCl_2 \text{ recovered} \tag{5}$$

With the above data on total organic material extracted, pyridine retention in pyridine extract, $ZnCl_2$ extracted, and weights of the benzene and pyridine extracts, the total organic solubilities could be calculated. The benzene solubility is the total weight of benzene extract, divided by the total organic material taken for extraction. The net pyridine solubility was corrected for $ZnCl_2$ and pyridine retention.

$$\text{Pyridine solubility} = \frac{(\text{gm pyridine extract} - \text{gm } ZnCl_2 \text{ extracted} - \text{gm pyridine in pyridine extract})}{\text{gm total organic material taken for extraction}} \tag{6}$$

The total pyridine solubility is the sum of the benzene and pyridine solubilities.

This total solubility was finally corrected to reflect the amount of coal-derived material which was solubilized by the process. To make this correction, it was assumed that all of the retained solvent was soluble in pyridine (rather than any part of it being insoluble); thus the corrected solubility is a measure of the minimum quantity of coal-derived organic matter solubilized by the process. With some algebraic rearrangement, this quantity was calculated as:

$$\text{Corrected Solubility} = 1 - (1 - \text{Total solubility})\,(1 + R) \qquad (7)$$

To illustrate this complex calculational procedure, the data for Run 43 are used in Table 2-4. The calculations were done using a CDC-6400 digital computer and Fortran program ZNCLOR (see Appendix B). Appendix A provides the computed results for all runs.

Additional Analyses

Scanning Electron Microscopy

Several samples representing a broad range of reaction conditions were selected for examination by scanning electron microscopy (SEM).

Samples of the dried MTC and extraction residues were mounted by sprinkling the samples over an aluminum stub which had been coated with a film of conductive carbon dissolved in acetone. The mounted samples were then sputter-coated with gold to render them conductive. The surfaces were then examined with 20 keV electrons in an AMR model-1000 scanning electron microscope.

Table 2-4. Sample Calculation Procedure for Run 43.

MTC recovered = 44.4 gm

Microlab Analysis	Wt. %	Wt. Recovered, gm	Wt. Fed, gm
C	59.76	26.53	23.9
H	5.82	2.60	1.95
N	0.77	0.34	0.33
Zn	9.89	4.39	0.0
Cl	6.47	2.87	0.0
Ash	16.00	7.10	5.51

Extraction data. MTC extracted = 2.158 gm; Bz extract = 0.6125 gm
Pyr. extract = 1.385 gm; residue = 0.588 gm

N analyses. Pyr extract 5.5% or 0.076 gm; residue 1.24% or 0.007 gm

$ZnCl_2$ in MTC = gm Cl + (gm Cl/(1.08 (gm Cl/gm Zn in $ZnCl_2$))
= 2.87 + (2.87/1.08) = 5.52 gm

"Excess Zn" = total Zn - Zn in $ZnCl_2$ = 4.39 - (2.87/1.08) = 1.74 gm
or 2.17 gm as ZnO

True ash = total ash - excess Zn (as ZnO) = 7.10 - 2.17 = 4.93

O + S = MTC - C - H - N - Zn - Cl - true ash
= 44.4 - 26.5 - 2.6 - 4.4 - 2.9 - 4.9 = 2.3

% recovery of each element = (gm recovered/gm feed) x 100

Element	% Recovery
C	111.00
H	133.33
N	103.03
O + S	35.06
Ash	89.47

Incorporation ratio (R) = (% C recovery - 95)/95 = (111 - 95)/95
= 0.168 gm incorporated C/gm coal C

$$\text{Organic matter extracted} = \frac{(\text{C + H + N + O + S recovered})(\text{MTC extracted})}{(\text{MTC recovered})}$$

= (26.53 + 2.60 + 0.34 + 2.3) (2.158) / (44.4)

= 1.54 gm

Table 2-4. Sample Calculation Procedure for Run 43 (continued).

Pyridine retention = Bz extract + pyr extract + residue - MTC extracted)
= 0.6125 + 1.385 + 0.588 - 2.158 = 0.4275 gm

Fraction pyridine in pyr extract = (gm N in pyr ext)/(gm N in res + pyr ext) = 0.076/(0.007 + 0.076) = 0.916

Pyridine retained in Pyridine extract = (gm pyr retained)
(fraction pyr in pyr ext)
= (0.4275)(0.916) = 0.392 gm

Benzene solubility = Bz extract/organics extracted
= 0.6125/1.54 = 39.77%

Pyridine solubility = $\frac{\text{Pyr ext - pyr ret in pyr ext - ZnCl}_2\text{ ext}}{\text{organics extracted}}$
= (1.385 - 0.392 - (5.52)(2.158/44.4)/1.54
= 0.725/1.54 = 47.08%

Total pyridine solubility = Bz sol. + pyr sol. = 39.77 + 47.08
= 86.85%

Corrected solubility (or minimum coal-derived solubility)
= 1 - (1 - total solubility) (1 + R)
= 1 - (1 - 0.8685) (1 + 0.168)
= 84.65%

In general, three magnifications were used. The first magnification (250x) allowed an overall view of a complete particle and easy scanning of the entire sample. The two larger magnifications (1000 x and 3000 x) provided more detailed examinations of specific areas of interest in the lower magnification.

Gel-Permeation Chromatography

MTC samples from the same runs which were examined by SEM were also examined by gel permeation chromatography (GPC).

Samples of the MTC were removed from the vacuum desiccator and extracted sequentially with benzene and pyridine in an atmospheric Soxhlet extractor. The solvent with fresh extract was immediately filtered through Millipore Teflon-type FH filters (0.5 μm pore size). Samples of 5 to 50 μl of the solutions were injected into the μ-Styragel (100 Å + 500 Å + 1000 Å) column with a pyridine flowrate of 1 ml/min and a chartspeed of 1 cm/min. Plots of uv absorbance at 365 and 313 nm versus retention time or volume were generated. Both benzene and pyridine extracts were examined separately. The effects of temperature, hydrogen pressure, reactor residence time, reaction solvent, and wash conditions on the elution of soluble products from the GPC column were determined.

The effect of the GPC column is to fractionate components in a mixture according to molecular size. High-molecular-weight products come out first, the lightest products last. The actual order of elution may be somewhat different, however, due to specific chemical interactions of some compounds with the column. Furthermore, the use of uv absorbance for detection creates the additional problem of unequal absorbances for different compounds which may obscure the actual concentration information. These difficulties with GPC analysis diminish its utility as an absolute measure of molecular weight distribution. Therefore, no attempt is made in this work to associate specific GPC tracings with molecular weight. Comparison of tracings from similar experiments where only one variable was altered has been used to examine the effect of this variable on the molecular-weight distribution.

Gas Analyses

For several runs, a sample of the product gas was collected for analysis, using an evacuated 150 ml stainless-steel sampling cylinder at the end of the reaction period just prior to quenching.

The gas samples were analyzed using a combination of gas chromatography (GC), mass spectrometry (MS) and coupled GC-MS. The Varian model temperature programmable GC with a 1/8" x 6' column packed with Chromosorb 106 was used. Hydrogen flowrate was set at 30 cc/min, with filament temperature at 150°C, and filament current at 186 ma. A one-ml sample was injected to the column at an initial temperature of 50°C (1 minute) with a 7°C/min rise to 200°C. A thermal conductivity cell was used for detection. The GC was calibrated using a mixture of methane, ethane, propane, propene, CO and CO_2.

GCMS Analysis, using a Finnigan model 4023 unit and MS analyses, using a CEC Model 21103 unit were carried out by Dr. Amos Newton and co-workers at Lawrence Berkeley Laboratory. A detailed description of this equipment is given elsewhere.(103)

Melting Behavior of the $ZnCl_2$-KCl-NaCl System

Early in the course of this investigation, it was thought that $ZnCl_2$ melts with lower viscosity or lower melting points would be desirable. Lower viscosity could enhance melt penetration; lower melting point could eliminate the requirement for water addition to make the $ZnCl_2$ liquid at 250°C.

In an effort to lower the viscosity and melting point of the $ZnCl_2$, a study was undertaken to determine the melting-freezing behavior of the $ZnCl_2$-KCl-NaCl system. Work done at Montana State University(102) had indicated that the addition of KCl to $ZnCl_2$ had little effect on activity at 450°C, while reducing melt viscosity so as to facilitate separation of product from the melt.

Melting-point experiments were conducted using various composition mixtures of NaCl, KCl and $ZnCl_2$. Liquidus points (temperature at which solid first forms on freezing) and solidus points (at which the last liquid disappears during freezing) were measured for mixtures as they were slowly heated or colled. The results are listed in Tables 2-5 and 2-6.

Increased conversion of coal to soluble materials has been reported using iodide and bromide salts with $ZnCl_2$.(101) We therefore investigated the melting behavior of the $ZnCl_2$-KBr-NaI system and tested its activity at 250°C relative to the activity of $ZnCl_2$-H_2O (see Table 2-7).

As can be seen from these data, significant reductions in $ZnCl_2$ melting point can be achieved through addition of alkali halides. The mixtures were also observed to exhibit significantly reduced viscosity, although no quantitative viscosity data were taken.

Table 2-5. Liquidus and Solidus Points of the $ZnCl_2$-KCl-NaCl System. Binary Experiments.

A. $ZnCl_2$-KCl Binary System

Mole Fraction $ZnCl_2$	Liquidus Temperature (°C)	Solidus Temperature (°C)
1.00	303	
.95	300	
.95[1]	293	283
.95[1]	290	271
.90	295	268
.85	287	248
.85[1]	281	240
.80	273	249
.75	260	243
.75[1]	260	246
.70	254	249
.55	225	217

B. $ZnCl_2$-NaCl Binary System

Mole Fraction $ZnCl_2$	Liquidus Temperature (°C)	Solidus Temperature (°C)
.95	298	289
.90	297	286
.80	287	257
.75	281	246
.70	274	250
.60[2]	254	246
.50	312	248

---

1 - Technical grade $ZnCl_2$ used in place of reagent grade.
2 - Eutectic point.

Table 2-6. Liquidus and Solidus Points of the $ZnCl_2$-KCl-Nacl System. Ternary Experiments.

Mole Fractions			Liquidus Temperature (°C)	Solidus Temperature (°C)
$ZnCl_2$	KCl	NaCl		
A. Zn/Na = 3/1				
.75	0.0	.25	281	246
.67	.11	.22	244	196
.63	.16	.21	224	194
.60	.20	.20[1]	200	194
.55	.27	.18	208	194
.50	.33	.17	206	192
.43	.43	.14	250	192
B. Zn/K = 3/1				
.75	.25	0.0	260	243
.67	.22	.11	239	197
.63	.21	.16	225	196
.60	.20	.20[1]	198	196
.55	.18	.27	234	196
.50	.17	.33	275	287
.46	.15	.39	310	296
C. Zn/Na = 8.5/1				
.85	.05	.10	292	220
.80	.11	.09	287	200
.73	.18	.09	270	200
.69	.23	.08	251	
.60	.33	.07	235	198
.53	.41	.06	215	202
.45	.50	.05	272	

---

[1] - Eutectic point.

Table 2-7. Liquidus and Solidus Points of the $ZnCl_2$-KBr-NaI System.

Mole Fractions			Liquidus Temperature (°C)	Solidus Temperature (°C)
NaI	KBr	$ZnCl_2$		
0.0	.10	.90	293	265
0.0	.20	.80	278	250
0.0	.25	.75	265	248
.11	.22	.67	186	158
.20	.20	.60[1]	170	140

---

[1] - Eutectic point.

Reproducibility - Replicate Experiments and Extractions

Several autoclave experiments were repeated to determine the reproducibility of solubilities and of solvent incorporation. Three runs were done in duplicate and one in triplicate (Table 2-8). Statistical analyses (Table 2-9) show that corrected solubilities have a standard deviation of 10% of the reported value; incorporation ratios have a 20% standard deviation. Table 2-7 and Tables 3-20 and 3-21 show that there are differences in elemental recoveries, product Zn/Cl ratios, and pressure-time behavior in replicate runs. These actual run-to-run differences, heterogeneity of the treated coal (of which only 1-2 gm were extracted), and inaccuracies in the extractions are likely to have contributed to variation in the solubilities for repeated runs.

Variability in replicate benzene extractions from the same MTC are seen in Table 2-10. Variations in benzene solubilities were found to be unrelated to either the amount of MTC extracted or the extraction time. These results underscore the need for a method more reliable than Soxhlet extraction for determining conversion. The solubility deviation encountered in repeat runs is probably largely due to the inaccuracies of this measurement technique.

Table 2-8. Replicate Autoclave Experiments. 273 gm $ZnCl_2$; 50 gm coal; 50 gm methanol; T = 250°C; to = 60 min.; water wash unless otherwise noted.

Run	P_{H_2} (psig)	Additive (gm)	Solubilities (Pct. daf)			R (gm/gm)	Percent Recovery			Zn/Cl in MTC (Weight)
			Uncorrected							
			Benzene	Bz+Pyridine	Corrected		C	H	O+S	
15	200		29.9	70.0	64.6	0.18	112.1	126.2	54.3	2.06
37	200		27.9	73.8	70.1	0.14	108.5	124.9	38.5	2.38
39[1]	500		45.0	76.3	72.3	0.17	110.7	127.4	39.6	1.96
75	500		37.7	73.6	68.2	0.20	114.2	131.8	47.0	2.33
57	500	ZnO - 9.0	26.1	67.2	64.1	0.10	104.1	134.9	86.8	6.69
69	500	ZnO - 9.0	29.2	77.0	74.3	0.12	106.1	126.9	51.4	5.21
43	800		39.7	86.5	84.2	0.17	111.0	132.5	35.3	1.53
72	800		38.5	93.4	92.0	0.20	114.0	136.0	17.6	1.37
73	800		35.9	81.9	78.9	0.16	110.6	130.5	33.2	2.59
72[2]	800		37.1	100.0	100.0	0.20	114.0	136.0	17.6	0.79
73[2]	800		38.9	100.0	100.0	0.16	110.6	130.5	33.2	0.98

1 - Benzene washed

2 - HCl washed

Table 2-9. Statistical Analysis of Replicate Autoclave Experiments.

	Solubilities (Pct. daf.)						Incorporation R (gm/gm)	
	Benzene		Benzene+Pyridine		Corrected			
Runs	Mean	Std.Dev.	Mean	Std.Dev.	Mean	Std.Dev.	Mean	Std.Dev.
15/37	33.9	8.0	71.9	3.8	67.3	5.4	0.16	0.04
39/75	diff wash		75.0	2.8	70.3	4.2	0.19	0.04
57/69	27.7	3.2	72.1	9.8	69.2	10.4	0.11	0.02
43/72/73	38.0	1.6	87.3	4.7	85.1	5.3	0.18	0.02

Table 2-10. Replicate Benzene Extractions

Run	Benzene Solubility (Pct. daf)	Extraction Time (hr:min)	Gm Extracted MTC
10	41.3	?	10.0
	47.3	5:00	1.179
15	24.4	?	7.014
	25.6	?	4.36
	27.7	4:00	
	26.1	?	4.24
	29.9	5:00	1.153
16	13.9	?	9.22
	11.2	3:50	1.476
26	39.2	?	9.798
	42.3	23:50	1.451
	38.9	4:30	1.214
22	5.6	?	9.974
	5.4	?	7.750
29	58.7	?	5.090
	56.0	?	2.774
	56.8	23:00	1.175
30	33.8	?	9.268
	26.3	?	5.929
	29.4	?	5.687
	31.0	5:00	6.617
	29.8	5:00	1.602
	30.3	3:00	3.029
33	14.8	?	5.546
	15.2	?	3.680
34	13.2	?	5.783
	14.8	?	6.441
36	23.2	?	4.561
	26.6	4:30	1.103
42	61.5	3:40	5.460
	65.9	5:30	1.226
43	39.7	4:30	4.753
	39.7	5:10	2.158
45	30.7	4:57	4.359
	29.1	19:45	2.672
50	35.6	5:00	3.731
	36.5	2:30	1.440
54	41.9	5:10	1.933
	38.7	5:00	1.155
55	34.2	4:20	1.966
	31.9	2:50	0.703
	31.5	22:50	0.795
57	30.2	16.25	1.315
	26.1	4:50	1.146

Table 2-10. Replicate Benzene Extractions (continued)

Run	Benzene Solubility (Pct. daf)	Extraction Time (hr:min)	Gm Extracted MTC
77(HCl wash)	22.0	4:57	1.452
	20.6	4:50	1.091
79(HCl wash)	39.6	4:50	1.237
	43.2	5:10	0.7175
80(HCl wash)	19.5	4:55	1.5925
	18.1	4:50	0.801

CHAPTER 3

RESULTS

Autoclave Experiments

The $ZnCl_2$-Water System

Preliminary experiments were focused on the effects of temperature and pressure (Table 3-1). Solubilization in pyridine is roughly first-order in hydrogen pressure at 250°C. There is a strong temperature effect with almost no conversion at 200°C and 50% at 300°C for a one-hour treatment.

Effects of certain inorganic additives are seen in Table 3-2. A low-melting mixture of 60% (molar) $ZnCl_2$ - 20% KBr - 20% NaI was much less active than an equal amount of $ZnCl_2$. The less viscous mixture of $ZnCl_2$-KCl-NaCl was similarly less active. However, addition of 10% $CaCl_2$ to the mixture had little effect on solubility. As ion-exchanged calcium from the coal ash would likely build up in a recycled $ZnCl_2$ melt, it is encouraging that calcium does not poison the activity.

Addition of Zn dust to the $ZnCl_2$-water system had the most pronounced positive effect of the inorganic additives, apparently promoting hydrogenation activity. The extent to which the zinc dissolved is not known. Slight increases in benzene and pyridine solubilities occurred, with a sharp increase in H/C ratio.

It can be concluded from this work and Derenscenyi's(49) that only modest increases in solubilization activity of the $ZnCl_2$-water melt will result through use of various co-catalysts. More promising

Table 3-1. Effect of Temperature and Hydrogen Pressure on the $ZnCl_2$-H_2O System. 273 gm. $ZnCl_2$; 27 gm H_2O; 50 gm Coal; t=60 min.

Run	T (°C.)	P_{H_2} (psig)	Solubilities Benzene	Total	H/C Atomic
62[3]	200	0	3.1	14.8	0.94
64	250	0	4.2	16.2	0.90
46	250	200	4.7	20.8	0.86
63[1]	250	500	5.3	23.8	0.89
22[2]	250	500	5.6	27.3	0.90
65	250	500	6.3	28.3	0.88
56	250	800	7.4	35.6	0.85
11	275	500	9.3	29.0	0.86
13	300	500	19.3	50.7	0.85
0[4]	25	0	1.8	12.2	0.98

---

[1] Pressure allowed to leak out to 275 psig by end of run.

[2] Pressure leak - refilled to maintain 500 psig H_2.

[3] Heater failure; T = 195 °C ± 20°C.

[4] Raw, untreated Wyodak coal.

Table 3-2. Effect of Inorganic Additives to $ZnCl_2$-H_2O Melt.
273 gm $ZnCl_2$; 27 gm H_2O; 50 gm coal; T = 250°C.; t = 60 min.

Run	Additive (gm)	P_{H_2} (psig)	Solubilities (Pct. daf)		Atomic H/C
			Benzene	Total	
3	KBr(45.3); NaI(57.1)[1]	500	3.6	13.1	0.90
5	KCl(37.6); NaCl(29.4)[1]	500	2.3	11.2	0.96
23	$CaCl_2$(24.7)	500	5.5	25.8	0.85
80	Zn(10.0)	800	10.8	37.4	1.11
82	Zn(10.1)[2]	1000	7.0	35.1	1.08
65	H_2O Alone	500	6.3	28.3	0.88
56	H_2O Alone	800	7.4	35.6	0.85

[1] Total melt weight (NaX + KX + $ZnCl_2$) = 273 gm.

[2] 225°C for 50 min followed by 275°C for 15 min.

results were found using solvent additives.(48) The focus of this work, therefore, shifted toward an investigation of the effects of solvents used with the $ZnCl_2$-water medium (Table 3-3).

Addition of piperidine to the melt produced an MTC only 4.4% pyridine-soluble: piperidine apparently poisoned the catalyst. Dihydroanthracene, while improving the solubility, was almost quantitatively retained in the MTC after vacuum oven drying.

In an effort to improve the ability of the medium to extract solubilized product and to expose the unconverted coal for further reaction, p-xylene was added. Unfortunately, the MTC from this treatment was only slightly more soluble than the raw coal; perhaps the xylene may have preferentially wet the coal, excluding the $ZnCl_2$ from contacting.

Ouchi and coworkers have shown that treatment of coal with paratoluenesulfonic acid (PTSA) in phenol is effective for depolymerization.(69-72) Incorporation of phenol by ortho-para alkylation of the coal limits the process potential of such a system, however. Addition of PTSA and t-butanol to $ZnCl_2$ resulted in a product with only 10% total solubility uncorrected, and virtually no coal-derived solubility when corrected for the retained solvent. The addition of mesitol (2,4,6-trimethyl phenol, i.e. ortho and para positions occupied) was examined to determine if positive action of a phenol could be gained without high incorporation. Only one-tenth gm mesitol/gm coal organics was retained, and a moderate increase in solubility to 39% resulted.

The best result using solvent additives with the $ZnCl_2$-water system was found using methyl naphthalene and tetralin. Neavel has postulated that naphthalene may act as a hydrogen shuttler, carrying

Table 3-3. Effect of Organic Solvents with $ZnCl_2$-H_2O Melt. 273 gm $ZnCl_2$; 27 gm Coal; 50 gm Solvent; T = 250°C; P = 500 psig; t = 60 min.

Run	Solvent	Corrected Solubility (Pct. daf)	R (gm Retained Solv/ gm Coal Organic)	Corrected Atomic H/C
2	Piperidine	4.4	.08	0.98
4	Dihydroanthracene	40.8	2.00	0.86
14	p-xylene[1]	14.7	.16	0.89
10	Methyl-naphthalene[2] + 10 gm tetralin	55.0	.37	0.96
7	Mesitol	39.4	.12	0.91
9	t-Butanol + PTSA[3]	0.0	.85	----
65	H_2O Alone	28.3	.00	0.88

---

[1] 24.7 gm $CaCl_2$ also present.

[2] 25 gm each of 1- and 2-methyl naphthalene

[3] PTSA = p-toluene sulphonic acid; 50 gm of each solvent. Reaction at 260°C ± 10°C.

hydrogen from hydrogen-rich portions of the coal to hydrogen-deficient areas.(125) Tetralin is a recognized hydrogen-donor. The combination of the two could add hydrogen-transfer capacity to the $ZnCl_2$ and enhance the dissolution of products. Solubility is enhanced to 55%, corrected, but with relatively large incorporation of about 0.4 gm/gm. This incorporation may be largely as methyl naphthalene, since Hershkowitz reports incorporations of only about 0.15 for runs using $ZnCl_2$-water-tetralin.(115)

$ZnCl_2$-Solvent Experiments

The next step in investigating the role of solvents was to replace the water with solvents which would themselves dissolve the $ZnCl_2$ (Table 3-4).

Acetic acid, although very effective in liquefying $ZnCl_2$, apparently had no impact on the coal. There was virtually no incorporation, and the MTC solubility was very similar to that of dried raw coal.

N,N-dimethyl formamide (DMF) apparently poisoned the $ZnCl_2$, and was retained in the product; MTC from this treatment was only 6% soluble (uncorrected), and contained about 0.15 gm DMF per gm coal organics.

The use of methanol proved very favorable. Methanol retention was reasonably low (0.2 gm/gm or less), and the solubility more than doubled compared to runs with $ZnCl_2$ and water. This high activity with low retention, combined with the potential of producing low-cost methanol from coal, make it a highly attractive solvent for coal conversion with $ZnCl_2$.

Table 3-4. Effect of Solvents in $ZnCl_2$-Solvent System. 273 gm $ZnCl_2$; 50 gm coal; 50 gm solvent; T = 250°C; P_{H_2} = psig; t = 60 min.

Run	Solvent	Solubility (Pct. daf)	R (gm Retained Solv/ gm coal organic)
25	N,N Dimethyl-formamide	0.0	0.14
38	Acetic Acid	10.5	0.00
15/37	Methanol[1]	67.3	0.17
54	Ethanol	100.0	0.39
33	i-Propanol	34.9	0.36
34	t-Butanol	12.2	0.34
36	Acetone	66.2	0.68
65	H_2O (27 gm)	28.3	0.00

[1] Average of duplicate runs.

The methanol result prompted investigation of other alcohols. Ethanol produces totally soluble product in one hour at 250°C, with roughly twice as much incorporation as methanol. Isopropanol and t-butanol incorporate nearly as much as ethanol, but produce considerably less solubility. Absence of normal pressure drop during these runs suggests that these alcohols were dehydrated by the $ZnCl_2$, producing alkenes.

Acetone was also tested as a $ZnCl_2$ solvent yielding a product with a solubility similar to that of $ZnCl_2$-methanol treated coal, but with roughly four times the incorporation.

The results of the $ZnCl_2$-solvent experiments made it unlikely that further investigation would reveal a medium which combined the high activity, low incorporation, and low solvent cost of the $ZnCl_2$-methanol system. It was decided to focus on the effects of additives to this medium, and to characterize its response to variations in temperature, pressure stoichiometry, and residence time.

The Effect of Inorganic Additives with $ZnCl_2$-Methanol Melt

Numerous inorganic additives were screened for their effects on product solubility and H/C ratio in the $ZnCl_2$-methanol melt (Table 3-5). Acidic and basic additives and possible hydrogenation additives were screened.

The proton acidity of the $ZnCl_2$ medium may be moderated by addition of either HCl or ZnO: HCl enhances Bronsted acidity while ZnO reduces Bronsted acidity by removing any HCl which may form in the reaction mixture. Since the activity of the $ZnCl_2$ could perhaps be due to

Table 3-5. Effect of Inorganic Additives to $ZnCl_2$-Methanol Melt.
273 gm $ZnCl_2$; 50 gm MeOH: 50 gm Coal; T = 250°C; t = 60 min.

Run	Additive (gm)	P_{H_2} (psig)	Corrected Solubility (Pct. daf)	R (gm Retained Solv/ gm Coal Organic)	Corrected Atomic H/C
58	HCl (100 psig)	500	100.0	0.16	0.84
69	ZnO (9.0)[3]	500	69.2	0.11	1.10
79	Zn (1.0)	500	73.6	0.15	0.86
27	$CdCl_2$ (38.5)[1]	200	44.3	0.16	0.76
28	$SnCl_2$ (42.1)[2]	200	0.0	0.19	0.55
39/75	None[3]	500	70.3	0.18	0.79
15/37	None[3]	200	67.3	0.17	0.76

[1] 11.4 gm water present with $CdCl_2$

[2] 36.0 gm water present with $SnCl_2$

[3] Average of two replicate runs

such Bronsted acidity, it was of interest to determine the effects of ZnO and HCl on the melt.

Addition of 100 psig HCl to the reaction mixture had a strongly positive effect on the product solubility. As will be seen, however, this effect is no greater than the effect of a dilute HCl wash.

ZnO addition (5 mole-%) had little effect on product solubility, but had a surprising effect on H/C ratio. This result could be due to analytical error, perhaps a CO_2 sink or a water source in combustion analysis, giving low carbon or high hydrogen values. The potential of using ZnO as a hydrogenation co-catalyst requires further investigation. It is notable that no sizeable negative effect is found from ZnO addition. A run containing 10 mole-% ZnO (Run 55) was also made, but different wash conditions do not allow direct comparison to the runs in Table 3-5. Attempts to produce a melt containing 20 mole-% ZnO resulted in a non-liquid medium.

In the hope of gaining hydrogenation activity, Zn metal, $SnCl_2$, and $CdCl_2$ were added in other runs. One gm Zn metal had virtually no effect on solubility but a slight positive effect on H/C ratio. Both $SnCl_2$ and $CdCl_2$ were added as hydrated salts and produced negative effects, which may be due to the presence of the added water.

The Effect of Organic Additives with $ZnCl_2$-Methanol Melt

Several solvents were screened for their effect with the $ZnCl_2$-methanol medium. The results range from deactivation to enhanced reaction (Table 3-6).

Table 3-6. Effect of Solvent Additives to $ZnCl_2$-Methanol Melt.
273 gm $ZnCl_2$; 50 gm MeOH; 50 gm Coal

Run	Solvent (gm)	P_{H_2} (psig)	Corrected Solubility (Pct. daf)	R (gm Retained MeOH/ gm Coal Organic)
21	n-Decane (50)	250	41.4	0.19
35	C_2Cl_6 (50)	200	40.5	0.43
53	o-Cl_2-benzene (30)	200	33.5	0.16
66	Pyrrolidine (10.5)	500	65.6	0.13
32	Cyclohexanol (10)	200	68.7	0.39
26	Anthracene Oil (10)	250	73.7	0.77
29	Tetralin (10)	200	77.4	0.65
59	Indoline (10)	500	81.5	0.27
39/75	Methanol only	500	70.3	0.18
15/37	Methanol only	200	67.3	0.17

Three of the solvents tested produced markedly lower MTC solubility. Addition of n-decane to the melt produced 40% pyridine-soluble MTC with about the same incorporation as $ZnCl_2$-methanol alone. A similar solubility is achieved using incorporate strongly. The best solvent additive tested was indoline, which in addition to having hydrogen-donor capacity of its own, may be even more prone to hydrogen-donation by interaction with $ZnCl_2$.

The Effect of $ZnCl_2$-Methanol Treatment Conditions on MTC Properties

The high solubilities and low incorporations resulting from use of methanol as the $ZnCl_2$ solvent prompted further investigation of this coal-conversion system. Effects of the key variables - time, temperature, pressure, and $ZnCl_2$/methanol ratio - on solubilization, incorporation, and H/C ratio are summarized here.

Experiments at two hydrogen pressures and three temperatures show the effect of temperature on MTC properties (Table 3-7 and Figure 3-1). A sharp increase in solubility is seen between 225 and 275°C. Near-total solubility results in one hour at 275°C, at either 200 or 800 psig H_2. Even at 225°C, significant changes in the coal are occurring, giving rise to 25 to 40% solubility. Apparent activation energies between 225 and 250°C for 200 psig and 800 psig hydrogen are 31 and 28 kcal/mole respectively, assuming first-order-irreversible kinetics.

The effect of temperature on incorporation ratio is less clear-cut. At 800 psig, there seems to be a leveling off of incorporation with higher temperatures between 0.15 and 0.20 gm/gm. At 200 psig, however, the incorporation continues to rise with increasing temperature.

Table 3-7. Effect of Reaction Temperature on the $ZnCl_2$-Methanol Melt. 273 gm $ZnCl_2$; 50 gm coal; 50 gm MeOH; t = 60 min.

Run	T(°C)	P_{H_2} (psig)	Corrected Solubility (Pct. daf)	R (gm Retained MeOH/ gm Coal Organic	Corrected Atomic H/C
52	225	200	26.4	0.12	0.83
15	250	200	64.6	0.18	0.76
37	250	200	70.1	0.14	0.86
30	275	200	95.6	0.32	0.72
30	275	200	95.6	0.32	0.72
49	225	800	40.0	0.11	0.88
43	250	800	84.2	0.17	0.86
72	250	800	92.0	0.20	0.80
73	250	800	81.9	0.16	0.85
48	275	800	99.1	0.17	0.86

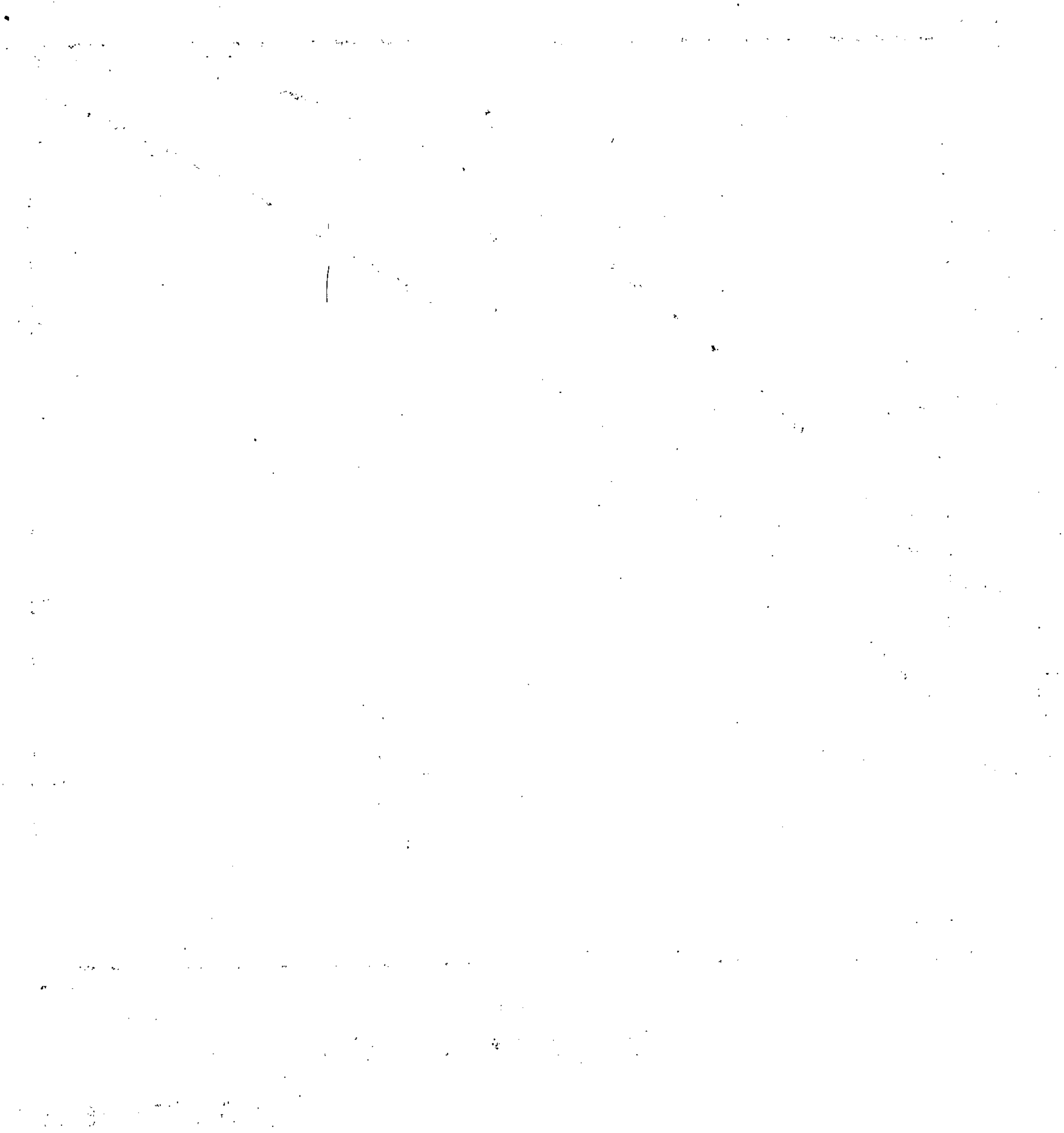
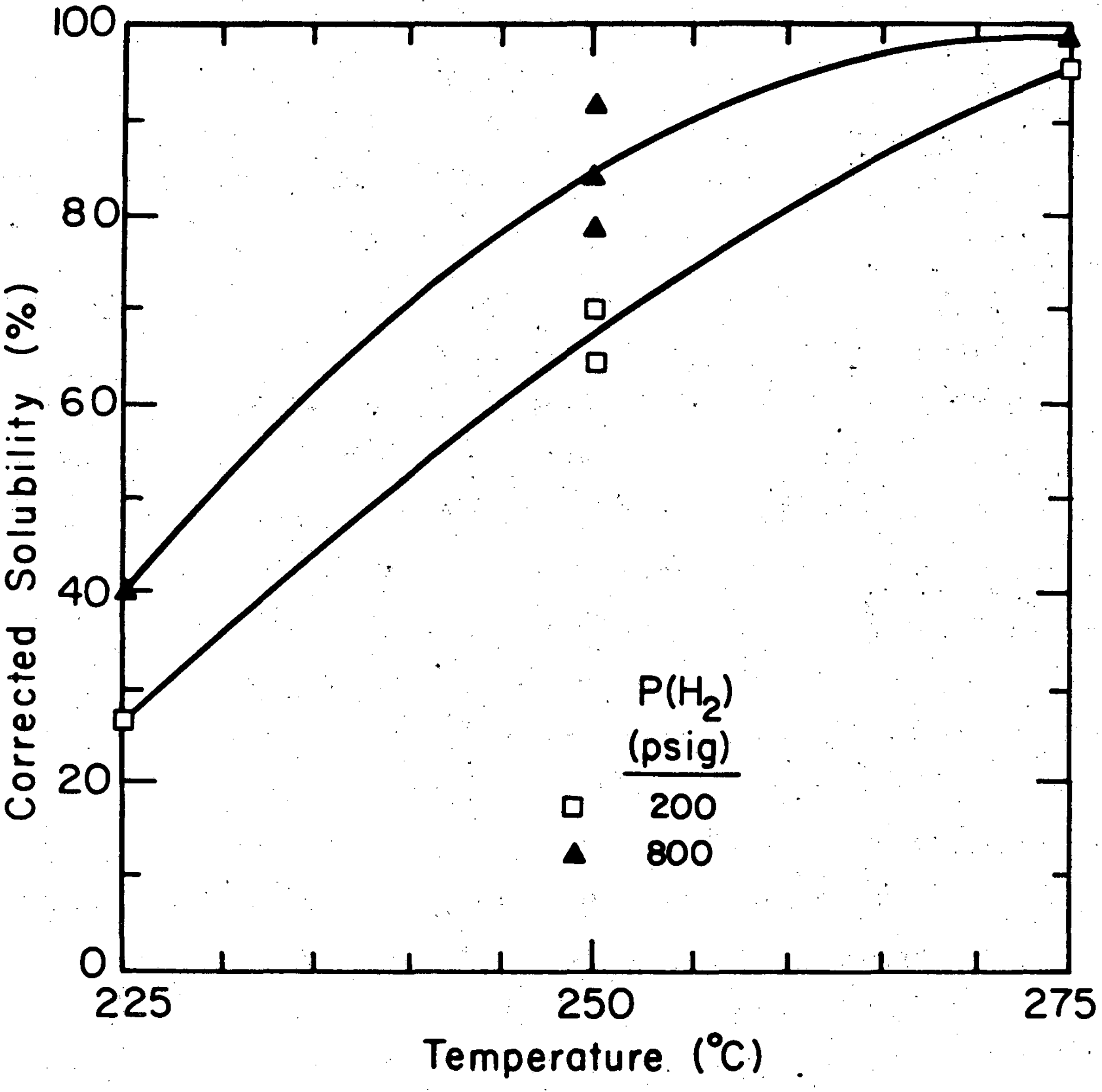


Figure 3-1. Effect of Temperature and Hydrogen Pressure on Solubility of $ZnCl_2$-Methanol Treated Coal.



XBL 796-6434

Figure 3-1.

This implies that at the higher bond cleavage rates, higher hydrogen pressures are necessary to prevent retention of the methanol.

