AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 2

A NOVEL CONCEPT FOR HIGH CONVERSION
OF COAL TO LIQUIDS

FINAL REPORT

Contract Period: 1 September, 1988 - 31 August, 1992

Wendell H. Wiser, Principal Investigator
Joseph Shabtai, Co-Principal Investigator

Department of Chemical and Fuels Engineering
University of Utah
Salt Lake City, Utah 84112

Prepared for the United States Department of Energy
under Contract No. DE-AC22-88PC88817

April, 1994

TABLE OF CONTENTS

	Page
ABSTRACT	iv
U.S PATENT	vi
 Chapter	
1. INTRODUCTION	1
2. BACKGROUND FOR THE RESEARCH	4
2.1 General	4
2.2 New Process Concept	13
2.3 Objectives	20
3. EXPERIMENTAL	22
3.1 The Micro-reactor System	22
3.1.1 General	22
3.1.2 Micro-reactor Description	23
3.1.3 Temperature Controller	25
3.1.4 Coal Sample Preparation	28
3.1.5 Catalysts	28
3.1.6 Procedure	32
3.1.7 Analysis of Coal Liquid Products	36
Elemental Analysis	36
Simulated Distillation	36
FTIR Analysis	37
Mass Spectrometric Analysis	37
NMR Analysis	38
3.2 The Continuous-flow System	38
3.2.1 General	38
3.2.2 Continuous-flow Reactor Description	38

4.	RESULTS AND DISCUSSION	42
4.1	The Micro-reactor System	42
4.1.1	Research Scheme	42
4.1.2	Experimental Results	43
	Effect of Temperature	43
	Effect of Pressure	44
	Effect of Time of Reaction	44
	Effect of Two Pass	48
	Effect of Catalyst Concentration	53
	Effect of Catalyst Type	59
4.1.3	Structural Analysis of Liquid Products	69
	Elemental Analysis of Liquid Product	69
	Simulated Distillation (SIMD) Analysis	69
	Molecular Weights in Liquid Products	71
	GC/MS Analysis	75
	NMR Analysis	75
	Carbon-13 NMR Analysis	87
	Proton NMR Analysis	89
	FTIR Analysis	93
4.1.4	Discussion	96
	Temperature and Hydrogen Pressure	96
	Effect of Contact Time	100
	Two-Pass Process	101
	Catalytic Activity	103
	Minimum Ferric chloride Concentration	111
4.1.5	Possible Components in Liquid Products	113
4.1.6	Reaction Scheme	120

4.2	The Continuous-flow Reactor System	122
4.2.1	Research Scheme	123
4.2.2	Experimental Results	124
4.2.3	Discussion	125
4.2.4	Liquid Product Analysis	129
5.	CONCLUSIONS	131
	LIST OF ABBREVIATIONS	134
	REFERENCES	135

ABSTRACT

A batch microreactor was designed and fabricated as a means of investigating maximum yields of liquids obtainable in very short reaction times of the order of a few seconds, and the maximum ratios of liquids/hydrocarbon (HC) gases obtainable under those conditions. A Wyodak sub-bituminous coal, crushed and sieved to -200 mesh particle size, was used in the experiments, with a temperature of 500 °C and a pressure of 1500 psi.

The fine coal particles were fed dry to the reactor and heated to reaction temperature in times of one to two seconds. At a time of 3 seconds at reaction temperature, in a single pass a liquid yield of 60% by weight of the coal was obtained, accompanied by a ratio of liquids/(HC) gases of 30/1. When the unreacted solids were recycled to the reactor, and the results combined with those of the first pass, a liquid yield of 82% by weight of the coal was achieved, accompanied by a ratio of liquids/HC gases of 30/1. This ratio represents only about 3 wt percent HC gases, much lower than is produced in current advanced technologies, and represents a large saving in hydrogen consumption.

A simulated distillation technique was applied to the liquids. The liquid product contained 86% by weight (of the liquids) total distillables (boiling point below 538 °C), including 70% by weight of low-boiling fractions in the gasoline, kerosene and gas oil range (boiling point up to

325 °C). The liquid product exhibited a H/C ratio of 1.5, which is considerably higher than observed in current advanced technologies for the primary liquids.

Several catalysts were investigated. Iron catalysts, specifically ferric chloride hexahydrate and ferric sulfate pentahydrate, each produced these high conversions and high ratios of liquids/HC gases.

A continuous-flow reactor system was also constructed and operated on the same coal. It was not possible to achieve turbulent flow in the reactor, due to hydrogen feed limitations. It also was not possible to feed -200 mesh coal, due to limitations in the feed system. These limitations combined to produce a much lower particle heat-up rate than desired. Conversions of the coal to liquids were about 50% by weight of the coal in a single pass, with ratios of liquids/HC gases of about 8/1, and about 78% by weight of the coal as liquids in a combined two-pass experiment, with combined ratios of liquids/HC gases of about 11/1. These ratios of liquids/HC gases were lower than in the micro-reactor, because times in the hot zone were longer, made necessary by the slower heat-up rate and larger particle diameters. However, it is believed that by feeding coal as -200 mesh particles, and full turbulent flow in the reactor, conversions and ratios of liquids/HC gases will approach those observed in the micro-reactor.

U.S. PATENT

A U.S. Patent has been granted covering the process described in the attached report.

Invention	METHOD FOR COAL LIQUEFACTION
Inventors	Wendell H. Wiser, et al.
Patent No.	5,308,477
Issue Date	May 3, 1993

CHAPTER 1

INTRODUCTION

U.S. Federal Government research and development efforts related to fossil energy have been mainly concerned with development of substitutes for petroleum and natural gas, supplemented more recently with efforts to use coal directly in a cleaner manner under a "Clean Coal Technology" funding program. At the outset, this direction of the nation's energy program resulted from the general belief that the world was running out of oil and substitutes would soon be required. However, it became apparent a few years ago that the oil supply of the world as a whole will last longer than predicted, and the urgency in producing fuels for reason of impending world shortages no longer appeared justified. The program of federal support in synthetic fuels was dramatically reduced.

Notwithstanding the reduced urgency for synthetic fuels as substitutes for petroleum and natural gas at the world level, there remains a measure of urgency at the U.S. level. At the present time, imports of petroleum in the United states represent about 50% of U.S. demand, and this fraction of demand is steadily increasing. In magnitude, the value of petroleum imports is about one-half of the magnitude of the trade imbalance of the country. This trade imbalance promises to become an economic problem of major proportions, if not addressed. Further, at present there exists a large amount of uncertainty relative to the direction to be

pursued by Russia as a world power, and the long-term intentions of its leaders. In fact, at present it is not at all clear who its leaders will be in a very few years. There remains reason for concern about the security of, and accessibility to, adequate petroleum resources as may be required to safeguard the national security of the United States and the free world, and the role which large and growing imports of petroleum may play relative to that security, especially imports from the unstable nations of the Middle East, where about two-thirds of the world's known and recoverable reserves of petroleum are located.

There exists a need for three main lines of research with respect to obtaining synthetic fuels from coal: (1) continue the fundamental research on the structure of coal, on coal liquefaction, and on coal gasification; (2) continue the search for innovative processes which can decrease the complexity of the technology and reduce the cost of producing synthetic fuels from coal; and (3) institute research leading to the development of new products from coal. The work pursued in this project has been concerned with Item 2.

Research activities pursued in the United States since World War II have been centered almost exclusively upon attempts to refine the technologies developed by German scientists and engineers prior to and during World War II. While these efforts have improved the reliability of the technologies, and in some cases reduced the pressure of the

process, they have accomplished relatively little toward reducing the cost of producing a synthetic crude from coal. These efforts, pursued over a period of many years, have always led to an estimated cost of a symthetic crude from coal ranging from 50% to 100%, or more, greater than natural petroleum with which it must compete in the market place, the comparisons being made with petroleum prices current at the time when such estimates have been made. It seems apparent that a novel, and very different, approach must be devised, if the cost of a synthetic crude from coal is to be brought more into line with petroleum prices. The work pursued in this project represents such a novel approach, reflecting a promise of a significant reduction in cost of production of a synthetic crude, perhaps even approaching the price of petroleum.

CHAPTER 2

BACKGROUND FOR THE RESEARCH

2.1. General.

For more than a decade, members of the Department of Fuels Engineering at the University of Utah have conducted research, and critically evaluated the literature, related to the chemical structure of coal. A concept was formulated of probable representative structures existing in coal, and the manner in which these units are joined in coal. This concept was reduced to a drawing by Professor W. H. Wiser, and is presented in Figure 2.1.

There is now general agreement among coal researchers that coals of greatest interest in liquefaction (in particular bituminous and sub-bituminous) consist of monocyclic and condensed aromatic and hydroaromatic rings, forming units (sometimes called clusters) varying in size from a single ring to perhaps four or five rings per unit. In such coals, from 15% to as much as 35% of the carbon atoms are hydroaromatic carbons, meaning carbon atoms in a naphthenic ring joined in a condensed configuration to one or more aromatic rings. These units are linked to each other by connecting bridges which are typically short aliphatic chains or etheric linkages. These types of units, and the connecting bridges, are represented in Figure 2.1.

When coal is heated to a temperature above about 375 °C, the connecting bridges begin to rupture, forming free radicals. It is now well established experimentally that

Figure 2.1. Schematic Representation of Structural Groups and Connecting Bridges in Bituminous Coal (Wiser Model)

this process proceeds via a free-radical mechanism. If a unit is completely severed from the coal mass by this means, and if the resulting free radicals can be capped with hydrogen before they have an opportunity to join together in a condensation reaction, the stable molecules formed may be of a size and structure characteristic of the coal units. Inasmuch as the free radicals are extremely reactive, the capping by hydrogen must be instantaneous, as it were. To achieve this, it is necessary to have an easily-available source of hydrogen present at the site of rupture of the bonds. Such a source will either be a hydroaromatic structure (from the coal itself or from a hydrogen-donor solvent, if present), or hydrogen adsorbed on a catalyst. If the free radicals are not capped in this manner, they will combine in condensation reactions to produce large structures, which will be solid at room temperature.

Traditionally, researchers conducting kinetic studies in coal liquefaction have concluded that the overall kinetics are first order, and have postulated that the slow and rate-determining step in the reaction sequence is thermal rupture of the bonds in the connecting bridges. However, very extensive kinetic studies in our laboratories have revealed that the overall kinetics are second order, rather than first order, over a range of 80 to 90% of the total reaction. Thermal bond rupture as the slow step could not represent a logical explanation for second order kinetics.

Extensive studies have led to the conclusion that the thermal rupture of the bonds in the connecting bridges occurs rapidly, when compared with capping of the radicals to form stable, volatile molecules. (It should be remembered that in kinetic studies on coal, the rate of reaction is measured by evolution of volatile products. One only "sees" the formation of molecules small enough to escape as vapor from the solid mass, and radical-radical reactions, leading to condensation, form entities too large to escape, and hence not observed in the kinetics.)

It has been observed that in the typical coal liquefaction reactor system, involving times in the hot zone of the order of 15 to 20 minutes, from 15% to as much as 20% of the weight of the coal is converted to HC gases, the principal component of which is methane. It is observed also that most of those HC gases appear to come from cracking of hydroaromatic units in the coal. A large amount of hydrogen is consumed as a participant in those reactions. In fact, hydrogen balance calculations reveal that most of the hydrogen consumed in the primary liquefaction process is consumed in the formation of these HC gases. It therefore became of primary interest to attempt to achieve satisfactory conversions of the coal to liquids, while greatly reducing the residence time of these liquids in the hot zone, thereby reducing the extent of cracking of the hydroaromatic units and reducing hydrogen consumption in the process.

It has been reported by Garrett Research and Engineering (now part of Occidental Petroleum) that small particles of the order of 25 microns diameter can be heated to a centerline temperature of 500 °C in times measured in milliseconds, using a product gas in turbulent flow as the heating medium. In the work of the present project, it was believed coal particle centerline temperatures of the order needed for high conversions to liquids should be achievable in times of one or two seconds.

As a consequence of our kinetic observations, and conclusions therefrom, examination of Figure 2.1 led us to wonder whether it may be possible, under appropriate conditions, to rupture the bonds in the connecting bridges throughout the coal structure, cap the free radicals thus formed, and remove the resulting molecules rapidly, in order to avoid cracking of the liquid molecules. particularly the saturated portions of the hydroaromatic structures. These thoughts led to a realization that a very short time in the heated zone is indicated, perhaps of the order of a few seconds. If this were to be achieved, it would be necessary to heat the coal essentially to the center of the particles in times as short as one or two seconds.

A further conclusion along this line of reasoning was the need for the particles to be very small (of the order of about -100 mesh, or smaller, Standard Tyler Screen Series), in order that the pathway for heating may be short. It is recognized that thermal conductivity in a coal particle is

not very rapid, due to the high porosity of the coal. The rate of heat transfer into such a particle may be greatly increased by using a hot gas (e.g. hydrogen) in turbulent flow to heat the particle. It has been observed that, at atmospheric pressure, the rate of diffusion of a gas in a gas phase is greater than in a liquid phase by a factor of about 2000. For rapid heat transfer into the coal particle by hot hydrogen gas, it then becomes necessary that a liquid phase should not be present in the coal pores during heat-up. This observation then dictates feeding the coal dry.

All of the above considerations, taken together, led to the following scheme for a reactor for high conversion of coal to liquids in very short times of a few seconds:

- (1) Crush the coal to fine particle sizes such as would pass through a fine screen, i.e. -100 mesh particle size, or smaller.
- (2) Place the coal in the reactor in a dry state.
- (3) If the experiment is to be conducted in a continuous-flow system, heat the coal particles with hot hydrogen gas in turbulent flow. If in a batch reactor, provide for rapid particle heat-up in times of the order of one or two seconds.
- (4) Provide a catalyst exhibiting hydrogenation/-hydrogenolysis activity, such as to be at or very near the site where connecting bridges are to be ruptured. These are the concepts incorporated into the reactors for the experimental work performed in this project.

One fundamental economic problem in direct coal liquefaction is the need to add hydrogen to coal.

Hydrogenation, hydrogenolysis and heteroatom removal are particularly important hydrogen-consuming reactions. Hydrogen stabilizes the reactive and unstable free radicals formed by thermal rupture of chemical bonds of the coal macromolecules. The hydrogen content of coal is about 5 wt% whereas for gasoline it is about 14%. Thus, it is necessary to add about 9 wt% hydrogen to produce gasoline and distillates. Hydrogenation/hydrogenolysis represent a serious economic burden from three viewpoints: (1) The cost of hydrogen is relatively high. The consumption of 5000 to 10,000 ft³ of hydrogen used to produce a barrel of oil from coal corresponds to a cost of hydrogen of \$1.25 to \$2.50, based upon a very modest hydrogen cost of 25 cents/1000 ft³. (2) The investment for a hydrogen production and compression facility is large, amounting in some cases to one third of the cost of the entire plant. (3) Hydrogenation occurs with difficulty unless catalyzed, and the coal environment is a hostile environment for most catalysts.

Weisz (1982) estimated the investment cost for various synfuel processes against the hydrogen deficiency of the resource. As seen in Figure 2-2, the investment cost escalates with increasing hydrogen requirement. For coal, the hydrogen content is the lowest of the available fossil fuel resources. Therefore, coal liquefaction processes must be developed to lower the amount of hydrogen needed.

One method of assisting in reducing costs is development of suitable catalysts to lower capital

Figure 2.2 Investment cost escalates with resource hydrogen deficiency.
Adapted from Weisz (1982)

investment and operating costs by improving the selectivity to the desired liquid products, reducing production of hydrocarbon gases and operating severity, and increasing throughput rates.

Another method is to reduce the reaction time, to aid in reducing hydrogen consumption by reducing formation of hydrocarbon gases, as identified above. For current state-of-the-art direct liquefaction processes, more than 50 percent of the total chemical hydrogen consumption goes into the formation of light hydrocarbons (C_1 - C_3 gases), but only 30% is consumed in the production of useful liquid products (Moroni and Fischer, 1980). Methane is undesirable because of the amount of hydrogen consumed to make methane. Gorbaty and Maa (1986) reported that hydrogen consumption increases sixfold at the higher temperatures and longer reaction times without adding to the liquid yield. Most of the additional hydrogen is consumed in producing methane. In hydropyrolysis of Wilmington distillate, Tsai (1987) found that hydrogen consumption is a linear function of gas production.

A large number of kinetic models have been put forward to characterize the rate of conversion. It is evident that there are a number of basic rates involved including physical disintegration of the particles, thermally induced bond rupture, repolymerization, and free radical stabilization from the coal-hydrogen inventory and the donor hydrogen, which may or may not be catalytically activated.

A number of studies have shown that the initial dissolution of some US and Australian coals occurs rapidly in direct liquefaction processes (Whitehust and Mitchell, 1977; Hill, et al., 1966; Wiser, 1968; Shabtai, 1974; Foster, 1983; Foster, 1984a; b; Abichandani, 1984). Some investigators (Gorin, 1981; Shah, 1981; Whitehurst, et al., 1980) suggested that limiting retrogressive reactions probably plays an important role, both during the early stages of liquefaction and in the absence of a H-donor solvent. Therefore, it is apparent that maximizing liquid hydrocarbon yield while minimizing hydrogen consumption could be the most important economic consideration in coal liquefaction.

A new concept of hydrogenation has been developed whereby a high yield of liquid is obtained under relatively low hydrogen pressure, using an inexpensive catalyst which may be disposable, in a few seconds reaction time.

2.2. New Process Concept.

In conventional approaches, the process for direct conversion of coal to liquids begins by slurring the coal in a liquid. Slurring the coal in a liquid is used to permit pumping the coal into the pressurized region. The presence of a liquid phase surrounding the coal particles after introduction into the reactor, as well as inside of the pores and channels of the coal, inhibits heat transfer into the particle by any means one may choose to use to heat

the coal particle to reaction temperature (generally 350-520°C), resulting in residence times in the hot zone of many minutes, characteristically between 15 minutes and 1 hour. One loses control over most of the chemistry of the process. Specifically, when the coal and its primary conversion products are exposed to temperatures above 350°C for such long periods time, many thermal degradation reactions occur, most of them undesirable. These reactions lead to high yields of hydrocarbon gases, hence high hydrogen consumption. They also lead to asphaltene production, making the downstream processing of the liquids more difficult.

Molecular diffusion rates in the gas phase are experimentally observed to be faster than in a liquid phase by some three orders of magnitude. Since coal itself is a rather poor conductor of heat, times required to completely heat the coal particles are dramatically shortened by avoiding a liquid phase within and surrounding the coal particles before liquefaction.

Indeed, the presence of a liquefaction solvent is not necessary to attaining high yields of liquids (Derbyshire and others, 1986; Weller, 1982; Zielke and others, 1966a, 1966b). Some years ago, Weller and other workers (Weller et al., 1950; Hawk and Hiteshue, 1965; Weller, 1982) studied the catalyzed liquefaction of coals in the absence of a vehicle oil. High liquefaction yields and good selectivities to distillate products were obtained in the

absence of a solvent. Weller and Pelipetz (1951a, b) also observed that iron which is inherently present in the mineral matter of coal exerts a positive catalytic effect.

Conversion of coal to low molecular weight distillate products requires extensive modification of the physical and chemical structure of the starting material. The molecular structures will rearrange during the heating of coal. The relative degrees of fragmentation and repolymerization are strongly influenced by time and temperature. At higher temperatures fragmentation is enhanced relative to repolymerization. Consequently, flash heating to high temperature results in extensive fragmentation of the coal structure to light species before stabilization or crosslinking of the fragments to larger structures. BTX and light saturated hydrocarbons are favored at the expense of heavier species.

High volatile bituminous and subbituminous coals are most responsive to direct conversion to liquids, while also producing the highest yields of liquids as a weight percent of the coal. Most of the clusters are in the range of two to three rings per cluster but with a substantial amount of single-ring aromatic units. The condensed structural units are joined to each other principally through short aliphatic bridges of one to three carbon atoms each, and by ether-type linkages (Heredy, 1965; Lazarov, 1968). Acid catalysts are believed to primarily cause hydrogenolytic cleavage.

Coal liquefaction in the presence of hydrogen will rupture the bonds in connecting bridges between clusters or units via cleavage reactions (hydrogenolysis) and ring hydrogenation reactions. An active hydrogenolysis catalyst is essential if this is to be accomplished as rapidly as the free radicals are formed, before they can recombine or polymerize.