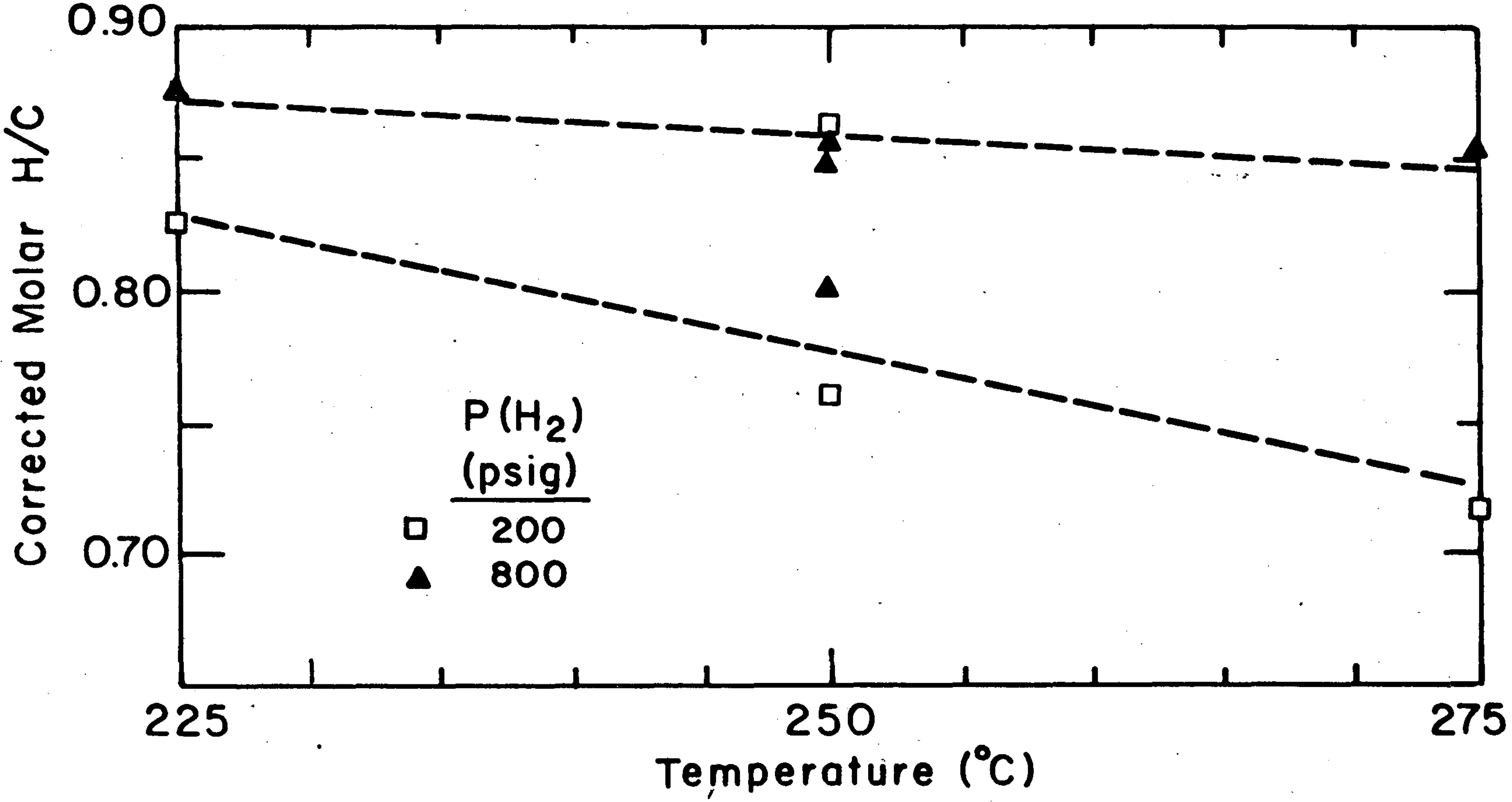
The desirability of higher pressures at higher temperatures is seen again in the behavior of the corrected product H/C ratio (Figure 3-2). (H/C ratios have been corrected by assuming incorporation of carbon as $-CH_3$ groups, and deducting the added methyl hydrogens to determine the H/C ratio of the coal-derived portion of the MTC.) Relative to the raw coal with an H/C of 0.97, the ratio remains near 0.85 at 800 psig but drops toward 0.7 at 200 psig.

The effect of hydrogen pressures up to 800 psig was examined at various methanol loadings and temperatures (Table 3-8). Data were taken at 250°C for hydrogen pressures of 0, 200, 500, and 800 psig. The incremental solubility appears to be first-order in hydrogen pressure (Fig. 3-3), rising from 60% with no hydrogen to 84% with 800 psig. The slope is somewhat less at 225°C, and also at 275°C where the reaction is near completion.

The same near-linear dependence on hydrogen pressure is seen at various methanol loadings (Figure 3-4). Here, the slopes are relatively independent of methanol loading.

The effect of hydrogen pressure on incorporation is seemingly dependent on methanol loading (Fig. 3-5). At 50 gm methanol, incorporation levels off around 0.17 gm/gm for hydrogen pressures above 200 psig. For 25 gm methanol, at 800 psig of hydrogen, incororation appears to decrease to as low as 0.05 gm/gm. The H/C ratio of the MTC is also dependent on methanol loading (Fig. 3-6).

Figure 3-2. Effect of Temperature and Hydrogen Pressure on Hydrogen-to-Carbon Ratio of $ZnCl_2$-Methanol Treated Coal.


0.90
0.80
0.70
Corrected Molar H/C
225
250
275
Temperature (°C)
P (H2)
(psig)
□ 200
▲ 800

XBL 796-6435

Table 3-8. Effect of Hydrogen Pressure on the $ZnCl_2$-Methanol Melt. 273 gm $ZnCl_2$; 50 gm coal; t = 60 min.

Run	T(°C)	P_{H_2} (psig)	Methanol Loading (gm)	Corrected Solubility (Pct. daf)	R (gm Retained MeOH/ gm Coal Organic)	Corrected Atomic H/C
40	250	200	25	54.8	0.16	0.70
47	250	800	25	73.6	0.05	0.96
45	250	0	50	55.7	0.31	0.52
50	250	0	50	66.9	0.31	0.54
15	250	200	50	64.6	0.18	0.76
37	250	200	50	70.1	0.14	0.86
39	250	500	50	72.3	0.17	0.82
75	250	500	50	68.2	0.20	0.75
43	250	800	50	84.2	0.17	0.86
72	250	800	50	92.0	0.20	0.80
73	250	800	50	78.9	0.16	0.85
52	225	200	50	26.4	0.12	0.83
49	225	800	50	40.0	0.11	0.88
30	275	200	50	95.6	0.32	0.72
48	275	800	50	99.1	0.17	0.86

Figure 3-3. Effect of Hydrogen Pressure at Various Temperatures on Solubility of $ZnCl_2$-Methanol Treated Coal. (Conditions as in Table 3-8)

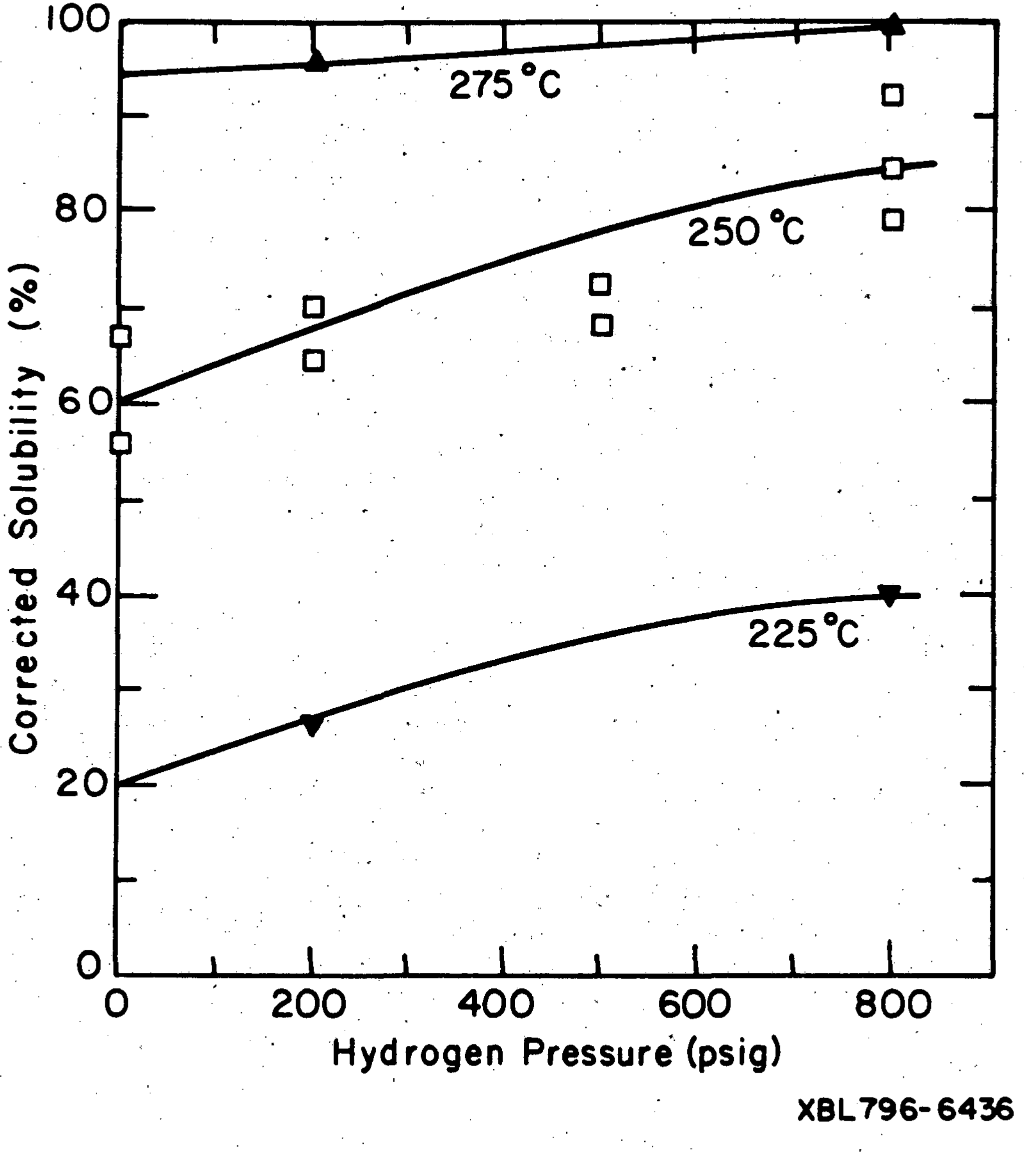
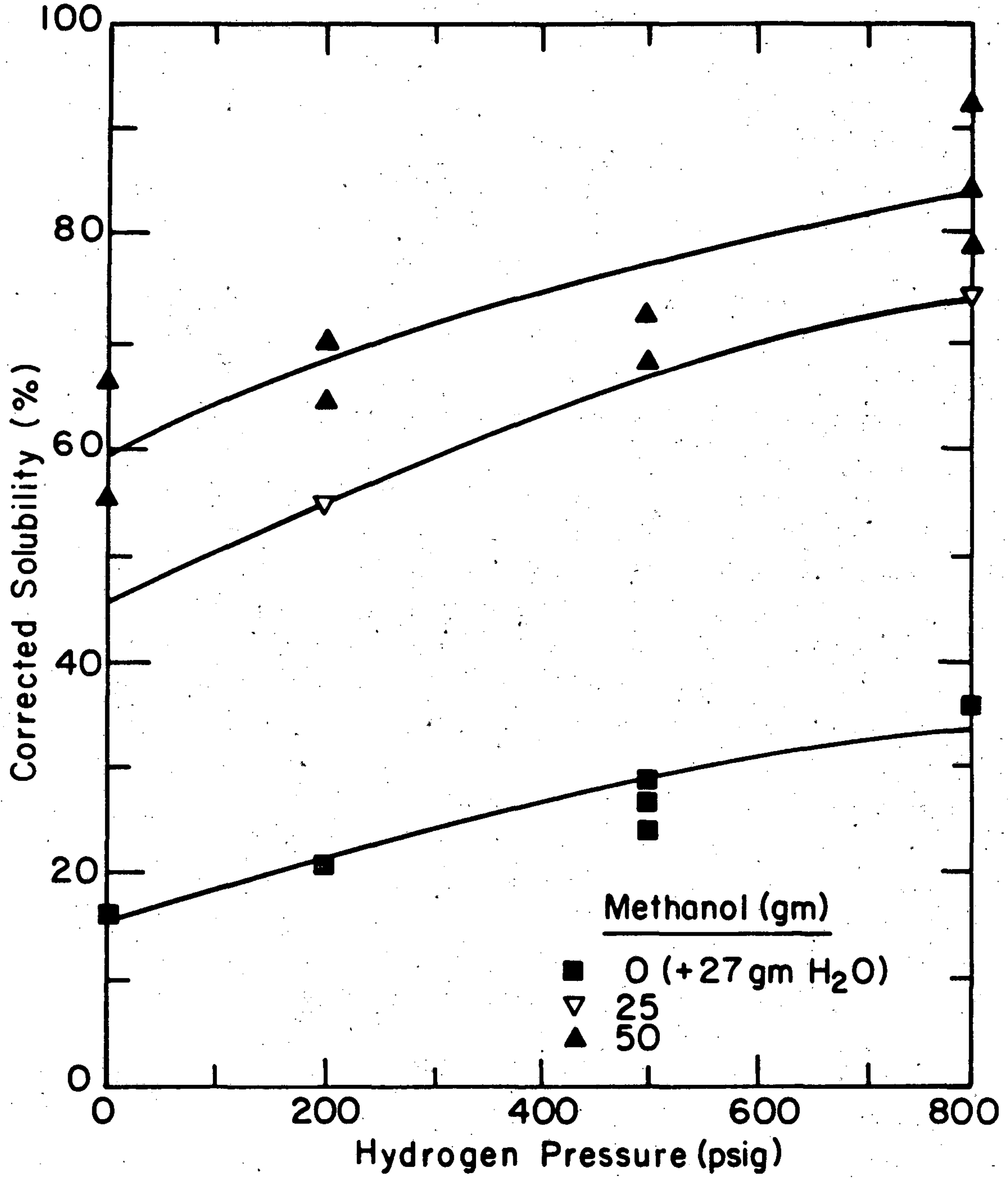

Corrected Solubility (%)
100
80
60
40
20
0
275 °C
250 °C
225°C
0
200
400
600
800
Hydrogen Pressure (psig)
XBL796-6436

Figure 3-3.

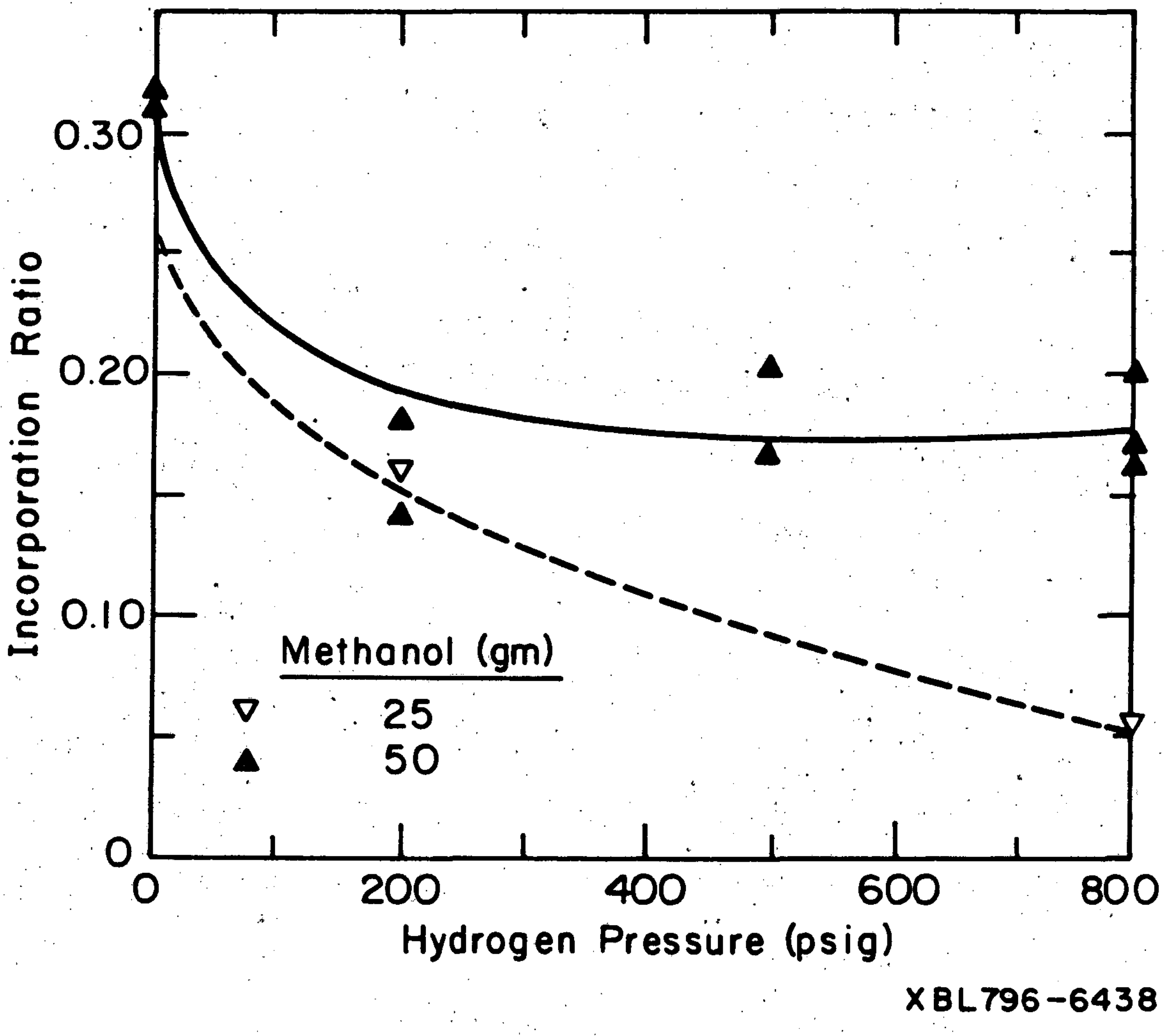
Figure 3-4. Effect of Hydrogen Pressure at Various Methanol Loadings on Solubility of $ZnCl_2$-Methanol Treated Coal.



XBL 796-6437

Figure 3-4.

Figure 3-5. Effect of Hydrogen Pressure at Various Methanol Loadings on Incorporation in $ZnCl_2$-Methanol Treated Coal.



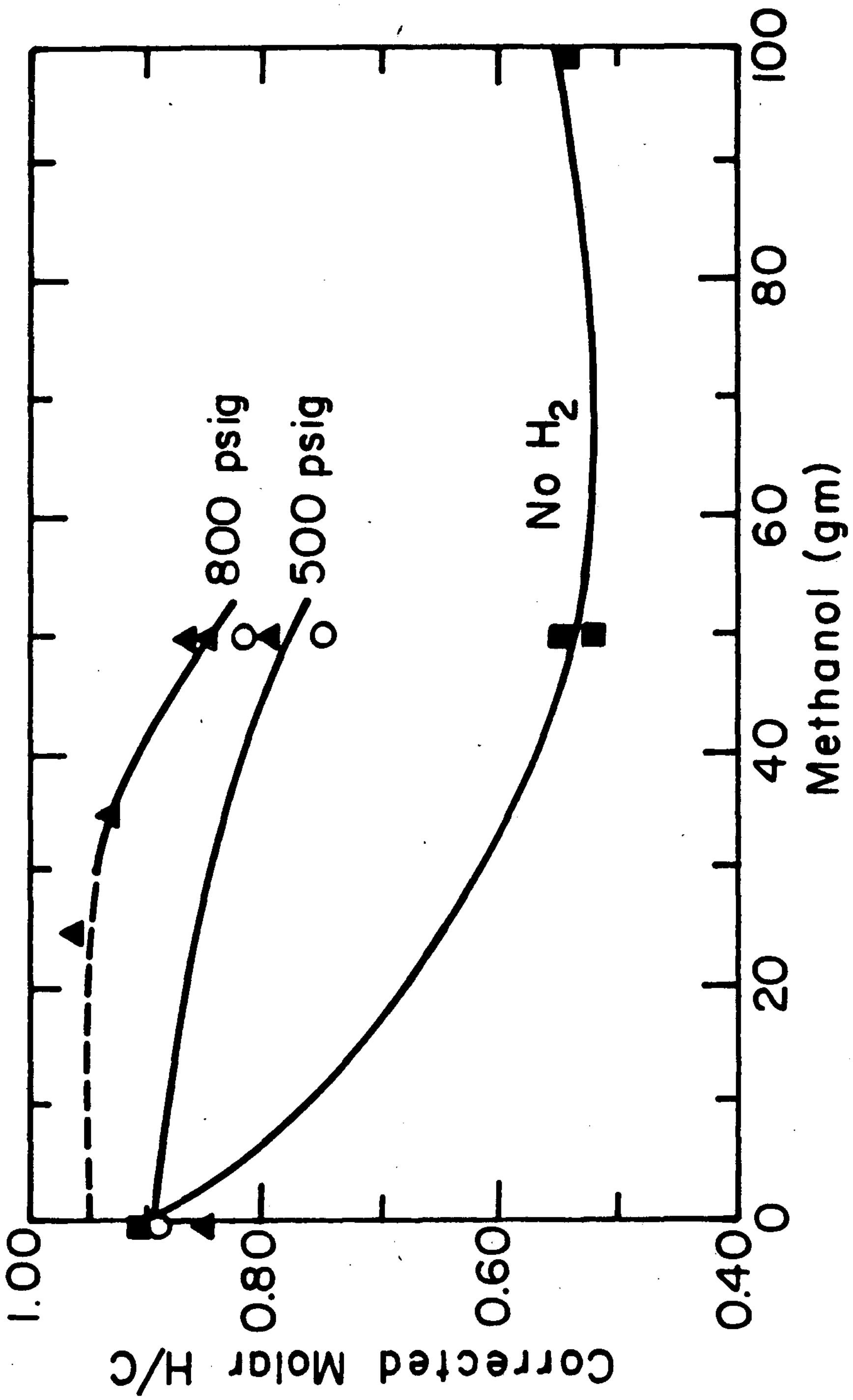
Incorporation Ratio
0.30
0.20
0.10
0
0
200
400
600
800
Hydrogen Pressure (psig)
Methanol (gm)
▽ 25
▲ 50
XBL796-6438

Figure 3-5.

Table 3-9. Effect of Methanol Amount on the $ZnCl_2$-Methanol Melt.
273 gm $ZnCl_2$; 50 gm Coal; T = 250°C; t = 60 min.

Run	Methanol Loading (gm)	P_{H_2} (psig)	Water Loading (gm)	Corrected Solubility (Pct. daf)	R (gm Retained MeOH/ gm Coal Organic)	Corrected Atomic H/C
64	0	0	27	16.2	0.00	0.90
45/50	50	0	0	61.3	0.31	0.53
17	100	0	0	25.3	0.27	0.55
46	0	0	0	25.3	0.27	0.55
44	10	200	10	39.4	0.07	0.94
40	25	200	0	54.8	0.16	0.70
15/37	50	200	0	67.3	0.17	0.81
41	75	200	0	47.5	0.24	0.62
65	0	500	27	28.3	0.00	0.88
39/75	50	500	0	70.3	0.19	0.79
56	0	800	27	35.6	0.00	0.85
47	25	800	0	73.6	0.05	0.96
51	35	800	0	70.2	0.10	0.93
43/72	50	800	0	88.1	0.19	0.83

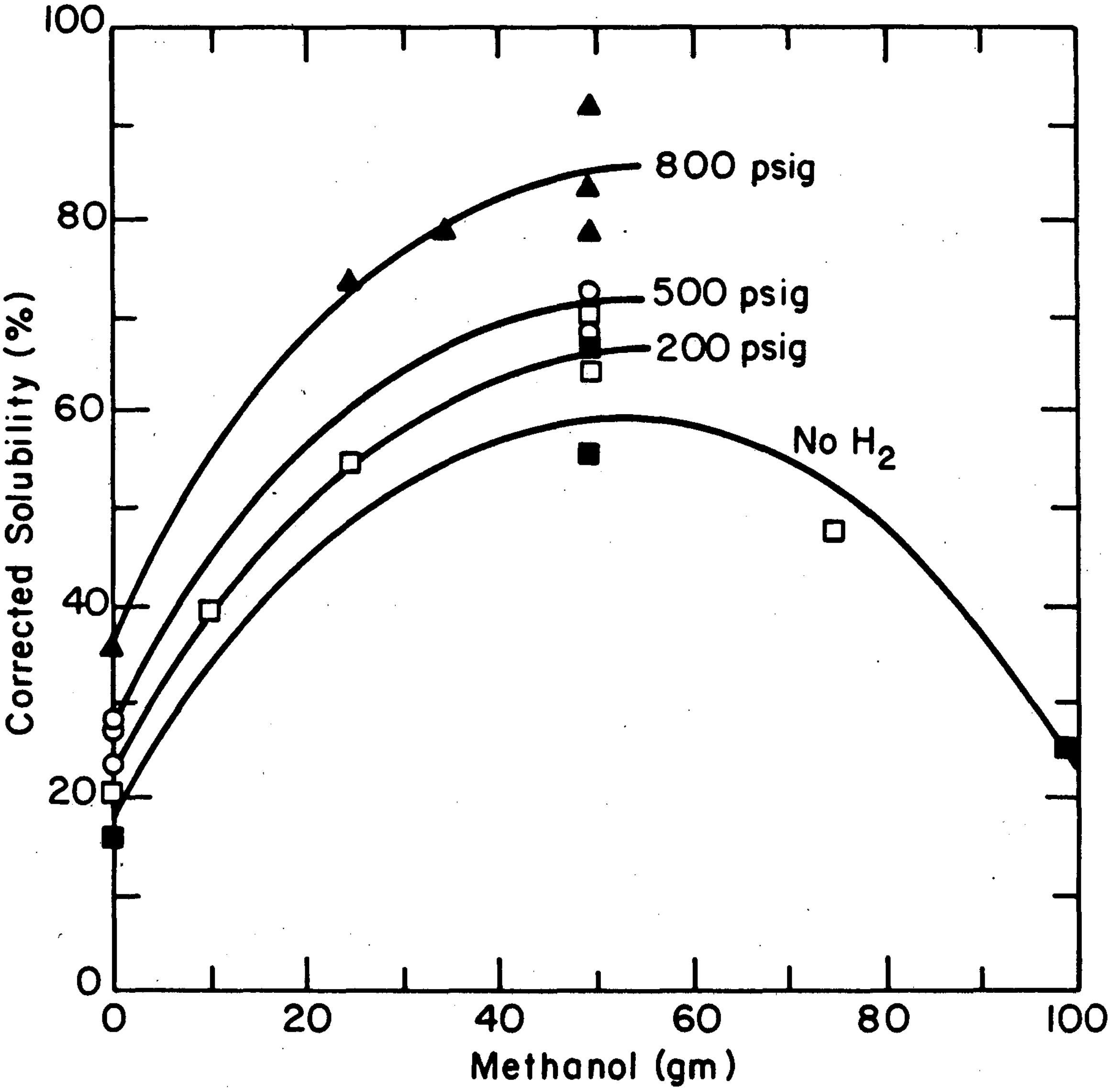
Figure 3-6. Effect of Methanol Loading and Hydrogen Pressure on Hydrogen-to-Carbon Ratios of $ZnCl_2$-Methanol Treated Coal.



XBL 796-6439

Figure 3-6.

Figure 3-7. Effect of Methanol Loading and Hydrogen Pressure on Solubility of $ZnCl_2$-Methanol Treated Coal.



XBL796-6440

Figure 3-7.

Several methanol loadings were examined at different hydrogen pressures (Table 3-9). Figure 3-7 shows that at all hydrogen pressures, the best conversion is obtained at 50 gm methanol per 273 gm $ZnCl_2$ (or 0.8 moles methanol per mole $ZnCl_2$).

Residence times between heatup only ("zero" residence time) and 60 minutes were used in experiments at 250^o and 275^oC (Table 3-10 and Fig. 3-8). Assuming Rate = k $\cdot$ Unconverted Coal , values of k are found as 3×10^{-2} min^{-1} and 1×10^{-1} min^{-1} at 250^oC and 275^oC, with nearly total conversion in less than 30 minutes at the higher temperature.

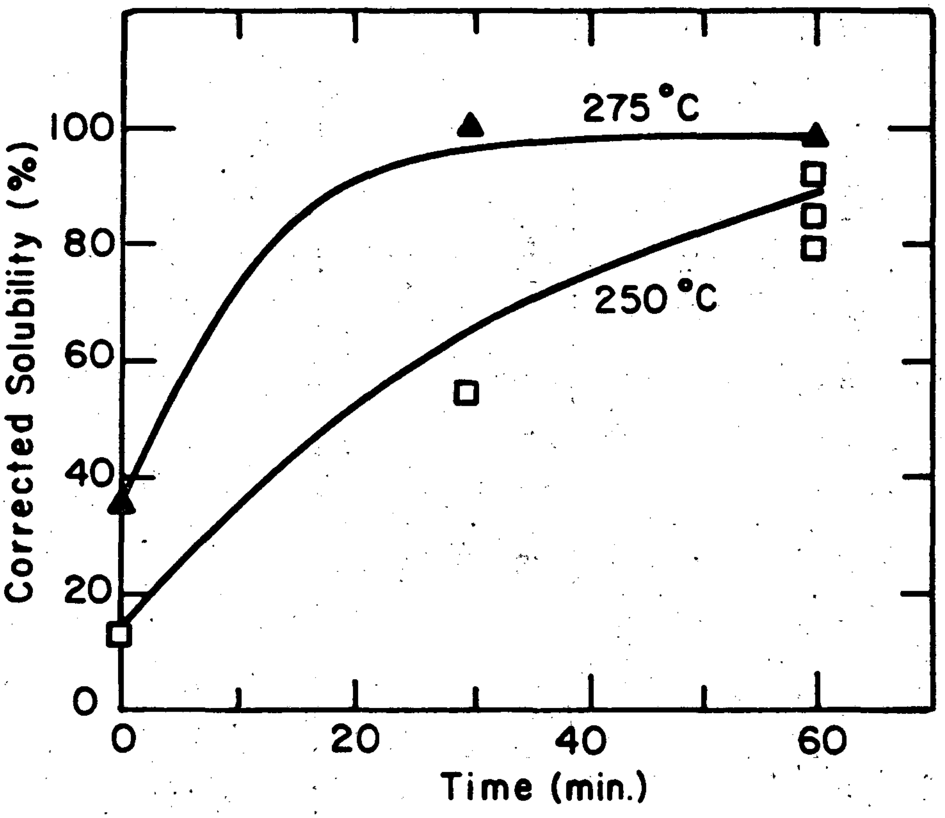
Incorporation is fairly constant between 0.15 and 0.20 for all runs between zero and 60 minutes residence time at these temperatures. One exception at 0 time, and 250^oC had very low incorporation but also very low conversion. The ratio of incorporation to conversion here is roughly constant.

The trend in H/C ratios with residence time is seen in Fig. 3-9. At 250^oC, H/C ratios decrease initially and then level off (or perhaps begin to increase) with longer reaction times. At 275^oC, the H/C ratio is lowest after simple heatup, and rises as the reaction proceeds. Considerable reaction occurs in the few minutes of heatup between 250^o and 275^oC. In this period, solubility rises 20 percent, incorporation approaches its maximum extent, and the H/C ratio drops to 0.75.

The effect of lowering melt-to-coal ratio to one-quarter the value used in previous experiments is seen in Table 3-11. Considerably less reaction takes place at the lower loading with lower solubility,

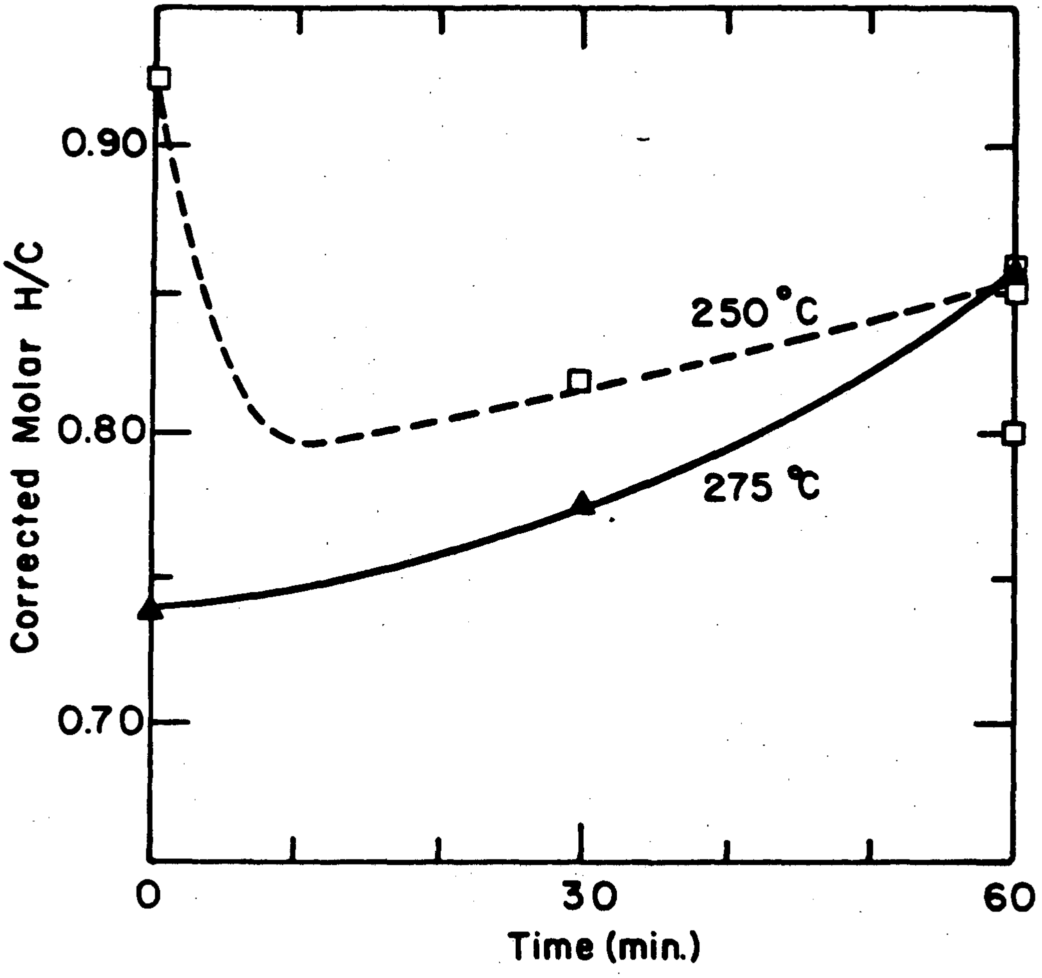
Table 3-10. Effect of Residence Time on the $ZnCl_2$-Methanol Melt.
273 gm $ZnCl_2$; 50 gm Coal; 50 gm Methanol; 800 psig H_2

Run	T(°C)	Residence Time (Min)	Corrected Solubility (Pct. daf)	R (gm Retained MeOH/ gm Coal Organic)	Corrected Atomic H/C
74	250	0	13.2	0.05	0.92
76	250	30	53.7	0.16	0.82
43/72/73	250	60	85.0	0.18	0.84
77	275	0	35.8	0.16	0.74
70	275	30	100.0	0.21	0.78
48	275	60	99.2	0.17	0.86



XBL 796-6441

Figure 3-8. Effect of Residence Time at Various Temperatures on Solubility of $ZnCl_2$-Methanol Treated Coal.



XBL 796-6442

Figure 3-9. Effect of Residence Time at Various Temperatures on Hydrogen-to-Carbon Ratios of $ZnCl_2$-Methanol Treated Coal.

Table 3-11. The Effect of Melt-To-Coal Ratio on Conversion.
T = 250°C; P = 500 psig; t = 60 min.

Run	Loadings (gm) Coal	 $ZnCl_2$	 MeOH	Corrected Solubility (Pct. daf)	R (gm/gm)	Corrected Atomic H/C
78	100	136.5	25	36.0	.05	.95
39/75[1]	50	273.0	50	67.3	.17	.76

---

[1] Average of duplicate runs.

Table 3-12. Comparison of Response of a Sub-Bituminous and a Bituminous Coal in the $ZnCl_2$-Methanol Melt. 273 gm $ZnCl_2$; 50 gm methanol; 50 gm Coal; T = 250°C; P_{H_2} = 500 psig; t = 60 min.

Run	Feed Coal	Corrected Solubility (Pct. daf)	R (gm Retained MeOH/ gm Coal Organic)	Pct. O Recovery
71	Illinois No. 6 (Bit)	76.2	0.51	69.5
39/75	Wyodak (Sub-Bit)	70.3	0.19	43.3

less incorporation and less reduction in H/C ratio. Insufficient mixing may have occurred due to the observed less-liquid nature of the lower melt run. Higher quantities of coal moisture per gm $ZnCl_2$ could also have diluted the catalyst causing the lower conversions.

The $ZnCl_2$-methanol melt was also used in treatment of Illinois no. 6 bituminous coal and Arabian heavy crude vacuum residuum. Table 3-12 compares the results with Illinois no. 6 with a Wyodak run under the same conditions. Similar product solubilities are achieved, but with considerably higher incorporation and lower oxygen removal.

The petroleum residuum sample was liquid at extraction temperatures and totally pyridine soluble, so gel-permeation chromatography was used as an initial determination of differences between the treated and untreated product. It appears that no substantial changes in molecular weight of the residuum was achieved, as essentially identical GPC elution curves were found before and after $ZnCl_2$-methanol treatment. No further analyses were performed on this sample.

Additional Results

In addition to corrected solubility, incorporation and product H/C ratio, other data were collected for each experiment. These include elemental recoveries (H, N, and O+S), total MTC solubilities in benzene and pyridine, and the effects of HCl or benzene washing of the MTC. Gel-permeation chromatography, various gas analyses, and examination of treated coal by scanning electron microscopy were also performed on selected runs.

Effect of Wash Conditions on MTC Properties

During the first experiment using ZnO as an additive (Run 55), a very high product solubility (90%) was found. This result was unexpected as ZnO was considered a potential poison for $ZnCl_2$ activity (the similar run with no ZnO was 70% soluble). A careful review of the experimental procedures in the two runs revealed only one other difference: the ZnO run was washed with dilute HCl to enhance removal of the ZnO in the water phase.

In subsequent experiments, the MTC was divided into two nearly equal portions after quenching, and half the product was washed with dilute HCl. Both the water-washed and HCl-washed samples were then dried and extracted in benzene and pyridine. The comparative results are shown in Table 3-13 and in Fig. 3-10, where the dashed line would represent a zero increase.

It is evident that HCl washing has a large effect on product solubility. Total solubility is most affected, with a maximum improvement of almost 50% (in solubility percentage units) in run 77. Benzene solubility is affected to a lesser extent, with a maximum increase of about 15% (in the same units).

In addition to changing the solubility, HCl rinsing enhances removal of Zn from the MTC. This is particularly apparent in runs 80 and 82 in which 10 gm Zn metal were present and run 69 where 10 gm ZnO were present. It is notable that only in these three runs were significant changes in H/C ratio of the MTC caused by HCl washing, suggesting that zinc somehow affects the analysis of hydrogen and carbon. Changes in (O+S)/C ratio are small, and are probably due

Table 3-13. Effect of HCl Rinsing on MTC Properties

Run	Uncorrected Solubilities (Pct. daf) Benzene Water Wash	Benzene HCl Wash	Pyridine + Benzene Water Wash	Pyridine + Benzene HCl Wash	Uncorrected Atomic H/C in MTC Water Wash	Uncorrected Atomic H/C in MTC HCl Wash
62	3.1	4.7	14.8	26.9	0.93	0.92
69	29.2	43.2	77.0	93.6	1.27	1.12
72	38.5	37.1	93.4	100.0	1.18	1.15
73	35.9	38.9	81.9	100.0	1.16	1.15
74	4.7	9.1	17.4	46.2	1.00	1.05
75	37.8	38.0	73.6	99.7	1.15	1.11
76	27.6	36.8	60.0	96.8	1.13	1.10
77	15.3	20.6	44.7	92.4	1.06	1.04
79	35.4	43.2	77.0	98.5	1.16	1.12
80	10.8	15.0	37.4	65.7	1.11	1.00
82	7.0	16.2	35.1	75.6	1.08	0.94
Raw Coal	2.0	-	13.0	-	0.98	-

Run	Atomic O+S/C in MTC Water Wash	Atomic O+S/C in MTC HCl Wash	Wt. % Zn in MTC Water Wash	Wt. % Zn in MTC HCl Wash	Wt. % Cl in MTC Water Wash	Wt. % Cl in MTC HCl Wash
62	0.19	0.22	3.96	0.24	0.33	0.16
69	0.13	0.09	23.60	1.30	4.53	1.30
72	0.03	0.04	9.78	6.42	7.12	8.11
73	0.09	0.05	9.14	4.98	3.53	5.06
74	0.20	0.19	5.71	0.13	0.38	0.11
75	0.11	0.07	6.08	2.27	2.61	3.69
76	0.11	0.10	6.94	0.65	1.19	1.19
77	0.14	0.13	8.10	0.10	0.78	0.21
79	0.09	0.09	8.04	4.88	6.44	2.44
80	0.14	0.15	20.00	0.04	3.48	0.59
82	0.14	0.16	21.30	1.48	3.70	0.35
Raw Coal	-	-	-	-	-	-

Figure 3-10. Effect of HCl Wash in Improving Benzene and Total Solubilities.