When the coal liquefaction temperature is above about 375°C, thermal rupture of aliphatic carbon-carbon and other labile bonds (C-O, C-N and C-S) begins to be extensive. The cleavage reactions become increasingly rapid as temperature increases, and at temperatures in the range 450-500°C the rupture of these bonds becomes essentially complete (Gibbins and Kandiyoti, 1991). This rupture process is accompanied by a large increase in free radical content.

The bonds primarily affected are the single carbon-carbon bonds and other bonds of similar energy. If the free radicals formed by these bond scissions can be stabilized or capped by the addition of hydrogen, without permitting condensation reactions involving the free radicals, the resulting molecules will be mostly (about 85% of the carbon in the coal) liquid-size molecules, or at least soluble in the liquids thus formed. Obviously, coals with a higher proportion of aliphatic carbon should convert more quickly.

Inasmuch as residence time in the heated environment is a key parameter influencing this chemistry, it could be expected that the extent of cracking of the primary liquid

products to form unwanted gases, thereby avoiding the high consumption of hydrogen associated with the production of these gases, could be greatly reduced by appropriately controlling the time.

The environment that can supply hydrogen to cap the free radicals also has the potential for partially hydrogenating the aromatic structures. At the temperatures in the liquefaction system, the saturated portions of these partially hydrogenated units also tend to crack, by a purely thermal route, thus yielding hydrocarbon gases which are usually unwanted. When this cracking occurs, an additional mole of hydrogen is consumed for each mole of bonds ruptured in these unwanted cracking reactions. To be able to reach quickly the intercluster linkages in the polymeric coal network, the prospective catalyst should be deeply intercalated in the small coal particle prior to heat-up, or, alternatively, it should be in the gas phase and have critical molecular dimensions allowing for fast diffusion in the coal particles before the coal particles reach the softening point.

Experimental work performed in the Fuels Engineering laboratories indicates that the thermal bond-scission reactions involving the connecting bridges between clusters in the coal occur extremely rapidly. Contrary to the views expressed in the literature by some investigators, these bond scission reactions do not represent the slow or rate-determining step in the sequence. If the highly reactive

fragments thus produced are to be capped by hydrogen, thus preventing undesirable condensation or recombination reactions, these units must either abstract hydrogen from the hydroaromatic structures in the coal, or in the donor solvent if one has been added to the system, or react with molecular hydrogen added to the system, this latter addition requiring a catalyst if it is to be at all extensive. Although some hydrogen addition directly from molecular hydrogen to coal units may occur noncatalytically, it is difficult and slow, and requires times of the order of several minutes to be significant. These hydrogen-abstraction reactions, whether from hydroaromatic structures in the coal or in the solvent, or from hydrogen chemisorbed on the catalyst, are believed by Wiser to represent the slow step in the liquefaction sequence, this conclusion supported by extensive experimental data from his laboratories (Wiser, 1988). According to the above discussion, increasing the yield of liquids in shorter times could result from assisting the addition of the essential hydrogen before recombination and/or condensation of the free radicals can occur.

In kinetic studies in coal liquefaction one only sees the formation of molecules formed through stabilization or capping. The product molecules of recombination and/or condensation reactions are generally too large to escape as volatiles.

A few results from the literature (Shroeder, 1961; Peterson, 1982), together with experimental results obtained in the laboratories at the University of Utah and supported by theoretical considerations, led to the conclusion that liquids in excess of 70% by weight of the coal are possible, and perhaps practical, while at the same time limiting the yields of hydrocarbon gases to only a few weight percent of the coal.

A key parameter must be the short residence time in the heated zone. The primary liquid products are exposed to elevated temperatures for a few seconds. This leads to a reduction of the gases produced and to an increase in the efficiency of hydrogen utilization.

To achieve the necessary reaction rates, leading to conversions in excess of 70% of the carbon in the coal to liquids in a few seconds (while being limited to temperatures not to exceed about 500°C), a catalyst will be required for speeding up the hydrogenolysis-hydrogenation of the coal. To facilitate this very rapid hydrogenolysis-hydrogenation process, the catalyst should either be effectively dispersed in the coal particle prior to introduction into the reactor, or introduced in the gas phase. FeCl_3 was found to be a very effective and selective catalyst at 250-290°C for hydrogenolytic cleavage of methylene and higher alkylene linkages between two aromatic rings, but a rather ineffective catalyst at these low temperatures for cleavage of diaryl etheric groups

(Skulthai, 1987). Under the high-temperature condition ($\sim 500^{\circ}\text{C}$), therefore, some highly effective hydrogenolysis catalysts (e.g., FeCl_3) are expected to show high activity for hydrogenolysis of both C-C and etheric intercluster linkages.

Therefore, as noted above, a principal objective in this work is to avoid large-scale use of hydrogen, to be achieved by minimizing the production of hydrocarbon gases in the conversion process. Coal crushed to -200 mesh (74 microns) is heated to a temperature of 500°C in about 2 seconds. Catalyst with chemisorbed hydrogen will be present within a few angstroms of the rupturing bond in the connecting bridge. The primary liquids will be removed from the heated zone before extensive cracking of these liquids can occur. Yields of liquids will be greater than 70% of the carbon in the coal, while yields of hydrocarbon gases will not exceed a few percent (i.e. 3-5%), and the hydrogen consumption will be much lower than in existing coal liquefaction processes.

2.3. Objectives.

The objectives of this research work are:

1. To design and construct a micro-reactor and a special temperature controller which provides for rapid heat-up to the required temperature, while avoiding temperature overshoot of more than a few degrees.
2. To construct a continuous-flow reactor, to compare results in a flow system with those in a batch system.

3. To investigate a variety of catalysts, particularly hydrogenation catalysts and acid catalysts, in a few seconds reaction time.
4. To demonstrate conversion of coal to high liquid yields greater than 50% by weight of the coal, with high ratios of liquids/HC gases greater than 10/1.
5. To determine the liquid yields and the ratio of liquid/HC gas under varying reaction conditions, and to evaluate reaction parameters in relation to maximizing ratios of liquids/HC gases.
6. To examine the chemistry that may occur when the coal particle is heated to reaction temperature in times of a few seconds, and the liquefaction process to form primary liquids is completed in times measured in seconds rather than minutes.
7. To investigate in detail the chemical composition of short time liquefied products from Wyodak coal.

CHAPTER 3

EXPERIMENTAL

3.1. The Micro-reactor System

3.1.1. General. From a review of proposed designs (Wiser and Shabtai, 1988), a small reactor system was constructed in which to define the maximum possible ratio of liquids to hydrocarbon gases, operating at short reaction time of a few seconds, temperatures of 450-550°C, hydrogen pressures as high as 2000 psig, at the same time converting more than 70% of the carbon in the coal to liquids.

Experimentally, such an environment is difficult to simulate in a small scale. Fundamental coal liquefaction studies have generally been performed using conventional batch autoclaves or continuous reactors. Also, conventional methods for hydrogenation of coal to liquids involve residence times of 20 minutes or more. It seemed reasonable that the residence time required for adequate conversions could be shortened by providing an excess of hydrogen, and by intimately mixing the coal with a catalyst. Occidental Petroleum Company has reported coal particle heatup rates of 5000 centigrade degrees per second, calculated from their experimental data for coal particles of 200 microns diameter, achieving a centerline particle temperature of 500°C in 0.1 second, the particles being heated by product recycle gases in turbulent flow (Sass, 1972). Several investigators have employed the captive sample techniques, where a fixed quantity of coal is heated in the presence of

hydrogen (Feldkirchner and Linden, 1963; Hiteshue, et al. 1962; Moseley and Paterson, 1965; and Feldkirchner and Johnson, 1968). Although this approach is experimentally simple, it does restrict achievable heating rates to perhaps 100°C/second at the most.

The chosen technique involves electrical heating of a thin strip of stainless steel screen upon which rested a small amount of coal. Cech (1950) has reviewed most of the early work with a "hot microscope stage" or electrical strip furnace. Finch and Taylor (1969) showed that a relatively simple DC timing circuit with batteries was capable of attaining heating rates of 10^3 to 10^4 °C/second. Variations of this approach have been used for studies of coal pyrolysis in vacuum and under nitrogen (Loison and Chauvin, 1964; Rau and Robertson, 1966; Juntgen and Van Heek, 1968; Mentser, et al., 1970).

3.1.2. Micro-reactor Description. A micro-reactor has been designed and constructed, patterned to a degree after a reactor operated by Anthony et al. (1974). The reactor was designed in order to rapidly heat a coal sample to reaction temperature, where the sample is held for a variable holding time. A sketch of the micro-reactor is shown in Figure 3-1.

The reactor has an internal volume of 106 ml, and is constructed of 304 stainless steel. It is designed to accommodate pressures up to 3000 psig at temperatures up to 600°C. The coal sample is supported on a 400 mesh (Standard

Figure 3-1 Micro-reactor

Tyler Screen Series) stainless steel screen (3.5×2.7 cm), attached to two electrodes to provide for electrical heating. Stainless steel screen has a high electrical resistance and a high tolerance against temperature and corrosion. A 0.002 in. diameter Chromel-Alumel fine wire K type thermocouple (Omega Eng. Inc.) is mounted immediately above the wire screen, not touching the screen but such that it will be embedded in the coal sample. A second metal-sheathed K-type thermo-couple is placed into the microreactor to read temperatures in the gas space between the coal sample and the wall of the reactor during the high-temperature reaction. Cooling coils are located in the walls of the reactor, but they have not been required for experiments at the short times of these experiments. Inasmuch as heat application occurs only to the screen supporting the coal sample, the walls of the reactor remain at a temperature far below the sample temperature in these short-time experiments, generally below 100 C. Details of the stage are illustrated in Figure 3-2.

3.1.3. Temperature Controller. This experiment requires rapid heat-up of the coal, in order to limit time in the reaction zone to a few seconds. To avoid temperature over-shoot of more than a few degrees, a special temperature controller was constructed in our laboratory (Figure 3-3). A typical time-temperature profile, at a pressure 1500 psig and reaction temperature 500°C, for a heating rate of about

Figure 3-2 Micro-reactor section view

Figure 3-3 Electrical circuit of temperature controller

250°C/second, is shown in Figure 3-4. The temperature profile of a typical experiment showed the temperature arrived at 500°C in about 2 seconds, then remained at 500°C about 20 seconds and the temperature varied only a few centigrade degrees.

3.1.4. Coal Sample Preparation. Wyodak sub-bituminous coal was used for all experiments in this investigation. In a typical experiment, coal was ground to pass through a 200 mesh Tyler series screen (coal particles -74 microns) using a ball mill grinder. Fine particles of coal were more reactive than large particles. The ground coal was dried under vacuum at a temperature of 80°C for about 4 hours, kept at ambient temperature overnight and stored in a brown glass bottle sealed under nitrogen. Table 3-1 shows the proximate analysis of the coal. Table 3-2 shows the ultimate analysis. The soluble acid catalyst was impregnated into the pores of the dry coal, and the solvent evaporated. The impregnated coal was re-sieved and stored under nitrogen. Then the sample was stored in a refrigerator for later use.

3.1.5. Catalysts. Catalysts added to the coal for the short-contact-time coal liquefaction experiments, described below, were:

(1) ZnCl_2 was used as a catalyst at 6.25% based on the moisture and ash free (maf) coal. The ZnCl_2 was dissolved

Figure 3-4 Typical time-temperature profile

Table 3-1
Proximate Analysis of Wyodak Subbituminous Coal

Component	Percent % by wt
Moisture	29.34
Volatile (Dry Basis)	55.79
Ash (Dry Basis)	10.22
Fixed Carbon (Dry Basis)	33.99

Table 3-2
Ultimate Analysis of Wyodak Subbituminous Coal

Element	Dry Basis % by wt	DAF % by wt
Carbon	65.5	72.96
Hydrogen	5.11	5.69
Nitrogen	0.92	1.02
Sulfur	0.87	0.97
Ash	10.22	—
Oxygen	17.38	19.36
H/C ratio	0.94	0.94

in sufficient water to wet the surface of the coal. The coal was then added to the solution, which was stirred at room temperature for about 30 minutes before the excess water was removed by vacuum drying. The ZnCl_2 -water-coal mixture was then dried in a vacuum at 80°C about 4 hours, then vacuum at room temperature about 8 hours.

(2) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (F.W. 270.3, purity 98%, Aldrich Chemical Company, Inc.) was used as a catalyst at concentration of 3%, 5%, 10% based on the Fe Cl_3 . The $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was impregnated from acetone solution, because acetone as the solvent can provide higher dispersions than water. The treatment step is the same as above.

(3) 12.3 wt% (3.45 wt% Fe) $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ (F.W. 489.96, Aldrich Chemical Company, Inc.) was impregnated into -200 mesh Wyodak coal from aqueous solution. The drying step is the same as above.

(4) $\text{Fe}_2\text{O}_3/\text{SO}_4^-$ was obtained from Pittsburgh Energy Technology Center. The solid catalyst was physically mixed with the coal, the catalyst weight being 0.35% by weight maf coal. The coal- $\text{Fe}_2\text{O}_3/\text{SO}_4^-$ mixture was stirred in an ultrasonic bath at room temperature for 1 hour, then stored in a brown glass bottle sealed under nitrogen.

(5) A coal sample was prepared by incipient wetness impregnation with an ammonium tetrathiomolybdate (ATM) $(\text{NH}_4)_2\text{MoS}_4$ solution. The procedure consisted of dissolving the quantity of the $(\text{NH}_4)_2\text{MoS}_4$ in enough distilled water to

give an approximate water-to-coal ratio of 1.5:1. The coal was then added to the solution. The coal sample (with catalyst) was then dried at vacuum condition, temperature 50°C, 4 hours. The dried coal sample was impregnated again with $(\text{NH}_4)_2\text{MoS}_4$, then dried. This procedure was repeated until an application of 0.05 wt. percent catalyst had been achieved. The assumption was made that ATM would convert entirely to MoS_2 . Mitchell (1989), et al. experiments showed that the thermal decomposition of ATM produces a molybdenum sulfide with an S/Mo atomic ratio in excess of 2.0.

(6) $(\text{NH}_4)_2\text{MoS}_4/\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$: 25 mmol FeCl_3 , 77mmol of $(\text{NH}_4)_2\text{MoS}_4$, about 1/3 ratio. First impregnate the coal sample with an aqueous solution of thiomolybdate, then dry the impregnated coal in a drying oven under N_2 at 50°C under vacuum. Finally impregnate with a solution of FeCl_3 and dry again under the same conditions.

(7) 10% by wt $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ based on FeCl_3 was physically mixed with -200 mesh coal.

3.1.6. Procedure. The experimental setup is schematically represented in Figure 3-5. The study was carried out in a micro-reactor which has been described above. Approximately 200 milligrams of dry Wyodak subbituminous coal, with catalyst impregnated, were carefully spread on the wire screen, exercising care to ensure that the coal particles completely surrounded the tip

1. Metering Valve	6. Temperature Controller
2. Micro-reactor	7. Temperature Recorder
3. Pressure Gauge	8. Relief Valve
4. High Amperage Circuit	9. Gas Sampling Port
5. Two 12V Batteries	10. Wet Test Flow-meter

Figure 3-5 Schematic arrangement of over-all experimental apparatus

of the thermocouple. The reactor was closed, evacuated and flushed two or three times with hydrogen gas to eliminate trace oxygen contamination, and pressurized with hydrogen to a pressure such that the pressure at operating temperature would be about 1500 psig. The coal was quickly heated to the desired reaction temperature in 1 to 2 seconds. The power supply consisted of two 12 volt lead-acid batteries connected in parallel to the circuit via a temperature controller. At the completion of the experiment at a predetermined time, the reactor system was cooled down quickly to room temperature and depressurized. The gases were carefully vented through a gas sampler, then to a wet-test meter. Gas samples were analyzed by gas chromatography (GC) using a HP 5890 gas chromatography. From the GC analysis and wet-test meter measurements, quantities of individual hydrocarbon (C_1 - C_4) gases were calculated. Also, the gases were measured by the weight difference between initial and final product weights. The two method difference is about 10%. It was not possible to perform a detailed analysis of the HC gases from 3 seconds run due to the very small amount of gas produced. The contents of the micro-reactor were thoroughly washed with THF and rinsed, then placed with tetrahydrofuran (THF) into a Soxhlet thimble. The mixture of liquid/solids was first extracted in a Soxhlet apparatus for 24 hours until the recycle extraction solvent was clear. The THF was then removed from the liquid product using a vacuum rotary evaporator with a

bath temperature of 50°C, and traces of THF solvent were further removed by spontaneous evaporation in a nitrogen-purged glove box until no THF remained. Then the liquids were weighed. The thimble containing the residue solids was dried overnight in a vacuum oven at a temperature of 50°C. Then the solids were weighed.

For the purpose of high conversion coal liquefaction with low HC gas, a two pass process was used. After the first pass, the weighed solids then were impregnated as for the first pass. Then, the procedure followed was the same as the first pass. Total conversion is the sum of the first and second pass conversions.

The yield of THF-soluble liquid product was calculated by dividing the weight of extracted liquid by the weight of the starting coal sample (maf basis). The liquid was then placed in a sample vial, under nitrogen, for subsequent analysis. The material balance of this process was about 98% by weight. Experiments were duplicated to verify the reproducibility of the data. It was observed that the reproducibility of the numbers was $\pm 5-8\%$. However, it was not possible to measure the water produced during the experiment, so the water was probably in the THF soluble liquid. Uncatalyzed test and the tests of activity of various catalysts were performed at 500°C and 1500 psig.

The advantages of this device are (1) relatively inexpensive design for high pressure studies, (2) direct

measurement of sample temperature, (3) very rapid particle heat-up, (4) very rapid quench of products.

3.1.7. Analysis of Coal Liquid Products. During production of liquids from coal, complex high-molecular-weight intermediate extracts are formed. To understand the processes occurring and make effective use of the products, it is important to carry out adequate chemical analyses of these extracts.

3.1.7.1. Elemental analysis. The elemental composition of the starting coal and of the liquid products were determined quantitatively for carbon, hydrogen, nitrogen and Sulfur. The oxygen content was determined by difference. The elemental analysis of the liquid products was done by Western Analytical Inc. The analysis of the starting coal is given in Table 3-1 and Table 3-2.

3.1.7.2. Simulated distillation. The boiling point distribution of the coal liquid product was determined by using simulated distillation. ASTM method D2887-73 was used. The analysis was performed on a programmed Hewlett Packard model 5730A gas chromatograph, using the following set points: initial temperature, -30°C (cooled by syphoned CO_2), holding for 0 minutes; temperature programming rate, $11^{\circ}\text{C}/\text{minute}$.; final temperature, 350°C ; final holding time, 4 minutes; temperature of injection port, 350°C ; temperature

of FID detection port, 400°C. The GC column consisted of a U-shaped 18 in × 1/4 in O.D. stainless steel tube packed with 3% Dexsil 400 on Anakrom Q, 90/100. Boiling point temperatures were calibrated with a standard mixture of alkylaromatics (50/50 by weight). Data obtained were fed, stored and analyzed directly, using a Hewlett-Packard model 21 MX-E series computer loaded with a simulated distillation program.

3.1.7.3. FTIR analysis. The starting coal and liquid product from a reaction of 5 seconds in the micro-reactor in the presence of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ catalyst were subjected to Fourier Transform Infrared (FTIR) analysis. Solid coal was examined by the KBr method. The liquid sample was analyzed in a CIRCIE cell. The spectrum was recorded on a Perkin Elmer 1600 Series spectrometer. The spectrum provides considerable information on the types of functional groups present in components of the coal liquid product.

3.1.7.4. Mass spectrometric analysis. The coal liquid product was analyzed by gas chromatography/Mass spectrometry (GC/MS). (1) A 4 m fused silica capillary column coated with 0.1 μm BP-1 was used, with He as carrier gas for liquid molecular weight distribution. (2) The reaction products were identified by EI/GC/MS analysis, using an HP Model 5985 instrument. This instrument had an impact voltage of 70 eV and was equipped with a 25m BP-5 capillary column.

3.1.7.5. NMR analysis. ^1H NMR and ^{13}C NMR spectra of the liquid products from 5 seconds coal liquid were obtained using deuterated THF as a solvent, and subjecting the solution to analysis using a nuclear magnetic resonance (NMR) spectrometer operated at 200 MHz. TMS was used as reference. The data obtained allowed for differentiation of various types of carbons and hydrogens present in the liquid product.