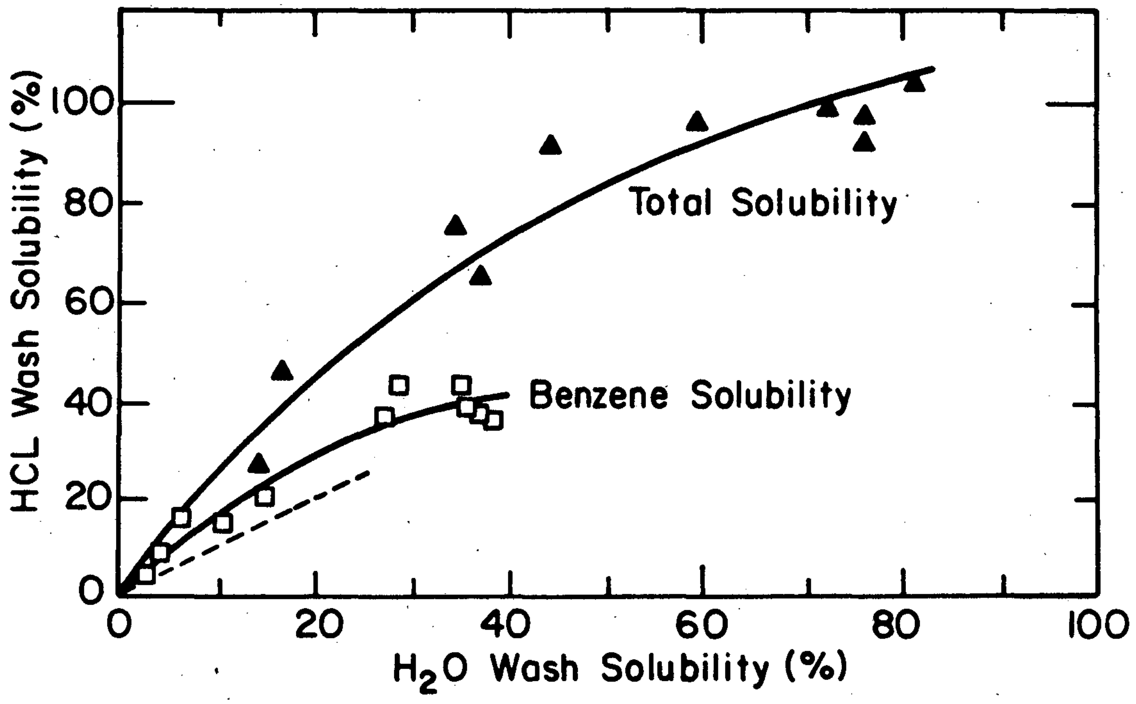


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Figure 3-10.

to the error involved in calculating O by difference rather than to any real changes in the MTC.

MTC products with high water-wash solubilities tend to have higher Cl values. This may be due to the fact that as the coal reaches high conversion levels, the MTC becomes more hydrophobic and impedes the removal of $ZnCl_2$ by water washing. In some experiments, the MTC could not be wetted by water, and a benzene wash was necessary to remove some of the hydrophobic material before hot water washing could be effective. To examine the effect of benzene washing, Table 3-14 compares results from runs 39 and 75, which were identical in all respects except that run 39 was washed with benzene prior to water washing. With the exception of a significant increase in benzene solubility, the two runs are identical to within experimental error.

Relationship Between Benzene and Pyridine Solubilities

In addition to corrected solubility, which measures the minimum quantity of coal-derived material which was solubilized by the treatment, it was of interest to know the properties of the MTC as a whole (i.e., before correction is made for solvent-derived material). Benzene and pyridine extractions were performed in series on the MTC, to obtain percent solubilities of dry ash-free (or daf) material. Appendix A lists the results of both extractions for every run.

For the wide range of reactions employed, there seems to be a general relationship between benzene and total (benzene + pyridine) solubility (see Fig. 3-11). Attempts to break this relationship into separate groups according to temperature, $ZnCl_2$ solvent, pressure, additive or residence time all produced significant overlapping.

Table 3-14. Comparison Between a Water-Washed and a Benzene-Washed Run. 273 gm $ZnCl_2$; 50 gm coal; 50 gm MeOH; T = 250°C; P_{H_2} = 500 psig; t = 60 min.

		Uncorrected Solubilities (Pct. daf)		Uncorrected Atomic Ratios		R
Run	Wash	Benzene	Benzene + Pyridine	H/C	O + S/C	(gm Retained MeOH/ gm Coal Organic)
39	Benzene	45.0	76.3	1.12	0.08	0.17
75	Water	37.8	73.6	1.15	0.11	0.20

Figure 3-11. Relationship Between Benzene and Total (Benzene + Pyridine) Solubility.

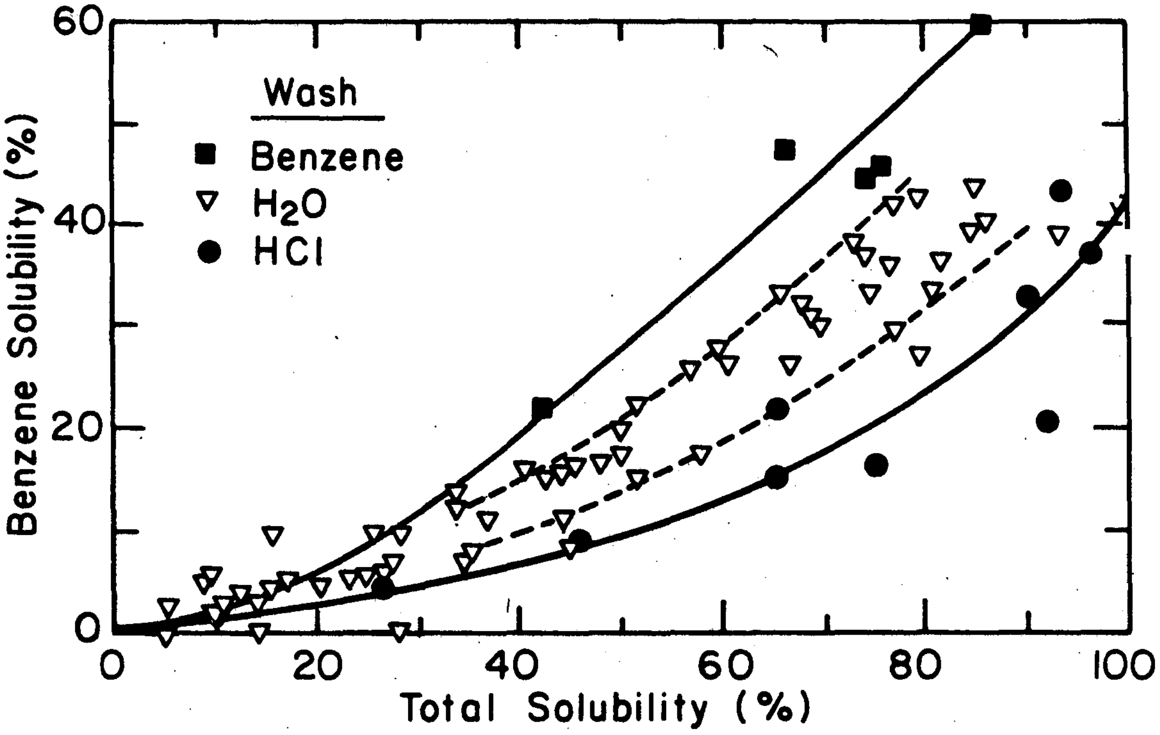

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Figure 3-11.

The single factor which clearly segregated the runs into separate groups was wash conditons. Acid washing produces significant increases in pyridine solubility and lesser increases in benzene solubility. As a result, the acid-wash runs all lie significantly below the other runs on the plot of benzene vs. total solubility. Benzene washing, on the other hand, tends to affect only the benzene solubility and not the pyridine solubility: thus benzene-washed runs are above the others on the plot.

Elemental Mass Balances

The fate of the chemical constituents of the coal during reaction can provide valuable information about the nature of the process. Elemental analyses of the MTC were combined with material balances on the reaction to assess the recovery of various elements in the product.

Drying experiments at 115°C under 50 millibars nitrogen on the raw coal revealed that about 23% of the mass of the raw coal was volatilized, mostly as water. The dried coal was then analyzed for C, H, N, S and ash (see Table 2-1). Thus, total recovery of coal from the autoclave would produce 38.5 gm from the 50 gm fed, including 23.9 gm C, 1.95 gm H, 0.33 gm N, 5.51 gm ash and 6.56 gm O+S. In the same way, the oven-dried weight and elemental analysis of each MTC may be used to obtain the weight of each element; Table 2-4 gives a sample calculation. Comparison with the untreated coal provides a measure of the fractional recovery of each element; Appendix A includes a summary of the recovery data.

The recovery of carbon in an MTC must be determined to estimate the degree of conversion to gas (mostly as CO_2 with some CO) which takes place during reaction. Data for the $ZnCl_2$-water system are free from interference of carbon in added solvents (see Table 3-15). These results show that between 90 and 95 percent carbon recovery can be expected at 250°C with $ZnCl_2$ treatment (the rest is presumably gas). Calculations of the amount of retained solvent in subsequent runs are based on the assumption of 95% coal carbon recovery.

Data on carbon recoveries for other runs have been listed as incorporation ratios (R), which gives an indication of the amount of additional carbon retained in the MTC over-and-above the 95% expected recovery of coal carbon. Attempts to correlate corrected solubility with carbon recovery (or incorporation) produced scatter, indicating that incorporation is not the only means of achieving solubilization.

As with carbon recovery, hydrogen recovery from MTC may be obscured by retention of solvent. To estimate the amount of hydrogen lost from the original coal material, the H/C ratio of the $ZnCl_2$-methanol treated coal was corrected assuming incorporation of three hydrogen atoms for each carbon atom (i.e., assuming methyl groups were retained from the methanol). Thus, the H/C ratios listed in previous tables are related to recovery of coal hydrogen.

In general, these corrected H/C ratios are considerably lower than the H/C of the original coal material. Uncorrected H/C ratios (see Appendix A) are usually higher than the raw coal, as the product is enriched in hydrogen through addtion of methyl groups (H/C = 3). As will be seen, significant oxygen removal occurs during the process,

Table 3-15. Elemental Recovery in the $ZnCl_2$-Water Melt. 273 gm $ZnCl_2$; 27 gm H_2O; 50 gm Coal; 250°C; 60 min.

	P_{H_2}	Percent Recovery			
Run	(psig)	C	H	N	O+S
64	0	90.2	82.9	83.9	87.5
46	200	92.4	81.4	100.0	66.8
22	500	87.8	80.3	95.5	71.0
63	500	93.9	85.3	100.0	64.7
65	500	94.3	85.2	94.0	65.2
56	800	94.0	81.7	96.0	57.8

and water formation is likely to be the sink for most of this lost hydrogen.

Removal of nitrogen from coal will be necessary to limit the environmental effects of burning coal-derived fuels. As may be seen from Appendix A, however, only limited nitrogen removal is accomplished under these reaction conditions, with typically 80 to 90 percent of the nitrogen recovered. Only one exception is noted: curiously, with the addition of nitrogen-containing indoline to the $ZnCl_2$-methanol melt, 80% of the nitrogen is apparently removed. This result needs further verification.

Studies of liquefaction in hydrogen-donor solvents above 325°C have shown a correlation between oxygen removal an formation of pyridine-soluble material.(126,127) Similarly, production of benzene-solubles has been associated with blocking or removal of hydroxyl groups from pyridine-soluble material. Preliminary work by Hershkowitz(128) has shown a relationship between oxygen removal and generation of pyridine-soluble material for reactions of the $ZnCl_2$-water-tetralin system.

Initial attempts to correlate oxygen recovery and product solubility for these experiments yielded a scatter plot. Further attempts to correlate oxygen removal and solubility led to segregation of runs into different classes (i.e., different temperatures, pressures, residence times, $ZnCl_2$-solvents, additives or wash conditions). The best result of these segregations is shown in Fig. 3-12. Reactions using water as $ZnCl_2$ solvent with no addtional solvent follow a single trend. A second broad grouping of points was observed for the $ZnCl_2$-methanol reactions. A third grouping was found for runs which were HCl washed.

Thus, oxygen removal and solubilization proceed in parallel, with different slopes generated by different solvents.

The overall reactions resulting in oxygen removal for methylation and simple hydogenolysis of ethers are:

$$R\text{-}O\text{-}R' + 2\ MeOH + 4(H) \longrightarrow R\text{-}Me + R'\text{-}Me + 3H_2O$$

$$R\text{-}O\text{-}R + 4(H) \longrightarrow 2\ RH + H_2O$$

Capping cleaved ethers with methyl groups requires two methyls per ether. Using Blom's estimates for ether content,(9) the 50 gm undried coal fed contain approximately 0.18 moles of ether O. An 80% conversion of this by methylation would require 0.29 moles $-CH_3$ (4.3 gm), and 0.58 moles H. An incorporation ratio of 0.14 is expected from this amount of methyl groups, close to the experimental values of 0.15 to 0.20. Simple hydrogenolysis and methylation both require the same amount of hydrogen; hydrogenolysis leaves half of it in the product, and methylation none. The hydrogen consumed may derive partly from hydroaromatics in the coal, causing a drop in the H/C ratio. If all the hydrogen were coal-derived, methylation would leave the remaining coal with a corrected H/C of about 0.7; hydrogenolysis leaves a product H/C of about 0.87. Certain runs with no gas-phase hydrogen which show lower H/C ratios than 0.7, probably involve over-correction for methanol incorporation.

Pressure-Time Data

Significant information about the course of an experiment can be obtained by following the variations in its total pressure, in cases where the run is totally enclosed an unsampled during its course. Beginning with Run 30, data were collected on total reaction pressure;

Figure 3-12. Relationship Between Solubility and Oxygen Recovery.

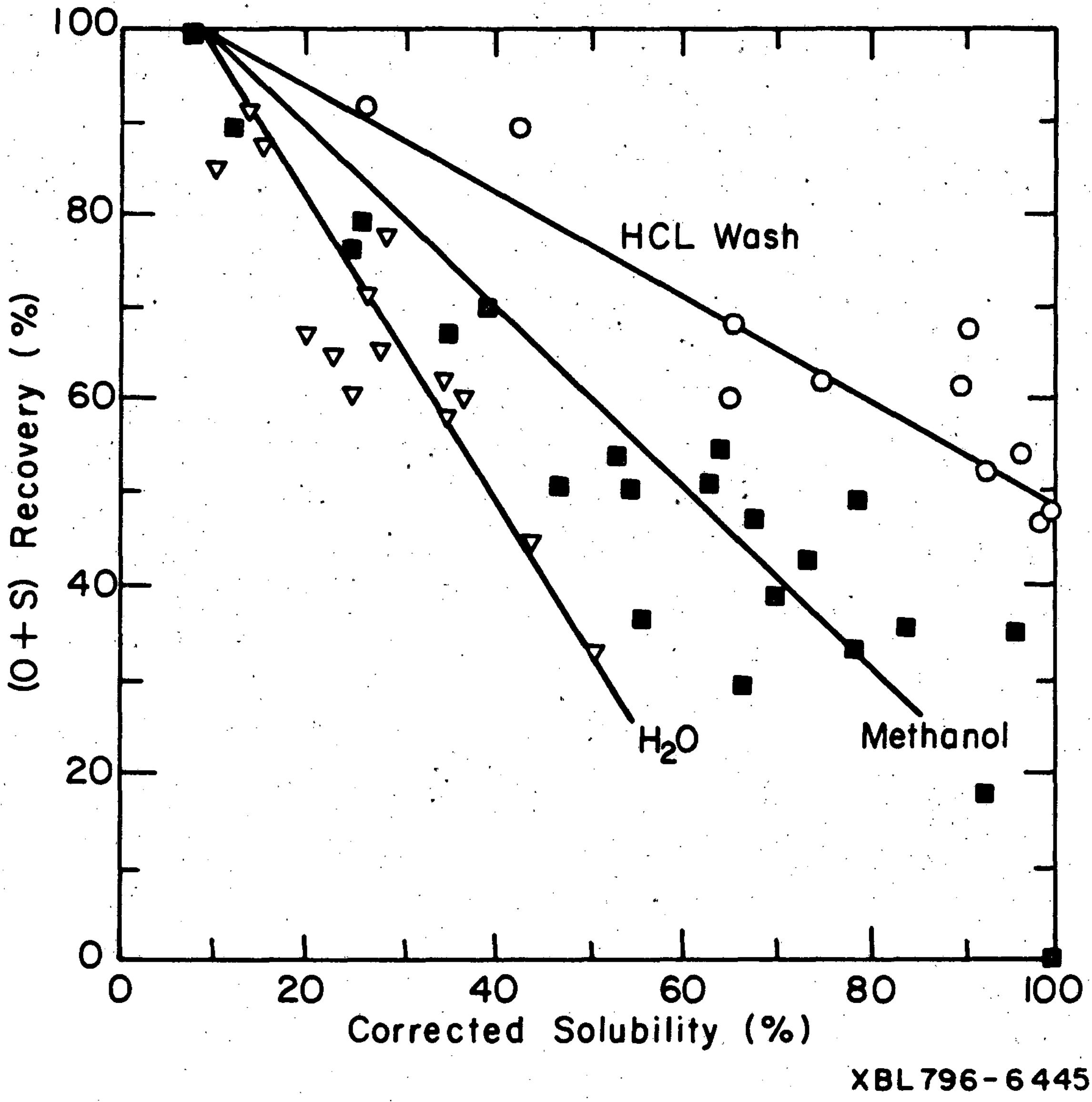
100
80
60
40
20
0
(O + S) Recovery (%)
0
20
40
60
80
100
Corrected Solubility (%)
HCL Wash
Methanol
H_2O
XBL796-6445

Figure 3-12.

Figure 3-13 presents a typical plot of total pressure history. The initial pressure build-up results from pressurization with hydrogen, and pressure continues to rise with heat up. When reaction temperature is reached, the pressure generally continues to rise for 5-10 minutes into the run, reaching a maximum, beyond which a drop occurs.

Some general remarks may be made concerning pressure-time behavior. Three quantities characterize a particular run. First, the amount by which the total pressure rises above the hydrogen partial pressure ($P_{max} - P_{H_2}$) indicates a contribution of components other than hydrogen. Second, the pressure drop from maximum pressure to the final pressure ($P_{max} - P_{final}$) is an indicator of gas consumption. Third, the time at which maximum pressure is reached indicates the balance between gas evolution and gas consumption.

For the $ZnCl_2$-methanol runs, the time at which maximum pressure occurs ($t_{P,max}$) is only a function of temperature. At 225°C, the maximum pressure occurs about 20 minutes into the run; at 250°C, generally within the first 10 minutes; at 275°C, at the start of the run. For these runs, only when the hydrogen partial pressure is 800 psig or greater does the pressure drop exceed the pressure rise.

The effect of temperature on pressure-time behavior is shown in Table 3-16. At higher temperatures, both the pressure rise ($P_{max} - P_{H_2}$) and the pressure drop ($P_{max} - P_{final}$) increase. Apparently, the reactions which produce the rise and those which consume the gas are both accelerated at higher temperatures.

Hydrogen partial pressure also has a definite effect on the pressure rise and pressure drop (see Table 3-17). Higher hydrogen

Figure 3-13. Typical Pressure-Time Autoclave Reactions. (Data from Run 72). Pressure continues to rise to peak about 5-10 minutes after heat up, with subsequent pressure drop.

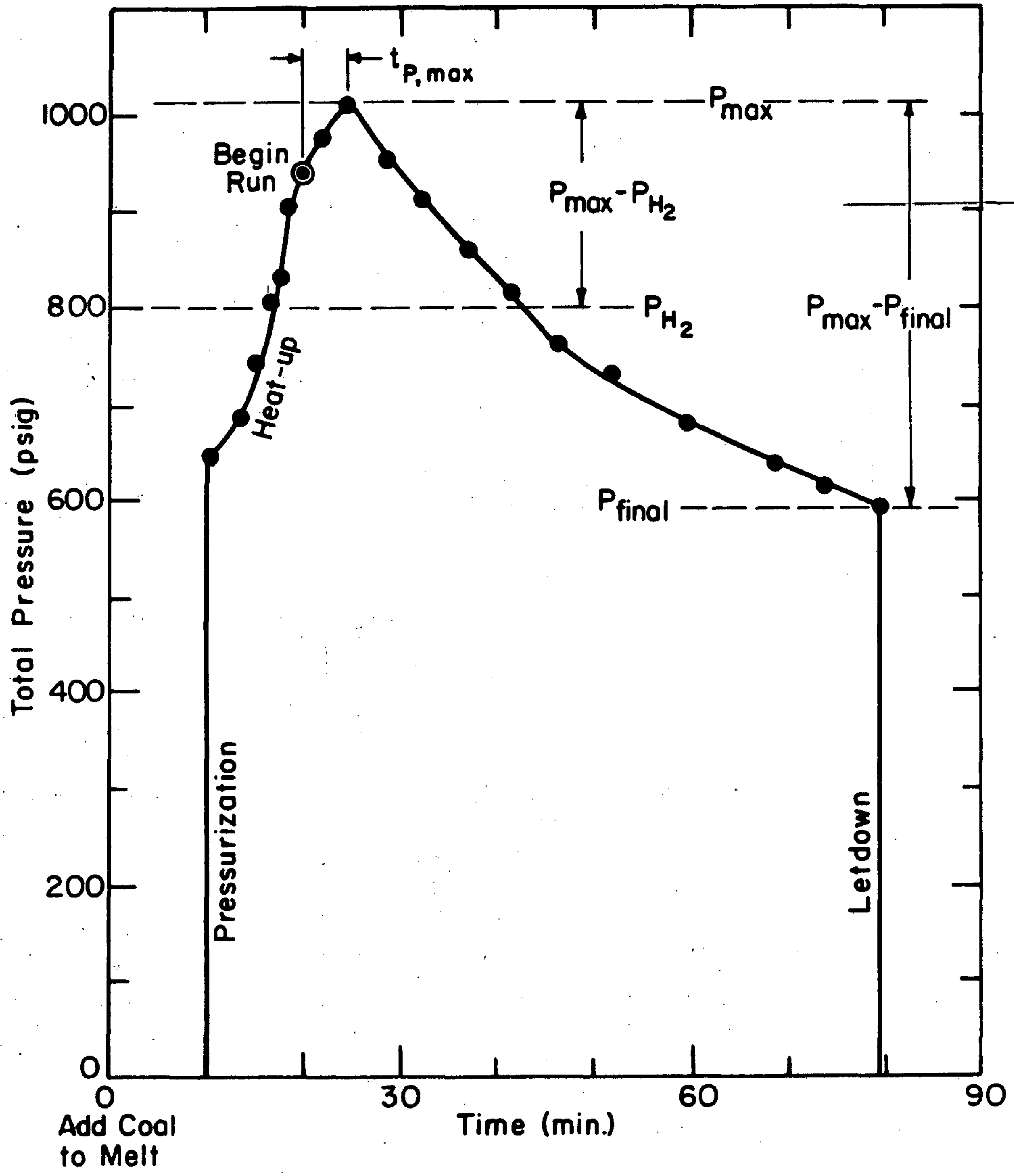

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Figure 3-13.

Table 3-16. Pressure-Time Behavior of Runs Illustrating the Effect of Temperature. 273 gm $ZnCl_2$; 50 gm Coal; 50 gm Methanol; 60 min.

Run	T(°C)	P_{max}	P_{H_2}	P_{final}	$P_{max}-P_{H_2}$	$P_{max}-P_{final}$	Time at P_{max}
49	225	1010	800	925	210	85	20
72	250	1010	800	595	210	420	5
48	275	1110	800	720	310	390	0
52	225	440	200	370	240	70	17
37	250	575	200	470	375	105	10
30	275	750	200	500	550	250	0

Table 3-17. Pressure-Time Data Illustrating the Effect of Hydrogen Pressure. 273 gm $ZnCl_2$; 50 gm Coal; 60 min.

Run	T(°C)	MeOH (gm)	P_{max}	P_{H_2}	P_{final}	$P_{max}-P_{H_2}$	$P_{max}-P_{final}$	Time at P_{max}
52	225	50	440	200	370	240	70	17
49	225	50	1010	800	925	210	85	20
45	250	50	390	0	310	390	80	3
37	250	50	575	200	470	375	105	10
39	250	50	790	500	615	290	165	8
72	250	50	1010	800	720	210	420	0
64	250	0	110	0	110	110	0	60
46	250	0	315	200	295	115	20	7
65	250	0	610	500	525	110	85	8
56	250	0	840	800	715	40	125	22
40	250	25	350	200	290	150	60	8
47	250	25	895	800	660	95	235	5
30	275	50	750	200	500	550	250	0
48	275	50	1110	800	720	310	390	0

pressures decrease the pressure rise, suggesting that hydrogen is consumed in a significant amount before the maximum pressure is reached. (This is consistent with the fact that higher hydrogen pressures also increase the pressure drop.)

Methanol loading causes different effects on pressure rise and drop (Table 3-18). The pressure rise increases monotonically with higher methanol loadings. The pressure drop, however, is greatest at 50 gm methanol. It is notable that corrected solubility exhibits the same behavior as pressure drop with respect to methanol loading (see Fig. 3-7). Thus, production of soluble material appears to be related to consumption of gas-phase hydrogen.

Table 3-19 provides pressure data for runs with different reactor residence times. It is seen that 70-90% of the pressure drop occurs in the first 30 minutes of reaction, consistent with data from individual runs. Melt/coal ratio has a sizeable effect (Table 3-20); reduction in melt/coal by a factor of approximately 4 results in a one-third increase in pressure rise, a one-third decrease in pressure drop, and a change in the time at which maximum pressure is reached from 8 minutes to 25 minutes.

Substitution of nitrogen for hydrogen provides some interesting data (Table 3-21). First, as seems reasonable, the nitrogen run shows very little gas consumption ($P_{max} - P_{final} = 60$ psi). The pressure rise (370 for N_2 vs. 310 for H_2) and the pressure at time zero (1110 for N_2 vs. 310 for H_2) are both significantly higher for nitrogen than for hydrogen. Hydrogen consumption at an early stage in the reaction, or hydrogen inhibition of volatiles production is inferred.

Table 3-18. Pressure-Time Data Illustrating the Effect of Methanol Loading. 273 gm $ZnCl_2$; 50 gm Coal; 250°C; 60 min.

Run	CH_3OH (gm)	P_{max}	P_{H2}	P_{final}	$P_{max}-P_{H2}$	$P_{max}-P_{final}$	Time at P_{max}
46	0	315	200	295	115	20	7
44	10	350	200	265	150	85	3
40	25	350	200	290	150	90	5
37	50	575	200	470	375	105	10
41	75	830	200	780	630	50	7
56	0	840	800	715	40	125	22
47	25	895	800	660	95	235	5
51	35	905	800	670	105	235	0
72	50	1010	800	590	210	420	5

Table 3-19. Pressure-Time Data Illustrating the Effect of Reaction Residence Time. 273 gm $ZnCl_2$; 50 gm Coal; 50 gm Methanol.

Run	T(°C)	Reaction Time (min)	P_{max}	P_{H2}	P_{final}	$P_{max}-P_{H2}$	$P_{max}-P_{final}$	Time at P_{max}
74	250	0	965	800	965	165	0	0
76	250	30	1045	800	795	245	250	6
72	250	60	1010	800	720	210	420	5
77	275	0	1160	800	1160	360	0	0
70	275	30	1095	800	755	295	340	0
48	275	60	1110	800	720	310	390	0

Table 3-20. Effect of $ZnCl_2$/Coal Ratio on Pressure-Time Behavior. $ZnCl_2$/Methanol = 273/50; 250°C; 60 min.

Run	$ZnCl_2$/Coal (gm/gm)	P_{max}	P_{H_2}	P_{final}	$P_{max}-P_{H_2}$	$P_{max}-P_{final}$	Time at P_{max}
39	273/50	790	500	615	290	175	8
78	137/100	910	500	800	410	110	25

Table 3-21. Reproducibility of Pressure-Time Data at 800 psig Hydrogen and Comparison to Data at 800 psig Nitrogen. 273 gm $ZnCl_2$; 50 gm Coal; 50 gm Methanol; 250°C; 60 min.

Run	$P_{t=0}$	P_{max}	P_{H_2}	P_{final}	$P_{max}-P_{H_2}$	$P_{max}-P_{final}$	Time at P_{max}
43	980	1160	800	810	360	350	5
72	940	1010	800	590	210	420	5
73	960	1030	800	440	230	590	4
50[a]	1110	1170	800	1110	370	60	6

[a] Nitrogen used in place of hydrogen.

Table 3-22. Reproducibility of Pressure-Time Data at 500 psig Hydrogen. 273 gm $ZnCl_2$; 50 gm Coal; 50 gm Methanol; 250°C; 60 min.

Run	P_{max}	P_{H_2}	P_{final}	$P_{max}-P_{H_2}$	$P_{max}-P_{final}$	Time at P_{max}
39	790	500	615	290	175	8
75	800	500	495	300	305	7

Table 3-22 provides more data on duplicate runs showing that while the pressure rise is fairly repeatable, the pressure drop may vary considerably. Undetected pressure leaks in the reactor system could be the cause of such descrepancies.

Inorganic additives have very little effect on pressure behavior (Table 3-23). Various loadings of ZnO produce the same pressure rise and drop and the same solubilities as a run with no ZnO. Zn metal produces an additional 100 psi pressure rise with a slightly lower pressure drop (perhaps due to generation of some hydrogen gas). Addition of 100 psig HCl causes an added pressure rise of somewhat less than 100 psi, with similar pressure drop to a run with no additives.

A comparison of pressure behavior for a series of different $ZnCl_2$ solvents is shown in Table 3-24. For the alcohols, the pressure drop increases from water to methanol to ethanol and then decreases rapidly with virtually no drop for iso-propanol or t-butanol. This behavior is in parallel with solubilization activity of the different solvents. The lack of a pressure drop for either t-butanol or i-propanol may indicate the production of an additional gas-phase component from these reactions. Alcohols are known to undergo dehydration in the presence of $ZnCl_2$ with reactivity in the order of tertiary secondary primary methyl. Production of butene from butanol and propene from propanol is known under these conditons. The behavior of pressure for the series of alcohols indicate that more than a vapor-pressure effect is responsible. Particularly, the large rise with ethanol compared to methanol leads one to suspect that some intermediate reaction is responsible for the large gas peak. With i-propanol and t-butanol,

Table 3-23. Effect of Inorganic Additives on Pressure-Time Behavior.
273 gm $ZnCl_2$; 50 gm coal; 50 gm Methanol; 250°C; 60 min.

Run	Additive (gm)	P_{max}	P_{H_2}	P_{final}	$P_{max}-P_{H_2}$	$P_{max}-P_{final}$	Time at P_{max}
39	None	790	500	615	290	175	8
57	ZnO-9.0	810	500	610	310	200	8
55	ZnO-18.8	790	500	575	290	215	3
79	Zn-1.0	920	500	760	420	160	5
58	HCL(100 psig)	870	500	660	370	210	5

Table 3-24. Effect of Various Solvents on Pressure-Time Behavior.
273 gm $ZnCl_2$; 50 gm coal; 50 gm Methanol; 250°C; 60 min.

Run	Solvent	$P_{max}-P_{H_2}$	P_{max}	P_{H_2}	P_{final}	$P_{max}-P_{final}$	Time at P_{max}
46	HOH(27 gm)	115	315	200	295	20	7
37	CH_3OH	375	575	200	470	105	10
54	EtOH	585	785	200	470	315	1
33	iPrOH	375	575	200	570	5	12
34	tBuOH	160	660	200	660	0	60
38	CH_3COOH	205	405	200	360	45	13
36	Acetone	360	560	200	560	0	60

the pressure curves virtually level out after maximum pressure is achieved, indicating that the intermediate formed from their reaction may be more stable.

Finally, the effect of different solvent additives on the $ZnCl_2$-methanol system is seen in Table 3-25. Perchloroethane, cyclohexanol, and o-dichlorobenzene all result in significantly less pressure drop during the run, implying that they may interfere with the reactions which consume gas (these solvents also produce solubility). Pyrollidine increases both the pressure rise and pressure drop with little effect on solubilization activity. Indoline has the strongest effect, reducing the pressure rise by 100 psi and increasing the pressure drop by more than 100 psi, making it the only run at less than 800 psig hydrogen in which the final pressure is below the initial hydrogen partial pressure. Indoline is enhancing gas consumption.

Drawing together the results of the pressure-time data, several conclusions may be arrived at:

1) Reactions proceed with an initial pressure rise followed by a significant pressure drop.
2) Pressure rise is larger with increasing temperature, decreasing hydrogen partial pressure, and increasing methanol loading.
3) Subsequent pressure drop is larger with higher temperature and higher hydrogen pressure, and goes through a maximum with increasing methanol loading, thus matching the solubilization behavior.
4) Inorganic additives have minor effects on pressure behavior.

Table 3-25. Effect of Solvent Additives to $ZnCl_2$-Methanol on Pressure-Time Behavior. 273 gm $ZnCl_2$; 50 gm Coal; 50 gm Methanol; 250°C; 60 min.

Run	Solvent (gm)	P_{max}	P_{H_2}	P_{final}	$P_{max}-P_{H_2}$	$P_{max}-P_{final}$	Time at P_{max}
35	Perchloro-ethane (50)	1250	200	1210	1050	40	6
32	Cyclohexanol (10)	685	200	620	485	65	2
53	o-Dichlor benzene (120)	440	200	390	240	50	1
66	Pyrollidine (10)	900	500	670	400	230	2
59	Indoline (10)	685	500	395	185	290	0
39	Methanol only	790	500	615	290	175	8
37	Methanol only	575	200	295	375	105	10

5) Solvents affect pressure drop and solubilization behavior in the same manner.
6) Substitution of nitrogen for hydrogen results in less pressure drop, implying that hydrogen is consumed during reaction.

Gas Analyses

To identify the gases produced during the autoclave experiments, gas analyses were performed on selected runs. Table 3-26 presents the results of mass spectrometry, gas chromatography, and combined gas chromatography and mass spectrometry analyses of four runs for which gas samples were collected. Hydrogen predominates, but significant quantities of dimethyl ether, methyl chloride, CO_2, CO, and hydrocarbons are also present.

Of primary interest in these analyses is the consumption of gas-phase hydrogen. Table 3-27 compares hydrogen consumption calculated by the gas analyses with the reactor pressure drop during the run. Runs 57 and 70 show virtual agreement between the actual hydrogen consumption and the consumption calculated assuming the total-pressure drop in the reactor represented only hydrogen disappearance. Run 72 shows about 8% more hydrogen consumption than the pressure drop would indicate; Run 75 shows about 20% less hydrogen consumption than pressure drop. In all cases, 80+% of the pressure drop is due to hydrogen consumption.

Comparison of Runs 75 and 72 shows that higher hydrogen pressures generally lead to higher hydrogen consumptions. Both Runs 75 and 57 (with 45 minutes residence time at 250°C) show hydrogen consumptions of approximately 0.30 gm/hr at 500 psig; Run 72 shows 0.53 gm/hr at

Table 3-26. Gas Analyses

A) Mass Spectrometer Results.

Run	Pressure at Sampling Time (psig)	Concentration, Mole %					
		CH_2	CO_2	CH_3OH	CH_3Cl	$(CH_3)_2O$	Hydrocarbons
57	615	49.4	11.7	0.4	6.4	22.8	9.7
70	755	62.3	12.3	0.2	1.4	0.2	23.6
72	595	58.3	9.9	0.5	6.7	2.3	18.3
75	495	49.7	13.9	0.3	9.7	4.7	18.9

Other gases: Run 70: CO 1.8%, Ch_4 2.9%
Run 75: CH_4 2.8%

B) Gas Chromatography Results

Run	Concentration, Mole %										
	CO_2	$(CH_3)_2O$	CH_3Cl	CO	CH_4	C_2H_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6-C_7
57	11.7	22.8	6.4	1.30	2.42	0.27	0.08	0.82	i=0.2 n=0.1	i=2.1 n=0.1	0.35
72	9.0	2.16	10.0	0.76	2.14	0.25	0.04	8.17	0.2	i=3.0 n=0.1	0.85
75	11.6	4.34	10.4	0.90	2.61	0.34	0.07	11.4	2.36	i=2.7 n=0.1	0.60

C) GCMS Results

Run 70 Largest peaks: Isobutane; isopentane; CO_2; propane; CH_3Cl; isohexane; 2,3-Me_2butane; 3-Me pentane; n-pentane 2-Me hexane; 3-Me hexane.

Run 75 Largest peaks: Propane; 2-Me butane; CH_3Cl; 2,3-Me_2 butane.

Table 3-27. Comparison of Reaction Pressure Drop with Measured Hydrogen Consumption. 273 gm $ZnCl_2$; 50 gm Methanol; 50 gm Coal.

Run	Pressure Drop During Reaction (psig)	H_2 Consumption (gm)		Run Conditions
		By Gas Analyses	If All P Drop Due to H_2 Loss	
75	305	0.30	0.36	250°C, 1 hr, 500 psig
72	420	0.53	0.49	250°C, 1 hr, 800 psig
57	200	0.23	0.23	250°C, 45 min, 500 psig, ZnO added
70	340	0.37	0.38	275°C, 30 min, 800 psig

Table 3-28. Major Gas Production in $ZnCl_2$-Methanol-Coal Reactions.

Run	$(CH_3)_2O$	CH_3Cl	CO_2	CO	CH_4	C_3H_8
	Total Moles in Gas Phase					
75	0.0132	0.029	0.037	0.0026	0.0075	0.0331
72	0.0078	0.029	0.033	0.0027	0.0075	0.0285
57	0.0823	0.023	0.042	0.0047	0.0087	0.0030
70	0.0009	0.0059	0.052	0.0076	0.012	--
	Total Grams in Gas Phase					
75	0.61	1.47	1.86	0.73	0.120	1.46
72	0.36	1.17	1.45	0.074	0.120	1.26
57	3.78	1.17	1.63	0.131	0.140	0.13
70	0.04	0.30	2.29	0.213	0.200	--

800 psig; combining to about 7 x 10^{-4} gm hydrogen consumed/hr psig at 250°C. At 275°C, hydrogen consumption increases to about 1 x 10^{-3} gm/hr psig.

Table 3-28 shows quantities of the major gases produced. Dimethyl ether and methyl chloride are present in significant quantities, as the result of side reactions of methanol. An unusually large amount of the ether was formed in Run 57; both dimethyl ether and methyl chloride production are relatively low in the 275°C reaction.

CO_2 in the product gases is likely to come from decomposition of carboxylic acids and perhaps of carbonyl groups in the coal. Relying on estimates from Blom,(6) the 50 gm of undried feed coal contained approximately 0.034 moles of -COOH and 0.03 moles of C-CO-C. Only the 275°C run shows significantly more CO_2 formed than carboxyl fed, and also shows 0.007 moles of CO (more than double the average of the 250°C runs).

Scant production of methane is found (less than 0.6% of the input carbon), and only traces of ethane and ethylene are produced. Some of these light hydrocarbons may be methanol-derived. Relatively large quantities of propane in Runs 72 and 75 (which could account for up to 4.5% of the input carbon) are believed to be the result of contamination, as may be the case for the higher hydrocarbons. The sum of CO_2, CO and C_1-C_2 hydrocarbons accounts for less than 3.6% of the input coal carbon in all cases.

Gel-Permeation Chromatography

Extracts from several runs were chosen for examination by gel-permeation chromatography (GPC) (see Table 3-29). Comparison of tracings

Table 3-29. Reaction Conditions and Yields for Runs Whose Extracts Were Examined by Gel-Permeation Chromatography

								Uncorrected Solubilities (Pct. daf)	
Run	T (°C)	P_{H_2} (psig)	t (min)	H_2O (gm)	CH_3OH (gm)	Additives (gm)	Wash	Benzene	Pyridine
72	250	800	60	0	50	-	H_2O	38.5	93.4
72	250	800	60	0	50	-	HCl	37.1	100.0
50	250	0	60	0	50	-	H_2O	36.5	74.7
49	225	800	60	0	50	-	H_2O	16.1	46.0
48	275	800	60	0	50	-	H_2O	41.6	99.2
77	275	800	0	0	50	-	H_2O	15.3	44.7
56	250	800	60	0	-	-	H_2O	7.4	35.6

from similar experiments with only one variable altered was used to examine the effect of this variable on the molecular-weight distribution.

Figure 3-14 compares GPC tracings (uv absorbance at 313 nm vs. elution volume of pyridine in ml) of fresh extracts from coal treated with $ZnCl_2$-methanol at three different temperatures (Runs 48,49 and 72). Two peaks (at 21.5 and 25 ml) are seen in the benzene extracts and a single peak (21 ml) in the pyridine extract. The curves for different temperatures are quite similar, the major effect being production of more high-molecular-weight pyridine-soluble material at elevated temperatures.

The effect of hydrogen pressure in $ZnCl_2$-methanol treatment is seen in Fig. 3-15 for Runs 72 and 50. The yields of benzene-solubles from the two runs are approximately the same: With no hydrogen present, the higher molecular-weight peak (at 21.5 ml) is larger than with hydrogen present. Pyridine-solubles for 0 hydrogen and 800 psig hydrogen are 75 and 95% respectively: The GPC profiles show more high-molecular-weight material when no hydrogen is used.

The effect of residence time in $ZnCl_2$-methanol treatment at 275°C is seen in Fig. 3-16. The small quantity of benzene-solubles produced during heatup is dominated by the lower molecular weight peak. One-hour residence time at 275°C produces almost three times the quantity of benzene-solubles with a larger proportion of high-molecular-weight materials in the extract. Similarly, a strong shift towards high-molecular-weight products at long reaction times is seen in the pyridine extract.