3.2. The Continuous-Flow System

3.2.1. General. The micro-reactor described in the previous section was designed to permit evaluating a concept for high conversion of coal to liquids, at the same time limiting production of HC gases to very low values, and hence limiting consumption of hydrogen. It is believed data from such a reactor may indicate the maximum theoretical ratios of liquids/HC gases achievable. However, in order to evaluate process economics, and study scale-up variables related to commercial operation, studies must also be conducted in a continuous process. For that purpose, a bench-scale continuous-flow system was constructed and operated as a part of this study.

3.2.2. Continuous-Flow Reactor Description. A schematic diagram of the continuous-flow reactor system is shown in Figure 3.6. The complete reactor system consists of seven components, each with a specific role, namely: gas

Figure 3.6. Schematic diagram of the ultrashort residence time coal liquefaction system

supply, hydrogen preheater, coal feed system, reactor, product collection and separation, gas sampling, and electronic control.

Coal is fed from a pressurized lock hopper by means of a star feeder. Hydrogen passes through a hydrogen preheater, after which it joins the coal, both entering the reactor tube together. The reactor tube, in which the liquefaction reactions are to be carried out, is a 3/16 inch inside diameter (ID) tube fabricated from 316 stainless steel. The reactor tube is heated by a series of electrical heating mantles which surround the tube. A temperature controller maintains a temperature of the hydrogen leaving the preheater at a predetermined value such that the coal-hydrogen mixture will enter the reactor tube at the appropriate temperature. A second temperature controller maintains the pre-set temperature in the reactor tube. As the length of the reactor tube was increased, as part of the program for establishing time in the heated zone, it became necessary to add additional temperatures controllers, one for each heating element. A power supply provides the electrical power for each temperature controller.

As the products leave the reactor tube, they pass through a series of separation vessels, where the gases are separated from the liquids and solids. The gases pass through a wet test meter, where their quantities are measured. A sample of the gases is then taken for analysis.

The liquids and solids are taken to another vessel, and cooled to ambient temperature.

A schematic diagram of the hydrogen preheater is shown in Figure 3.7. In designing the preheater to provide for adequate control of the temperature of the hydrogen as it joins the coal feed, it was necessary to treat the preheater tube as three zones, A, B, and C, each exhibiting different performance reflecting different rates of heat transfer from heating element to the hydrogen, and different hydrogen viscosities. A well-mixed hydrogen flow was assumed in the calculations.

A schematic diagram of the reactor is shown in Figure 3.8. Predicting the performance of the reactor was difficult. The stream is a two-phase system (solid coal and hydrogen gas) at the beginning, but changes to a three-phase flow as the stream moves through the tube. To assist in predicting operation of the reactor, and therefore the required heat flux, the tube was considered as consisting of three Regions, represented in Figure 3.9.

In Region I, the hot hydrogen and dry coal sample mixture is considered to be a two-phase, two-component mixture. The viscosity of the hydrogen in this region decreases smoothly with increasing temperature. There is virtually no change in the flow rates of the components. Region I ends when the coal particle temperature reaches its softening temperature. The flow pattern in this region is assumed to be non-back-mixing plug flow.

Figure 3.7. Schematic diagram of the preheater

* This drawing is not in scale.

Figure 3.8. Schematic view of the reactor

Figure 3.9. A simplified thermodynamic model of the reactor

Region II is characterized by a sharp increase in viscosity of the mixture, due to softening and swelling of the coal particles. In this region, physically adsorbed gases and moisture in the pore structure of the coal will be desorbed. Chemical bonds in the bridges which join the clusters rupture, and stabilization of the resulting free radicals commences. Region II ends when a significant amount of chemical reaction has occurred.

In Region III, the rates of chemical reaction, including formation of free radicals, and stabilization of those radicals, have become more steady. Bulk viscosity may decrease, but some local viscosity change is possible due to endothermic reactions. The flow pattern in this region becomes very complicated, and local turbulent, three-phase flow may occur.

In order to eliminate pressure drop and temperature distribution deviation in the axial direction of the reactor, a back-pressure adjusting valve was used (see Figure 3.8) to ensure that the whole reaction system pressure is uniform.

The functions of catalyst selection and preparation, coal sample preparation, catalyst application, and product analysis were carried out in the same manner as described for the experiments with the micro-reactor.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. The Micro-reactor System

4.1.1. Research Scheme. Studies were undertaken to find a way to convert coal into a high yield of liquids with a low yield of HC gases, in order to reduce the consumption of hydrogen, an expensive reactant. Wyodak sub-bituminous coal was used in this research (coal properties are given in Table 3-1 and Table 3-2). As described in Chapter 3, coal was ground and sieved to -200 mesh. In a typical experiment 200 mg of coal were subjected to short-contact-time liquefaction using a specially designed micro-reactor described in Chapter 3. The reaction temperature was 500°C, the hydrogen pressure was 1500 psig, and the reaction contact time ranged from 3 to 60 seconds. The effects of reaction time, catalysts and catalyst concentration upon the liquid yield and ratio of liquid/HC gases were investigated.

To obtain high conversion of coal to liquids with low HC gas production, a two-pass process was used, intended to simulate recycle of unreacted solids. Catalysts were applied to the coal by impregnation from solution.

Catalysts tested included:

zinc chloride (ZnCl_2),
ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$),
sulfated iron oxide ($\text{Fe}_2\text{O}_3/\text{SO}_4$),
ammonium tetrathiomolybdate $[(\text{NH}_4)_2\text{MoS}_4]$,
ferric sulphate pentahydrate $[\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}]$,

ammonium tetrathiomolybdate/ferric chloride hexahydrate

A detailed study was carried out on the liquids produced with ferric chloride hexahydrate. The liquids formed using the other catalysts were studied in less detail but were compared with the ferric chloride hexahydrate results. The impregnated coal was heated with hydrogen in the micro-reactor. The yields of char residue and liquids were determined gravimetrically. The yield of gaseous products was calculated from peak areas following calibration using standard gas mixtures, and by mass balance difference.

4.1.2. Experimental Results. The concept for coal liquefaction was investigated as a function of several variables, i.e., hydrogen pressure, reaction temperature, reaction time, catalyst type and catalyst concentration.

Total conversion of coal (dmmf) was calculated using the following expression:

$$\text{Conversion} = \frac{\text{wt liquid (THF soluble)} + \text{wt HC gas}}{\text{wt coal (dmmf)}} \times 100$$

Following is a description of the results obtained.

4.1.2.1. Effect of temperature. The effect of temperature on the conversion of Wyodak coal was investigated. A -200 mesh Wyodak coal sample was used, with 6.25% ZnCl_2 , to find the effects of temperature and hydrogen pressure on product distribution. It was found that ZnCl_2 concentrations in the

range 5-20% were suitable for preparation of ZnCl_2 -coal impregnates (Oblad, 1982). Figure 4-1 shows the effect of temperature on product distribution at 1000 psig of hydrogen pressure and a ZnCl_2 loading of 6.25% by weight, and a reaction time of 60 seconds. The experimental results are summarized in Table 4-1. At 500°C the yield of THF-soluble liquid reached a maximum in 60 seconds. The yield of C_1 - C_4 hydrocarbon gases increased steadily with temperature.

4.1.2.2. Effect of pressure. The effect of hydrogen pressure on the product distribution obtained at 500°C and between 800 and 2000 psig and a time of 60 seconds is shown in Figure 4-2. It can be seen that liquid yield for the catalyzed reaction reached 50.2% by wt at 1500 psig and 500°C. A further increase of H_2 pressure did not substantially increase the yield. The experimental results are summarized in Table 4-2.

4.1.2.3. Effect of time of reaction. Experiments were designed to investigate the dependence of coal liquid conversion and liquid/HC gas ratio upon contact time. In order to achieve a conversion greater than 70% (by weight) of the coal, with ratios of liquid/HC gas of 10/1 or greater, a short contact time was used. Two sets of experiments were performed at the same reaction conditions. They were: (1) 10% by wt FeCl_3 (3.45% Fe) (as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) as

Figure 4-1. Effect of temperature on the conversion of Wyodak coal.

Table 4-1
The Effect of the Temperature on the Conversion of
Wyodak Coal by Using 6.25% by wt ZnCl_2^a

Experimental No.	Temperature °C	Liquid Conv.	Gas Conv.	Total Conv.
#1	450	38.4	7.5	45.9
#2	475	42.3	8.1	50.4
#5	500	46.8	9.2	56.0
#3	540	44.7	11.5	56.2
#4	550	42.1	13.0	55.1

^a. Pressure is 1000 psig. Contact time is 60 seconds.

Table 4-2
The Effect of Hydrogen Pressure on the Conversion of
Wyodak Coal by Using 6.25% by wt ZnCl_2^a

Experimental No.	Pressure psig	Liquid Conv.	Gas Conv.	Total Conv.
#6	800	30.0	6.5	36.5
#5	1000	46.8	9.2	56.0
#7	1500	50.2	8.1	58.3
#8	1700	51.1	9.0	60.1
#9	2000	51.0	9.1	60.1

^a. Temperature is 500°C. Contact time is 60 seconds.

Figure 4-2. Effect of hydrogen pressure on the conversion of Wyodak coal.

catalyst and (2) 12.3% by wt $\text{Fe}_2(\text{SO}_4)_3$ (3.45% Fe) [as $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$] as catalyst.

THF conversion profiles were measured at time periods of 3, 5, 7, 10, 15, 20, 40 and 60 seconds to elucidate the effect of contact time. In (1), all runs were carried out with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10% FeCl_3). Experimental results are summarized in Table 4-3 and Figure 4-3. It is observed that the conversion is 66.3% and the liquid/HC gas ratio is 8.8 in 40 seconds. Figure 4-3 presents data for coal conversion and liquid/HC gas ratio as a function of time. It can be seen that the conversion did not change to a major extent with time of reaction from 5 to 40 seconds, but the liquid/HC gas ratio decreased considerably. At 5 seconds, the liquid/HC gas ratio reached 26 and conversion (in a single pass) was 60.6% by weight. These results generally reflect the expected trends for short contact time on the high liquid/HC gas ratio.

For a Wyodak coal sample containing 12.3 wt% $\text{Fe}_2(\text{SO}_4)_3$, the ratios of liquid/HC gas as a function of contact time at constant temperature and H_2 pressure, are summarized in Table 4-4 and Figure 4-4. As seen in Figure 4-4, the ratio of liquid/HC gases reached as high as 25.5, with 57.9% conversion in 5 seconds.