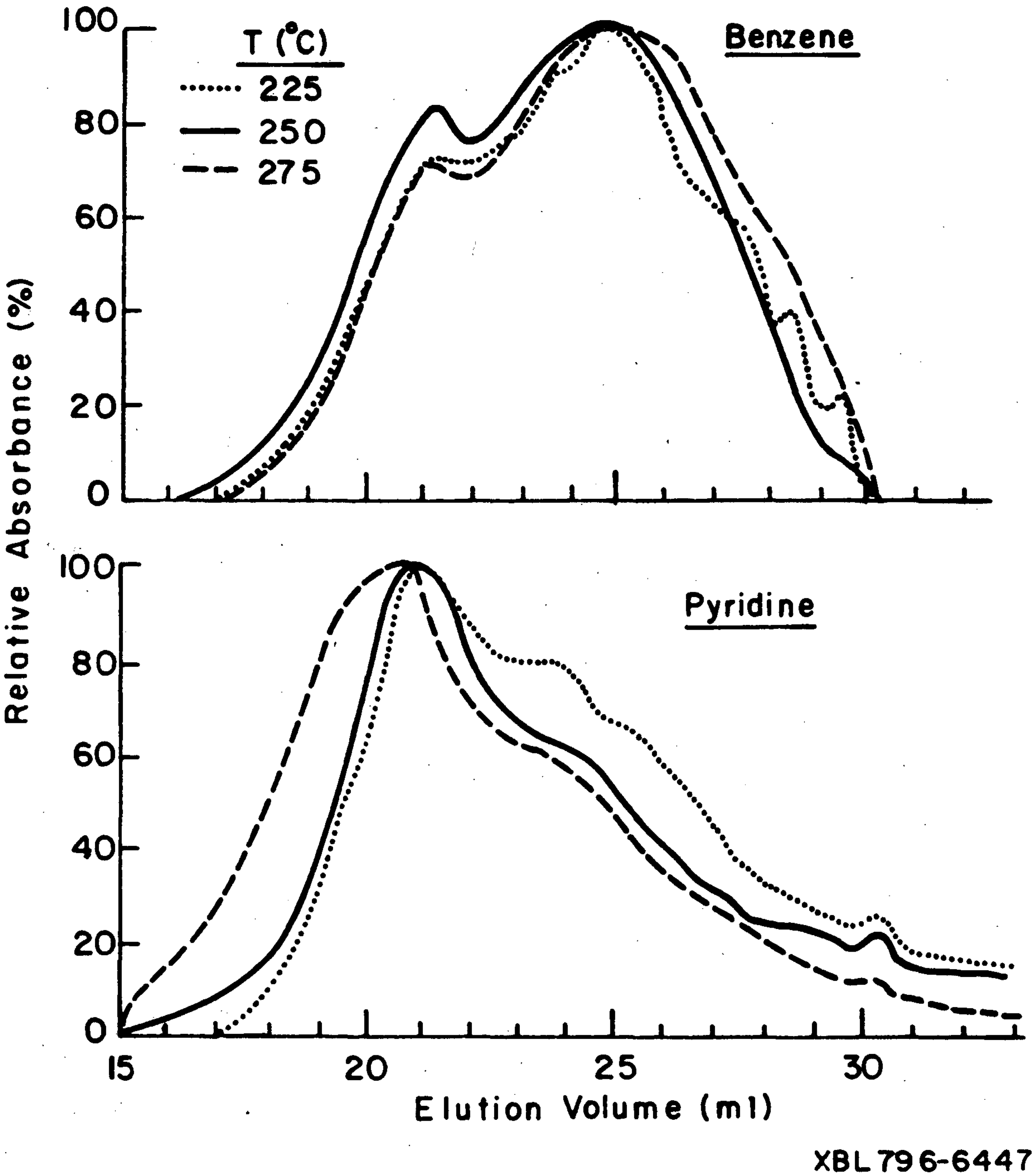

Figure 3-14. Effect of Temperature on Elution of Benzene- and Pyridine-Soluble Materials from a Gel Permeation Column.

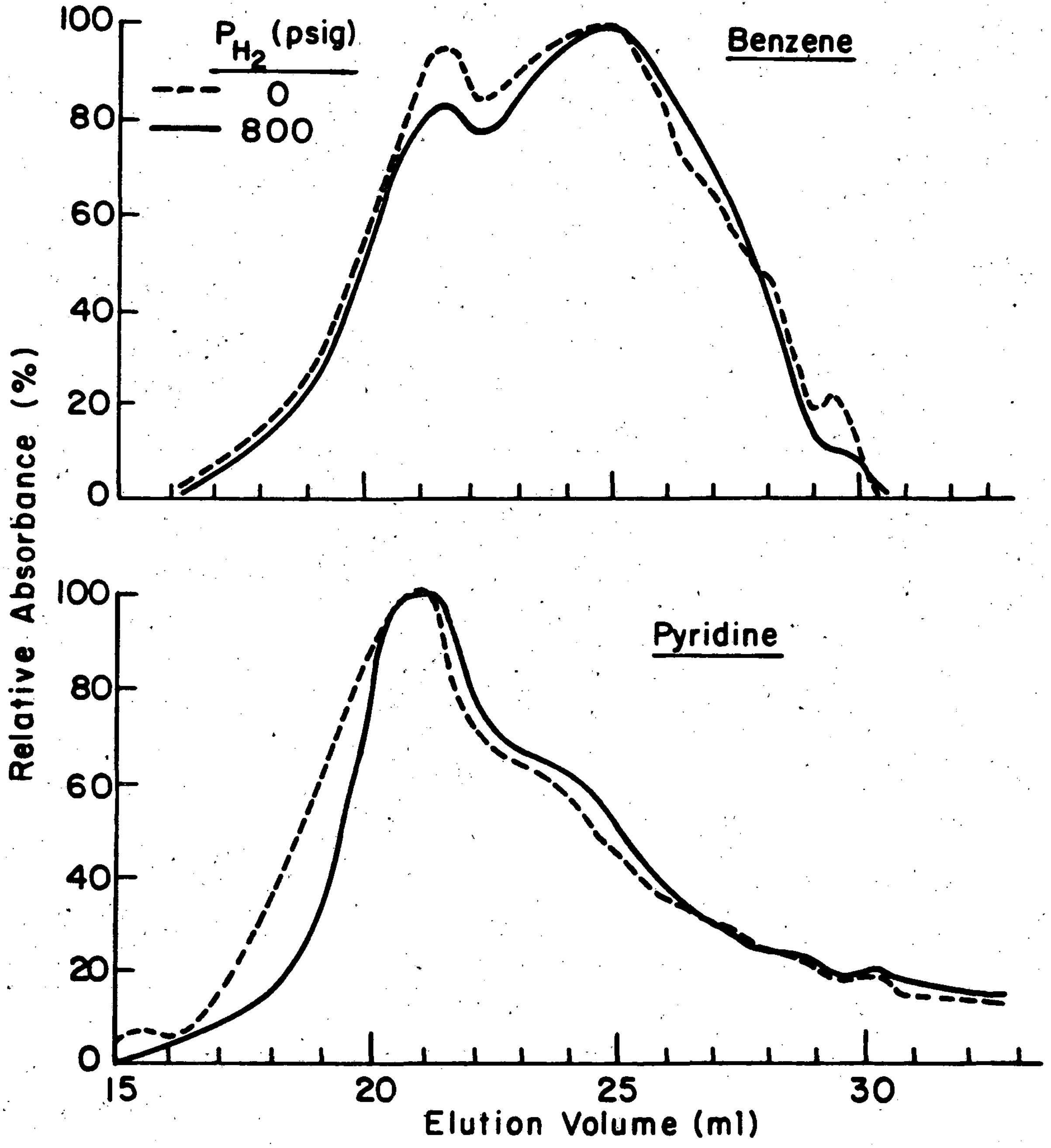

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Figure 3-15. Effect of Hydrogen Pressure on Elution of Benzene- and Pyridine-Soluble Materials from a Gel-Permeation Column.

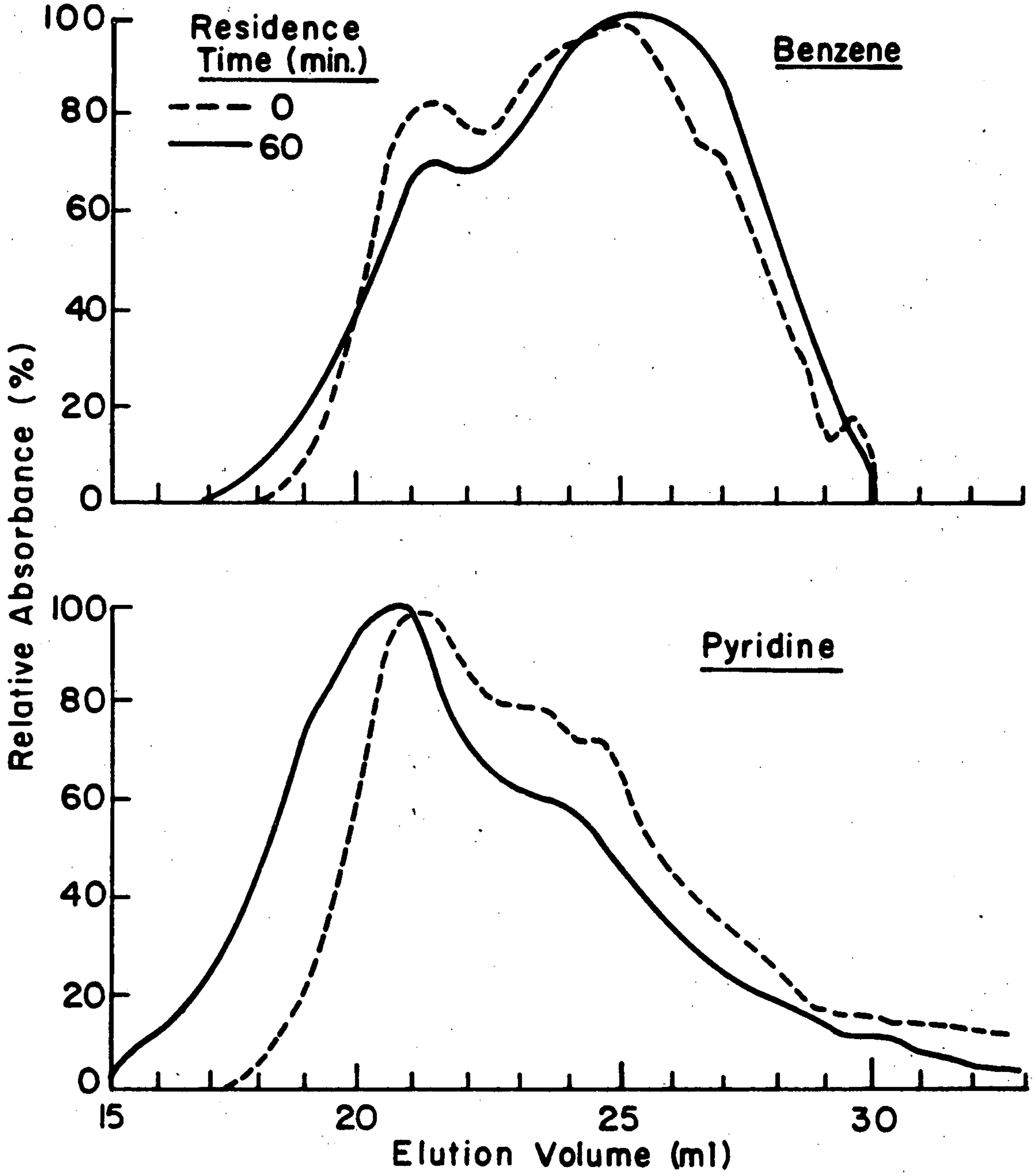

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Figure 3-16. Effect of Residence Time on Elution of Benzene- and Pyridine-Soluble Material from a Gel-Permeation Column.

HCl washing produces the same trend towards higher-molecular-weight extracts with increased yield. Figure 3-17 shows almost identical tracings for water- and HCl-washed MTC, with a slightly higher 21.5 ml peak (benzene-solubles) and substantial increase in materials eluting in less than 20 ml (pyridine-solubles) for the extracts from acid-washed MTC.

As in solubilization activity, the greatest change in GPC tracings is found in changing the $ZnCl_2$ solvent from water to methanol (Fig. 3-18). With $ZnCl_2$-water treatment, which produces only 7% benzene-solubles, most of the product has a fairly low molecular weight (i.e., the elution volume is over 25 ml). Roughly five times more benzene-solubles are produced with methanol, materials with elution volumes below 25 ml predominating. Pyridine-solubles exhibit a similar trend.

In summary, higher conversions (by raising temperature or residence time, washing with HCl, or using methanol instead of water) produce a higher proportion of high molecular weight material. Only for higher hydrogen pressures is greater extractability accompanied by reduced molecular weight.

Scanning Electron Microscopy

The mechanism for reaction of a solid with a liquid is always highly dependent upon the extent of heterogeneity of the solid and upon the extent to which the liquid can reach the solid by capillary uptake or direct imbibition. In coal liquefaction, the surface tension and sorbability of the treating liquid may have major effects upon the liquefaction rate. This is especially true in connection with the current study in which lower-than-usual temperatures are employed in the conversion, and the coal does not self-decompose.

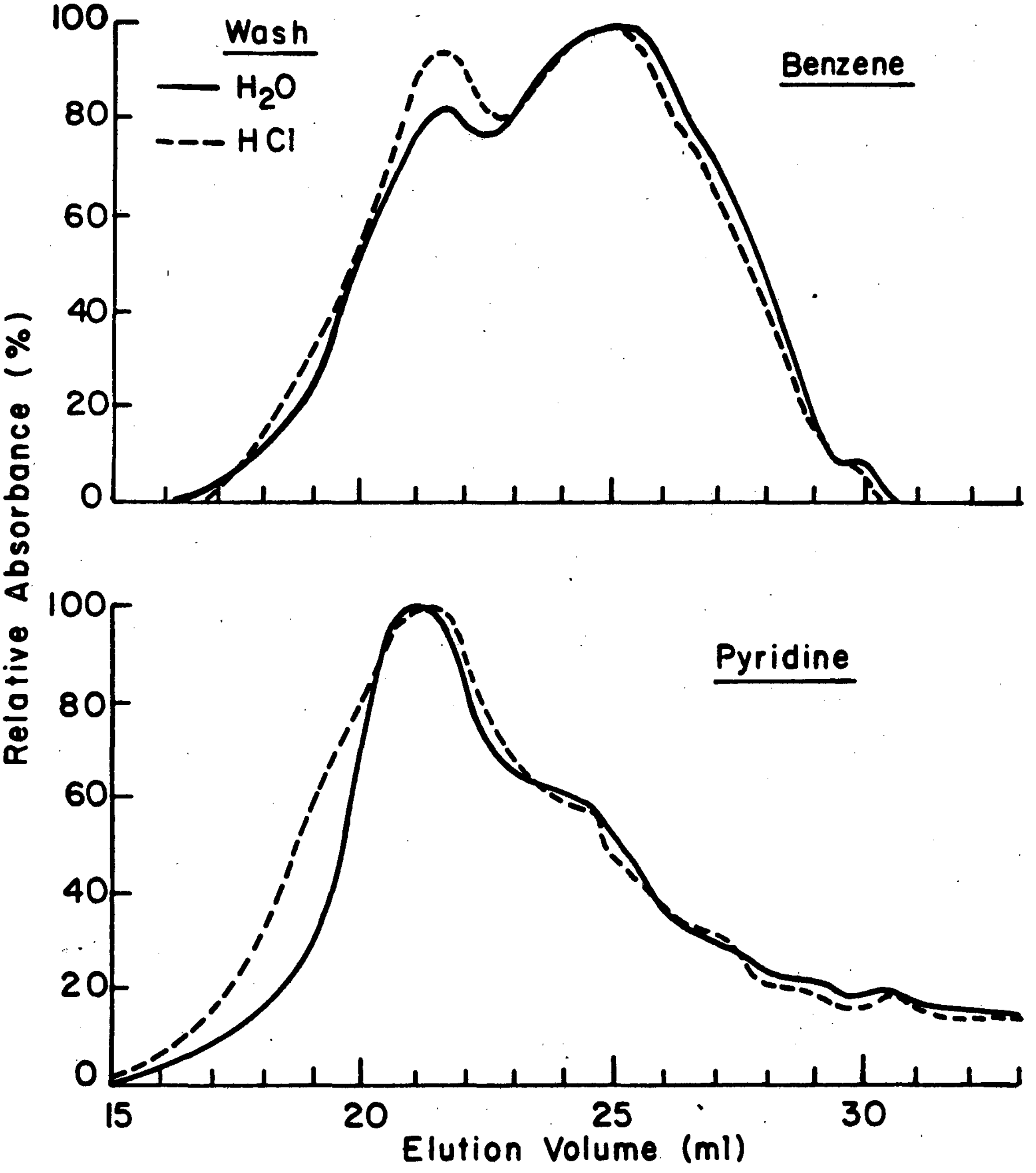

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Figure 3-17. Effect of Wash Conditions on Elution of Benzene- and Pyridine-Soluble Materials from a Gel-Permeation Column.

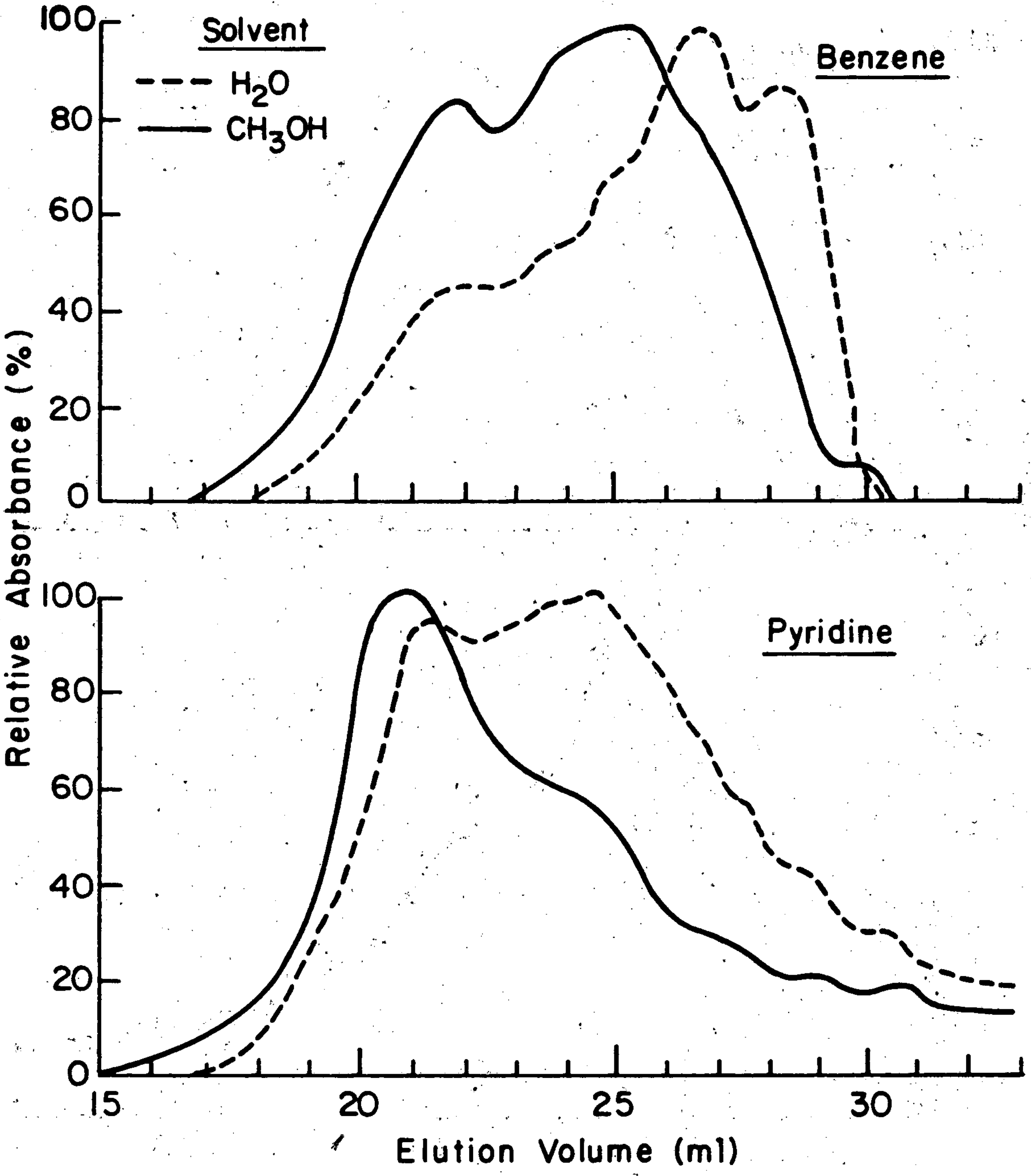

Figure 3-18. Effect of Reaction Solvent on Elution of Benzene- and Pyridine-Soluble Material from a Gel-Permeation Column.

In order to gain some insight into the physical factors which may affect the activity of $ZnCl_2$-catalyzed coal conversion, samples of the treated coals were examined with a scanning electron microscope. Coal particles have been examined before treatment, after treatment, and after pyridine extraction.

Table 3-30 provides the reaction conditions and pyridine solubilities of the MTCs examined in this study. For all of the treatments listed in the table, both the MTC and the extraction residue were examined.

Figure 3-19 compares the untreated coal and its extraction residue with the $ZnCl_2$-H_2O treated coal. Little detail is seen in the raw coal at these magnifications; even after extraction, only 25% of the organic matter is removed by extraction. Treatment with $ZnCl_2$-water only causes minor changes with some "corn-popping" opening up cracks in the particles. Minor change is seen in the bulk of the organic matter between the cracks, however, indicating poor penetration of the melt into this material.

Figure 3-20 examines the role of tetralin in solubilization. Samples treated with tetralin without $ZnCl_2$ (none shown here) are virtually identical to the untreated coal shown in Fig. 3-19. Combination of tetralin with $ZnCl_2$ may be highly effective, however, as seen in Figs. 3-20a and 3-20b. The crack-forming action of the $ZnCl_2$ is still evident, but is combined with some extraction action of the tetralin. The high product solubility and sizeable changes in morphology of MTC suggest that the $ZnCl_2$ and tetralin work together chemically as well as physically. The fine-grain material on the surface

Table 3-30. Treatment Conditions and Extraction Yields for Coal Samples Examined by Scanning Electron Microscopy.

Run	T (°C)	p_{H_2} (psig)	t (min)	H_2O (gm)	$ZnCl_2$ (gm)	CH_3OH (gm)	Additives (gm)	Total Solubility (Pct. daf)
0[a]	25	0	0	0	0	0	-	12
FH3[b]	250	500	60	27	273	0	-	25
FH6[b]	250	500	60	27	273	0	Tetralin-50	65
72	250	800	60	0	273	50	-	85
77[c]	275	800	0	0	273	50	-	36
48	275	800	60	0	273	50	-	99

[a] Untreated coal.

[b] Samples supplied by Frank Hershkowitz, UC Berkeley, Dept. of Ch.E.

[c] Heatup only to 275°C (less than 5 min above 225°C).

Figure 3-19. Coal before and after treatment with $ZnCl_2$-Water at 250°C for one hour. a,b. Untreated coal. c,d. Same, after pyridine extraction. e,f. Treated Coal. g,h. Same, after pyridine extraction.

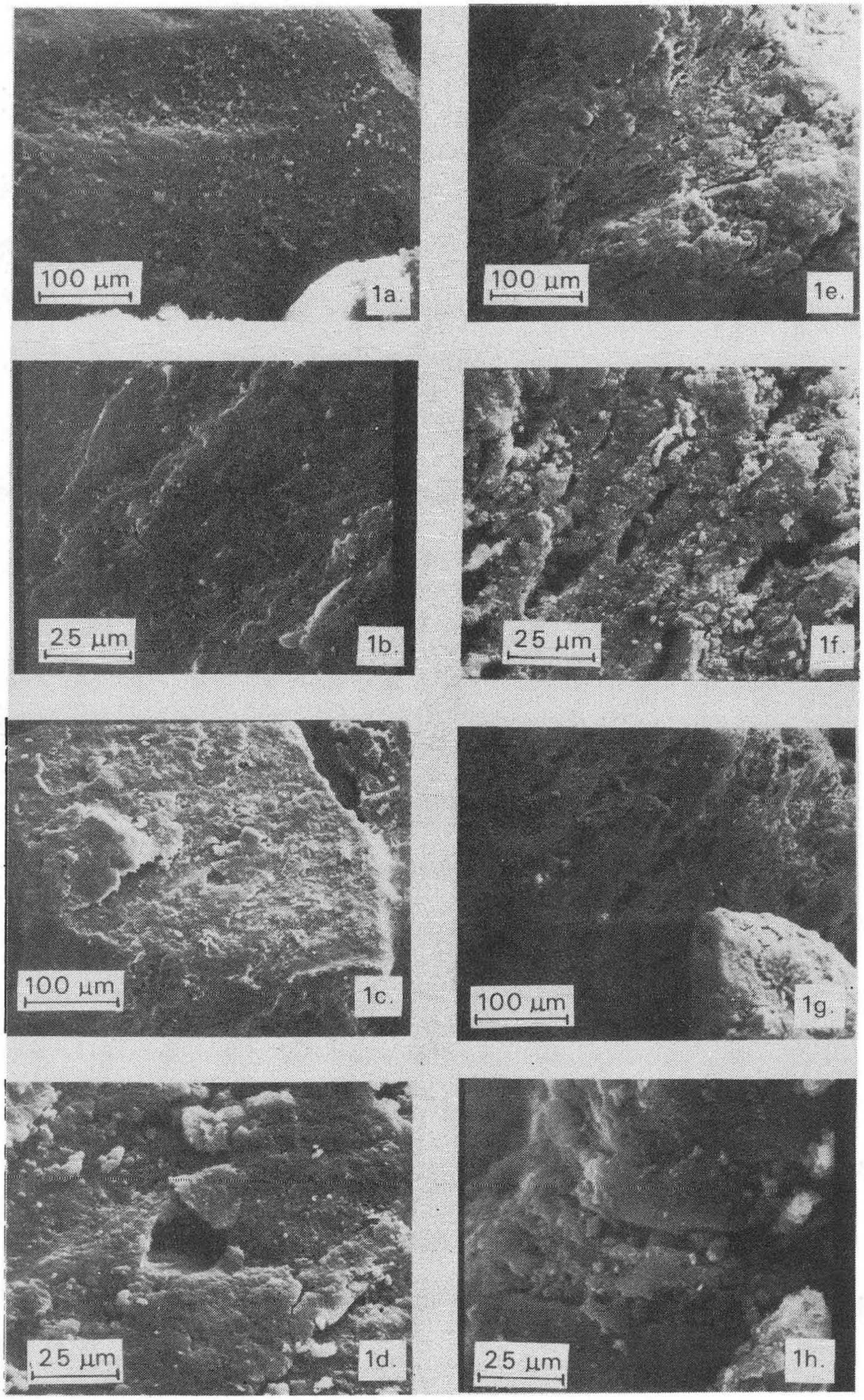

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Figure 3-19.

Figure 3-20. Effect of organic additives in $ZnCl_2$ treatment (250°C, one hour). a,b. Tetralin and water present. c,d. Same, after pyridine extraction. e,f. Methanol present. g,h. Same, after pyridine extraction.

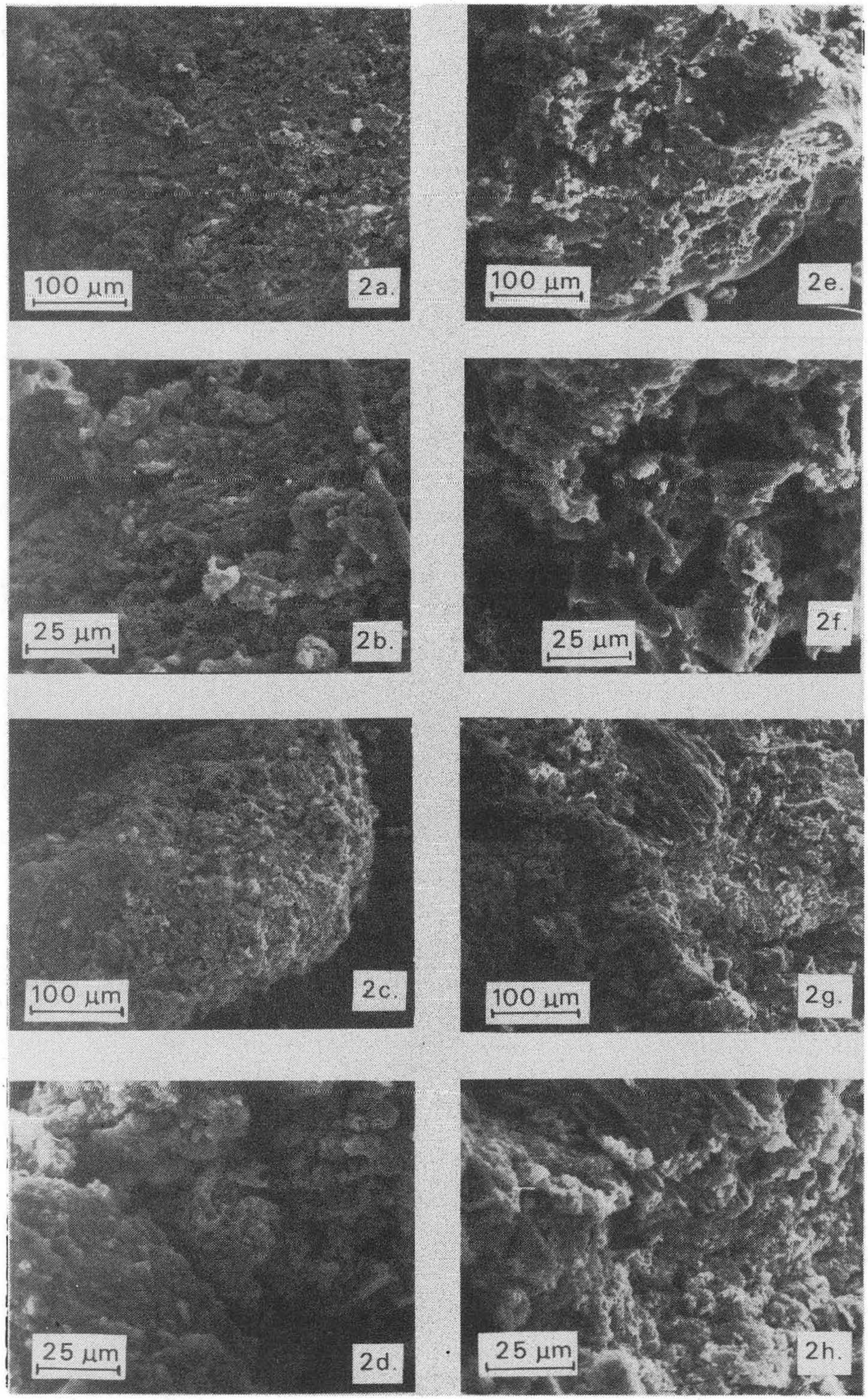

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Figure 3-20.

is reminiscent of micrographs of asphaltenes taken by Rebagay and Mori,(104) suggesting that such material may have been extracted during reaction with tetralin and then deposited on the surface during drying.

Pyridine extraction of the $ZnCl_2$-tetralin treated coal (Figs. 3-20c and 3-20d) removes about 65% of the organic matter, leaving heavily pitted regions in the particles where organic matter has been removed. Figure 3-22 examines this pitted area in more detail. The material which remains after extraction represents some part of the organic matter in the coal which is more resistant to conversion than the extracted material. Bacterial membranes or cell walls from plant matter may be the source of such relatively resistent material, with the remaining cell contents coalified to more reactive materials.

With $ZnCl_2$-methanol treatment, greater changes occur in the morphology of the MTC particles (Fig. 3-20e and 3-20f). The particles are extensively pitted and show evidence of product removal similar to that in the extraction residues of the $ZnCl_2$-tetralin treatment. Apparently addition of methanol to the $ZnCl_2$ allows the catalyst to penetrate the particles more effectively, and aids in the extractive removal of reaction products from inside the particles. Very smooth wax-like areas on the outside of the MTC particles suggest that some of the material may have been molten during reaction, and resolidified on cooling. Pyridine extraction of the $ZnCl_2$-methanol treated coal removed 85% of the organic matter: the particles no longer retain their integrity, the residue being an agglomerated mass of randomly orientated fragements of ash and residual insoluble organic matter in about equal volume.

Figure 3-21. Effect of residence time at 275°C for $ZnCl_2$-Methanol treatment. a,b Heatup only. c,d. Same, after pyridine extraction. e,f. One hour residence time. g,h. Same, after pyridine extraction.

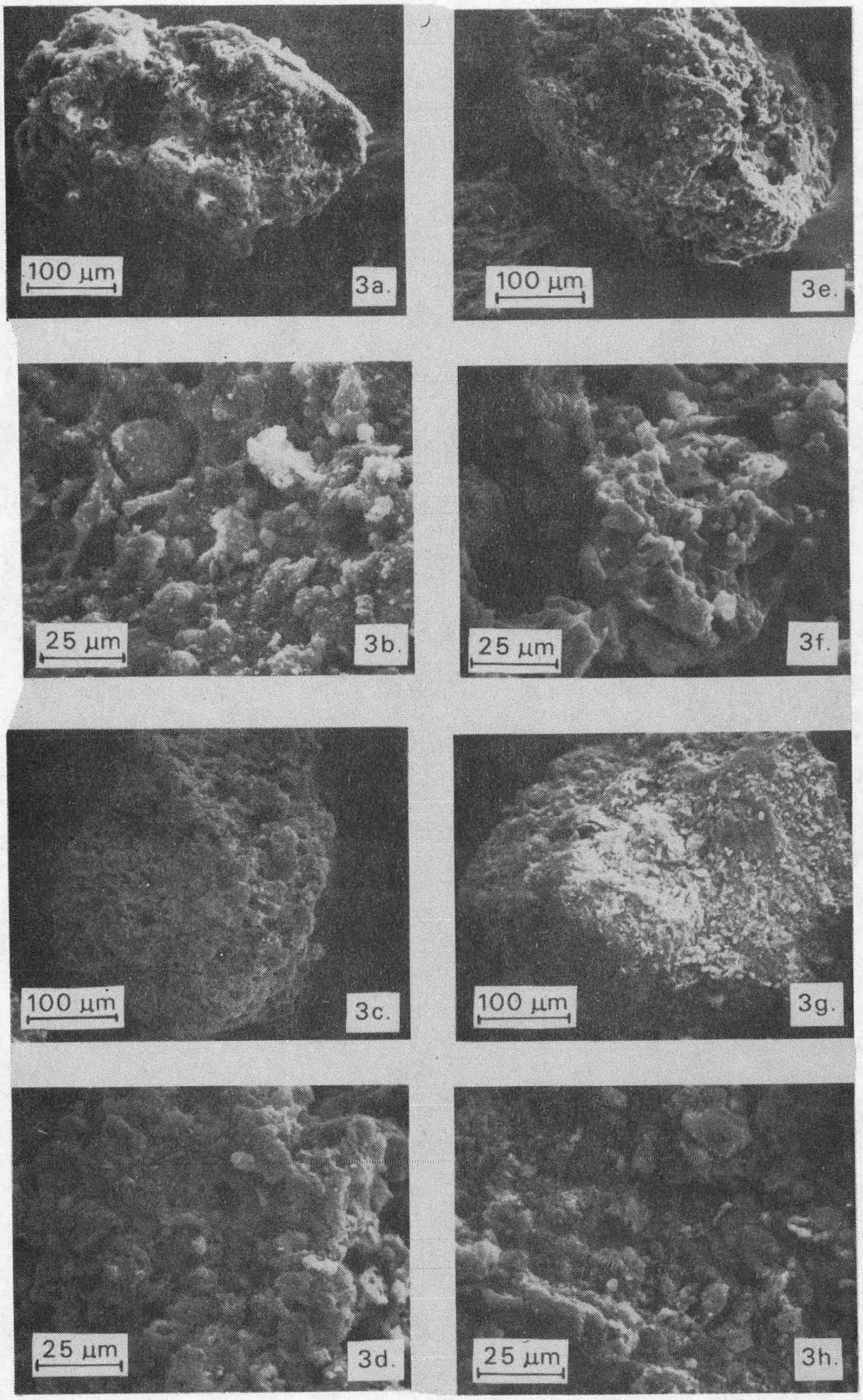

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Figure 3-21.

Figure 3-22. Electron Micrograph of $ZnCl_2$-Tetralin Treated Pyridine-Extracted Coal.

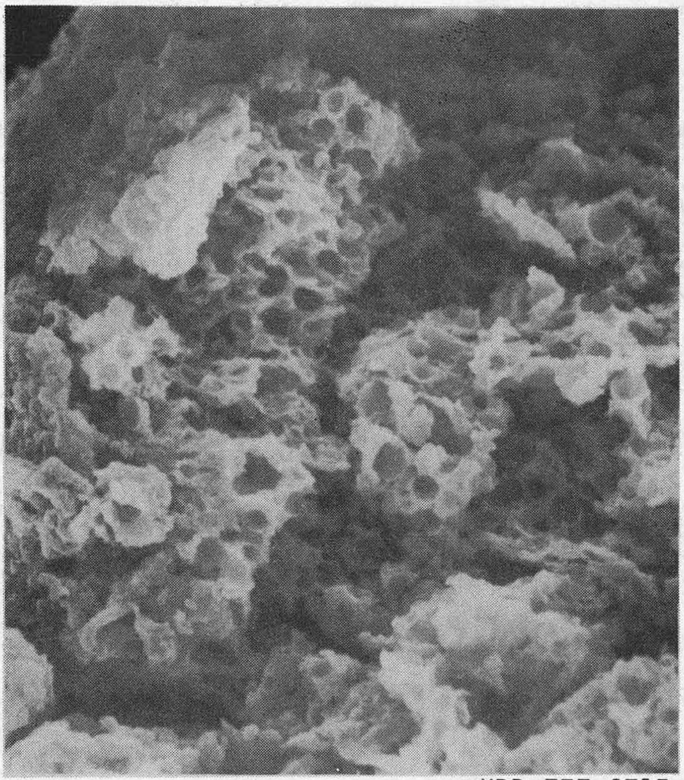

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Figure 3-22.

The effect of raising the reaction temperature to 275°C in the $ZnCl_2$-methanol system is seen in Fig. 3-21. Even for heatup alone to 275°C, significant changes in particle morphology are already taking place. Deep pits open up in the particles, and extraction removes some 36% of the organic material. Apparently the particles are rapidly penetrated by melt at these temperatures. Reaction at 275°C for one hour continues the disintegration of the particles, creating long deep pits and causing many of the particles to fragment. Pyridine extraction removes essentially all of the organic material in this case, leaving a residue of agglomerated ash particles.

This information on the physical changes which accompany the conversion of coal to soluble material will be useful in establishing a mechanism for the solubilization.

Summary of Results

$ZnCl_2$ is more effective when dissolved in methanol than in water for conversion of coal to soluble material.

At all hydrogen pressures, the best conversion is obtained at 0.18 gm methanol/gm $ZnCl_2$ (or 0.8 mole methanol/mole $ZnCl_2$).

Solubilization increases linearly with hydrogen pressure at constant temperature and methanol loading.

A strong temperature effect on rate leads to complete solubilization of coal at 275°C in less than 30 minutes, for $ZnCl_2$ with methanol.

H/C ratios are less in the MTC than in the raw coal except when ZnO or Zn is used as an additive; H/C ratios increase with increasing hydrogen pressure.

Addition of reactive solvents is far more effective than addition of inorganic additives in promoting $ZnCl_2$ solubilization activity.

ZnO has little effect on solubilization; HCl addition during treatment causes no greater effect than a dilute HCl wash after treatment.

Extractive solvents reduce solubility; hydrogen-donor solvents increase both solubility and incorporation.

Incorporation of solvent in the MTC is reduced by lower methanol loadings and higher hydrogen pressures.

HCl washing sharply increases pyridine solubility with a smaller effect on benzene solubility. Benzene washing increases benzene solubility with no effect on total (benzene + pyridine) solubility.

Benzene and pyridine solubilities increase together, with their ratio dependent on the wash conditons.

Nitrogen removal is small, typically 20%.

Oxygen removal and corrected solubility are related, the relation dependent on reaction solvent and wash conditions.

Sizeable pressure drops occur during the runs, caused primarily by consumption of gas-phase hydrogen.

The additional pyridine-solubles resulting from treatments at higher temperatures, at longer reaction times, by HCL washing, or by using methanol in place of water are of higher molecular-weight than the initial products. Only higher hydrogen pressures yield more product that also has lower-molecular-weight.

As evidenced by scanning electron micrographs of the treated coal, substituting methanol for water greatly enhances contacting of the catalyst with the coal, and tends to extract product from the coal particles during treatment.

CHAPTER 4

CHEMISTRY OF ZINC CHLORIDE-ALCOHOL-COAL SYSTEMS

The goal of this work has been to seek means of converting coal at temperatures below that at which thermal degradation takes place. Solvent extractions in the absence of catalysts performed by Grens and co-workers on Wyodak coal have shown relatively small rise in extractability with temperature until approximately 325-350°C.(114) At these temperatures, extraction yields begin to rise rapidly with increasing temperature, indicating that the coal has begun to self-decompose.

The results of this work shows that in the presence of $ZnCl_2$ and alcohols, the same coal may be converted to pyridine-soluble materials at temperatures at or below 275°C. It is therefore concluded that the catalyst system plays an important role in activating the coal for depolymerization into soluble components.

To understand more fully the role of $ZnCl_2$ in the conversion process, the chemistry of this catalyst is being explored. As a first step, reaction of $ZnCl_2$ and alcohols in the absence of coal will be discussed to indicate compounds possibly present in the reaction mixture. Next, the reactions of these compounds with various chemical groups in the coal (specifically, aromatic centers and etheric and aliphatic crosslinks) in the presence of $ZnCl_2$ will be discussed.

$ZnCl_2$-Alcohol Reactions

Kuchkarov and colleagues have investigated the reactions of various alcohols with $ZnCl_2$.(105) Their primary finding was that the catalyst does not decompose the alcohol to form HCl and alkoxyzinc compounds. Instead, a one-to-one $ZnCl_2$-alcohol complex is formed (except in the case of cyclohexanol, which forms a 1:2 complex), which decomposes with further heating. Table 4-1 lists the conditions under which the various complexes form and decompose, and the products of the decomposition.

The products of the complex decomposition are seen to be primarily dehydration products. For all alcohols except methanol, a water molecule may be removed from a single alcohol molecule, and the predominant product is the alkene. $ZnCl_2$-ethanol complex decomposes to ethanol, ethylene, and acetaldehyde. The acetaldehyde is particularly interesting since it is an oxidation product from the ethanol, implying the presence of some unreported reduced species (perhaps ethane from ethylene) or perhaps an O_2 impurity in the reaction system.

$$CH_3CH_2OH + CH_2{=}CH_2 \xrightarrow{ZnCl_2} CH_3CHO + CH_3CH_3 \qquad (?)$$

Such reactions could indicate evidence of reversible hydrogen donation by an alcohol in the presence of $ZnCl_2$. It is also somewhat surprising that no ether is formed.

Decomposition of the $ZnCl_2$:methanol complex takes place with two methanol molecules forming water and dimethyl ether. Unfortunately, no rate data are available for this reaction. Gas analyses from runs

Table 4-1. $ZnCl_2$-Alcohol Complexes and Their Decomposition Products (after Kuchkarov, 105).

Alcohol	Complex Formation Temperature (°C)[1]	$ZnCl_2$:ROH	Decomposition Temperature (°C)	Decomposition Products
CH_3OH	150-155	1:1	180	CH_3OCH_3
C_2H_5OH	140-145	1:1	170-175	C_2H_5OH, CH_3CHO, C_2H_4
n-C_3H_7OH	160-165	1:1	205-210	$CH_3CH{=}CH_2$
i-C_3H_7OH	130-140	1:1	175-185	$CH_3CH_2CH{=}CH_2$
n-C_4H_9OH	140-150	1:1	-	-
CH_2OHCH_2OH	150-155	1:1	-	-
cyclo-$C_6H_{11}OH$	120-125	1:2	140	Cyclohexene + oil

---

[1] Complexes were synthesized by heating the alcohol in dry $ZnCl_2$ at the temperature noted for 4-6 hours. The reaction product was vacuum distilled or washed in ether and analyzed for Zn, Cl, C and H.

57, 72, and 75 all show significant quantities of dimethyl ether (with lesser amounts of methanol and methyl chloride), confirming the dehydration reaction of methanol.

Gas analyses from the $ZnCl_2$-methanol reactions also show the presence of methyl chloride and methane. The first may be the result of chlorination of methanol by $ZnCl_2$. The methane (beyond the small amount from the coal) may be formed from reaction of the methyl chloride or of the methanol; Schlosberg has cited evidence for formation of propane from isopropyl chloride in BF_3 at lower temperatures.(106)

Kuchkarov also investigated the chemical reactivity of the $ZnCl_2$-alcohol complexes.(105) He found them to have catalytic activities in excess of those of anhydrous $ZnCl_2$ or $ZnCl_2 \cdot 2H_2O$. Acylations, esterifications, alkylations (with alkyl chlorides and higher alcohols), and acetal production were all found to occur substantially, at temperatures between 70 and 220°C; see Table 4-2.

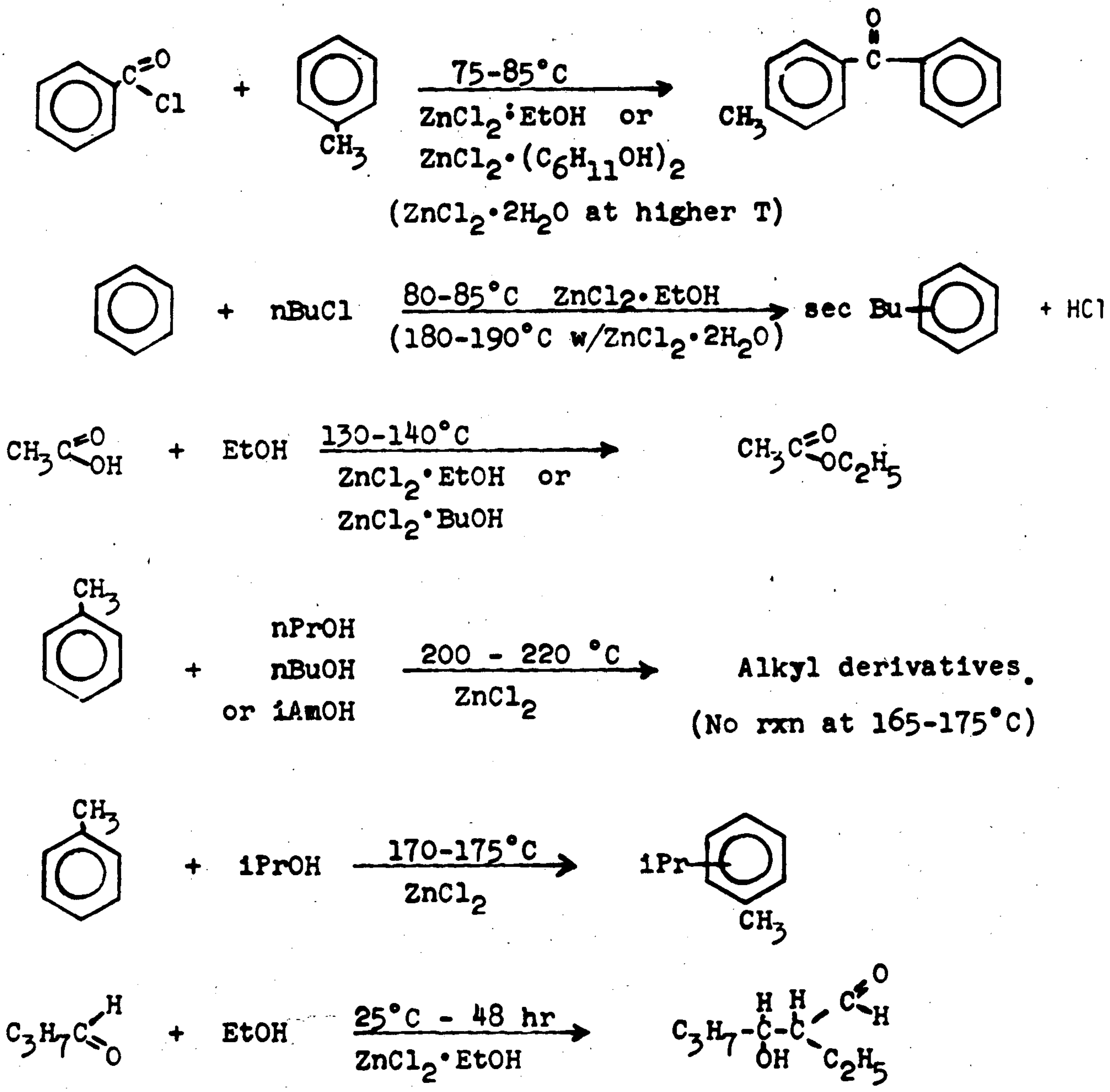
The catalytic properties of $ZnCl_2$-alcohol complexes are purported to be due to complex acid formation, as Meerwein(107) has reported for $ZnCl_2 \cdot 2H_2O$.

$$ZnCl_2 + 2\ H_2O \longrightarrow ZnCl_2 \cdot (OH)_2H_2 \longrightarrow ZnCl_2 \cdot (OH)_2^{2-} + 2\ H^+$$

However, the extent to which this reaction occurs is open to question. Hydrolysis with HCl production may follow the complex acid formation, i.e.

$$2\ ZnCl_2 + H_2O \rightleftharpoons 2\ HCl + ZnO$$

Table 4-2. Reactions Catalyzed by $ZnCl_2$-Alcohol Complexes (after Kuchkarov, 105) (continued)



The equilibrium constant for this reaction at 250^{o}C is about 10^{-16} however, indicating that HCl production would be small. Chemical analyses of the reaction off-gases failed to reveal any HCl.

$ZnCl_2$-Alcohol-Coal Reactions

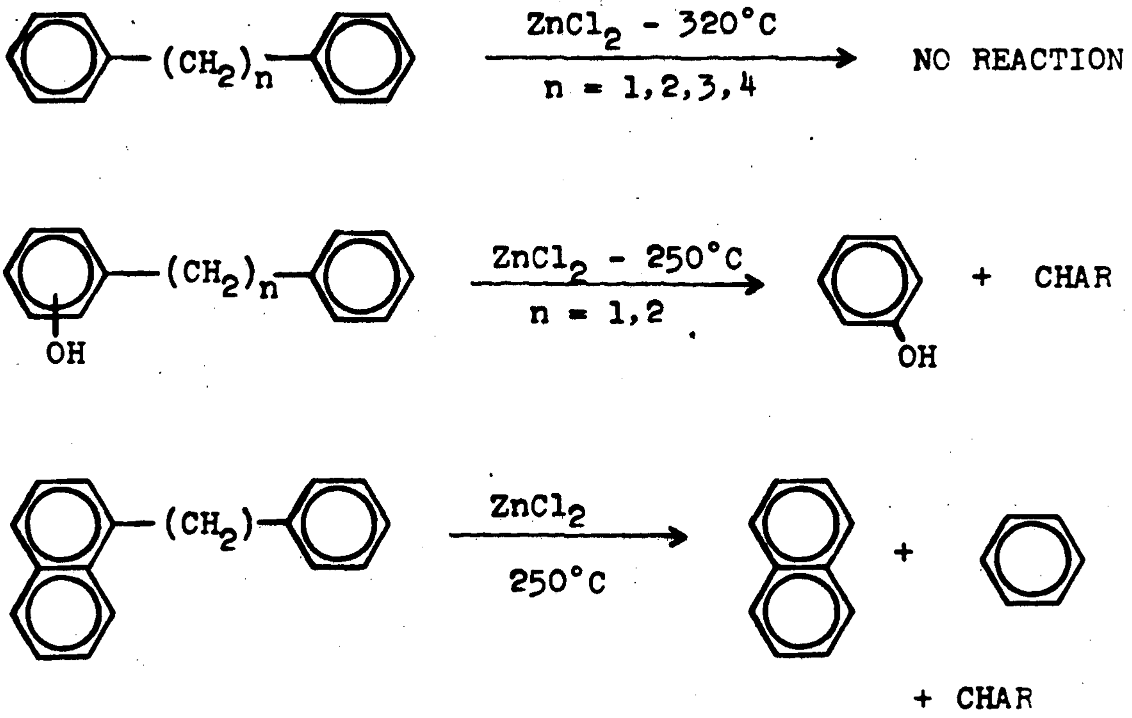
As noted in Chapter 1, coal is composed of a wide variety of organic functional groups and aromatic and aliphatic moieties. Of particular interest for this study are the reactivities of bonds which hold together the individual pieces of the coal polymer. Cleavage of these interconnecting bonds can result in solubilization of the coal organic matter. Also of interest will be the reactions - specifically hydrogenation and alkylation - of the aromatic centers.

Two major types of crosslinks, aliphatic and etheric, are considered important in crosslinking the coal structure. Collins et al have shown that these bonds are cleaved in donor solvent media at temperatures in the ranage of 400-500^{o}C.(32)

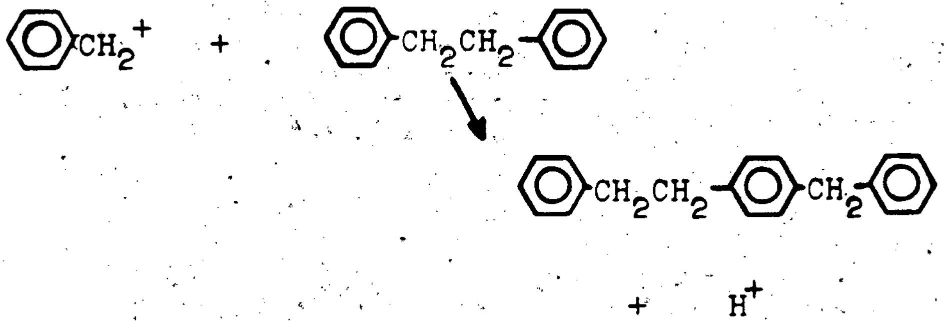
Aliphatic Linkages

Taylor has studied reactions of model compounds containing aliphatic linkages in the presence of $ZnCl_2$ at temperatures between 200 and 325^{o}C.(103) Some of his results are shown in Table 4-3. It is interesting to note that $ZnCl_2$ can cleave hydroxy-substituted diphenylalkanes or naphthylaryl alkanes, but not diphenylalkanes as such. Addition of 1000 psig H_2 to the reaction medium has no effect, or some positive effect, on reactant conversion. HCl is a strong promoter, but also may produce conversions without $ZnCl_2$.

Table 4-3. Cleavage of Aliphatic Crosslinks by $ZnCl_2$ (Taylor, 103).



Taylor finds his results consistent with carbonium ion chemistry for such systems; hydroxyl substitution on the aromatic rings leads to more stable intermediate carbonium ions and thus to higher reactivity. It is notable that Taylor had no material in the system which could readily quench the reactive carbonium ions formed by $ZnCl_2$ cleavage of the aliphatic bridges. As a result, polymeric material was formed from part of the reactant, and this was interpreted to occur through Scholl-type condensation:



The aromatic centers in coal are likely to be substituted, often by phenolic groups; furthermore, there are many multiple ring systems. Therefore, Taylor's findings would lead one to expect that $ZnCl_2$-alcohol systems could cleave most of the aliphatic bridges in coal at 300°C, if not at 250°C. The presence of alcohol may or may not enhance the catalytic activity, but it should reduce the tendency of cleavage fragments to polymerize, by serving as a primary capping agent.

Ether Linkages

Mobley(108, 109) has reported work on cleavage of aryl ether and thioether bonds with $ZnCl_2$ in various solvents, as summarized in Tables 4-4, 4-5 and 4-6. Only the diphenyl ethers are found to be refractory. In the reaction, ether cleavage is accompanied by incorporation of the solvent. When the ether oxygen is attached to

Table 4-4. Ether Cleavage by Zinc Chloride. Data of Mobley(108). 0.025 Moles Ether; 3/1 $ZnCl_2$/Ether (Molar); 50 ml Solvent; 1 Hr Reaction Time.

Ether	Solvent	Gas	Reactant Conversion (%)	T (°C)	P (MPa)	Product and Yield (%)
Diphenyl[1]	Benzene	H_2	0	327	13.6	-
	Tetralin	H_2	6.5	230	9.7	-
Phenyl-benzyl	Benzene	H_2	100	226	3.9	Phenol - 61 Diphenyl methane - 59 o-Benzyl phenol - 14
Naphtyl-Benzene		N_2	100	226	5.0	Naphthol - 29 Benzyl naphthols - 20 Diphenyl methane - 14
Dibenzyl	Benzene	H_2	100	232	4.8	Diphenyl methane - 80
	Benzene[2]	N_2	100	228	5.1	Diphenyl methane - 88
	Tetralin	H_2	100	233	4.1	Benzyl tetralins - 66
	Tetralin	N_2	100	227	4.4	Benzyl tetralins - 62
	Cyclohexane	N_2	94	230	4.8	Tar
	Methanol	H_2	100	225	6.2	Methyl benzyl ether - 90

[1] 2.5/1 molar $ZnCl_2$/ether

[2] 0.3 moles $ZnCl_2$/ether

Table 4-5. Cyclic Ether Cleavage by Zinc Chloride. Data of Mobley.(108)
325°C; 1 Hr.; 21.5/1 Molar Benzene/Ether; 2.9/1 Molar $ZnCl_2$/Ether.

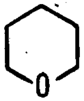
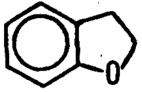
Ether	P_{H_2} (MPa)	Reactant Conversion (%)	Product	Yield (%)
	14.2	31.1	--	0.0
	14.0	100	s-amyl benzene	8.2
			1-methyl tetralin	5.2
			i-propyl benzene	4.5
			t-amyl benzene	3.3
			1,3-dimethyl benzene	2.9
			ethyl benzene	1.6
			1,1-dimethyl,2-propenyl benaene	1.4
			2-methyl naphthalene	1.2
			1,1-dimethyl indan	1.0
			1-methyl naphthalene	1.0
			s-butyl benzene	0.9
			toluene	0.6
	14.1	-	s-butyl benzene	11.8
			i-propyl benzene	4.8
			n-butyl benzene	4.5
			1-methyl indan	3.7
			ethyl benzene	0.8
			tetralin	0.4
			toluene	0.3
	15.3	98.3	phenol	27.5
			hydroxy 1,2-diphenly ethane	10.8
			ethyl benzene	9.5
			2-ethyl phenol	5.0
			1,1-diphenyl ethane	4.2
			4-ethyl phenol	1.8
			diphenyl methane	1.4
			toluene	0.7
			bibenzyl	0.2

Table 4-6. Thioether Cleavage by Zinc Chloride. Data of Mobley.(109)

Reactant	Solvent	Moles Solvent Mole Reactant	Moles $ZnCl_2$ Mole Reactant	Reaction Temperature (°C)	Reaction Pressure (MPa)	Products	% Theoretical Yield of Product	% Conversion of Reactant
Diphenyl sulfide	Cyclohexane	16.8	0	324	14.4	Benzene Thiophenol	15.7(1) 11.0(2)	32.5
Diphenyl sulfide	Cyclohexane	16.7	2.80	323	12.1	Benzene	7.4(1)	6.0
Diphenyl sulfide	Benzene	19.8	2.67	325	13.8	No identifiable products	-	21.9
Diphenyl disulfide	Benzene	24.0	0	321	13.8	Thiophenol Diphenyl sulfide	54.5(1) 30.6(2)	100
Diphenyl sulfide	Benzene	24.0	3.28	323	13.1	Diphenyl sulfide Thiophenol	52.1(2) 21.2(1)	82.8
Dibenzyl sulfide	Benzene	23.4	3.18	325	13.6	Toluene Bibenzyl Stilbene Diphenylmethane	24.9 17.5 14.3 11.8	100
Dibenzyl sulfide	Benzene	23.7	0	325	14.1	Bibenzyl Toluene Stilbene	43.5 33.0 7.8	100
Dibenzyl disulfide	Benzene	17.8	2.42	225	13.8	Diphenylmethane	58.75	98.5
Dibenzyl disulfide	Benzene	27.1	3.67	320	14.2	Bibenzyl Toluene Stilbene Diphenylmethane	27.4 26.2 7.1 2.9	100
Dibenzyl disulfide	Benzene	27.3	0	321	13.7	Bibenzyl Toluene Stilbene	52.0 32.0 3.8	100
Thiophene	Benzene	21.3	2.95	325	14.8	No reaction	-	5.9
Dibenzothiophene	Benzene	20.2	2.79	325	13.7	No reaction	-	8.0

Table 4-6. Thioether Cleavage by Zinc Chloride. Data of Mobley.(109)
(Continued)

Reactant	Solvent	Moles Solvent Mole Reactant	Moles $ZnCl_2$ Mole Reactant	Reaction Temperature (°C)	Reaction Pressure (MPa)	Products	% Theoretical Yield of Product	% Conversion of Reactant
Tetrahydrothiophene	Benzene	21.7	2.93	226	13.6	Complex with $ZnCl_2$		91.7
Tetrahydrothiophene	Benzene	21.5	2.98	321	15.8	Butanes	15.0	91.2
						Propane	13.0	
						Hydrogen sulfide	6.0	
						Ethane	3.0(1)	
						Methane	2.0(3)	
						sec-Butylbenzene	2.4	
						Toluene	1.3(2)	
						Isopropylbenzene	0.9(2)	
						n-Butylbenzene	0.8	

---

[1] Based on 2 moles product per mole reactant

[2] Based on 1 mole product per mole reactant

[3] Based on 4 moles product per mole reactant

the aromatic ring a phenol results, whereas otherwise oxygen is removed in forming the daughter compounds.

When cyclohexane is used as solvent for dibenzylether cleavage, the parent compound incorporates and a polymer results. This result is similar to cases where aliphatic bridges were cleaved in the absence of a suitable capping agent.

Mobley's result with methanol as solvent is of particular interest in this present study. A single major product, methyl benzyl ether, is formed at 225°C. However, in the presence of some available form of hydrogen at 250°C or above, one would expect this compound to undergo oxygen removal and form toluene and methanol.

Newer work by Mobley has shown that the addition of powdered nickel to the $ZnCl_2$-benzene medium does result in significant toluene yield from dibenzyl ether, implying that the solid nickel serves as a hydrogenating co-catalyst.

The reaction of methanol with dibenzyl ether fits into a category of reactions which were investigated by Briller,(110) involving $ZnCl_2$-catalyzed exchange of phenolic proton by an alkyl group previously attached to another oxygen-containing species (see Figure 4-1). The existence of this type of ether-hydroxyl interchange implies that similar reactions can occur with ethers and phenols in the coal.

Thus, the primary crosslinks in the coal, which are in fact cleaved by $ZnCl_2$ catalysis as observed in this study, are most likely etheric and aliphatic. A summary of the reactions which would be expected to occur is shown in Fig. 4-2. Although these may represent the essential reactions resulting in solubilization of the coal, numerous

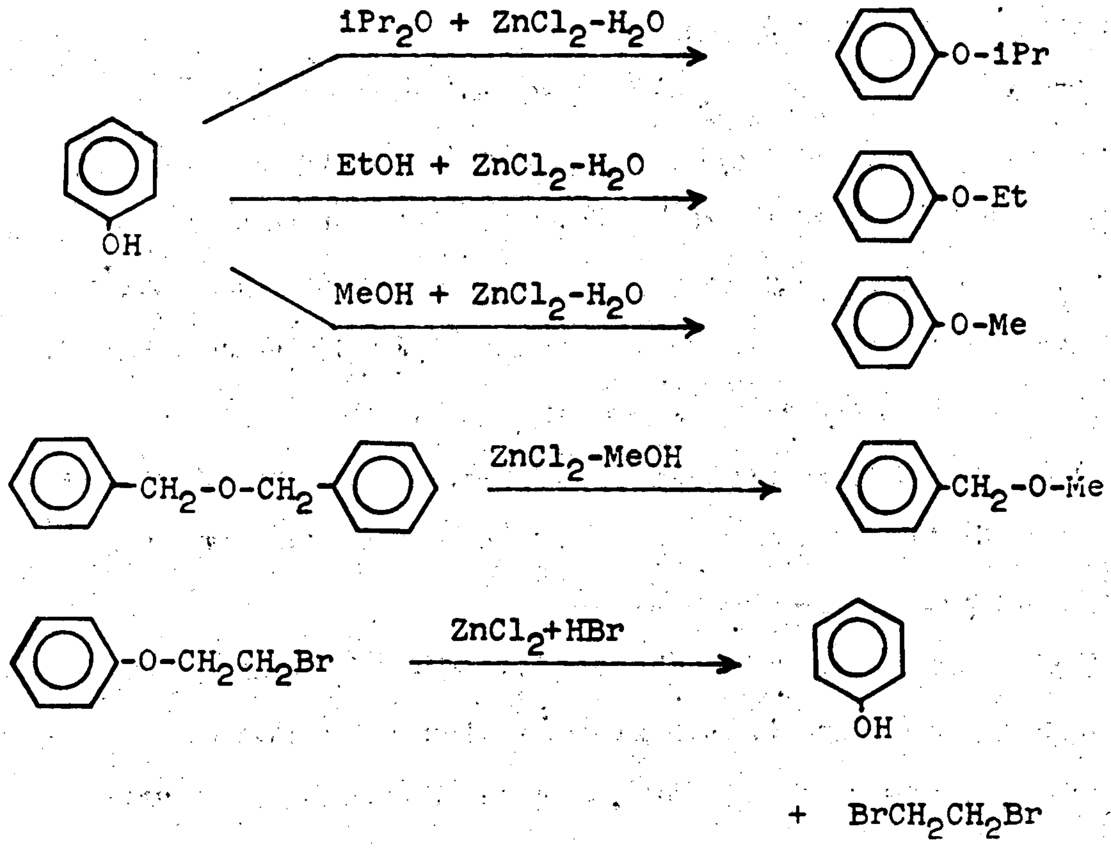


Figure 4-1. Exchange Reactions of Phenols, Ethers, and Alcohols (after Briller, 110)

$$\text{Ar-(CH}_2\text{)}_n\text{-Ar} \xrightarrow{\text{ZnCl}_2} \text{Products}$$

if $n \geq 1$ and

Ar ≥ Naphthyl

or

Ar is a phenol.

$$\text{Ar-Ch}_2\text{-O-Ch}_2\text{-Ar} \xrightarrow{\text{ZnCl}_2} \text{Ar-CH}_2\text{-Solvent} + \text{H}_2\text{O}$$

$$\text{Ar-CH}_2\text{-O-Ar'} \xrightarrow{\text{ZnCl}_2} \text{Ar-CH}_2\text{-Solvent} + \text{Ar'OH}$$

Figure 4-2. Cleavage of Crosslinks Between Aromatic Centers by Zinc Chloride (based on work of Taylor and Mobley, 103, 108, 109) side reactions may accompany these cleavages. Of particular interest are the reactions which involve the aromatic centers; such reactions may lead to further bond cleavage, alkylation or, in some cases, condensation.

Aromatic Centers

Friedel-Crafts alkylation of aromatic centers with Lewis-acid catalysts has been conducted on a wide variety of compounds for many years. An extensive review of these reactions has been published work by Olah.(112) Table 4-7 lists some of the alkylations catalyzed by $ZnCl_2$ with alcohols, ethers and olefins.

Although it is difficult to alkylate benzene or toluene with alcohols and $ZnCl_2$, it is seen to be easy to alkylate phenol and aniline. $ZnCl_2$ supported on Al_2O_3, SiO_2, or silica gel is also a good catalyst for alkylating aromatics with olefins or ethers. Such alkylations seem not to occur with unsupported $ZnCl_2$, and the acidic support may be needed to adsorb or activate the olefin; similarly, such reactions may take place in the coal medium due to clay in the coal mineral matter.

The question of whether or not methanol will alkylate aromatic centers remains unresolved. Olah makes no reference to alkylations by methanol or dimethyl ether. Mobley found no alkylation products with methanol and dibenzyl ether at 225°C. Kuchkarov has postulated that alkylation by alcohols occurs via production of the olefin intermediate, which would exclude the possibility of alkylation by methanol.(105) Model compound studies are needed to resolve this debate.

Table 4-7. Alkylation of Aromatic Centers with Alcohols, Ethers, and Olefins by Zinc Chloride (after Olah, 112).

Aromatic	Alcohol	Ether	Olefin	Catalyst-Conditions
Benzene	n-Propanol i-Propanol n-Butanol Cyclohexanol	Diethyl Dibutyl Diisopropyl Diisoamyl	Ethylene Propene 2-Butene i-Butylene 2-Methyl-2 Butene 1,3-Butadiene Cyclohexene	$ZnCl_2$ and Al_2O_3, SiO_2 or silica gel
Benzene	Ethanol			$ZnCl_2$-poor yield at 300°C
	i-Butanol			$ZnCl_2$-260°C, 48-72 hr
Toluene	i-Butanol n-Butanol			$ZnCl_2$-300°C, 24 hr
Toluene	i-Propanol	Diisopropyl		$ZnCl_2$ on Al_2O_3, SiO or silica gel
Phenol			3-Methyl Propene	$ZnCl_2$-H_2O
Phenol			Ethylene	$ZnCl_2$ + $HgCl_2$
			Propene	Zn
			Higher olefins	$ZnCl_2$ + HCL
			1,3 Butadiene	$ZnCl_2$
o-Cresol	i-Butanol			$ZnCl_2$-180°C
m-Cresol			1-Pentene	$ZnCl_2$ on Al_2O_3 3-Methyl-1-Butene 2-Methyl-2-Butene
Aniline	n-Propanol i-Propanol i-Butanol i-Amyl t-Amyl n-Octyl s-Octyl			$ZnCl_2$- 200-280°C
Tetralin			1-Nonene	$ZnCl_2$- 250°C or $ZnCl_2$ on Al_2O_3
Naphthalene	i-Propanol Cyclohexanol	Diisopropyl	Ethylene Propene	$ZnCl_2$ on Al_2O_3

Table 4-7. Alkylation of Aromatic Centers with Alcohols, Ethers, and Olefins by Zinc Chloride (after Olah, 112). (Continued)

Aromatic	Alcohol	Ether	Olefin	Catalyst-Conditions
Anthracene	n-Butanol i-Amyl i-Butanol			$ZnCl_2$+HCl, 150°C, 4 hr
Toluene Naphthalene Methyl-Naphthalene Tetralin Biphenyl	Allyl			$ZnCl_2$

Salim and Bell have studied reactions of aromatics with $ZnCl_2$ without alkylating agents, in runs using cyclohexane as solvent at 325°C for 1 hour at 1500 psig H_2; see Tables 4-8 and 4-9.(113) Among the aromatics, naphthalene and phenanthrene are unreactive, whereas anthracene is hydrogenated with minor cracking. The presence of a methyl group on naphthalene has a minor activating effect for hydrogenation: presence of hydroxyl is a strong activator for hydrogenation, with the hydroxyl group being removed. In the absence of hydrogen (1500 psig N_2), the conversion of these compounds is almost exclusively to polymers. (Table 4-10)

Hydroaromatic model compounds generally show less than 12 percent conversion under these conditions. Most reactive of these is dihydroanthracene, which is primarily hydrogenated (or perhaps disproportionated) to form octahydroanthracene. A hydroxyl group on hydrogenated naphthalene enhances the reactivity slightly if attached to the aromatic ring, and greatly enhances reaction (with hydroxyl removal) if attached to the aliphatic ring. Dihydronaphthalene is rapidly converted to tetralin. Cracking of hydroaromatic or aromatic rings is slight. Under the conditions of the $ZnCl_2$-alcohol-coal experiments (250°C, 500 psig), we would expect these hydrogenation and cracking reactions to be considerably slower.

Several other reactions are worthy of note.(112) $ZnCl_2$ promotes rearrangements in aromatic structures; for instance, rearrangements of aryl ethers (Fries rearrangement),

Table 4-8. Conversion of 2-Ring Aromatics with $ZnCl_2$ and Hydrogen. 325°C; 1500 psig H_2; 1 hr.; 2 mole % Substrate in Cyclohexane; $ZnCl_2$/Substrate = 1/2 Molar (Data of Salim, 113).

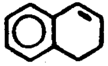
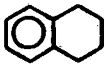
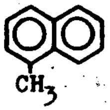
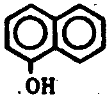
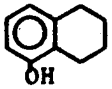
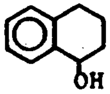
Substrate	Conversion, Mole % Total	Hydrogenation Only	Ring Cracking	Other Products
	0.5	0.5	t	-
	78	60	0.1	-
	1.3	0.4	0.4	1
	5.1	3.6	0.1	Tetralin - 1.1 Naphthalene - 0.3
	26	5.8	0.1	Tetralin - 16 Naphthalene - 3.4
	3.6	t	1.3	Decalin + Tetralin - 0.5 Naphthalene - f0.4
	80	t	0.1	Decalin + Tetralin - 66 Naphthalene - 12

Table 4-9. Conversion of 3-Ring Aromatics with Zinc Chloride and Hydrogen. 325°C; 1500 psig H_2; 2 Mole % Substrate in Cyclohexane; $ZnCl_2$/Substrate = 1/2 Molar (data of Salim, 113).

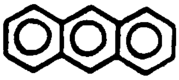
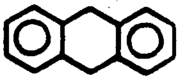
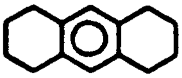
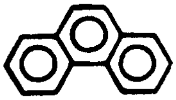
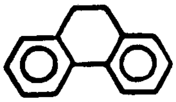
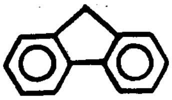
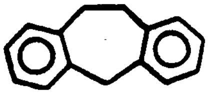
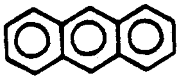
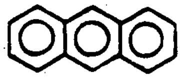
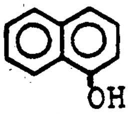
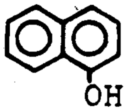
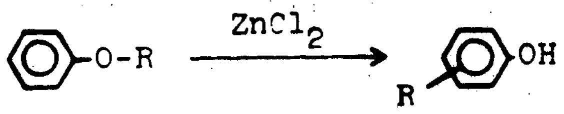
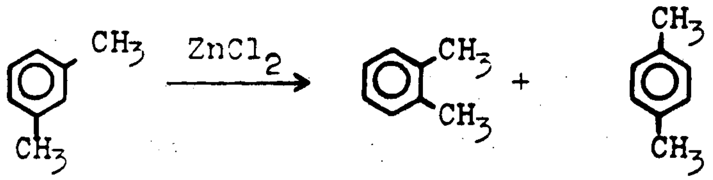
SUBSTRATE	CONVERSION, mole %		
	TOTAL	HYDROGENATION	CRACKING
	68	67.7	0.5
	12	6.9	0.6
	T	0	t
	1.3	1.3	t
	2.7	0.7	0.3
	0	0	3.0
	3.8	0	3.0

Table 4-10. Effect of Hydrogen Pressure in Conversion of Aromatics to Liquid Products. 325^oC; 1500 psig; 2 Mole % Substrate in Cyclohexane; $ZnCl_2$/Substrate = 1/2 Molar (data of Salim, 113).

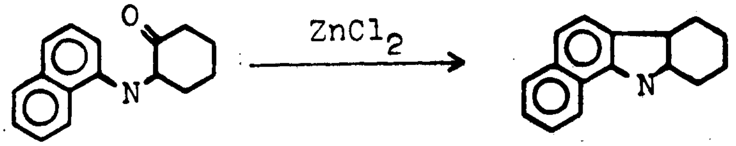
SUBSTRATE	GAS	SUBSTRATE CONVERSION, mole%		
		LIQUID PRODUCTS	UNREACTED	POLYMERIZED
	H_2	68	32	0
	N_2	0.1	5	95
	H_2	26	74	0
	N_2	4	20	76



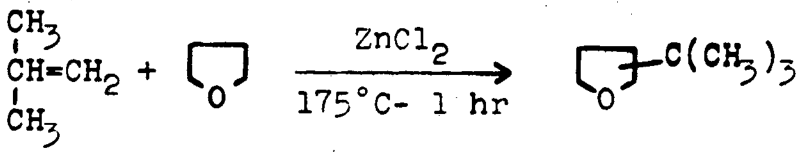
and isomerization of xylenes (or, by inference, trimethyl- and tetramethylbenzenes).



Decarboxylation of carboxylic acids is expected as well as removal of carbonyls, in some cases with cyclialkylation, e.g.



Aklylation of aliphatic ethers is also promoted by $ZnCl_2$.



Haloalkylkations with formaldehyde, para-formaldehyde or haloethers by $ZnCl_2/HCl$, alkylations of alkenes by haloalkenes, and acylations by acyl chlorides (or anhydrides) and $ZnCl_2$ would also be rapid at 250^oC. The necessary reactants for such events would not likely be present in the $ZnCl_2$-alcohol-coal medium, however.

Summarizing, many reactions may be taking place in the complex $ZnCl_2$-alcohol-coal system. The major reactions include: (1) cleavage of aliphatic and etheric crosslinks between aromatics; (2) alkylations of aromatic centers by alcohols (larger than ethanol), alkenes and perhaps ethers; (3) hydrogenation of anthracene; (4) hydroxyl removal from hydroaromatics whose aliphatic rings are hydroxy-substituted; and (5) rearrangements of alkyl-substituted aromatics and aryl-alkyl ethers.

No cracking of aromatic or hydroaromatic rings is anticipated. In the cleavage of aliphatic and etheric crosslinks, depolymerized products only result when there is a suitable capping agent available for the cleaved bond sites; otherwise polymer results. Hydrogen appears to be a slow capping agent at 250°C and 500 psig hydrogen pressure; alcohols, alkenes and aromatics are more active capping agents through their susceptibility to alkylation.

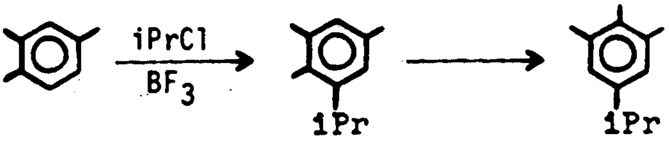
Thus the $ZnCl_2$-alcohol-coal medium contains all of the necessary components for successful depolymerization of the bridges between the aromatic centers in coal. These reactions are evidently sufficient to bring about increased pyridine solubility through $ZnCl_2$-alcohol treatment.

Related Chemistry

In addition to bond scission, there are several other potential mechanisms by which coal may be converted with $ZnCl_2$ and alcohols. Larsen(55) has asserted that $ZnCl_2$ may activate oxygen and nitrogen bases in the coal for hydrogen donation.(55) Hydrogenation of aromatics in such a manner may lead to easier crosslink cleavage. Holten(48) and Hershkowitz and Grens(115) have found evidence for activation of tetralin for hydrogen donation by $ZnCl_2$ between 250 and 300°C; thus it would be possible for hydroaromatics in the coal to behave similarly. In further support of Larsen's theory, the addition of indoline to the $ZnCl_2$-methanol solution resulted in higher solubility and higher H/C ratio in the treated coal.

If one assumes a model of coal consisting of acid-base pairs such as that proposed by Sternberg,(7) production of soluble material could result from $ZnCl_2$ dissociation of such pairs. The proposed model for Wyodak coal (Chapter 1) contains many hydrogen-bonded and acid-base bonded pairs. Even if not important to the breakdown of the coal itself, these pairs would be likely to occur in the products. The effect of HCl washing in producing pyridine solubles from insoluble coal may well be due to acid-base dissociation.

The rearrangement of alkyl groups on aromatic centers may lead to yet another mechanism of solubilization. Schlosberg has reported isopropylation of coal with BF_3/isopropylchloride, with the product coal giving higher yields in liquefaction and gasification.(106) Steric interaction of the isopropyl group on aromatic rings in the coal is believed to weaken the associative forces of Van derWaals attraction and pi-bonding, leaving the coal more unstable and more reactive.



Since $ZnCl_2$ is a known catalyst for xylene rearrangement, such reactions may take place in the $ZnCl_2$-alcohol-coal medium.

Although hydrogen donation by oxygen and nitrogen bases, acid-base cleavage and alkyl-aromatic rearrangements may all have some role in the conversion process, it is unlikely that these effects predominate. Etheric and aliphatic crosslink scission remain the most likely chemical mechanism for $ZnCl_2$ action.

Thus, in order to convert coal at 250°C, it is necessary to contact the aliphatic and etheric crosslinks in the coal with a cleavage catalyst in the pressence of a suitable capping agent which prevents repolymerization. Since the coal is a semi-porous solid under these conditions, problems may be encountered in the catalyst contacting. Recognizing this, the chemical mechanism will be joined with the physical phenomena which also play an important role in the conversion.

CHAPTER 5

REACTION SEQUENCE LEADING TO COAL SOLUBILIZATION USING ZINC CHLORIDE IN ORGANIC MEDIA

As the reactions of $ZnCl_2$ with various components of coal have now been examined, it is appropriate to fit this information into a larger picture of the interaction of the catalyst-organic medium with the coal particles, in which physical phenomena, such as wetting and solvation may play an important role.