4.1.2.4. Effect of two pass. In order to increase the liquid yields, while limiting the HC gas products, a two pass process was used. The extracted char from the first

Table 4-3
Dependence of Coal Conversion and Liquid/HC Gas Ratio upon
Reaction Time by Using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ^{a, b}

Experimental No.	Reaction Time (sec.)	Conversion (wt%)	Liquid/HC Gas Ratio
#10	60	65.5	7.3
#40	40	66.3	8.8
#23	20	60.0	10.6
#39	15	62.9	21.4
#42	10	61.7	22.4
#45	7	61.7	25.4
#48	5	60.6	26.0
#50	3	55.2	31.2

^a 10% FeCl_3 by wt (as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) -Wyodak coal (-200 mesh) sample was used.

^b Short contact time liquefaction was performed at 1500 psig initial hydrogen pressure and 500°C temperature.

Figure 4-3 Dependence of coal conversion and liquid/HC gas ratio upon reaction time by using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

Table 4-4

Dependence of Coal Conversion and Liquid/HC Gas Ratio Upon
Reaction Time by Using $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ^{a, b}

Experimental No.	Reaction Time (sec.)	Conversion (wt%)	Liquid/HC Gas Ratio
#64	20	69.8	11.9
#67	10	54.6	20.8
#90	7	58.1	22.7
#66	5	57.9	25.6
#68	3	50.3	28.1

- ^a 12.3% $\text{Fe}_2(\text{SO}_4)_3$ by wt [as $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$]-Wyodak coal sample was used.
- ^b The experiment was carried out at temperature 500°C and initial hydrogen pressure 1500 psig.

Figure 4-4. Dependence of coal conversion and liquid/HC gas ratio upon reaction time by using $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$.

pass was used as the solid feed for a second pass, with catalyst again applied to the char. A total reaction time of 40 seconds, divided between the two passes in different ratios, was used. The experimental results are summarized in Table 4-5, and plotted in Figure 4-5 and Figure 4-6. As seen, in the first pass (10, 15, 20 seconds, respectively), the conversion of the Wyodak coal did not change with time to a major extent, but the liquid/HC gas ratio in the first pass increased substantially as the reaction time in the first pass was decreased. In Figure 4-6, as seen, after the second pass, the overall ratios of liquid/HC gas in the combined products were 15, 21.5, 22.4, respectively. Compared with the one pass total for 40 seconds, a two pass approach can achieve very high liquid/HC gas ratios and high coal conversions.

A second set of two-pass experimental results is summarized in Table 4-6 and Figure 4-7. Again it can be seen, the shorter the contact time of the first pass, the higher the liquid/HC gas ratio achieved.

4.1.2.5. Effect of catalyst concentration. The effect of catalyst ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) concentration on the liquid/HC gas ratio and coal conversion was studied. The -200 mesh Wyodak coal sample was impregnated with ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in 3 different concentrations, namely 3%, 5%, and 10% by weight, respectively. The experiments were carried out at 500°C, 1500 psig and times of 3-10 seconds.

Table 4-5
Two Pass Coal Conversion and Liquid/ HC Gas Ratio
by Using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ^a

Experimental No.	Reaction Time (sec.)	Conversion (wt%)	Liquid/HC Gas Ratio
#40	40	66.3	8.8
#23-1	20	60.0	10.6
#23-2	20	79.0	15.0
#39-1	15	61.9	21.4
#39-2	25	86.3	21.5
#42-1	10	61.7	22.4
#42-2	30	87.9	22.6

^a. 10% FeCl_3 by wt (as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) coal sample was used.

Figure 4-5. Two pass liquid conversion vs. reaction

Figure 4-6. Two pass liquid/HC gas ratio vs. reaction

Table 4-6
Two Pass Coal Conversion and Liquid/HC Gas Ratio
by Using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}^a$

Experimental No.	Reaction Time (sec.)	Conversion (wt%)	Liquid/HC Gas Ratio
#50	3	59.2	31.2
	3	82.0	30.0
#48	5	60.6	26.0
	5	85.9*	26.6
#45	7	61.7	25.4
	7	79.9	24.5
#51	10	61.7	24.7
	10	80.2	24.2
#53	15	63.9	20.0
	15	84.0	20.0
#23	20	60.0	10.6
	20	79.0	15.0

a. 10% FeCl_3 by wt (as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) coal sample was used.

Figure 4-7 Two pass total liquid/HC gas ratio vs. reaction time.

The effect of the concentrations of catalyst on the yield of THF soluble products and the ratio of liquid/HC gases are summarized in Table 4-7, Table 4-8, Table 4-9 and Table 4-10, and plotted in Figure 4-8 and Figure 4-9. As seen, under the experimental condition, the increase in yield of THF soluble products was modest for the catalyst concentration of 10%, compared with a concentration of 5%, by weight. At a concentration of 3% by wt, the conversion yield was substantially less than that at 5% or 10% by wt. These experimental results showed that at a temperature of 500°C, H_2 pressure 1500 psig and reaction time 5 seconds, the application of 10% or 5% by wt $FeCl_3$ ($FeCl_3 \cdot 6H_2O$) exhibited a relatively mild catalytic activity for short-contact-time coal liquefaction. The last row of Table 4-9, was a dry coal sample with 10% $FeCl_3$ (ferric chloride hexahydrate) physically mixed by blue agate mortar (rather than impregnated) to obtain a uniform mixture. It can be seen that ferric chloride hexahydrate physically mixed with coal can yield almost the same amount of liquid as impregnated coal. The effect of catalyst physical properties will be discussed in section 4.1.4.

4.1.2.6. Effect of catalyst type. The effect of catalyst type on the conversion to liquids and liquid/HC gas ratio was investigated. Zinc chloride ($ZnCl_2$), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sulfated iron oxide (Fe_2O_3/SO_4), ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$), ferric sulphate

Table 4-7
Effect of Catalyst Concentration (3% by wt FeCl₃) on the
Liquid/HC Gas Ratio and Coal Conversion

Experimental No.	Contact Time (Sec.)	Conversion (wt%)	Liquid/HC Gas Ratio
#69	10	50.8	19.3
#72	7	51.8	22.3
#70	5	51.6	22.7
#71	3	43.3	22.5

Table 4-8
Effect of Catalyst Concentration (10% by wt FeCl₃) on the
Liquid/HC Gas Ratio and Coal Conversion

Experimental No.	Contact Time (Sec.)	Conversion (wt%)	Liquid/HC Gas Ratio
#42	10	61.7	22.4
#45	7	61.7	25.4
#48	5	60.6	26.0
#50	3	55.2	31.2

Table 4-9
Effect of Catalyst Concentration (5% by wt FeCl_3) on the
Liquid/HC Gas Ratio and Coal Conversion

Experimental No.	Contact Time (Sec.)	Conversion (wt%)	Liquid/HC Gas Ratio
#55	3	51.1	34.5
#60	5	59.7	24.5
#58	10	58.6	22.2

Table 4-10
Effect of Catalyst Concentration on the Liquid/HC
Gas Ratio and Coal Conversion^a

Experimental No.	Catalyst Conc.(wt%)	Conversion (wt%)	Liquid/HC Gas Ratio
#70	3% FeCl_3	51.6	22.7
#60	5% FeCl_3	59.7	24.5
#48	10% FeCl_3	60.6	26.0
#82	10% FeCl_3 (dry) ^b	57.7	21.7

- a. Reaction conditions: 500°C temperature ; 1500 psig
initial H_2 pressure; 5 seconds reaction contact time.
- b. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was physically mixed with -200 mesh Wyodak
coal by blue agate mortar.

Figure 4-8 Effect of catalyst concentration on the conversion

Figure 4-9. Effect of catalyst concentration on the liquid/HC gas ratio.

pentahydrate $[\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}]$, ammonium tetrathiomolybdate/ferric chloride hexahydrate and ferric chloride hexahydrate (physically mixed with coal) were used as catalyst for hydrogenation-hydrogenolysis of Wyodak coal in short-contact-time liquefaction. A recent investigation using ammonium tetrathiomolybdate and sulfated iron oxide as catalysts for the coal liquefaction was reported by Bockrath, et al. (1990) and Huffman, et al. (1992). Bockrath, et al. used molybdate ranging from 250 to 2000 ppm (parts per million). They found that molybdenum as low as 500 ppm results in a high coal conversion. Pradhan, et al. have synthesized very fine particle sizes of sulfated iron oxide (30-100 Å) and have shown that even in small amounts (3500 ppm Fe) it would result in about 80% conversion for direct coal liquefaction.

Therefore, a study was performed on the possible use of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3/\text{SO}_4$, $(\text{NH}_4)_2\text{MoS}_4$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, as catalysts in the short-contact-time liquefaction. Results obtained are summarized in Table 4-11, Figure 4-10 and Figure 4-11. The data of Figure 4-10 resulted from a reaction time of 40 seconds, and the data of Figure 4-11 are for 5 seconds, single pass. As seen, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{MoS}_4$ gave a high yield of THF-soluble and high liquid/HC gas ratio. Also, it should be noted that the $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ shows a relatively high activity. It is seen in Table 4-11 that all of the catalyzed experiments produced significantly more liquid than the noncatalytic case.

Table 4-11

Effect of the Catalysts on the Coal Conversion
and Liquid/HC Gas Ratio

Catalyst	Concen. wt%	Conv. wt%	Liquid/HC Gas Ratio
ZnCl ₂ ^a	6.25	56.0	7.0
	ZnCl ₂		
FeCl ₃ ·6H ₂ O	10.0	79.0	15.0
	FeCl ₃		
Fe ₂ O ₃ /SO ₄	0.35	59.8	13.1
	Fe ₂ O ₃		
(NH ₄) ₂ MoS ₄	0.05	72.3	13.9
	Mo		
FeCl ₃ ·6H ₂ O ^b	10.0	60.6	26.0
	FeCl ₃		
Fe ₂ (SO ₄) ₃ ·5H ₂ O	12.3	57.9	25.6
	Fe ₂ (SO ₄) ₃		
FeCl ₃ ·6H ₂ O/ (NH ₄) ₂ MoS ₄ ^c	25/77	61.5	20.7
FeCl ₃ ·6H ₂ O(dry)	10.0	57.7	21.7
	FeCl ₃		
No Catalyst	----	24.5	8.2

Table 4-11 continued

- a. Experiments were performed at 500°C temperature, 1500 psig hydrogen pressure and 40 seconds contact time.
- b. Reaction temperature, hydrogen pressure and contact time are 500°C, 1500 psig and 5 seconds respectively
- c. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} / (\text{NH}_4)_2\text{MoS}_4$ ratio is 25 mmol Fe/77 mmol Mo.

Figure 4-10. Effect of the catalysts on the conversion and liquid/HC

Figure 4-11 Effect of the catalysts on the conversion and liquid/HC

Table 4-11 shows that $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10% by wt FeCl_3), physically mixed or impregnated, give almost the same yield.

4.1.3. Structural Analysis of Liquid Products. The purpose of this part of the work is to analyze in detail the liquid (THF-soluble) products obtained by the short contact time (5 seconds) liquefaction. The products were analyzed by a combination of elemental analysis, simulated distillation, molecular weight determination, GC/MS, FTIR, ^{13}C and ^1H NMR. Results obtained are described below.

4.1.3.1. Elemental analysis of the liquid product. The elemental composition of the liquid (THF soluble) is listed in Table 4-12. It can be seen that the hydrogen content was considerably increased, and oxygen and nitrogen contents were reduced, as compared with those of the original coal (see Table 3-2). Compared to the original coal, the liquid had lower heteroatom content, e.g., N, S content, whereas its H/C ratio increased from 0.94 in the original coal to 1.5 in the liquid. About 80% of the oxygen in the original coal is present in the liquid. However, about half of the nitrogen remained in the char. Some of the sulfur probably converted to H_2S (trace amount).

4.1.3.2. Simulated distillation (SIMD) analysis. The boiling point distribution of the liquid was determined by a simulated distillation procedure (see section 3.1.7.2) and

Table 4-12

Elemental Analysis of 5 Seconds

Wyodak Coal Liquid

Element	wt%
Carbon	72.8
Hydrogen	9.21
Nitrogen	0.58
Sulfur	0.70
Oxygen (by difference)	16.7
H/C	1.5

the results are summarized in Table 4-13. As seen, the oxygen-rich Wyodak coal liquid product contained 86 % (by weight) of total distillables, including 70.3% by wt of low-boiling fractions (gasoline, kerosene, and gas oil; b.p. up to 325°C).

4.1.3.3. Molecular weight distribution of liquid (THF-soluble) products. The molecular weight of the products is a more meaningful parameter. An MS technique for obtaining molecular weight distribution profiling of coal liquid products was developed by The Center of Micro Analysis & Reaction Chemistry at the University of Utah. In general, the mass spectra were recorded in the M/Z 100-650 mass range.

A 4m length capillary column, known to allow for rapid elution of relatively large and polar molecules, was used in the analysis. Such a short column provides not only short analysis times, but also the ability to observe the distribution profile of the eluting liquid components as a function of column temperature. This concept is similar to that of simulated distillation.

The molecular-weight-distribution mass spectra of liquid products at two different reaction times are shown in Figure 4-12 and Figure 4-13. As seen, the components for the products from 5 seconds contact time eluted between M/Z 100-450, and for the products from 20 seconds contact time, at M/Z 100-350.

Table 4-13
Boiling Point Distribution of 5 Seconds Coal
Liquid Product of Wyodak Coal

Fraction	Total wt%	Cumm. wt%
Gasoline (<200 °C)	2.8	2.8
Kerosene (200-275 °C)	46.7	49.5
Gas Oil (275-325 °C)	20.8	70.3
Heavy Gas Oil (325-400 °C)	10.0	80.4
Vacuum Gas Oil (400-538 °C)	5.6	86.0
Total Distillable (below 538 °C)	86.0	
Atmospheric Res. (above 350 °C)	25.7	
Vacuum Residue (above 538 °C)	14.0

Figure 4-12 Summed mass spectrum of 20 seconds liquid product of Wyodak coal by GC/MS

Figure 4-13 Summed mass spectrum of 5 seconds liquid product of Wyodak coal by GC/CIMS

4.1.3.4. GC/MS analysis. The characterization of the coal-derived liquid materials was explored by high resolution mass spectrometry. The positive structural identification of the various types of components presented in the liquid (THF-soluble) can be carried out by using GC/MS techniques, which have an upper molecular weight limit of about 500.

Figure 4-14 presents typical GC/MS chromatography spectrum profiles of the liquid from the 5 seconds contact time experiment, using Wyodak coal, in which the major components are identified. The results are summarized in Table 4-14. These compounds correspond to the peak numbers in Figure 4-14. It can be seen that the liquid products mainly contain two and three ring components, e.g., alkylnaphthalenes, benzofluorenes, phenanthrenes and other two and three-ring aromatic compounds. Also, some alkylbenzenes and alkylated fluorenes were found.

Figure 4-15 and Figure 4-16 show some typical single ion fragments of the compounds. The EI spectrum corresponds to the GC peak.

4.1.3.5. NMR analysis. Nuclear magnetic resonance (NMR) is used as a spectroscopic technique for characterization of coal liquefaction products. It can obtain information directly about the average carbon skeletons of the molecules present in the liquid. The THF soluble products derived from the Wyodak coal were analyzed by carbon NMR

Figure 4-14 Typical GC/MS chromatography spectrum profile of 5 seconds liquid product of Wyodak coal

Table 4-14 GC/MS Analysis of Products from Short Time Liquefaction of Wyodak Coal.
Structure Assignments ^a (5 seconds).

GC Peak Number	Mol. Peak M/e	Major Fragments M/e	Assignments ^a	
			Mol. Formula	Structure
34	56	51, 50, 41, 27	C ₄ H ₈	CH ₂ =CH-CH ₂ -CH ₃
38	58	43, 42, 39, 29, 27	C ₄ H ₁₀	CH ₃ -CH ₂ -CH ₂ -CH ₃
49	70	57, 46, 41, 39, 29	C ₄ H ₈ N
54	88	59, 57, 42, 31, 29	C ₅ H ₁₂ O	CH ₃ -CH ₂ -CH ₂ -CH ₃ -OCH ₃
56	72	43, 41, 39, 29, 27	C ₄ H ₈ O

Table 4-14 continued

GC Peak Number	Mol. Peak M/e	Major Fragments M/e	Assignments	
			Mol. Formula	Structure
144	118	101, 87, 71, 57, 41, 31	C ₈ H ₆ O
204	122	93, 78, 57, 47, 41, 31	C ₈ H ₁₀ O
302	86	74, 70, 56, 42, 29	C ₅ H ₁₀ O	b

Table 4-14 continued

GC Peak Number	Mol. Peak M/e	Major Fragments M/e	Assignments	
			Mol. Formula	Structure
540	159	140, 130, 114, 101, 87, 71, 57, 43, 31, 27	$C_{11}H_{13}N$
594	146	140, 133, 128, 115, 102, 87, 70, 57, 43, 29,	$C_{10}H_{10}O$
620	146	130, 110, 103, 98, 87, 71, 59, 43, 31, 29	$C_{10}H_{10}O$

Table 4-14 continued

GC Peak Number	Mol. Peak M/e	Major Fragments M/e	Assignments	
			Mol. Formula	Structure
666	172	155, 145, 133, 127, 113, 100, 87, 71, 59, 41, 31, 29	$C_{12}H_{12}O$
862	220	205, 192, 177, 163, 149, 135, 121, 107, 91, 87, 77, 67, 57, 41, 29	$C_{17}H_{16}$
875	236	221, 205, 193, 180, 165, 151, 137, 123, 111, 91, 87, 83, 71, 57, 43, 29	$C_{18}H_{20}$

Table 4-14 continued

GC Peak Number	Mol. Peak M/e	Major Fragments M/e	Assignments	
			Mol. Formula	Structure
956	252	237, 219, 196, 181, 153, 137, 127, 111, 95, 83, 67, 57, 43, 29	$C_{19}H_{24}$
985	226	215, 197, 182, 173, 157, 145, 129, 113, 102, 87, 71, 59, 43, 31, 29	$C_{16}H_{18}O$

Table 4-14 continued

GC Peak Number	Mol. Peak M/e	Major Fragments M/e	Assignments	
			Mol. Formula	Structure
1146	234	219, 203, 191, 175, 159, 147, 131, 115, 102, 88, 77, 65, 57, 41, 29	$C_{18}H_{18}$
1290	292	277, 261, 247, 231, 221, 203, 189, 175, 161, 147, 129, 105, 94, 80, 57, 41, 29	$C_{22}H_{28}$

Table 4-14 continued

GC Peak Number	Mol. Peak M/e	Major Fragments M/e	Assignments	
			Mol. Formula	Structure
1431	322	282, 259, 237, 215, 201, 173, 161, 145, 129, 113, 100, 87, 71, 43, 28	$C_{22}H_{26}O_2$
1573	392	377, 346, 336, 321, 305, 291, 275, 261, 249, 235, 217, 203, 189, 175, 161, 147, 133, 105, 91, 69, 57, 41, 29	$C_{25}H_{28}O_4$

Table 4-14 continued

a For some product components two or more alternative molecular structures can be considered.

b. : residual solvent from product extraction.

c. Or this structure:

d. Or either one of these structure:

AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

2 of 2

Figure 4-15 EI fragmentogram at M/Z 204

Figure 4-16 EI fragmentogram at M/Z 956

spectroscopy and proton NMR spectroscopy which give a statistical average composition.