Overall Reaction

The sequence of reactions which lead to coal solubilization during catalytic conversion with $ZnCl_2$ in organic media is depicted in Fig. 5-1. The primary steps include catalyst penetration, coal activation, capping reactions, and solvent extraction of products.

Catalyst Penetration

The first step of the reaction involves penetration of the catalyst into the pores of the coal. $ZnCl_2$, a liquid-phase or so-called "homogeneous" catalyst, in combination with solid coal is truly a heterogeneous system. Indeed, it constitutes "inverse" heterogeneous catalysis; the catalyst must diffuse into pores of the reactant and adsorb onto reactive sites, instead of reactant diffusing into pores of the catalyst and absorbing onto catalyst sites. Such a system proves considerably more complex to model than conventional heterogeneous catalytic systems, because as the coal reacts, one must consider the changing size and possibly changing nature of the pores - including

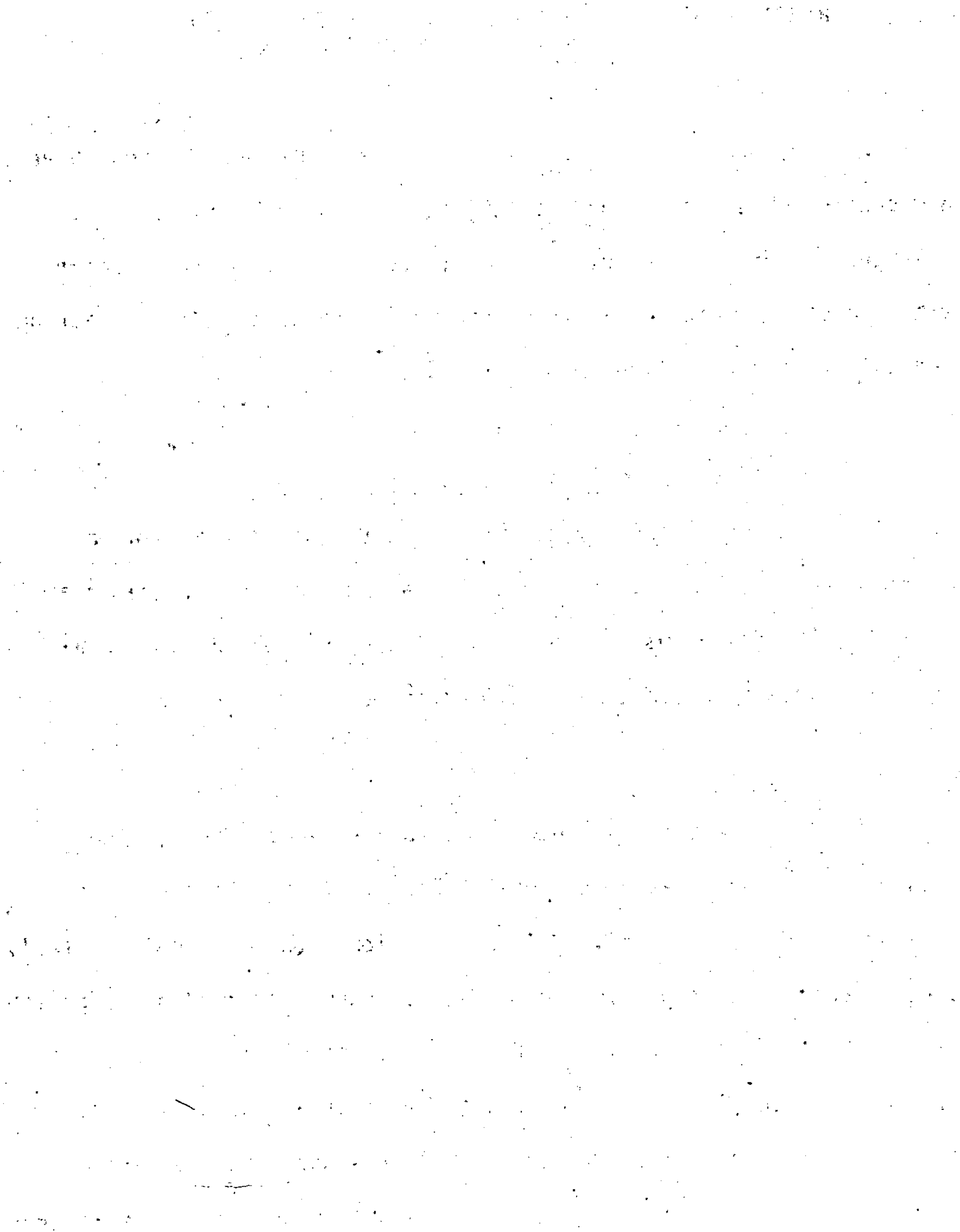


Figure 5-1. Sequence of Reactions Leading to Coal Solubilization During Catalytic Coal Conversion.

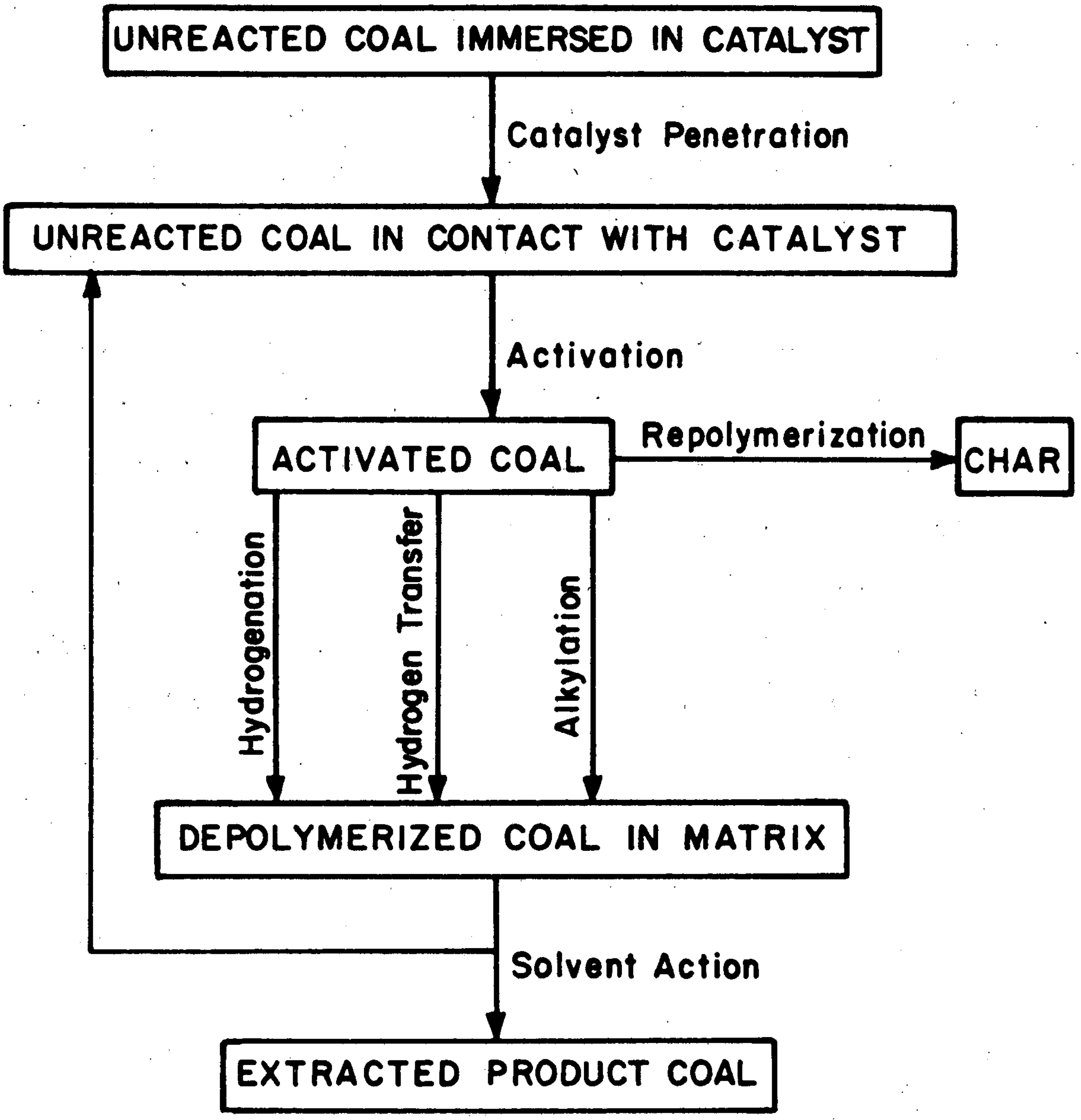


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Figure 5-1.

especially surface wettability. Thus, catalyst solutions of differing properties may have very different pore-penetration rates.

A slow rate of contacting may limit the effective reactivity of some $ZnCl_2$ melts. Scanning electron micrographs show poor contacting of coal with $ZnCl_2$-H_2O, but rapid and extensive penetration with $ZnCl_2$-methanol. This difference in wettability, accompanied by a lower viscosity for the methanol melt, is consistent with the observation that coal mixes with $ZnCl_2$-H_2O more slowly than with $ZnCl_2$-methanol.

The nature of the pores in Wyodak coal serves to explain these findings. The model for Wyodak coal shows a preponderance of polar groups attached to the organic matrix. Thus a reaction medium having a polar organic character should be best able to penetrate the coal. Alcohols and phenols would appear desirable, particularly lower-molecular-weight alcohols which could penetrate smaller pores. In this connection, it is noteworthy that Larsen found that gas chromatographic columns packed with coal retain methanol and ethanol in tailing peaks.(78) It is also of interest to note that other successful reactive breakdowns of coal have involved media which readily penetrate a polar organic structure (e.g., BF_3-phenol, p-toluene sulfonic acid with phenol, NaOH with C_2H_5OH, potassium with naphthalene or tetrahydrofuran).

Activation

Penetration alone is insufficient to cause breakdown of the coal without a catalyst; otherwise methanol alone would convert the coal. The relative ability of different media to split reactive cross-linkages of the coal is a crucial factor in obtaining conversion;

as previously noted, $ZnCl_2$-alcohol melts may have considerably greater chemical activity than $ZnCl_2$-water.

Excessive amounts of any solvent are likely to diminish activation by occupying catalyst sites leaving too few for attack on coal. The maximum in the curve of conversion vs. methanol amount (Fig. 3-7) is probably due to a trade-off between contacting and capping (for which methanol is necessary) and activity. Chlorinated and nitrogen-containing solvents may play a role in reducing activation similar to that of excess methanol.

As noted in the previous chapter, numerous side reactions may take place. With the higher alcohols, alkylation of aromatic centers and alkene production may tie up the catalyst, allowing less reaction with the important linkages. Evidence of these reactions is seen in the lower solubility and higher incorporation for isopropanol and t-butanol runs.

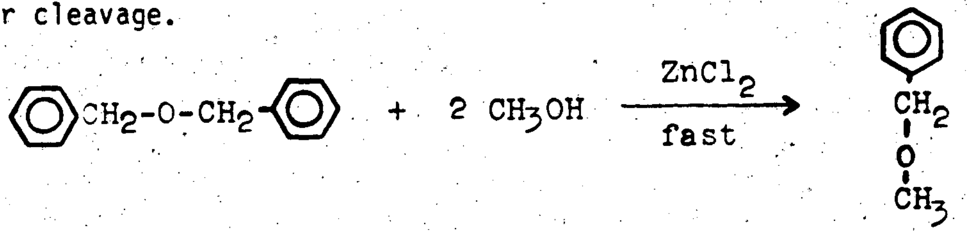
Capping Reactions

Once activation is achieved, it is critically important to have a suitable capping agent to prevent polymerization leading toward coke. As shown in Fig. 5-1, there appear to be three major capping mechanisms in the $ZnCl_2$-alcohol-coal system: hydrogenation, hydrogen transfer, and alkylation.

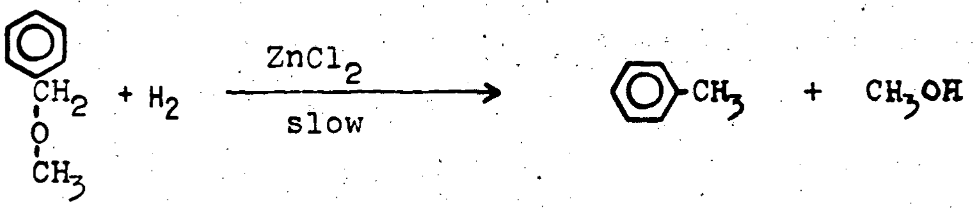
Hydrogenation by gas-phase hydrogen is likely to be the slowest of these capping reactions. The gas analyses shown rates of hydrogen consumption on the order of 6-7 x 10^{-4} gm/hr psig at 250°C and about 1 x 10^{-3} gm/hr psig at at 275°C. Increased product H/C ratio with increasing hydrogen pressure is further evidence of participation of gas-phase hydrogen.

Hydrogen transfer may take place by: (1) direct transfer from hydroaromatic groups in the initial products to the reaction site; (2) shuttling of hydrogen by aromatics such as naphthalene from hydrogen-rich segments of the coal; or (3) hydrogen transfer from added donors such as tetralin. Mineral matter in the coal may catalyze the rehydrogenation of donors by gas-phase hydrogen. Notably, such donors tend to incorporate by alkylation.

Due to the ability of alcohols and ethers to complex with the catalyst, these compounds are the most likely capping agents when present. As shown by Mobley, dibenzyl ether incorporates methanol after cleavage.



Higher hydrogen pressures reduce methanol incorporation indicating either competing hydrogenation and alkylation or subsequent hydrogenation of the initial alkylation product.



If this secondary conversion with oxygen removal is slow relative to alkylation, this reaction sequence could explain why less oxygen is removed in the $ZnCl_2$-methanol system than in the $ZnCl_2$-water system for a similar level of solubilization.

Indeed, the lack of a rapid capping reaction may be another reason for the lower conversion in the $ZnCl_2$-water system. Since hydrogenation is slow under reaction conditions, there is no suitable capping mechanism in the $ZnCl_2$-water solution. Addition of Zn to the medium may enhance hydrogenation leading to more efficient capping and 10% higher conversion (presumably through less repolymerization). Zinc addition has a negligible effect in the $ZnCl_2$-methanol medium where another capping agent is available.

The necessity of capping at a comparable rate to bond activation cannot be overstressed. The lack of sufficient capping may be the major reason behind the failure of more active catalysts to produce soluble products; the major products from such reactions are gas and insoluble char. $AlCl_3$, superacids (Lewis acid-Bronsted acid combinations such as SbF_5-HF, or $AlCl_3$-HCl), phosphoric acid, and sulfuric acid are all likely to have failed because activation ran too far ahead of capping.

Solvent Action

As solubilization may be impeded by inability of the catalyst to reach the reactive sites in the coal structure, a final process of solvation and removal of products by the reaction medium may play an important role. A medium which causes physical disruption of the coal structure may enhance reactivity by increasing the reactant surface area, enlarging the pores so as to promote intraparticular mass transfer, and making the initial reaction products mobile for hydrogen shuttling and donation.

Scanning electron micrographs of the $ZnCl_2$-methanol treated coal show that significant extraction takes place during reaction, consistent with a large total extent of reaction. The inability of purely extractive solvents to promote solubilization may be due to negative effects in earlier stages of the dissolution (inhibition of catalyst penetration, catalyst dilution or inhibition of catalyst activity). Increased product solvation and dissolution may also be a factor in faster solubilization at higher temperatures.

Thus, an effective medium for truly catalytic conversion of coal to soluble components involves a critical combination of components: (1) a catalyst phase which is suitably mobile in the coal; (2) a catalyst with sufficient reactivity for conversion of the crosslinks in the coal structure; (3) a capping agent which can react with bond fragments at a rate similar to that at which they are formed; and (4) a solvent medium to remove solubilized products. Certainly other media exist beside $ZnCl_2$-methanol which may perform these functions.

Effect of HCl Wash

One final result still requires explanation: the effect of HCl washing. It has been noted by other investigators that benzene-solubles may be created from pyridine-solubles or pentane-solubles from benzene solubles by acid treatment.(56,116,117) The assumed mechanism for such effects is the cleavage of acid-base pairs in the products.

In the case of $ZnCl_2$ treatment, a second possibility exists. The bivalent zinc ion may serve as a bridge between two high-molecular-weight fragments in the coal. Such a Zn-bridged compound is likely to be insoluble in pyridine. Treatment of this compound with HCl should liberate $ZnCl_2$ and the two fragments, each of which is pyridine-soluble. There is some evidence that this may be the case: (1) extra zinc is present in the product, beyond the amount that would balance, as $ZnCl_2$, the chlorine present; (2) this excess zinc is also present in the extraction residues; (3) removal of the excess zinc by HCl washing accompanies the increase in pyridine solubility.

The extent to which acid-base cleavage or zinc-bridge removal accounts for the increased solubility awaits further experimentation.

Comparison with Current Processing Techniques

It is appropriate at this point to compare $ZnCl_2$-methanol catalyzed coal conversion with conventional thermolytic processing. Figure 5-2 presents in schematic form the conversion of coal to various products under different processing conditions. Pyrolytic processing heats the coal to over 450°C, causing cleavage of many bonds in rapid succession. Distillable products may be formed directly in this manner, but the rapid rate of bond cleavage generally does not allow suitable capping, and significant quantities of char and gas are produced from condensation and fragmentation of the activated coal. Overly active catalysts (e.g., concentrated sulfuric acid,(129) or $AlCl_3$(84)) may also lead to similar results.

In an effort to limit the side reactions, the conventional processes utilize diverse methods of activating hydrogen in conjunction with lower reaction temperatures (375-450°C). This moderate activation initially produces a depolymerized coal product consisting of mostly preasphaltenes, with some asphaltenes and oils, the total product having reduced nitrogen, sulfur, and oxygen levels relative to the original coal. This product may be used as a clean-burning boiler fuel, or may be reactivated by catalysts or hydrogen-rich recycle solvents to yield distillable products. Some char and gas formation still accompanies the moderate activation and reactivation steps, although significantly less than that which is formed by intense activation.

Figure 5-2. Schematic Illustration of the Conversion of Coal to Distillable Products, Char, and Gas.

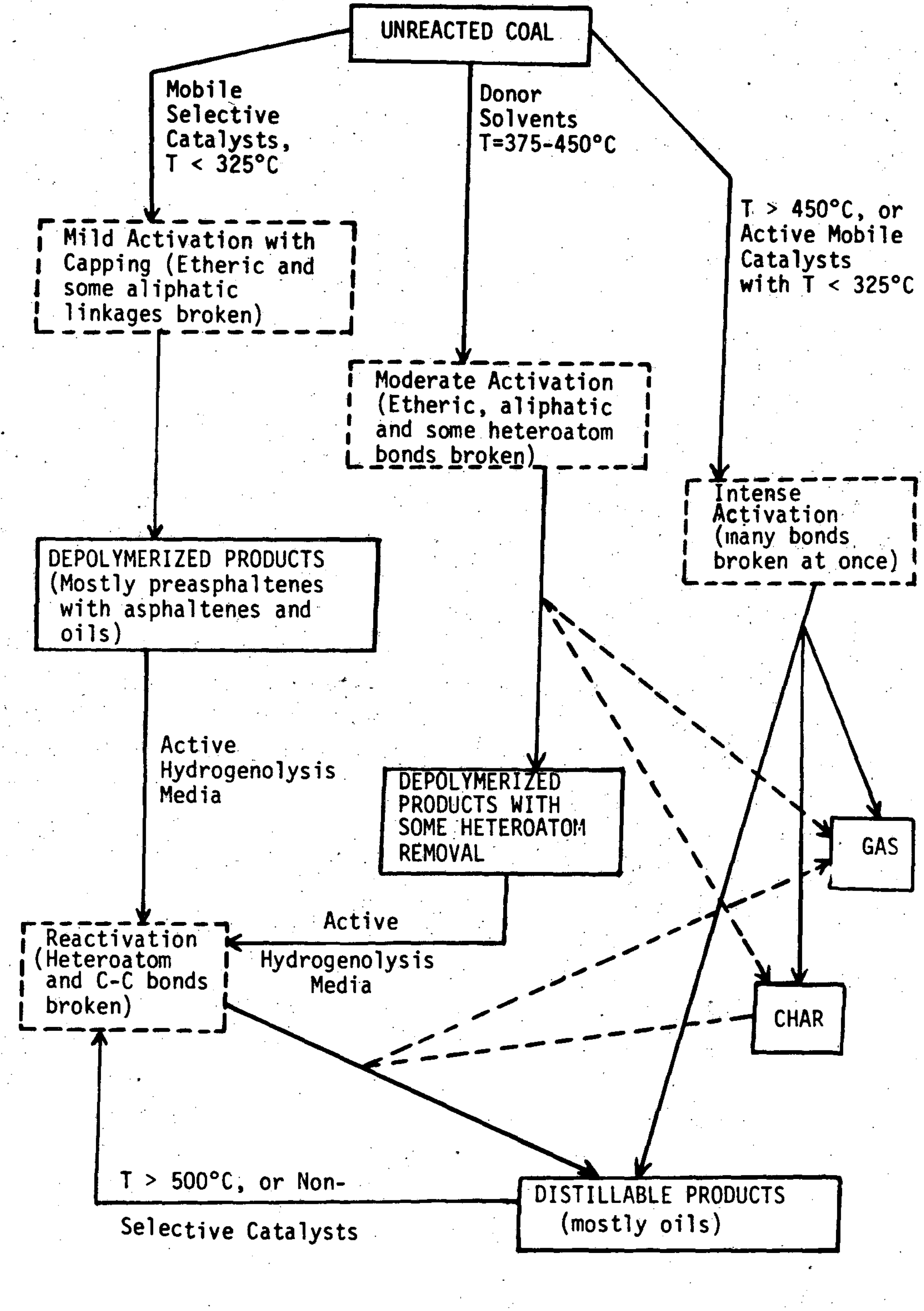


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Figure 5-2.

Our new catalytic route utilizes a mobile catalyst to contact the coal and perform the activation at lower temperatures under more controllable conditions. Suitable capping produces depolymerization products almost exclusively, avoiding the side reactions that form char and gas. Experiments in this laboratory have shown that this process may be extended, activating the less reactive sites, with the same catalyst at higher temperatures (e.g., 300°C), using hydrogen-donor solvents, higher hydrogen pressures, or hydrogenation co-catalysts with the $ZnCl_2$.(115,122,123)

A thermodynamic advantage allowing the use of lower hydrogen pressures accompanies the use of lower temperatures for coal conversion. Figure 5-3 shows a plot of hydrogen pressure versus temperature for aromatic-hydroaromatic equilibria (benzene to cyclohexane, biphenyl to phenyl cyclohexane and bicyclohexyl, naphthalene to tetralin and decalin, phenanthrene to tetrahydro-, octahydro-, and perhydro-phenanthrene.(130) The region in which the equilibrium concentration of aromatic and hydroaromatic are equal is shown as a diagonal band on the plot; the hydroaromatic form is thermodynamically favored above this region, the aromatic favored below. Thus, this plot shows that as the temperature is reduced, less hydrogen is needed to make dehydrogenation unfavorable. Since char formation results from dehydrogenation and condensation, reduction in conversion temperature allows lower hydrogen pressures to be utilized without the threat of char formation. Therefore, liquid-catalyzed coal conversion can produce desired products with higher selectivity under lower hydrogen pressures than the thermolytic route.

Figure 5-3. Hydrogen pressure versus temperature for hydroaromatic - aromatic equilibria. Lower hydrogen pressures are needed to favor hydroaromatics during lower temperature processing.

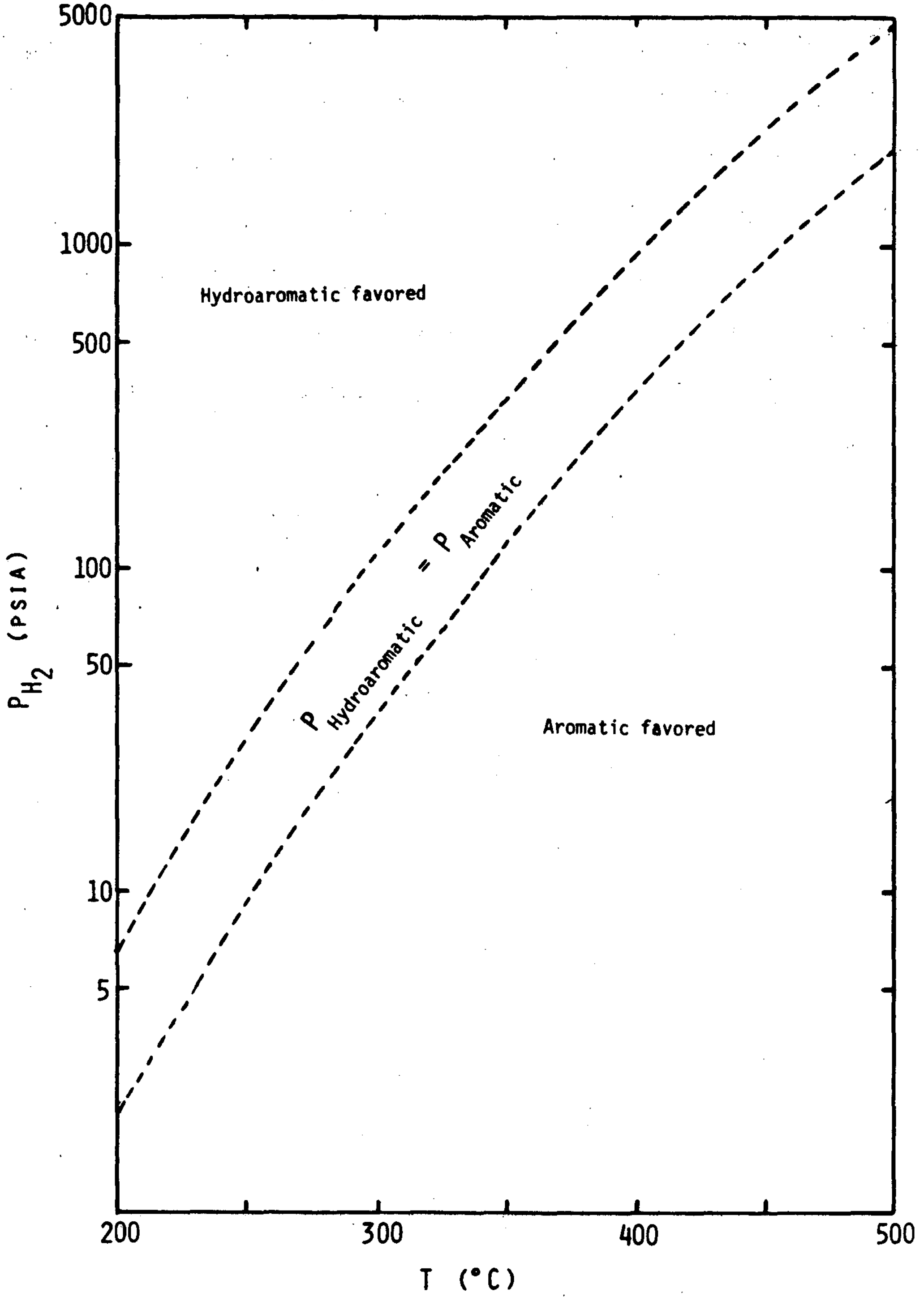

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Figure 5-3.

This work demonstrates that such catalytic conversion is indeed possible, and outlines the direct process requirements for successful low-temperature operation. Indirect process requirements not yet studied are the potential corrosive properties of wet $ZnCl_2$ in various containing materials and the question of nearly complete recovery of such a catalyst. More important, however, the ground work is set for investigation of media with similar liquefaction properties.

CHAPTER 6

CONCLUSIONS

Zinc chloride combined with a suitable solvent is an active liquid-phase catalyst for cleavage of bonds which crosslink the polymeric structure of coal. With $ZnCl_2$-methanol at 275°C, 800 psig H_2, and 30 minutes residence time, the cleavage products from Wyodak coal are roughly 60% pyridine-soluble in addition to 40% benzene-soluble; the original coal is 12% pyridine-soluble, including less than 1% benzene-solubles.

The mechanism for solubilization involves contacting coal with catalyst, promoted by solvent, coal activation by the catalyst, "capping" of reactive bond fragments by hydrogen or solvent, and extraction of primary products which enhances further catalyst-coal contact. A marked reduction in oxygen content of the coal takes place in parallel with conversion to pyridine-soluble material, suggesting that ether-bond cleavage is an important step in the overall conversion. Such a mechanism is supported by experiments in which $ZnCl_2$ cleaves benzylic ethers and certain other aryl ethers (Mobley).(108)

In one-hour runs at 250°C and 500 psig hydrogen pressure, the activity of the $ZnCl_2$ is found to be strongly related to the medium in which it is dissolved. $ZnCl_2$-water solutions effectuate relatively little conversion (only 30% pyridine-solubility or less) unless accompanied by methyl-naphthalene and/or tetralin (55% solubility). Solutions of $ZnCl_2$ in primary alcohols are effective; methanol gives 70% solubility and ethanol gives complete conversion. Solutions in secondary and tertiary alcohols are less effective; isopropanol gives 33% and t-butanol gives no conversion beyond the 12% extractibility before treatment.

Thus $ZnCl_2$-methanol mixtures are particularly effective in catalytic coal conversion. Methanol appears responsible for enhancing coal-catalyst contacting, increasing catalyst activity, capping reactive fragments, and extracting products. Some methanol is retained in the products (0.1 to 0.2 gm methanol/gm coal organic), probably due to alkylation of cleaved bond sites and possibly alkylation of aromatic centers. Higher hydrogen pressures increase conversion and decrease methanol retention, indicating either that hydrogenation competes with methylation or that once methylation occurs, hydrogenolysis occurs with accompanying demethylation.

A variety of inorganic and solvent additives were screened with the $ZnCl_2$-methanol and $ZnCl_2$-water systems. Inorganic additives generally have either no effect ($CaCl_2$, ZnO) or a negative effect (NaCl + KCl, NaI + KBr, $SnCl_2$, $SbCl_2$); a positive effect is found with Zn metal addition. Extractive solvents (n-decane, perchloroethane, o-dichlorobenzene, pyrollidine, cyclohexane, p-xylene) decrease the conversion in proportion to the amount of solvent added. Reactive solvents (indoline, anthracene oil, tetralin, dihydroanthracene) increase the conversion but also incorporate strongly. Piperidine and N,N-dimethyl formamide poison the catalyst.

This work demonstrates that coal conversion may take place under conditons considerably less severe than those employed in current coal processing technology (400°C, 2000 psig H_2 and up). The understanding of the mechanism of catalytic coal conversion with $ZnCl_2$

in organic media at 250^{o}C may well pave the way for catalytic coal conversion processes which could be less capital-intensive, more energy-efficient, and give better product distributions than the conventional thermolytic processes.

CHAPTER 7

RECOMMENDATIONS FOR FUTURE WORK

The high conversion levels which may be achieved with $ZnCl_2$ in organic media open many new areas for further investigation. Such studies may serve to improve the understanding of $ZnCl_2$ catalysis and coal chemistry, and may lead to advanced coal processing concepts.

Suggestions for future study fall into five major categories: (1) the $ZnCl_2$-methanol system alone; (2) $ZnCl_2$-methanol with model compounds; (3) $ZnCl_2$-methanol coal conversion; (4) coal conversion catalysis in non-$ZnCl_2$-media; and (5) investigation of acid washing and other product-washing techniques.

The $ZnCl_2$-Methanol System

Significant gaps in the understanding of the chemistry of $ZnCl_2$-alcohol systems could be filled by further experimentation.

1) As $ZnCl_2$-alcohol systems are alleged to have significant acidity, a study of the pH of $ZnCl_2$-methanol solutions as a function of methanol concentration and temperature would be of interest.

2) The kinetics of conversion of methanol to dimethyl ether and other products in the presence of $ZnCl_2$ would help to determine the quantities of each component present in the reaction medium. The effects of silica, pyrite, and clay (from coal ash), and hydrogen pressure on the reaction may also be important.

$ZnCl_2$-Methanol Reactions with Model Compounds

To help determine the chemical behavior of the $ZnCl_2$-methanol system on the coal, a detailed study of the reactions of etheric and aliphatic crosslinks between aromatic centers with this medium would be useful. Areas of focus should include:

1) Study the competition between hydrogenation and alkylation which was found in the coal studies.

2) Include donor solvents to determine their effect in this medium.

3) Seek out a temperature-pressure regime where the reactions are most selective toward achieving high conversion with minimal methanol incorporation.

4) If a selective regime is found, these reactions may be used with C^{13}-methanol to depolymerize a variety of different coals for the purpose of coal chemistry studies.

$ZnCl_2$-Methanol Coal Conversion

I) Improvements in the run procedure.

1) Avoid effect of heatup by injecting a coal slurry into the preheated $ZnCl_2$-methanol solution.

2) Perform more detailed gas collection and analysis.

3) Improve the method of separating organic constituents from the aqueous or alcoholic phase.

4) Perform analysis for trace constituents in the water stream.

5) Develop a procedure whereby the MTC may be extracted by the $ZnCl_2$-methanol solution at reaction temperature to determine the

portion of the coal dissolved by this medium. Scanning electron microscopy of the residue from this procedure may prove valuable.

6) Analyze the materials volatized during vacuum oven drying by performing vacuum distillation of the washed MTC.

7) Develop a simple, more precise, and meaningful measure of reaction yield. Exxon has found room-temperature cyclohexane extractions to correlate well with pilot-plant distillate yields. Amoco research has suggested extractions with THF using Millipore filters. These and other extraction methods should be investigated as a replacement to the tedious and unreliable Soxhlet extractions.

8) More accurate oxygen determinations are needed. A neutron-activation analysis developed by Volbrath and Miller(119) may be useful. Wet-chemical analyses for phenolic and carbonyl groups should be performed.

9) More detailed product analyses including C^{13} and H^{1} NMR, GPC, SEM, multiple fractionations such as employed by Mobil,(11) oxidations (with GCMS) for aromatic group determination,(23) inverse oxidations for aliphatic group determinations,(28) or functional group determinations by trifluoracetylation followed by F^{19}-NMR(120) could provide useful information on the chemical transformations which accompany conversion.

II) Improved reaction rate and reduction of methanol incorporation.

1) Investigate the further conversion of pyridine-insolubles.

2) if the $ZnCl_2$-methanol reaction studies show a sizable conversion of methanol to dimethyl ether during reaction heatup, it will be important to investigate the effect of mixtures of methanol and dimethyl ether on conversion (or test the effect of various heatup times on conversion if the coal can be injected after heatup).

3) Attempt further upgrading of the product by higher temperatures and pressures with $ZnCl_2$, or by addition of a more active catalyst and more effective capping agent ($ZnCl_2$-HCl- tetralin, for example).

4) Use additives which enhance hydrogenation in preference to methylation. Among the most promising prospects would be HI or I_2, metals (Ni, Co, Mo, Fe, Sn or Zn), metal carbonyls, and various organic and inorganic hydrides.

5) Attempt to substitute CO or a CO/H_2 mixture for H_2.

III) Process-related improvements.

1) Reduce the corrosion problems by using a reactor lining of Zn, ZnO or char, or by adding sufficient qauantities of ZnO or some other HCl 'getter' to minimize the effect of HCl.

2) Develop a process which uses less $ZnCl_2$ or more effectively recovers the catalyst for recycle. Less may be used by impregnating the coal with $ZnCl_2$ followed by methanol treatment, or by diluting the catalyst with inert salts (e.g., $CaCl_2$). Approaches to better separation of $ZnCl_2$ from the products include: (i) gravity separation of product and melt; (ii) further conversion in a second stage with product removal by distillation and ash + solids removal by filtration; or (iii) critical solvent separation of organics from melt by methods such as Kerr-McGee has employed with the SRC-I pilot plant at Wilsonville.(122)

IV) Related studies.

1) Develop a model for the three-phase reaction system which includes mass transfer, diffusion of liquid catalyst into the coal, reaction, repolymerization, capping, and product extraction. Considerable data on

reaction and mass transfer rates would need to be gathered for such a model.

Coal Conversion Catalysis in Non-$ZnCl_2$ Media

1) As outlined in this study, effective coal conversion catalysis involves creating a catalyst-solvent combination which enhances catalyst-coal contacting, promotes bond cleavage at a rate comparable to bond capping (limiting repolymerization), and promotes product removal. For contacting, quenching, and removal, methanol has been found to be a very effective choice of solvent.

A variety of catalysts, from acidic to basic, may be effective for the activation step. From the standpoint of process potential, the cheapest active catalyst is desirable. A great advantage could be gained if such a catalyst could be derived from the coal itself. In this light, the H_2SO_4-methanol system should be a top priority, followed by H_3PO_4-methanol or NaOH-methanol. A wide range of concentrations should be tested to insure the proper rate of activation and capping.

Associated with these reaction studies could be: (i) scanning electron microscopy for information on contacting; (ii) use of hydrogenation co-catalysts or recycled solvents; (iii) use of other oxygen-containing solvents should undesirable side reactions develop from the methanol solutions.

2) Product upgrading is also worthy of continued catalytic research. Particularly lacking is examination of dehydroxylation catalysts to remove phenols from pyridine-solubles producing benzene-solubles. Nitrogen and sulfur removal have received more attention,

but much work could be done using Lewis acids to attack these basic functionalities.

Washing Techniques

The effect of HCl washing in improving pyridine solubility remains largely a mystery. Further studies dealing with the effects of HCl concentration and wash time are needed. Washing with other acids and bases could help determine whether this wash effect is due to Zn bridge removal or cleavage of acid-base complexes.

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Coal Conversion Processes

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Overall Reaction Sequence

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Appendix A

Summary of Data from Individual Runs

Run No.	C Added to MTC (gm)	H Added to MTC (gm)	N Added to MTC (gm)	Ash Added to MTC (gm)	O+S Added to MTC (gm)	H/C Atomic Ratio	(O+S)/C Atomic Ratio	N/C Atomic Ratio	Other Zn in MTC (gm)	$ZnCl_2$ in MTC (gm)	Pyridine Retention (gm)	Benzene Soly. (daf%)	Pyridine Soly. (daf%)	Total Solubility(daf%)	Incorporation Ratio	Corr. Solubility (%)	Coal to Solubles (%) Basis: All incorp'd Solvent in Residue.	Coal C to Solubles (%)
2.0	.6	.1	.1	11.0	-2.7	1.003	.125	.015	.81	.432	-.000	1.6	9.8	11.4	.079	4.4	12.3	4.2
3.0	-5.6	-.6	-.1	-1.5	.8	.896	.322	.012	.44	.024	.466	3.6	9.5	13.1	0.	13.1	13.1	12.5
4.0	43.4	2.9	-.1	3.0	-6.6	.859	0.	.003	.40	1.969	1.115	42.2	37.8	80.0	1.963	40.8	237.0	38.7
5.0	-3.3	-.3	-.1	-1.3	-1.0	.957	.216	.011	.40	.023	.390	2.3	8.9	11.2	0.	11.2	11.2	10.7
7.0	1.4	-.0	-.1	-.9	-2.5	.909	.128	.007	.30	.102	.314	8.6	37.1	45.7	.115	39.4	50.9	37.5
9.0	18.2	.8	-.1	1.2	5.2	.780	.224	.006	4.02	.031	.078	5.1	5.2	10.3	.853	0.	19.1	0.
10.0	7.1	.5	.0	-.9	4.0	.964	.272	.010	.68	.068	.096	47.3	19.7	67.0	.365	55.0	91.5	52.2
11.0	-1.6	-.4	-.0	-1.2	-1.5	.860	.183	.012	.27	.017	.972	9.3	19.8	29.0	0.	29.0	29.0	27.6
12.0	36.9	2.5	.4	-1.0	-2.6	.884	.052	.010	1.06	.464	.236	44.6	30.4	75.1	1.677	33.3	201.0	31.6
13.0	-6.2	-.7	-.0	-1.9	-4.4	.846	.097	.015	.45	.116	.444	19.3	31.4	50.7	0.	50.7	50.7	48.2
14.0	2.4	.0	-.0	-.8	-1.3	.893	.159	.010	.80	.092	.408	9.2	17.1	26.3	.157	14.7	30.4	14.0
15.0	2.9	.5	-.0	-.9	-3.0	1.102	.106	.009	1.27	.060	.110	29.9	40.1	70.0	.180	64.6	82.6	61.4
16.0	-3.0	-.4	-.0	-1.1	-3.6	.882	.112	.012	.36	.017	.100	10.9	33.8	44.7	0.	44.7	44.7	42.5
17.0	4.9	.6	.0	.3	-1.6	1.068	.139	.010	.68	.089	.204	15.9	25.3	41.1	.269	25.3	52.2	24.1
19.0	2.5	.5	-.0	-.5	-3.2	1.119	.100	.010	1.46	.258	.099	31.7	36.8	68.6	.163	63.5	79.8	60.3
20.0	1.2	-.0	-.1	.3	-5.2	.928	.042	.008	1.50	.368	.365	16.3	32.4	48.8	.104	43.4	53.8	41.2
21.0	3.1	.6	-.0	.4	-3.0	1.121	.104	.009	5.15	.362	.302	16.8	33.9	50.7	.191	41.4	60.4	39.3
22.0	-2.9	-.4	-.0	-1.3	-1.9	.895	.177	.013	.52	.038	.909	5.6	21.7	27.3	0.	27.3	27.3	25.9
23.0	-2.1	-.4	.1	-1.5	-2.6	.847	.145	.017	.65	.067	.769	5.5	20.4	25.8	0.	25.8	25.8	24.5
24.0	-4.0	.1	-.1	-.1	-2.1	1.257	.178	.011	8.35	1.233	.810	21.8	44.0	65.8	0.	65.8	65.8	62.5
25.0	2.0	.7	.1	12.5	-5.2	1.235	.043	.016	19.19	.650	.609	0.	5.6	5.6	.141	0.	6.4	0.
26.0	16.3	1.7	-.0	1.1	-4.8	1.094	.035	.006	0.	.092	.102	38.9	46.3	85.1	.770	73.7	150.7	70.0
27.0	2.5	.4	-.0	-1.5	-1.5	1.074	.154	.009	.64	.122	.186	22.1	29.9	52.0	.161	44.3	60.4	42.1
28.0	3.1	.2	-.1	2.4	-1.1	.936	.160	.008	11.82	.106	.428	2.2	3.4	5.6	.188	0.	6.7	0.
29.0	13.5	1.6	-.1	-.7	-3.5	1.153	.065	.006	.26	.031	.072	59.7	26.6	86.3	.648	77.4	142.2	73.5
30.0	6.1	1.2	-.1	.1	-4.3	1.273	.061	.008	1.72	.438	.613	29.3	67.3	96.6	.322	95.6	127.7	90.8
31.0	5.2	.3	.0	.6	-3.1	.932	.096	.010	.66	.514	.368	9.1	7.1	16.2	.281	0.	20.8	0.
32.0	7.6	1.2	-.1	1.1	-4.1	1.215	.062	.007	.71	.455	.135	41.7	35.8	77.5	.387	68.7	107.5	65.3
33.0	7.0	.7	-.0	-1.4	-1.5	1.025	.130	.008	.83	.027	.007	14.9	37.3	52.2	.362	34.9	71.1	33.2
34.0	6.5	.7	-.1	-.7	-1.1	1.044	.144	.007	1.88	.251	.019	13.2	21.2	34.4	.338	12.2	46.0	11.6
35.0	8.6	.5	-.1	-2.1	-2.9	.920	.089	.007	0.	.082	.159	16.8	41.6	58.4	.430	40.5	83.5	38.5
36.0	14.1	1.0	-.1	-1.4	-2.4	.943	.087	.006	0.	.009	.015	26.6	53.2	79.8	.675	66.2	133.6	62.9
37.0	2.0	.5	-.1	-.4	-4.0	1.127	.078	.008	2.25	.347	.290	37.9	35.9	73.8	.142	70.1	84.3	66.6
38.0	-1.1	-.5	-.1	-1.0	-1.8	.786	.166	.010	0.	.011	.427	2.1	8.6	10.7	.002	10.5	10.7	10.0
39.0	2.6	.5	-.1	-.5	-4.0	1.126	.079	.009	.86	.153	.556	45.0	31.3	76.3	.166	72.3	85.9	68.7
40.0	2.4	.3	-.0	-1.0	-3.3	1.021	.099	.009	.62	.067	.156	25.7	35.3	61.0	.160	54.8	70.7	52.0
41.0	4.2	.6	-.1	-.2	-3.3	1.078	.094	.008	1.34	.106	.086	25.7	31.8	57.6	.237	47.5	71.2	45.1
42.0	2.8	.2	-.2	.2	-5.2	.989	.041	.006	.10	.194	.076	65.9	17.4	83.3	.175	80.4	97.9	76.4
43.0	2.6	.6	.2	-.6	-4.2	1.169	.079	.011	1.74	.269	.427	39.7	46.8	86.5	.168	84.2	101.0	80.0
44.0	.4	.1	-.0	-.0	-3.3	.915	.038	.011	.22	.139	.200	14.6	28.5	43.1	.076	37.4	40.4	[illegible]
45.0	.3	.8	-.0	.1	-4.2	1.119	.064	.003	2.09	.221	.266	22.6	33.7	[illegible]	.315	55.7	87.1	[illegible]
46.0	-1.0	.4	.0	-.4	-2.2	.862	.139	.011	.80	.021	.304	4.7	16.2	20.9	0.	23.8	20.8	19.3
47.0	.3	.3	.0	-.5	-1.9	1.079	.071	.011	.77	.051	.120	29.8	42.3	[illegible]	.355	[illegible]	77.1	70.3

Run No.	C Added to MTC (gm)	H Added to MTC (gm)	N Added to MTC (gm)	Ash Added to MTC (gm)	O+S Added to MTC (gm)	H/C Atomic Ratio	(O+S)/C Atomic Ratio	N/C Atomic Ratio	Other Zn in MTC (gm)	$ZnCl_2$ in MTC (gm)	Pyridine Retention (gm)	Benzene Soly. (daf%)	Pyridine Soly. (daf%)	Total Solubility(daf%)	Incorporation Ratio	Corr. Solubility (%)	Coal to Solubles (%) Basis: All incorp'd Solvent in Residue	Coal C to Solubles (%)
48.0	2.6	.6	-.0	1.0	-6.6	1.162	0.	.010	0.	.575	.730	41.6	57.6	99.2	.166	99.1	115.9	94.2
49.0	1.3	.3	-.0	-.9	-2.0	1.089	.145	.011	1.34	.044	.223	16.1	29.9	46.0	.111	40.0	51.1	38.0
50.0	5.8	.8	-.1	-1.1	-4.6	1.125	.052	.008	2.19	.115	.108	36.5	38.3	74.7	.309	66.9	97.9	63.6
51.0	1.0	.4	-.1	-2.1	-3.4	1.115	.103	.010	1.60	.112	.181	33.1	47.9	81.0	.096	79.2	88.8	75.3
52.0	1.5	.3	-.0	-1.0	-1.4	1.056	.163	.010	2.38	.026	.118	12.0	22.2	34.2	.119	26.4	38.3	25.1
53.0	2.5	.4	-.0	1.0	-3.4	1.070	.095	.009	2.95	.171	.090	22.1	20.8	42.8	.164	33.5	49.8	31.8
54.0	-.3	.3	-.1	-1.4	-2.6	1.123	.135	.008	.18	.134	.082	38.7	66.0	104.7	.389	106.5	145.4	101.2
55.0	7.7	1.2	-.0	.2	-3.9	1.208	.067	.008	.09	.009	.057	32.6	58.0	90.6	.040	90.2	94.2	85.7
56.0	-1.4	-.4	-.0	-1.1	-2.8	.851	.135	.012	.65	.024	.051	7.4	28.2	35.6	0.	35.6	35.6	33.8
57.0	1.0	.7	-.0	-2.3	-.9	1.268	.183	.011	10.02	.073	.063	26.1	41.1	67.2	.096	64.1	73.6	60.9
58.0	2.3	.5	-.1	1.0	-2.1	1.129	.135	.008	0.	.146	.149	33.9	72.1	106.0	.155	106.9	122.4	101.6
59.0	5.0	.9	-.3	-.7	-2.9	1.182	.100	.002	2.10	.039	.019	43.1	42.3	85.4	.271	81.5	108.6	77.4
60.0	-2.8	-.2	.0	1.5	2.3	.997	.336	.014	0.	0.	.239	0.	28.5	28.5	0.	28.5	28.5	27.1
62.0	-7.9	-.7	-.1	-1.6	-2.1	.922	.221	.012	.02	.006	.197	4.7	22.2	26.9	0.	26.9	26.9	25.6
62.5	-17.4	-1.4	-.2	-4.5	-5.0	.935	.194	.014	.37	.013	.218	3.1	11.7	14.8	0.	14.8	14.8	14.1
63.0	-1.5	-.3	.0	-1.2	-2.3	.889	.151	.013	.92	.012	.152	5.3	18.5	23.8	0.	23.8	23.8	22.6
64.0	-2.3	-.3	-.1	-1.4	-.8	.899	.213	.011	.98	.007	.189	4.2	12.0	16.2	0.	16.2	16.2	15.4
65.0	-1.4	-.3	-.0	-1.5	-2.3	.884	.152	.012	.78	.039	.214	6.3	21.9	28.3	0.	28.3	28.3	26.9
66.0	1.7	.7	-.0	1.0	-2.6	1.245	.124	.010	6.32	.084	.049	30.6	38.8	69.5	.127	65.6	78.3	62.3
67.0	.1	.0	.0	-.7	.9	.991	.249	.012	.73	.092	.566	0.	14.5	14.5	.057	9.6	15.3	9.2
68.0	-.9	-.0	-.0	-.3	-.1	1.004	.227	.011	0.	0.	.252	4.7	4.9	9.7	.011	8.7	9.8	8.2
69.0	-7.6	-.4	-.2	-2.6	-4.7	1.117	.092	.009	0.	.029	.074	43.2	50.4	93.6	.117	92.8	104.5	88.2
69.5	-14.8	-1.0	-.2	-4.0	-5.0	1.266	.133	.011	3.83	.093	.111	29.2	47.8	77.0	.117	74.3	86.0	70.6
70.0	3.7	.7	-.1	-.2	-5.4	1.169	.034	.008	.58	.219	.193	38.8	61.6	100.4	.214	100.5	121.9	95.5
72.0	-9.1	-.5	-.2	-2.3	-5.9	1.153	.036	.008	0.	.139	.145	37.1	74.4	111.5	.200	113.8	133.8	108.1
72.5	-11.5	-.7	-.2	-3.0	-6.1	1.184	.032	.008	.65	.146	.100	38.5	54.9	93.4	.200	92.0	112.0	87.4
73.0	-8.0	-.4	-.2	-2.2	-5.6	1.154	.050	.007	.08	.106	.083	38.9	65.9	104.8	.164	105.6	121.9	100.3
73.5	-13.4	-.9	-.2	-3.8	-5.4	1.157	.091	.008	.99	.068	.055	35.9	46.0	81.9	.164	78.9	95.3	75.0
74.0	-11.2	-.8	-.2	-3.1	-3.5	1.045	.193	.012	.01	.005	.185	9.1	37.1	46.2	.051	43.4	48.6	41.3
74.5	-12.7	-1.0	-.2	-3.8	-3.8	1.003	.199	.012	.97	.016	.254	4.7	12.7	17.4	.051	13.2	18.3	12.5
75.0	-11.4	-.8	-.2	-3.5	-5.4	1.111	.071	.009	0.	.051	.088	38.0	61.7	99.7	.202	99.7	119.9	94.7
75.5	-9.2	-.5	-.2	-2.9	-4.6	1.145	.107	.009	.85	.074	.097	37.8	35.8	73.6	.202	68.2	88.4	64.8
76.0	-9.6	-.6	-.2	-3.2	-4.7	1.104	.102	.009	0.	.017	.049	36.8	59.9	96.8	.158	96.3	112.0	91.5
76.5	-11.9	-.8	-.2	-3.7	-4.9	1.129	.112	.010	1.08	.035	.058	27.6	32.4	60.0	.158	53.7	69.5	51.0
77.0	-10.1	-.7	-.2	-3.7	-4.3	1.044	.128	.010	0.	.002	.025	20.6	71.7	92.4	.160	91.2	107.2	86.6
77.5	-11.4	-.8	-.2	-3.7	-4.4	1.061	.139	.009	1.47	.030	.107	15.3	29.3	44.7	.160	35.8	51.8	34.0
79.0	-10.1	-.7	-.2	-4.0	-4.9	1.123	.094	.008	.53	.034	.025	43.2	55.3	98.5	.150	98.3	113.2	93.4
79.5	-11.6	-.8	-.2	-2.8	-5.1	1.157	.093	.010	.44	.181	.132	35.4	41.6	77.0	.150	73.6	88.5	69.9
80.0	-14.2	-1.1	-.2	-3.6	-4.8	1.004	.146	.012	0.	.001	.046	15.0	50.5	65.7	0.	65.7	65.7	62.4
80.5	-11.7	-.8	-.2	-1.8	-4.4	1.109	.141	.011	4.50	.104	.159	10.8	26.5	37.4	0.	37.4	37.4	35.6
82.0	-16.9	-1.4	-.2	-4.3	-5.2	.937	.159	.012	.12	.007	.036	16.2	59.4	75.6	0.	75.6	75.6	71.8
82.5	-9.1	-.6	-.1	-2.4	-3.9	1.031	.143	.011	5.62	.103	.053	7.0	24.1	35.1	0.	35.1	35.1	[illegible]

Run No. (.5 = Split Wash)	Temperature (°C)	H_2 Pressure (lb/in^2)	Residence Time (min)	Methanol Loading (gm)	Water Loading (gm)	Run Group	1,H_2O;2,HCl;3,C_6H_6	Wash Conditions 1, Split H2O/HCl	Additive A	Add. A Loading (gm)	Additive B	Add. B Loading (gm)	Carbon Recovery (%)	Hydrogen Recovery (%)	Nitrogen Recovery (%)	Ash Recovery (%)	O and S Recovery (%)
2.0	250.	500.	60.	0.	27.	3.	1.	0.	PIPERIDINE	50.0		0.	102.5	105.1	126.4	299.5	58.4
3.0	250.	500.	60.	0.	27.	2.	1.	0.	KBR	45.3	NAI	57.1	76.7	70.2	80.5	71.9	112.6
4.0	250.	500.	60.	0.	27.	3.	1.	0.	DIHYDROANT	50.0		0.	281.4	246.9	81.7	154.1	0.
5.0	250.	500.	60.	0.	27.	2.	1.	0.	KCL	37.6	NACL	29.4	86.1	84.2	81.8	76.9	84.8
7.0	250.	500.	60.	0.	27.	3.	1.	0.	MESITOL	50.0		0.	105.9	98.4	64.9	82.9	61.8
9.0	250.	500.	60.	0.	27.	3.	1.	0.	T-BUTANOL	50.0	PTSA	50.0	176.1	140.4	83.0	122.0	179.9
10.0	250.	500.	60.	0.	27.	3.	3.	0.	ME-NAPHTHA	50.0	TETRALIN	10.0	129.7	127.8	108.3	83.2	160.5
11.0	275.	500.	60.	0.	27.	1.	1.	0.		0.		0.	93.3	81.9	95.8	77.9	77.6
12.0	250.	500.	60.	0.	27.	3.	3.	0.	ANTHRA OIL	50.0		0.	254.3	229.7	213.3	82.5	60.3
13.0	300.	500.	60.	0.	27.	1.	1.	0.		0.		0.	74.2	64.1	91.4	66.4	32.7
14.0	250.	500.	60.	0.	27.	3.	1.	0.	P-XYLENE	50.0	CACL2	24.7	109.9	100.3	92.1	85.8	79.5
15.0	250.	200.	60.	50.	0.	5.	1.	0.		0.		0.	112.1	126.2	89.3	84.2	54.3
16.0	275.	500.	60.	0.	27.	2.	1.	0.	CACL2	24.7		0.	87.3	78.7	90.5	79.2	44.6
17.0	250.	0.	60.	99.	0.	5.	1.	0.		0.		0.	120.5	131.5	104.0	105.9	76.1
19.0	275.	650.	20.	50.	0.	5.	1.	0.		0.		0.	110.5	126.3	96.2	91.3	50.5
20.0	320.	400.	60.	25.	0.	7.	1.	0.	N-DECANE	100.0		0.	104.9	99.5	74.7	105.2	20.2
21.0	250.	250.	60.	50.	0.	7.	1.	0.	N-DECANE	50.0		0.	113.1	129.6	86.5	107.7	53.5
22.0	250.	500.	60.	0.	27.	1.	1.	0.		0.		0.	87.8	80.3	95.5	76.1	71.0
23.0	250.	500.	60.	0.	27.	2.	1.	0.	CACL2	24.7		0.	91.2	78.9	128.2	73.4	60.2
24.0	250.	200.	60.	50.	0.	6.	2.	0.	ZN	25.0		0.	83.4	107.2	78.8	99.0	67.8
25.0	250.	250.	60.	0.	0.	4.	1.	0.	N,N-DMF	100.0		0.	108.4	136.7	144.7	326.3	21.2
26.0	250.	250.	60.	50.	0.	7.	1.	0.	ANTHRA OIL	10.0		0.	168.1	187.9	91.4	120.9	27.1
27.0	250.	200.	60.	50.	0.	6.	1.	0.	CDCL2	38.5		0.	110.3	121.1	85.4	72.1	77.7
28.0	250.	200.	60.	50.	0.	6.	1.	0.	SNCL2	42.1		0.	112.8	108.0	80.8	143.4	82.5
29.0	250.	200.	60.	50.	0.	7.	3.	0.	TETRALIN	10.0		0.	156.6	184.4	80.8	87.3	46.1
30.0	275.	200.	60.	50.	0.	5.	1.	0.		0.		0.	125.6	163.4	81.8	102.6	35.1
31.0	200.	200.	60.	50.	0.	7.	1.	0.	ANTHRA OIL	10.0		0.	121.7	115.8	105.0	110.9	53.5
32.0	250.	200.	60.	50.	0.	7.	1.	0.	CYCHEXANOL	10.0		0.	131.8	163.6	81.8	119.3	37.5
33.0	250.	200.	60.	0.	0.	4.	1.	0.	I-PROPANOL	50.0		0.	129.4	135.5	90.0	74.3	76.9
34.0	250.	200.	60.	0.	0.	4.	1.	0.	T-BUTANOL	50.0		0.	127.1	135.6	80.0	87.2	83.3
35.0	250.	200.	60.	50.	0.	7.	1.	0.	C2CL6	50.0		0.	135.9	127.7	79.5	61.7	55.2
36.0	250.	200.	60.	0.	0.	4.	1.	0.	ACETONE	50.0		0.	159.1	153.3	84.8	75.3	63.0
37.0	250.	200.	60.	50.	0.	5.	1.	0.		0.		0.	108.5	124.9	75.1	92.5	38.5
38.0	250.	200.	60.	0.	0.	4.	1.	0.	ACETIC ACD	50.0		0.	95.2	76.4	84.0	81.0	72.1
39.0	250.	500.	60.	50.	0.	5.	3.	0.		0.		0.	110.7	127.4	82.6	90.8	39.6
40.0	250.	200.	60.	25.	0.	5.	1.	0.		0.		0.	110.2	115.0	86.4	82.6	49.7
41.0	250.	200.	60.	75.	0.	5.	1.	0.		0.		0.	117.5	129.5	80.8	96.4	50.4
42.0	250.	500.	60.	0.	27.	3.	3.	0.	TETRALIN	50.0		0.	111.6	112.8	54.0	103.1	20.7
43.0	250.	800.	60.	50.	0.	5.	1.	0.		0.		0.	111.0	132.5	103.6	89.6	35.3
44.0	250.	200.	60.	10.	10.	3.	1.	0.		0.		0.	101.6	97.2	93.6	89.0	40.9
45.0	250.	0.	60.	50.	0.	5.	1.	0.		0.		0.	124.9	142.0	97.4	102.0	36.4
46.0	250.	200.	60.	0.	27.	1.	1.	0.		0.		0.	92.4	81.4	100.5	84.9	66.8
47.0	250.	800.	60.	25.	0.	5.	1.	0.		0.		0.	100.2	109.5	91.7	82.9	42.5

Run No. (.5 = Split Wash)	Temperature (°C)	H_2 Pressure (lb/in^2)	Residence Time (min)	Methanol Loading (gm)	Water Loading (gm)	Run Group	1,H_2O:2,HCl:3,C_6H_6	Wash Conditions 1, Split H_2O/HCl	Additive A	Add. A Loading (gm)	Additive B	Add. B Loading (gm)	Carbon Recovery (%)	Hydrogen Recovery (%)	Nitrogen Recovery (%)	Ash Recovery (%)	O and S Recovery (%)
48.0	275.	800.	60.	50.	0.	5.	1.	0.		0.		0.	110.8	131.6	93.5	117.7	0.
49.0	225.	8C0.	60.	50.	0.	5.	1.	0.		0.		0.	105.5	117.4	99.3	82.9	69.6
50.0	250.	0.	60.	50.	0.	5.	1.	0.		0.		0.	124.4	143.0	81.3	80.3	29.2
51.0	250.	800.	60.	35.	0.	5.	1.	0.		0.		0.	104.1	118.6	84.7	61.3	48.9
52.0	225.	200.	60.	50.	0.	5.	1.	0.		0.		0.	106.3	114.8	85.7	81.6	78.8
53.0	250.	200.	60.	50.	0.	7.	3.	0.	O-DICL-BEN	60.0		0.	110.5	120.8	88.2	118.3	47.6
54.0	250.	200.	6C.	0.	0.	4.	1.	0.	ETHANOL	50.0		0.	98.8	113.4	69.4	74.7	60.9
55.0	250.	500.	60.	50.	0.	6.	2.	0.	ZNO	18.8		0.	132.0	162.9	85.3	104.4	40.5
56.0	250.	800.	60.	0.	27.	1.	1.	0.		0.		0.	94.0	81.7	96.0	80.2	57.8
57.0	250.	500.	60.	50.	0.	6.	1.	0.	ZNO	9.0		0.	104.1	134.9	94.0	59.0	87.0
58.0	250.	500.	60.	50.	0.	6.	1.	0.	HCL(PSIG)	100.0		0.	109.7	126.6	73.5	117.3	67.7
59.0	250.	500.	60.	50.	0.	7.	1.	0.	INDOLINE	10.0		0.	120.8	145.9	20.0	87.9	55.2
60.0	250.	500.	60.	0.	0.	4.	1.	0.	DECANE+TET	250.4	HCL(PSIG)	100.0	88.4	90.0	106.6	127.0	135.1
62.0	200.	0.	60.	0.	27.	1.	2.	1.		0.		0.	94.1	89.0	98.5	89.0	91.3
62.5	200.	0.	60.	0.	27.	1.	1.	1.		0.		0.	94.1	89.0	98.5	89.0	91.3
63.0	250.	500.	60.	0.	27.	1.	1.	0.		0.		0.	93.9	85.3	103.9	77.6	64.7
64.0	250.	0.	60.	0.	27.	1.	1.	0.		0.		0.	90.2	82.9	83.9	73.9	87.5
65.0	250.	500.	60.	0.	27.	1.	1.	0.		0.		0.	94.3	85.2	94.0	72.6	65.2
66.0	250.	500.	60.	50.	0.	7.	1.	0.	PYROLIDINE	10.5		0.	107.1	136.2	90.3	118.4	60.7
67.0	40.	0.	999.	0.	0.	4.	1.	0.	ETHYLETHER	306.0		0.	100.4	101.7	105.0	86.7	113.8
68.0	235.	0.	60.	99.	0.	5.	1.	0.		0.		0.	96.1	98.6	90.6	94.4	99.2
69.0	250.	500.	60.	50.	0.	6.	2.	1.	ZNO	9.0		0.	106.1	126.9	87.9	81.1	51.4
69.5	250.	500.	60.	50.	0.	6.	1.	1.	ZNO	9.0		0.	106.1	126.9	87.9	81.1	51.4
70.0	275.	800.	30.	50.	0.	5.	1.	0.		0.		0.	115.4	137.8	78.2	96.0	18.1
72.0	250.	800.	60.	50.	0.	5.	2.	1.		0.		0.	114.0	136.0	76.9	102.7	17.6
72.5	250.	800.	60.	50.	0.	5.	1.	1.		0.		0.	114.0	136.0	76.9	102.7	17.6
73.0	250.	800.	60.	50.	0.	5.	2.	1.		0.		0.	110.6	130.5	68.8	90.2	33.2
73.5	250.	800.	60.	50.	0.	5.	1.	1.		0.		0.	110.6	130.5	68.8	90.2	33.2
74.0	250.	800.	0.	50.	0.	5.	2.	1.		0.		0.	99.9	104.7	100.8	74.0	89.0
74.5	250.	800.	0.	50.	0.	5.	1.	1.		0.		0.	99.9	104.7	100.8	74.0	89.0
75.0	250.	500.	60.	50.	0.	5.	2.	1.		0.		0.	114.2	131.8	85.6	83.7	47.0
75.5	250.	500.	60.	50.	0.	5.	1.	1.		0.		0.	114.2	131.8	85.6	83.7	47.0
76.0	250.	800.	30.	50.	0.	5.	2.	1.		0.		0.	110.0	125.3	88.6	74.8	53.5
76.5	250.	800.	30.	50.	0.	5.	1.	1.		0.		0.	110.0	125.3	88.6	74.8	53.5
77.0	275.	800.	0.	50.	0.	5.	2.	1.		0.		0.	110.2	118.4	88.0	64.2	67.1
77.5	275.	800.	0.	50.	0.	5.	1.	1.		0.		0.	110.2	118.4	88.0	64.2	67.1
79.0	250.	500.	6C.	50.	0.	6.	2.	1.	ZN	1.0		0.	109.2	127.1	79.9	76.8	46.4
79.5	250.	500.	60.	50.	0.	6.	1.	1.	ZN	1.0		0.	109.2	127.1	79.9	76.8	46.4
80.0	250.	800.	60.	0.	27.	2.	2.	1.	ZN	10.0		0.	91.6	99.4	90.7	102.3	59.7
80.5	250.	800.	60.	0.	27.	2.	1.	1.	ZN	10.0		0.	91.6	99.4	90.7	102.3	59.7
82.0	225.	999.	60.	0.	27.	2.	2.	1.	ZN	10.1		0.	91.1	96.5	86.2	80.0	61.5
82.5	225.	999.	60.	0.	27.	2.	1.	1.	ZN	10.1		0.	91.1	96.5	86.2	80.0	61.5

Appendix B

Calculations and Plotting Programs

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      PROGRAM ZNCLOR(INPUT,OUTPUT,PUNCH,TAPE99)
C    CALCULATIONS PROGRAM --  ACCEPTS RAW DATA AND CALCULATES ELEMENTAL
C    RECOVERIES, INCORPORATION, SOLUBILITIES.  PUNCHES CARDS FOR PLOTTING
C    PROGRAM INPUT AND GENERATES TABLES WHEN THE IDENTIFIER NOPRNT IS GT 0.
      COMMON/EXCUND/ADTYPA(100),ADTYPB(100),ADAMTB(100),ADAMTA(100)
      COMMON/EXTTOT/BSOL(100),PSOL(100),TSOL(100),XMINSL(100),XMAXSL(100
     1),YIELD(100)
      COMMON/RECEXT/NX,TSI(100),CDORG(100),GMTC(100),ZNCL2(100),TOTORG(1
     100),ICODE(100),REC(100,7)
      COMMON/RECTOT/HTOC(100),OSTOC(100),XNTCC(100)
      COMMON/ALLSUB/PCTR(100,7),RUN(100),R95C(100),MM
      COMMON/CONTAB/TAB(100),HP(100),TI(100),TE(100),ALC(100),WAT(100),A
     1DIT(100)
      COMMON/CHOPLD/YPL(100),XPL(100),XMIN,XMAX,YMIN,YMAX,NPTS,ICH(100)
      COMMCN/NEWEST/Z(100),XTRA(100),XZN(100),XNET(100,7),ANW(100),NOPRN
     1T,LBL(7),LBLW(3),WASH(100)
      DIMENSION SPECS(30)
      DIMENSION XMTC(100),BE(100),PYE(100),RES(100),FPYRNE(100)
      DIMENSION OREC(100)
      DIMENSICN WP(100,7)
    1 FORMAT(8F5.2)
    9 FORMAT(4F6.4,F3.2)
   13 FORMAT(I1)
      NOPRNT=0
      MM=0
      READ 16,(LBLW(I),I=1,3)
      READ 16,(LBL(I),I=1,7)
   16 FORMAT(7A3)
   99 MM=MM+1
      ANW(MM)=0.
      READ 1,(WP(MM,I),I=1,6),GMTC(MM),RUN(MM)
      READ 9,XMTC(MM),BE(MM),PYE(MM),RES(MM),FPYRNE(MM)
      CALL CCNDNS
      READ 13,ICODE(MM)
      WASH(MM)=ICODE(MM)
      IF(ICODE(MM).EQ.2)GO TO 99
      CALL RECOVR(WP)
      CALL EXTRAC(XMTC,BE,PYE,RES,FPYRNE)
      IF(ICODE(MM).GT.0)GO TO 99
      ICODE(MM)=1
      WASH(MM)=1.
      CALL TOTALS
      DO 104 I=1,MM
      PUNCH 101,RUN(I),TE(I),HP(I),TI(I),ALC(I),WAT(I),TAB(I),WASH(I),AN
     1W(I),ADTYPA(I),ADAMTA(I),ADTYPB(I),ADAMTB(I)
      PUNCH 102,PCTR(I,1),PCTR(I,2),PCTR(I,3),PCTR(I,6),PCTR(I,7),XNET(I
     1,1),XNET(I,2),XNET(I,3),XNET(I,6),XNET(I,7),HTOC(I),OSTOC(I),XNTOC
     2(I)
  101 FORMAT(1X,F4.1,3(1X,F4.0),2(1X,F3.0),3(1X,F2.0),2(A10,F5.1))
  102 FORMAT(1X,10(F5.1,1X),3(F5.3,1X))
  103 FORMAT(1X,F5.2,1X,2(F5.3,1X),3(F5.1,1X),F5.3,1X,3(F5.1,1X))
  104 PUNCH 103,XZN(I),Z(I),XTRA(I),BSOL(I),PSOL(I),TSOL(I),R95C(I),XMIN
     1SL(I),XMAXSL(I),YIELD(I)
      STOP
      END
      SUBROUTINE RECCVR(WP)
```

```
   DIMENSION OC(7),TOT(100),ZNOH2(100),FCR(100),XASH(100),ZNO(100),R9
  1OC(100),R8OC(100),CORREC(100,7)
   DIMENSION WP(100,7)
   COMMON/NEWEST/Z(100),XTRA(100),XZN(100),XNET(100,7),ANW(100),NOPRN
  1T,LBL(7),LBLW(3),WASH(100)
   COMMON/ALLSUB/PCTR(100,7),RUN(100),R95C(100),MM
   COMMON/RECTOT/HTOC(100),OSTOC(100),XNTOC(100)
   COMMON/RECEXT/NX,TSI(100),CDORG(100),GMTC(100),ZNCL2(100),TOTORG(1
  100),ICODE(100),REC(100,7)
80 FORMAT(*1*)
 3 FORMAT(* RUN NUMBER*,F5.1,3X,A3,* WASH*,//,* GMS MTC RECOVERED=*,F
  17.2,/,* GMS ZNCL2=*,F7.3,/,* EXCESS ZN=*,F7.3,* GMS*,/,*  AS ZNO=*
  2,F9.3,/,*  AS ZNOH2=*,F7.3)
 4 FORMAT(7(1XA3,2(F7.3,3X),5X,F7.3,4X,F10.3,2X,F10.3,/))
19 FORMAT(///,* (INCORPORATED CARBON/COAL CARBON) IN MTC*,/,* .IF 95
  1PCT OF COAL CARBON RECOVERED *,F7.3,/,* .IF 90 PCT OF COAL CARBON
  2RECOVERED *,F7.3,/,* .IF 80 PCT OF COAL CARBON RECOVERED*,F8.3,/,/
  3/,* ASSUMING 95 PCT OF COAL CARBON RECOVERY...*,/,* .TOTAL ORGANIC
  4S=*,F7.3,* GMS*,/,* .COAL DERIVED ORGANICS=*,F7.3,* GMS*,/,* SOLVE
  5NT INCORPORATION= *,F7.3,* GMS *)
20 FORMAT(/,* ELEMENTAL RATIOS*,/,*  H/C   C+S/C    N/C*,/,1X,F5.3,2X
  1,F5.3,3X,F5.3,/)
21 FORMAT(//,3X,*  WT.PCT.  GMS RECOV.   CORR. FOR ZN   NET GAIN   PC
  1T.RECOV.*)
   OC(1)=23.91
   OC(2)=1.95
   OC(3)=0.33
   OC(4)=0.
   OC(5)=0.
   OC(6)=5.51
   OC(7)=6.56
   IF(NOPRNT.EQ.0)GO TO 60
   PRINT 80
60 NX=1
   N=MM
   IF(MM.EQ.1)GO TO 99
   IF(ICODE(MM-1).EQ.2)NX=0
   IF(NX.EQ.0)N=N-1
99 WP(N,7)=0.
   TOT(N)=0.
   TSI(N)=0.
   CDORG(N)=0.
   DO 2 I=1,7
   REC(N,I)=WP(N,I)*GMTC(N)/100.
   CORREC(N,I)=REC(N,I)
 2 TOT(N)=TOT(N)+CORREC(N,I)
   ZNCL2(N)=REC(N,5)+(REC(N,5)/1.084)
   XZN(N)=REC(N,4)-(REC(N,5)/1.084)
   IF(XZN(N).GE.0.)GO TO 18
   XZN(N)=0.
   ZNCL2(N)=2.084*(REC(N,4))
18 ZNOH2(N)=1.52*XZN(N)
   ZNO(N)=1.245*XZN(N)
   XASH(N)=ZNO(N)
   CORREC(N,6)=REC(N,6)-XASH(N)
   REC(N,7)=GMTC(N)-TOT(N)
```

```
      CORREC(N,7)=GMTC(N)-ZNCL2(N)-REC(N,6)-REC(N,1)-REC(N,2)-REC(N,3)
      IF(CORREC(N,7).LT.0.)CORREC(N,7)=0.
      IF(REC(N,7).LT.0.)REC(N,7)=0.
      KW=ICODE(N)
      IF(NOPRNT.EQ.0)GO TO 96
      PRINT 3,RUN(N),LBLW(KW),GMTC(N),ZNCL2(N),XZN(N),ZNO(N),ZNOH2(N)
   96 XNTOC(N)=(6.*CORREC(N,3))/(7.*CORREC(N,1))
      HTOC(N)=12.*CORREC(N,2)/CORREC(N,1)
      OSTOC(N)=.8*CORREC(N,7)/CORREC(N,1)
      IF(NOPRNT.EQ.0)GO TO 61
      PRINT 20,HTOC(N),OSTOC(N),XNTOC(N)
      PRINT 21
   61 DO 7 I=1,7
      XNET(N,I)=CORREC(N,I)-OC(I)
    7 PCTR(N,I)=100.*CORREC(N,I)/OC(I)
      FCR(N)=CORREC(N,1)/OC(1)
      TOTORG(N)=CORREC(N,1)+CORREC(N,2)+CORREC(N,3)+CORREC(N,7)
      PRINT 4,(LBL(I),WP(N,I),REC(N,I),CORREC(N,I),XNET(N,I),PCTR(N,I),I
     1=1,7)
   62 IF(N.EQ.100)GO TC 95
      IF(N.EQ.MM)GO TO 97
      N=N+1
      GO TO 99
   97 IF(NX.EQ.1)GO TO 93
      ANW(MM)=1.
      ANW(MM-1)=1.
      IF(NOPRNT.EQ.0)GO TO 63
      PRINT 92
   92 FORMAT(//# COMBINED WATER AND ACID WASH#,/)
   63 DO 90 I=1,7
      REC(100,I)=REC(MM,I)+REC(MM-1,I)
      CORREC(100,I)=CORREC(MM,I)+CORREC(MM-1,I)
      GMTC(100)=GMTC(MM)+GMTC(MM-1)
   90 WP(100,I)=CORREC(100,I)/GMTC(100)
      N=100
      GO TO 96
   95 DO 94 I=1,7
      PCTR(MM,I)=PCTR(100,I)
   94 PCTR(MM-1,I)=PCTR(100,I)
   93 R95C(N)=(FCR(N)-.95)/.95
      R90C(N)=(FCR(N)-.90)/.90
      R80C(N)=(FCR(N)-.80)/.80
      IF(FCR(N).LT..95)R95C(N)=0.
      TSI(N)=(R95C(N)*TOTORG(N))/(1.+R95C(N))
      CDORG(N)=TOTORG(N)-TSI(N)
      IF(NX.EQ.1)GC TC 89
      R95C(MM)=R95C(100)
      R95C(MM-1)=R95C(100)
   89 IF(NOPRNT.EQ.0)GC TU 64
      PRINT 19,R95C(N),R90C(N),R80C(N),TOTORG(N),CDORG(N),TSI(N)
   64 RETURN
      END
      SUBROUTINE EXTRAC(XMTC,BE,PYE,RES,FPYRNE)
      COMMON/ALLSUB/PCTR(100,7),RUN(100),R95C(100),MM
      COMMON/NEWEST/Z(100),XTRA(100),XZN(100),XNET(100,7),ANW(100),NOPRN
     1T,LBL(7),LBLW(3),WASH(100)
```

```
      COMMON/RECEXT/NX,TSI(100),CDORG(100),GMTC(100),ZNCL2(100),TOTORG(1
     100),ICODE(100),REC(100,7)
      COMMON/EXTTOT/BSOL(100),PSOL(100),TSOL(100),XMINSL(100),XMAXSL(100
     1),YIELD(100)
      DIMENSION RATIO(100),ASH(100),PYORG(100),CDORGX(100),TSIX(100),TOR
     1GX(100)
      DIMENSION XMTC(100),BE(100),PYE(100),RES(100),FPYRNE(100)
   10 FORMAT(//,* EXTRACTION DATA(GMS)      *,A3,* WASH*,/,* EXTRACTED MT
     1C=*,F7.4,*    BENZENE EXTRACT=*,F7.4,*    PYRIDINE EXTRACT=*,F7.4,/,
     2* RESIDUE=*,F7.4,*    PYRIDINE RETENTION=*,F7.4,/,* FRACTION OF RET
     3AINED PYRIDINE IN EXTRACT=*,F5.3)
   11 FORMAT(* ZNCL2=*,F7.3,*    ASH=*,F7.3,*    PYRIDINE SOL ORGANICS=*,F
     17.3,/,* COAL DERD ORGANICS=*,F7.3,*    SOLVENT=*,F7.3,*    TOTAL ORG
     2ANICS=*,F7.3,//,* TOTAL SOLUBILITIES(PCT DAF)*,/,*   BENZENE   PYRI
     3DINE      TOTAL*,/,3F10.3,//,* COAL DERIVED SOLUBILITY(PCT DAF)*,/,
     4*     MINIMUM   MAXIMUM*,/,2F10.3,/)
   12 FORMAT(/,* THEORETICAL SOLUBLE YIELD=*,F10.3,*  PCT DAF*)
      N=MM
      IF(NX.EQ.0)N=N-1
   51 TSI(N)=(R95C(N)*TOTORG(N))/(1.+R95C(N))
      CDORG(N)=TOTORG(N)-TSI(N)
      XTRA(N)=RES(N)+PYE(N)+BE(N)-XMTC(N)
      RATIO(N)=XMTC(N)/GMTC(N)
      Z(N)=RATIO(N)*ZNCL2(N)
      ASH(N)=REC(N,6)*RATIO(N)
      PYORG(N)=PYE(N)-Z(N)-(XTRA(N)*FPYRNE(N))
      CDORGX(N)=CDORG(N)*RATIO(N)
      TSIX(N)=TSI(N)*RATIO(N)
      TORGX(N)=TSIX(N)+CDORGX(N)
      BSOL(N)=100.*BE(N)/TORGX(N)
      PSOL(N)=100.*PYORG(N)/TORGX(N)
      TSOL(N)=BSOL(N)+PSOL(N)
      XMINSL(N)=100.*((BE(N)+PYORG(N)-TSIX(N))/CDORGX(N))
      IF(XMINSL(N).LT.0.)XMINSL(N)=0.
      XMAXSL(N)=100.*((BE(N)+PYORG(N))/CDORGX(N))
      YIELD(N)=.95*XMINSL(N)
      IF(NOPRNT.EQ.0)GO TO 60
      L=ICODE(N)
      PRINT 10,LBLW(L),XMTC(N),BE(N),PYE(N),RES(N),XTRA(N),FPYRNE(N)
      PRINT 11,Z(N),ASH(N),PYORG(N),CDORGX(N),TSIX(N),TORGX(N),BSOL(N),P
     1SOL(N),TSOL(N),XMINSL(N),XMAXSL(N)
      PRINT 12,YIELD(N)
   60 IF(N.EQ.MM)GO TO 50
      N=N+1
      GO TO 51
   50 RETURN
      END
      SUBROUTINE TOTALS
      COMMON/ALLSUB/PCTR(100,7),RUN(100),R95C(100),MM
      COMMON/RECTOT/HTOC(100),OSTOC(100),XNTOC(100)
      COMMON/EXTTOT/BSOL(100),PSOL(100),TSOL(100),XMINSL(100),XMAXSL(100
     1),YIELD(100)
      COMMON/NEWEST/Z(100),XTRA(100),XZN(100),XNET(100,7),ANW(100),NOPRN
     1T,LBL(7),LBLW(3),WASH(100)
      IF(NOPRNT.EQ.0)GO TO 9
      PRINT 1
```

```
    1 FORMAT(#1DATA SUMMARY#/,10X,#S  O  L  U  B  I  L  I  T  I  E  S#,/
     1,10X,# TOTAL ORGANICS#,10X,# COAL#,12X,# PCT C#,5X,#
     2 #,/,# RUN  BENZENE PYRIDINE  TOTAL   MIN     MAX   YIELD RECOVERY
     3     R#)
    2 FORMAT(1X,F4.1,1X,2F7.3,1X,F7.3,2X,3(F7.3,1X),2F7.3)
    7 FORMAT(1X,F4.1,2X,2(F6.3,2X),F7.3,2X,F7.3,2(1X,F7.3),4X,F7.3)
    8 FORMAT(#1 ELEMENTAL RATIOS IN MTC AND PERCENT RECOVERY OF ELEMENTS
     1 FROM COAL FEED#,///,#  RUN    H/C    O+S/C      N/C    PCT C   PCT
     2 H   PCT N     PCT O+S#,/)
      DO 3 I=1,MM
    3 PRINT 2,RUN(I),BSOL(I),PSOL(I),TSOL(I),XMINSL(I),XMAXSL(I),YIELD(I
     1),PCTR(I,1),R95C(I)
      PRINT 8
      DO 6 I=1,MM
    6 PRINT 7,RUN(I),HTOC(I),OSTOC(I),XNTOC(I),PCTR(I,1),PCTR(I,2),PCTR(
     1I,3),PCTR(I,7)
    9 RETURN
      END
      SUBROUTINE CONDNS
      COMMON/EXCOND/ADTYPA(100),ADTYPB(100),ADAMTB(100),ADAMTA(100)
      COMMON/CONTAB/TAB(100),HP(100),TI(100),TE(100),ALC(100),WAT(100),A
     1DIT(100)
      COMMON/ALLSUB/PCTR(100,7),RUN(100),R95C(100),MM
      READ 1,HP(MM),TI(MM),TE(MM),ALC(MM),WAT(MM),ADIT(MM)
    1 FORMAT(3F4.0,2F3.0,F2.0)
      READ 10,ADTYPA(MM),ADAMTA(MM),ADTYPB(MM),ADAMTB(MM)
   10 FORMAT(2(A10,F5.1))
      IF(ADIT(MM).EQ.0.)GO TO 5
      IF(ADIT(MM).EQ.1.)GO TO 3
      IF(ALC(MM).GT.0.)GO TO 2
      IF(WAT(MM).GT.0.)GO TO 6
      TAB(MM)=4.
      GO TO 8
    6 TAB(MM)=3.
      GO TO 8
    2 TAB(MM)=7.
      GO TO 8
    3 IF(ALC(MM).EQ.0.)GO TO 4
      TAB(MM)=6.
      GO TO 8
    4 TAB(MM)=2.
      GO TO 8
    5 IF(ALC(MM).GT.0.)GO TO 7
      TAB(MM)=1.
      GO TO 8
    7 TAB(MM)=5.
    8 RETURN
      END
```

```
      PROGRAM PLOTS(INPUT,OUTPUT,TAPE99)
C     PLOTTING PROGRAM -- ACCEPTS PUNCHED DATACARDS FROM CALCULATICNS PROGRAM
C     AND MAKES PLOTS AS COMMANDED (SEE EXAMPLE PLOTTING COMMAND)
      COMMON/CONTAB/TAB(100),HP(100),TI(100),TE(100),ALC(100),WAT(100)
      COMMON/EXCESS/WASH(100),ANW(100),R95C(100)
      COMMON/EXCOND/ADTYPA(100),ADTYPB(100),ADAMTB(100),ADAMTA(100)
      COMMON/CHOPLO/YPL(100),XPL(100),XMIN,XMAX,YMIN,YMAX,NPTS,ICH(100)
      COMMON/RECVRY/RUN(100),CREC(100),HREC(100),XNREC(100),ASHREC(100),
     1OSREC(100),CNET(100),HNET(100),XNNET(100),ASHNET(100),CSNET(100),H
     2TOC(100),OSTGC(100),XNTOC(100)
      COMMCN/PLTAD/SPECS(100)
      COMMON/EXTCTN/XZN(100),ZNCLEX(100),PYRRET(100),BSOL(100),PSOL(100)
     1,TSOL(100),XMINSL(100),XMAXSL(100),YIELD(100)
      COMMON/LBLWMM/MM,LBLW(3)
      DIMENSICN CORHTC(100)
  101 FORMAT(1X,F4.1,3(1X,F4.0),2(1X,F3.0),3(1X,F2.0),2(A10,F5.1))
  102 FORMAT(1X,10(F5.1,1X),3(F5.3,1X))
  103 FORMAT(1X,F5.2,1X,2(F5.3,1X),3(F5.1,1X),F5.3,1X,3(F5.1,1X))
      MM=0
      READ 1,(LBLW(I),I=1,3)
    1 FORMAT(3A3)
    2 MM=MM+1
      READ 101,RUN(MM),TE(MM),HP(MM),TI(MM),ALC(MM),WAT(MM),TAB(MM),WASH
     1(MM),ANW(MM),ACTYPA(MM),ADAMTA(MM),ADTYPB(MM),ADAMTB(MM)
      IF(RUN(MM).EQ.0.)GO TO 3
      READ 102,CREC(MM),HREC(MM),XNREC(MM),ASHREC(MM),OSREC(MM),CNET(MM)
     1,HNET(MM),XNNET(MM),ASHNET(MM),OSNET(MM),HTOC(MM),OSTOC(MM),XNTOC(
     2MM)
      READ 103,XZN(MM),ZNCLEX(MM),PYRRET(MM),BSGL(MM),PSGL(MM),TSOL(MM),
     1R95C(MM),XMINSL(MM),XMAXSL(MM),YIELD(MM)
      GO TC 2
    3 MM=MM-1
      DO 600 I=1,MM
      IF(TAB(I).EQ.5..OR.TAB(I).EQ.6.)GO TO 602
      CORHTC(I)=HTOC(I)
      GO TC 601
  602 CORHTC(I)=((.0103)*HREC(I))-(3.*((CREC(I)/95.)-1.))
  601 PRINT 603,RUN(I),HTOC(I),CORHTC(I)
  6C3 FORMAT(1X,F4.1,2(2X,F5.2),/)
  600 CONTINUE
C     SAMPLE SET OF PLCTTING COMMANDS
      CALL CHCCSE(ALC,50.,TI,60.,TE,275.,XMINSL,HP,1)
      CALL TABULA
      CALL PLCT(0.,0.,1.,23HHYDROGEN PRESSURE(PSIG),25HCORRECTED SOLUBIL
     1ITY(PCT))
      CALL LSTSQR(1,0,0)
      CALL CHOOSE(ALC,50.,TI,60.,TE,250.,XMINSL,HP,1)
      CALL TABULA
      CALL PLCTAC(5.)
      CALL LSTSQR(1,0,0)
      CALL CHOOSE(ALC,50.,TI,60.,TE,225.,XMINSL,HP,1)
      CALL TABULA
      CALL PLOTAD(4.)
      CALL LSTSQR(1,0,0)
C     END SAMPLE SET OF PLOTTING COMMANDS
      CALL GDSEND(SPECS)
```

```
      STOP
      END
      SUBROUTINE TABULA
      COMMON/EXCESS/WASH(100),ANW(100),R95C(100)
      COMMON/EXCOND/ADTYPA(100),ADTYPB(100),ADAMTB(100),ADAMTA(100)
      COMMON/CHOPLO/YPL(100),XPL(100),XMIN,XMAX,YMIN,YMAX,NPTS,ICH(100)
      COMMON/LBLWMM/MM,LBLW(3)
      COMMON/RECVRY/RUN(100),CREC(100),HREC(100),XNREC(100),ASHREC(100),
     1OSREC(100),CNET(100),HNET(100),XNNET(100),ASHNET(100),CSNET(100),H
     2TOC(100),OSTOC(100),XNTOC(100)
      COMMON/EXTCTN/XZN(100),ZNCLEX(100),PYRRET(100),BSOL(100),PSOL(100)
     1,TSOL(100),XMINSL(100),XMAXSL(100),YIELD(100)
      COMMON/CONTAB/TAB(100),HP(100),TI(100),TE(100),ALC(100),WAT(100)
      NOPRNT=1
      IF(NOPRNT.EQ.0)GO TO 50
      PRINT 1
    1 FORMAT(≠1≠,11X,≠RUN CONDITIONS≠,7X,≠ SOLUBILITIES   INCOR≠,/,7X,≠G
     1MS GMS (C)  PSIG MINS  COAL+SOLVT   COAL RATIO         PCT RECOVERY
     2 FROM COAL≠,/,≠  RUN MEOH H2O  T  P(H2) TIME  BENZ TOTAL   MINM
     3R    H/C     C     H     N     O+S WASH   A D D I T I V E S ( G M S
     4 )≠,/)
    2 FORMAT(2(1X,F4.1),1X,F3.0,3(1X,F4.0),2X,F4.1,1X,2(F5.1,2X),F4.2,2X
     1,F4.2,2X,4(F5.1,1X),1X,A3,1X,2(A10,≠=≠,F5.1,1X),/)
    3 FORMAT(2(2X,F8.2))
    4 FORMAT(//,≠    Y VALUES   X VALUES≠)
      DO 99 I=1,MM
      IF(ICH(I).NE.1)GO TO 99
      L=WASH(I)
      PRINT 2,RUN(I),ALC(I),WAT(I),TE(I),HP(I),TI(I),BSOL(I),TSOL(I),XMI
     1NSL(I),R95C(I),HTOC(I),CREC(I),HREC(I),XNREC(I),OSREC(I),LBLW(L),A
     2DTYPA(I),ADAMTA(I),ADTYPB(I),ADAMTB(I)
   99 CONTINUE
      PRINT 4
      DO 98 I=1,NPTS
      PRINT 3,YPL(I),XPL(I)
   98 CONTINUE
   50 RETURN
      END
      SUBROUTINE CHOOSE(CA,CAV,CB,CBV,CC,CCV,YIN,XIN,IADWSH)
      DIMENSION YIN(100),XIN(100)
      DIMENSION CA(100),CB(100),CC(100)
      COMMON/CHOPLO/YPL(100),XPL(100),XMIN,XMAX,YMIN,YMAX,NPTS,ICH(100)
      COMMON/EXCESS/WASH(100),ANW(100),R95C(100)
      COMMON/LBLWMM/MM,LBLW(3)
      COMMON/EXCOND/ADTYPA(100),ADTYPB(100),ADAMTB(100),ADAMTA(100)
      XMIN=0.
      XMAX=0.
      YMIN=0.
      YMAX=0.
      NPTS=0.
      DO 99 I=1,MM
      ICH(I)=0
      IF(IADWSH.EQ.0)GO TO 98
      IF(WASH(I).EQ.2.)GO TO 99
      IF(ADAMTA(I).GT.0.)GO TO 99
   98 IF(CA(I).NE.CAV)GO TO 99
```

```
      IF(CB(I).NE.CBV)GO TO 99
      IF(CC(I).NE.CCV)GO TO 99
      NPTS=NPTS+1
      ICH(I)=1
      YPL(NPTS)=YIN(I)
      XPL(NPTS)=XIN(I)
      IF(YIN(I).GT.YMAX)YMAX=YIN(I)
      IF(YIN(I).LT.YMIN)YMIN=YIN(I)
      IF(XIN(I).GT.XMAX)XMAX=XIN(I)
      IF(XIN(I).LT.XMIN)XMIN=XIN(I)
   99 CONTINUE
      RETURN
      END
      SUBROUTINE PLOT(XDEC,YDEC,SYMB,BCTITL,LFTITL)
      COMMON/CHOPLO/YPL(100),XPL(100),XMIN,XMAX,YMIN,YMAX,NPTS,ICH(100)
      COMMON/PLTAD/SPECS(100)
      DIMENSICN GIVEN(5)
      SPECS(20)=0.0
      GIVEN(1)=XMAX
      GIVEN(2)=XMIN
      GIVEN(3)=10.
      GIVEN(4)=10.
      GIVEN(5)=1.1
      SPECS(27)=0.
      SPECS(11)=1.
      SPECS(26)=0.
      SPECS(25)=0.
      SPECS(24)=0.
      SPECS(12)=99.
      CALL NXTFRM(SPECS)
      CALL FAGLIX(GIVEN,SPECS)
      GIVEN(1)=YMAX
      GIVEN(2)=YMIN
      GIVEN(5)=.8
      CALL FAGLIY(GIVEN,SPECS)
      SPECS(11)=1.0
      CALL AXLILI(SPECS)
      SPECS(25)=-.15
      SPECS(27)=-.15
      CALL SAXLIT(SPECS)
      CALL SAXLIR(SPECS)
      SPECS(13)=NPTS
      SPECS(14)=1.
      SPECS(15)=1.
      SPECS(16)=SYMB
      SPECS(17)=.15
      SPECS(18)=.15
      CALL PSLILI(XPL,YPL,SPECS)
      SPECS(19)=0.
      SPECS(21)=1.
      SPECS(24)=0.05
      SPECS(28)=XDEC
      SPECS(17)=.25
      SPECS(18)=.25
      CALL NCDLIE(SPECS)
      SPECS(28)=YDEC
```

```
      SPECS(26)=0.05
      CALL NODLIL(SPECS)
      SPECS(17)=.3
      SPECS(18)=.3
      CALL TITLEB(BOTITL,SPECS)
      CALL TITLEL(LFTITL,SPECS)
      RETURN
      END
      SUBROUTINE PLOTAD(SYMB)
      COMMON/CHOPLO/YPL(100),XPL(100),XMIN,XMAX,YMIN,YMAX,NPTS,ICH(100)
      COMMON/PLTAD/SPECS(100)
      SPECS(17)=.15
      SPECS(18)=.15
      SPECS(13)=NPTS
      SPECS(16)=SYMB
      CALL PSLILI(XPL,YPL,SPECS)
      RETURN
      END
      SUBROUTINE LSTSCR(LINPLT,IPARPL,LIM)
      COMMON/CHOPLO/YPL(100),XPL(100),XMIN,XMAX,YMIN,YMAX,NPTS,ICH(100)
      COMMON/PLTAD/SPECS(100)
      DIMENSION YLIN(100),YPAR(100),YPLUS(100),YMINUS(100),Y(100),X(100)
      XN=NPTS
      NP=SPECS(13)
      SX=0.
      SY=0.
      SXY=0.
      SXX=0.
      SXXX=0.
      SXXXX=0.
      SXXY=0.
      DO 1 I=1,NPTS
      SX=SX+XPL(I)
      SY=SY+YPL(I)
      SXX=SXX+(XPL(I)**2.)
      SXXX=SXXX+(XPL(I)**3.)
      SXXXX=SXXXX+(XFL(I)**4.)
      SXXY=SXXY+((XPL(I)**2.)*YPL(I))
1     SXY=SXY+(XPL(I)*YPL(I))
      A=((XN*SXY)-(SX*SY))/((XN*SXX)-(SX**2.))
      B=(SY-(A*SX))/XN
      DE=XN*((SXX*SXXXX)-(SXXX**2.))+SX*((SXXX*SXX)-(SXXXX*SX))+SXX*((SX
     1*SXXX)-(SXX**2.))
      IF(DE.EQ.0.)GO TO 98
      C0=(SY*((SXX*SXXXX)-(SXXX**2.))+SX*((SXXX*SXXY)-(SXXXX*SXY))+SXX*(
     1(SXY*SXXX)-(SXXY*SXX)))/DE
      C1=(XN*((SXY*SXXXX)-(SXXY*SXXX))+SY*((SXXX*SXX)-(SXXXX*SX))+SXX*((
     1SX*SXXY)-(SXX*SXY)))/DE
      C2=(XN*((SXX*SXXY)-(SXXX*SXY))+SX*((SXY*SXX)-(SXXY*SX))+SY*((SX*SX
     1XX)-(SXX**2.)))/DE
      SEL=0.
      SELS=0.
      SEP=0.
      SEPS=0.
      DO 99 I=1,NPTS
      YLIN(I)=(A*XPL(I))+B
```

```
      YPAR(I)=C0+(C1*XPL(I))+(C2*(XPL(I)**2.))
      EL=YPL(I)-YLIN(I)
      EP=YPL(I)-YPAR(I)
      SEL=SEL+((EL*EL)**.5)
      SEP=SEP+((EP*EP)**.5)
      SELS=SELS+(EL*EL)
      SEPS=SEPS+(EP*EP)
   99 CONTINUE
      AVGERL=SEL/XN
      AVGERP=SEP/XN
      STDDEL=(SELS/XN)**.5
      STDDEP=(SEPS/XN)**.5
      PRINT 2
    2 FORMAT(/,* CURVE FITS---------Y=A*X+B , Y=C0+(C1*X)+(C2*X**2)*,/,6X
     1,*A*,10X,*B*,1CX,*C0*,9X,*C1*,9X,*C2*)
      PRINT 3,A,B,C0,C1,C2
    3 FORMAT(5(1X,1PE10.3))
      PRINT 4,AVGERL,STDDEL,AVGERP,STDDEP
    4 FORMAT(/,* AVERAGE ERROR  STD.DEVIATION*,/,* LIN*,2(1X,1PE10.3),/,
     1* PAR*,2(1X,1PE10.3))
      XINC=(XMAX-XMIN)/100.
      SPECS(13)=100
      IF(LINPLT.EQ.0)GO TO 5
      DO 7 I=1,100
      XI=I-1
      X(I)=XMIN+(XINC*XI)
      Y(I)=(A*X(I))+E
      YPLUS(I)=Y(I)+(2.*STDDEL)
      YMINUS(I)=Y(I)-(2.*STDDEL)
      IF(YPLUS(I).GT.YMAX)YPLUS(I)=YMAX
      IF(YMINUS(I).LT.YMIN)YMINUS(I)=YMIN
    7 CONTINUE
      CALL SLLILI(X,Y,SPECS)
      IF(LIM.EQ.0)GC TO 5
      CALL DLLILI(X,YPLUS,.1,.05,SPECS)
      CALL DLLILI(X,YMINUS,.1,.05,SPECS)
    5 IF(IPARPL.EQ.0)GO TO 98
      DO 8 I=1,1C0
      XI=I-1
      X(I)=XMIN+(XINC*XI)
      Y(I)=C0+(C1*X(I))+(C2*(X(I)**2.))
      YPLUS(I)=Y(I)+(2.*STDDEP)
      YMINUS(I)=Y(I)-(2.*STDDEP)
      IF(YPLUS(I).GT.YMAX)YPLUS(I)=YMAX
      IF(YMINUS(I).LT.YMIN)YMINUS(I)=YMIN
    8 CONTINUE
      CALL SLLILI(X,Y,SPECS)
      IF(LIM.EG.0)GC TC 98
      CALL DLLILI(X,YPLUS,.1,.05,SPECS)
      CALL DLLILI(X,YMINUS,.1,.05,SPECS)
   98 SPECS(13)=NP
      RETURN
      END
      SUBROUTINE LABELS(PROGRM,SZ,XST,YST,SYM,ALBL)
      COMMON/PLTAD/SPECS(100)
      SYMBCL=SPECS(16)
```

```
SIZE=SPECS(17)
SPECS(16)=SYM
SPECS(17)=SZ
SPECS(18)=SZ
SPECS(22)=XST
SPECS(23)=YST
IF(PROGRM.EQ.1.)CALL SYMKEY(1.,ALBL,SPECS)
IF(PROGRM.EQ.2.)CALL TITLEG(1.,ALBL,SPECS)
SPECS(16)=SYMBCL
SPECS(17)=SIZE
SPECS(18)=SIZE
RETURN
END
```

Appendix C

Raw Data for Calculations Program

Data fed to the calculations program (ZNCLOR) - elemental analyses of the MTC, extraction weights, and run conditions - are listed exactly in the form in which it was fed to the program.

The first line provides weight percents of each element, followed by the weight of MTC recovered and the run number, all in F5.2 format. The second line gives extraction weights in gm (four values in F6.4 format), followed by the fraction of retained pyridine which was found in the pyridine extract (in F3.2). The third line gives run conditions: hydrogen pressure (psig), residence time (min) and temperature (^{o}C) in F4.0; methanol loading and water loading (gm) in F3.0; and type of additive (0. = none, 1. = inorganic, 2. = organic) in F2.0. The fourth line identifies the additive and gives its loading in gm. The fifth line is for program control and instructs the computer that a new set of data is coming. (1 indicates an altogether new run; 2 indicates that the upcoming data is to be combined with the previous data as they are from the same run with different run conditions; 3 serves the same as a 1, but indicates that the previous run was benzene-washed.)

For example, the first set of data is interpreted as follows: 47.6003.9800.8104.5303.2134.0051.5002.00 indicates 47.60% C, 3.98% H, 0.81% N, 4.53% Zn, 3.21% Cl, 34.00% ash, 51.50 gm MTC recovered, and run number 2. The second line - 6.99920.06600.84406.0892.20 - indicates 6.9992 gm MTC extracted yielding 0.0660 gm benzene extract, 0.84406 gm pyridine extract, and 6.0892 gm residue with 20% of the incorporated pyridine in the pyridine extract. The third line - 500.060.250.00.27.2 - indicates 500 psig hydrogen pressure, 60 minutes reaction time, 250°C, 00 gm methanol, 27 gm water, an organic additive present. The fourth line identifies the additive as 50 gm piperidine.

```
H2CHCL BZ
 C   H   N  ZN CLASHO+S
47.6003.9800.8104.5303.2134.0051.5002.00
6.99920.06600.84406.0892.20
500.060.250.00.27.2.
PIPERIDINE 50.0            000.0
1
57.3204.2800.8301.5600.2014.1032.0003.00
6.36060.19480.56606.0660.05
500.060.250.00.27.1.
       KBR 45.3         NAI 57.1
1
67.3604.8200.2710.9011.3809.0099.9004.00
9.00202.75005.47401.8930.93
500.060.250.00.27.2.
DIHYORCANT 50.0            000.0
1
62.5404.9900.8201.3900.1814.4032.9005.00
6.66320.13130.55306.3685.06
500.060.250.00.27.1.
       KCL 37.6        NACL 29.4
1
68.6205.2000.5801.4000.6313.4036.9007.00
8.41700.61952.88805.2240.39
500.060.250.00.27.2.
    MESITOL 50.0           000.0
1
59.9703.9000.3906.7901.1616.7070.2009.00
1.38650.05750.10501.3025.20
500.060.250.00.27.2.
 T-BUTANOL 50.0        PTSA 50.0
1
59.8604.8100.6903.1502.0010.4751.8010.00
1.75700.71250.41200.7280.50
500.060.250.00.27.2.
ME-NAPHTHA 50.0  TETRALIN 10.0
3
65.6004.7000.9300.8800.1013.6034.0011.00
8.74000.69801.73907.2750.24
500.060.275.00.27.0.
          000.0            000.0
1
76.0005.6000.8803.8402.7307.3380.0012.00
8.84393.45102.99702.6319.76
500.060.250.00.27.2.
ANTHRA OIL 50.0            000.0
3
68.2304.8101.1602.3600.7016.2026.0013.00
8.65501.37702.61205.1100.57
500.060.300.00.27.0.
          000.0            000.0
1
65.7204.8900.7602.6100.6714.3040.0014.00
7.13350.55551.17255.8135.13
500.060.250.00.27.2.
  P-XYLENE 50.0       CACL2 24.7
1
64.5805.9300.7105.5602.7015.0041.5015.00
1.15250.27500.51650.4710.80
200.060.250.50.00.0.
          000.0            000.0
1
67.7904.9800.9701.7100.6015.6030.8016.00
1.47600.13450.46200.9795.30
500.060.275.00.27.1.
     CACL2 24.7            000.0
1
65.5005.8300.7802.2000.7015.2044.0017.00
6.61300.87501.54004.4020.27
000.060.250.99.00.0.
          000.0            000.0
1
64.0405.9700.7705.7402.3916.6041.2519.00
5.61151.40401.94702.3600.61
650.020.275.50.00.0.
          000.0            000.0
1
65.1605.0400.6406.6903.0319.9038.5020.00
6.31600.76702.15103.7630.72
400.060.320.25.00.2.
  N-DECANE100.0            000.0
```

```
1
55.8805.2200.5913.3002.8925.5048.4021.00
6.52400.75602.04604.0240.52
250.060.250.50.00.2.
  N-DECANE 50.0            000.0
1
64.6004.8200.9701.7900.2014.9032.5022.00
9.97400.47202.02708.3840.17
500.060.250.00.27.0.
          000.0            000.0
1
66.4604.6901.2902.3200.3714.8032.5023.00
9.41000.43601.79307.9500.14
500.060.250.00.27.1.
     CACL2 24.7            000.0
1
39.9004.1800.5223.8007.7031.7050.0024.00
8.33100.97303.88904.2790.86
200.060.250.50.00.1.
       ZN 25.0             000.0
1
32.5503.3500.6028.5004.7652.6079.6025.00
7.10700.00001.35106.3650.90
250.060.250.00.00.2.
   N,N-DMF100.0            000.0
1
70.6406.4400.5303.6304.5211.7056.9026.00
1.21400.38100.63300.3020.86
250.060.250.50.00.2.
ANTHRA OIL 10.0            000.0
1
 66.4505.9500.7102.5901.0712.0039.7027.00
 5.94201.12901.72903.2700.42
 200.060.250.50.00.1.
      CDCL2 38.5           000.0
 1
 46.5203.6300.4620.8900.5539.0058.0028.00
 9.99300.13300.39409.8940.20
 200.060.250.50.00.1.
      SNCL2 42.1           000.0
 1
 74.4207.1500.5301.3200.8810.2050.3029.00
 1.82500.96000.49750.4400.54
 200.060.250.50.00.2.
   TETRALIN 10.0           000.0
 3
 50.0405.3100.4516.0014.2313.0060.0030.00
 1.60200.28001.66400.2710.95
 200.060.275.50.00.0.
          000.0            000.0
 1
 64.6505.0200.7704.5203.3115.4045.0031.00
 8.08200.57401.00206.8740.10
 200.060.200.50.00.2.
 ANTHRA OIL 10.0           000.0
 1
 63.0306.3800.5406.3205.3214.9050.0032.00
 4.44701.38701.74701.4480.74
 200.060.250.50.00.2.
 CYCHEXANOL 10.0           000.0
 1
 68.7305.8700.6602.8701.1111.4045.0033.00
 1.28550.16600.44500.6815.50
 200.060.250.00.00.2.
 I-PROPANOL 50.0           000.0
 1
 63.3105.5100.5506.0102.2614.9048.0034.00
 5.78300.61701.24603.9390.26
 200.060.250.00.00.2.
  T-BUTANOL 50.0           000.0
 1
 75.5505.7900.6100.8302.6307.9043.0035.00
 4.71700.71501.96602.1950.69
 200.060.250.50.00.2.
      C2CL6 50.0           000.0
 1
 76.0805.9800.5600.3900.6708.3050.0036.00
 1.10300.26650.55300.2990.68
 200.060.250.00.00.2.
    ACETONE 50.0           000.0
```

```
1
61.7805.8000.5908.7203.6518.8042.0037.00
4.94001.39001.85001.9900.65
200.060.250.50.00.0.
            000.0           000.0
1
67.3504.4100.8200.1100.8713.2033.8038.00
4.75600.08550.58014.5170.50
200.060.250.00.00.2.
ACETIC ACD 50.0             000.0
1
67.0306.2900.6904.1102.1015.3739.5039.00
3.78101.37001.44051.5270.60
500.060.250.50.00.0.
            000.0           000.0
3
69.3205.9000.7502.3200.7514.0038.0040.00
4.07251.01431.52542.2890.40
200.060.250.25.00.0.
            000.0           000.0
1
66.4305.9700.6304.4401.3816.5042.3041.00
4.30800.83401.19852.0620.70
200.060.250.75.00.0.
            000.0           000.0
1
65.8905.4300.4405.3105.4814.3540.5042.00
1.84600.91400.50400.5040.90
500.060.250.00.27.2.
  TETRALIN 50.0             000.0
3
59.7605.8200.7709.8906.4716.0044.4043.00
2.15800.61251.38500.5880.92
800.060.250.50.00.0.
            000.0           000.0
1
68.4605.3400.8702.1501.6514.6035.5044.00
4.39100.53501.31022.7460.70
200.060.250.10.10.0.
            000.0           000.0
1
65.0606.0600.7006.9802.6417.9045.9045.00
4.35901.09431.57841.9520.85
000.060.250.50.00.0.
            000.0           000.0
1
64.6104.6400.9702.5200.1916.6034.2046.00
5.80600.22420.82725.1190.07
200.060.250.00.27.0.
            000.0           000.0
1
67.3006.0000.8503.3901.2615.6035.6047.00
2.11400.56900.86050.8050.65
800.060.250.25.00.0.
            000.0           000.0
1
60.0805.8200.7009.4011.3014.7044.1048.00
2.93700.81402.37420.4790.92
800.060.275.50.00.0.
            000.0           000.0
1
64.6805.8700.8403.8800.4716.0039.0049.00
4.86850.65001.39953.0420.65
800.060.225.50.00.0.
            000.0           000.0
1
65.3706.1300.5908.6404.1615.7045.5050.00
1.44000.40050.62800.5200.85
000.060.250.50.00.0.
            000.0           000.0
1
64.9906.0400.7306.9803.0514.0038.3051.00
1.91400.50801.00150.5860.85
800.060.250.35.00.0.
            000.0           000.0
1
62.0205.4600.6906.3000.5318.2041.0052.00
2.57450.25050.58851.8540.85
200.060.225.50.00.0.
            000.0           000.0
```

```
1
57.2105.1000.6310.3404.2822.0746.2053.00
2.08000.32000.55301.2970.90
200.060.250.50.00.2.
O-DICL-BEN 60.0             000.0
3
63.8906.4300.5705.9506.0512.1049.4054.00
1.15500.34100.78100.1150.80
200.060.250.00.00.2.
   ETHANOL 50.0             000.0
1
68.0706.3700.6600.8400.6212.2034.7055.00
0.79500.22450.43700.1905.50
500.060.250.50.00.1.
       ZNO 18.8             000.0
1
66.6604.7300.9402.3600.4815.5033.7056.00
2.63900.16300.66101.8660.30
800.060.250.00.27.0.
            000.0           000.0
1
47.3205.0000.5922.1003.3029.9052.6057.00
1.14600.19100.42350.5950.80
500.060.250.50.00.1.
       ZNO  9.0             000.0
1
58.4405.5000.5405.3909.6614.4044.9058.00
1.29800.32750.97600.1440.90
500.060.250.50.00.1.
 HCL(PSIG)100.0             000.0
1
65.4706.4500.1506.1101.4716.9044.1059.00
1.36500.47250.51200.4000.50
500.060.250.50.00.2.
  INDOLINE 10.0             000.0
1
54.0404.4900.9000.0000.0017.9039.1060.00
1.91200.00000.46001.6910.05
500.060.250.00.00.2.
DECANE+TET250.4 HCL(PSIG)100.0
1
61.8404.7500.8500.2400.1615.2025.9062.00
2.07300.08260.41551.7720.10
000.060.200.00.27.0.
            000.0           000.0
2
63.6504.9601.0303.9600.3314.3010.2062.50
2.04800.05350.23901.9740.10
000.060.200.00.27.0.
            000.0           000.0
1
65.4504.8501.0002.9300.2715.8034.3063.00
2.27400.10150.37111.9535.05
500.060.250.00.27.0.
            000.0           000.0
1
62.3404.6700.8002.9900.1615.3034.6064.00
2.42300.08500.27272.2540.10
000.060.250.00.27.0.
            000.0           000.0
1
66.1004.8700.9102.7700.5114.6034.1065.00
3.93700.21020.81053.1300.20
500.060.250.00.27.0.
            000.0           000.0
1
50.7105.2600.5915.9003.6728.5050.5056.00
1.18600.23400.40500.5960.50
500.060.250.50.00.2.
PYROLIDINE 10.5             000.0
1
59.5704.9200.8602.7701.0514.1040.3067.00
4.53650.00000.81304.2895.30
000.999.040.00.00.2.
ETHYLETHER306.0             000.0
1
62.2405.2100.8100.0000.0014.1036.9068.00
4.50100.18300.20304.3670.05
000.060.235.99.00.0.
            000.0           000.0
```

```
1
69.5106.4700.7601.3001.6112.6023.4069.00
1.08000.39500.55300.2060.85
500.060.250.50.00.1.
       ZNO  9.0            000.0
2
46.2604.8800.5723.6004.5331.9019.7069.50
1.07300.18600.49230.5055.85
500.060.250.50.00.1.
       ZNO  9.0            000.0
1
61.5906.0400.5808.6007.9213.5044.5070.00
1.43600.39701.03300.1995.95
800.030.275.50.00.0.
          000.0            000.0
1
63.4906.1000.5906.4208.1113.6023.4072.00
1.03800.28100.84600.0555.99
800.060.250.50.00.0.
          000.0            000.0
2
61.0906.0300.5709.7807.1216.2020.3072.50
1.06400.28700.65050.2270.95
800.060.250.50.00.0.
          000.0            000.0
1
65.5006.3000.5104.9805.0613.9024.3073.00
1.09400.32500.73950.1130.99
800.060.250.50.00.0.
          000.0            000.0
2
62.2506.0000.6109.1403.5217.3016.9073.50
1.00600.27400.47250.3150.95
800.060.250.50.00.0.
          000.0            000.0
1
65.2105.6800.9000.1300.1112.3019.5074.00
2.32650.18550.77801.5485.10
800.000.250.50.00.0.
          000.0            000.0
2
61.8505.1700.8705.7100.3816.0018.0574.50
2.24150.08800.27902.1285.10
800.000.250.50.00.0.
          000.0            000.0
1
70.5206.5300.7302.2703.6911.2017.8075.00
1.07500.34350.68800.1315.90
500.060.250.50.00.0.
          000.0            000.0
2
63.8306.0900.6606.0802.6115.9023.1075.50
1.46700.43800.56700.5595.80
500.060.250.50.00.0.
          000.0            000.0
1
70.8906.5200.7600.6501.1911.4020.2076.00
1.21850.39150.68350.1930.60
800.030.250.50.00.0.
          000.0            000.0
2
64.7206.0900.7506.9401.1917.1018.5076.50
1.52300.33900.47950.7630.80
800.030.250.50.00.0.
          000.0            000.0
1
71.9806.2600.8000.1000.2109.2019.2077.00
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          000.0            000.0
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          000.0            000.0

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800.060.250.00.27.1.
       ZN 10.0            000.0
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1.55800.09850.48951.1290.90
800.060.250.00.27.1.
       ZN 10.0            000.0
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0.98600.13750.51850.3660.20
999.060.225.00.27.1.
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2
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999.060.225.00.27.1.
       ZN 10.1            000.0
0
```

Appendix D

Extract Analyses

	WEIGHT %						
Run	C	H	N	S	Ash	Zn	Cl
Benzene Extracts							
3	82.30	10.80	0.13	1.00	-	-	-
4	89.22	6.31	0.12	0.20	-	0.60	0.61
5	81.83	10.61	0.19	0.31	-	-	-
7	81.71	8.45	0.18	0.61	1.30	0.09	0.51
9	83.35	8.08	0.05	6.34	0.30	0.07	-
11	83.62	9.53	0.03	-	-	-	-
13	86.05	7.95	0.47	-	-	-	-
48	83.76	8.80	0.44	-	-	-	-
55	82.14	8.43	0.42	-	-	-	-
Pyridine Extracts							
3	73.70	6.85	1.16	0.44	-	-	-
4	51.90	3.92	7.29	0.03	3.00	16.40	16.20
5	73.70	6.92	1.26	0.61	-	2.50	-
7	74.70	5.52	1.37	0.46	3.00	-	-
9	61.00	5.05	2.49	7.75	8.80	6.73	-
11	76.30	5.73	2.25	-	-	-	-
13	74.30	4.76	3.18	-	-	-	-
15	60.60	4.93	4.08	-	13.50	-	-
17	74.00	6.18	2.31	-	4.90	3.69	-
19	65.53	5.32	3.71	-	-	10.50	-
20	-	-	4.67	-	-	-	-
21	-	-	4.22	-	-	-	-
22	-	-	2.12	-	-	-	-
23	-	-	1.66	-	-	-	-
24	-	-	5.78	-	-	-	-
26	-	-	4.03	-	6.10	8.58	7.45
27	-	-	2.69	-	-	-	-
30	51.19	4.14	7.19	-	7.00	14.90	16.24
31	-	-	1.73	-	-	-	-
32	-	-	4.28	-	10.80	-	-
33	-	-	1.40	-	-	-	-
34	-	-	1.97	-	-	-	-
35	76.60	5.41	2.58	-	-	-	-
36	79.83	5.63	1.54	-	-	-	-
37	67.53	5.46	2.98	-	8.41	-	-
40	76.18	6.03	1.90	-	-	-	-
43	60.13	4.81	5.50	-	-	-	-

Appendix D

Extract Analyses

	WEIGHT %						
Run	C	H	N	S	Ash	Zn	Cl
47	73.11	5.76	3.00	-	-	-	-
48	56.96	4.58	6.02	-	-	-	-
54b	57.49	4.84	3.91	-	9.90	-	9.39
55x	71.85	5.54	1.98	-	5.50	-	1.33
58	58.47	4.87	3.42	-	7.50	8.80	10.20

	WEIGHT %						
Run	C	H	N	S	Ash	Zn	Cl
Residues							
Blank	62.86	4.59	2.69	-	-	-	-
3	62.92	3.87	2.06	0.28	21.10	-	-
4	61.61	3.53	1.41	0.77	21.70	1.61	0.12
5	60.15	3.97	1.82	0.84	12.70	-	-
7	58.23	3.59	1.21	1.32	30.70	-	-
9	60.46	3.63	1.33	8.91	74.70	8.77	-
11	68.56	4.32	1.85	-	14.30	-	-
13	61.20	3.64	1.22	-	26.20	-	-
15	51.30	4.37	1.83	-	30.40	-	-
16	63.30	3.95	2.11	-	25.00	-	-
17	58.90	4.51	2.14	-	20.70	-	-
19	51.22	4.11	1.74	-	30.60	-	0.13
20	-	-	1.05	-	-	-	-
21	-	-	1.94	-	-	-	-
22	-	-	2.50	-	-	-	-
23	-	-	2.29	-	-	-	-
24	-	-	0.84	-	-	-	-
26	-	-	1.67	-	21.90	-	-
27	-	-	1.97	-	-	-	-
30	26.38	2.58	0.83	-	60.10	-	-
30b	-	-	-	-	42.10	-	-
31	-	-	2.64	-	14.90	-	0.09
32	-	-	1.85	-	-	-	-
33	-	-	1.64	-	-	-	-
34	-	-	1.75	-	-	-	-
35	-	-	1.04	-	-	-	-
36	-	-	1.39	-	-	-	-
37	42.41	3.79	1.50	-	39.20	-	0.24
40	53.69	4.16	1.72	-	27.50	3.61	0.09
43	38.56	2.94	1.24	-	-	-	-
47	47.79	3.70	1.83	-	-	-	-
48	37.65	3.27	1.44	-	-	-	-
55	26.26	2.62	0.68	-	60.50	-	-

Extract-Run	C	H	N	Ash	Zn	Cl
Other Extract Analyses						
Cyclohexane Wash - 10	63.80	4.60	0.97	15.60	4.70	-
Cyclohexane-10	51.90	5.25	0.10	-	-	-
Benzene-10	84.20	7.27	0.39	-	-	-
Pyridine-10	64.60	4.69	4.53	-	-	-
Residue-10	67.60	4.31	1.36	19.70	-	-
Cyclohexane-12	91.97	6.30	0.18	-	-	-
Benzene-12	88.95	6.14	0.61	-	-	-
Pyridine-12	63.61	4.58	5.87	-	-	-
Residue-12	65.80	3.93	2.11	17.50	-	-
Cyclohexane-14	86.43	9.49	0.28	-	-	-
Benzene-14	83.97	9.06	0.75	-	-	-
Pyridine-14	75.30	6.22	2.05	-	-	-
Residue-14	61.71	3.94	2.51	17.10	-	-
Benzene Wash-29	87.90	9.45	0.12	0.30	0.16	0.11
Pyridine-29	73.90	6.06	2.77	-	-	-
Residue-29	52.05	4.34	1.87	-	-	-
Benzene Wash-39	86.69	9.50	0.16	-	-	-
Pyridine-39	57.95	4.76	2.45	-	-	-
Residue-39	47.72	4.03	1.47	-	-	-
Benzene Wash-42	88.27	7.46	0.18	-	-	-
Pyridine-42	62.46	4.47	5.65	4.90	-	12.10
Residue-42	27.31	2.38	1.02	-	-	-
Benzene Wash-53	81.97	8.95	0.28	1.30	-	1.21

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