4.1.3.5.1. ^{13}C NMR analysis. The spectrum of the THF-soluble products of the short time procedure is shown in Figure 4-17, and the interpretation is summarized below. Based on the chemical shifts of various model compounds and some reference data, the carbon types in the hydrocarbon can be identified. The major separation is between aromatic and aliphatic resonances. As seen, the spectrum shows a number of peaks both in the aliphatic C and aromatic C (plus oxygenated C) ranges. Various types of aliphatic carbons due to paraffins and hydroaromatic rings generally appear between 10 and 50 ppm. The spectrum indicates the presence of a variety of aromatic carbons in the 110-165 ppm region, including oxygenated aromatic carbons. The aromatic carbon resonances are further subdivided into two groups at 150 ppm. The shoulder between 105 and 120 ppm is caused by ring carbons that are ortho and para to aromatic ether, phenolic and benzofuran carbons. The peak between 120 to 150 ppm identifies aromatic carbon atoms bound to hydrogen (Ar-H), and bridgehead and substituted aromatic carbon atoms bound to hydroaromatic CH_2 carbon and alkyl side chains (Ar-C). The aromatic resonances resulting from C-O groups (150-165 ppm) are well separated from other aromatic resonances. It is clearly seen that some aromatic carbons (150-165 ppm) are attached to oxygen. The peak between 150 and 165 ppm is due

Figure 4-17 ^{13}C Carbon NMR spectrum of 5 seconds liquid from Wyodak coal

to aromatic ethers and 2-alkylbenzofurans and the signal around 170 ppm is due to aryl ethers. The peak around 180 ppm is due to carboxylic acids. Also, a peak observed about 92 ppm is due to terminal olefinic carbons in $\text{CH}=\text{CH}_2$ groups. Carbon atoms adjacent to oxygen atoms in alcohols or aliphatic ether groups are present in the region 55-90 ppm.

4.1.3.5.2. Proton NMR analysis The proton spectrum of the liquid (THF soluble) is shown in Figure 4-18. The distribution of hydrogens into various types was calculated and is summarized in Table 4-15. The major separation is between the aliphatic and aromatic hydrogen resonances, aliphatic resonances occurring in the chemical shift region 0.5-5.0 ppm, and aromatic resonances in the region 6-9 ppm. The phenolic resonances are between 5.0-9.0 ppm. Resonances in the aliphatic region (0.5-5.0 ppm) are due to methylene alpha to aromatics, methyl alpha to aromatics, and other methylene and methyl groups. The total concentration of α -hydrogens (between 2.0 and 3.4 ppm) viz., those attached to a saturated carbon in an α - position relative to an aromatic ring, is found to be about 28 percent. The total concentration of β -hydrogens (between 1.0 and 2.0 ppm), those incorporated in paraffinic CH_2 , and naphthenic CH_2 groups, as well as in CH_2 and CH_3 groups in a β -, or γ - (0.5-1.0 ppm) or farther position relative to an aromatic ring is about 57%. Signals just beyond 4 ppm indicate hydroxyl or carboxyl protons. Signals in the chemical shift

Figure 4-18 ^1H spectrum of 5 seconds liquid from Wyodak coal

Table 4-15
Distribution of Hydrogens in the Liquid Products of Short Contact
Time (5 seconds) Wyodak Coal Liquefaction ^a

Hydrogens Type	Chemical Shift Region, ppm	Distribution (Wyodak Coal)
<u>Aliphatic</u> (total)	0.5-4.8	85^b
alpha (total) ^e	1.6-4.8	28.1(33) ^c
beta+gamma ^f (total)	0.5-1.6	56.9(67)
<u>Phenolic</u>	5.0-9.0	15.0
<u>Aromatic</u> (total)	6.2-9.0	10.6
1 and 2 ring	6.2-7.5	8.0(75) ^d
3-ring	7.5-9.0	2.6(25)

^a As determined by proton NMR analysis, using deuterated THF as solvent.

^b Bold numbers represents the percentages of total aliphatic, total olefinic, and total aromatic

Table 4-15 continued

hydrogens in the liquid products.

- ^c Numbers in parenthesis represent percent of hydrogens of a given type out of the total aliphatic hydrogens.
- ^d Numbers in parenthesis in this column represent percent of hydrogens in 1-ring, 2-ring, or 3-ring compounds out of the total nonsubstituted aromatic hydrogens.
- ^e CH₃, CH₂, and CH alpha (α) to an aromatic
- ^f β -CH₃, CH₂, and CH beta (β) or further from an aromatic ring + paraffinic CH₂ and CH; CH₃ gamma (γ) or further from an aromatic ring + paraffinic CH₃.

range of 6.2-9.0 ppm are due to protons on aromatic rings with different extent of substitution. Table 4-16 also shows the distribution of aromatic hydrogens into 1-, 2-, and 3-ring components.

4.1.3.6. FTIR analysis. Fourier transform infrared (FTIR) spectroscopy is a valuable analytical tool for the characterization of coal and coal-derived products. In this part of the analytical study, the FTIR spectra of coal and coal liquid products were measured in order to provide further corroboration of the data obtained by GC/MS and NMR.

The Wyodak coal and THF soluble products obtained by the short-contact-time coal liquefaction technique were subjected to FTIR spectroscopy (see Experimental section).

Wyodak coal (-200 mesh) was analyzed using the KBr pellet technique. The FTIR spectrum of the Wyodak coal sample is given in Figure 4-19. The absorption maxima are listed and assignments are given in Table 4-16.

Wyodak coal contains a large amount of oxygen (19.36%) and has a relatively high atomic hydrogen to carbon ratio (0.94). The FTIR spectrum of the coal was consistent with these findings. Part of the oxygen was found in the form of phenolic groups which show as a broad band between 3100 and 3600 cm^{-1} . The strong aromatic ring breathing band near 1610 cm^{-1} (compared to the relatively weaker CH stretching bands at 2852 and 2923 cm^{-1}) is consistent with the medium-high carbon aromaticity of this coal. Hydrogen-rich alkyl

Table 4-16

Assignments of Infrared Absorption
Maxima Shown by Wyodak Coal

Band Position cm ⁻¹	Assignment
3600-3100	OH stretching (phenols)
2950	CH stretching (CH ₃ groups)
2922	CH stretching (CH ₂ groups)
1610	Aromatic ring breathing mode
1440	CH symmetric bending in CH ₃ groups and CH bending in CH ₂ groups
1382	CH symmetric bending in CH ₃ groups
1276	C-O stretching (aryl ethers), OH deformation in phenols
1195	C-O stretching (benzofurans)
1100-1095	C-O stretching of aliphatic ethers
540,470	Kaolinite

Figure 4-19 FTIR absorption maxima (cm⁻¹) of starting Wyodak coal

groups (CH_3 , CH_2 and CH) are apparent from the CH stretching bands at 2852 and 2923 cm^{-1} . The shoulder near 1700 cm^{-1} is assigned $\text{C}=\text{O}$ stretching of carbon-containing functional groups). The medium bands between 1150-1280 cm^{-1} can be assigned to $\text{C}-\text{O}$ stretching vibrations of aryl ethers. Aliphatic deformation absorptions appear at 1440 cm^{-1} and 1382 cm^{-1} . Absorption bands for kaolinite are seen at 540 and 470 cm^{-1} . The mineral bands also overlap with the aromatic CH out-of-plane bending vibrations. Several distinct bands for these vibrations appear in coal liquid products (see below).

Figure 4-20 shows the FTIR spectrum of the liquid product of the short contact time (5 second) liquefaction of Wyodak coal. The assignments of the absorption maxima are summarized in Table 4-17. The spectrum indicates the presence of several types of functional groups and characteristic aromatic ring substitution patterns in components of the liquid product.

4.1.4. Discussion

4.1.4.1. Temperature and hydrogen pressure. It is noted (Figure 4-1) that the yield of THF-soluble liquid products decreases and the yield of HC gases increases linearly when the temperature is increased above 500°C, when the pressure is 1500 psig. The yield of total product however does not increase appreciably over these ranges of pressure and temperature. Hence the increase in yield of HC gases must

Figure 4-20 FTIR absorption maxima (cm⁻¹) of 5 seconds liquid from Wyodak coal

Table 4-17

Assignments of Infrared Absorption Maxima of Liquid Products
Obtained by Short Contact Time (5 seconds) Liquefaction of
Wyodak Coal^a

Band Position cm ⁻¹	Assignment
3641	OH stretching (free OH groups in phenols, alcohols and carboxylic acids)
3450-3200	OH stretching (associated OH groups)
3066	CH stretching (aromatic rings)
2955	CH stretching (CH ₃ groups)
2926	CH stretching (CH ₂ groups)
2861	CH stretching (CH ₃ , CH ₂ , and CH groups)
1730	C=O stretching (aromatic esters; ketones)
1771	C=O stretching (saturated esters; α-ketoesters)
1602	aromatic ring breathing mode
1437	CH symmetric bending in CH ₃ groups and CH bending in CH ₂ groups
1366	CH symmetric bending in CH ₃ groups
1470-1340	CH bending in CH ₃ , CH ₂ , CH groups

Table 4-17. continued.

Band Position cm ⁻¹	Assignment
1310-1150	C-O stretching (aryl ethers, dibenzofurans), OH bending in phenols
885	CH out-of-plane bending of a single nonsubstituted aromatic hydrogen (penta-substituted aromatic rings)
861	CH out-of-plane bending of 1 or 2 adjacent nonsubstituted aromatic hydrogens (tetra- and penta-substituted aromatic rings)
811	CH out-of-plane bending of 2 or 3 adjacent nonsubstituted aromatic rings (tri- and tetra-substituted aromatic rings)
767-745	CH out-of-plane bending of 4 adjacent nonsubstituted aromatic hydrogens (ortho-disubstituted aromatic rings)
697	monosubstituted aromatic rings (5 adjacent aromatic hydrogens)

- a. Reaction contact time: 5 seconds; Temperature: 500°C;
H₂ initial pressure: 1500 psig.

be due to conversion of liquids to HC gases, when temperature is increased above 500°C.

A temperature of 500°C and initial hydrogen pressure of 1500 psig were observed to be suitable values to achieve a high liquid yield with low hydrocarbon gas yield. Therefore, these values were used to set the conditions for the short contact time tests with the other catalysts at various contact times.

4.1.4.2. Effect of contact time. One of the objectives of this research was to investigate whether high conversions of coal to liquids could be achieved in very short contact times, of the order of a few seconds. A second objective was to determine whether high ratios of liquids to HC gases could be achieved, by reducing the time of exposure of the liquids to high temperatures, thereby limiting thermal cracking of the liquids to form HC gases. The rationale behind the investigation is as follows: When the small coal particles, with an appropriate catalyst applied, are brought to a temperature of the order of 500°C in one or two seconds, thermal rupture of the bonds between the condensed units (clusters) in the coal, consisting principally of short aliphatic and other labile bonds (C-O, C-N, and C-S), is completed in a few seconds (i.e., less than five seconds). The free radicals formed by rupture of these bonds are capped very rapidly by the addition of hydrogen to form THF-soluble liquids compounds. Dobner, et al. (1976)

observed that the time required for formation of liquids from coal was significantly shorter than the time required for production of methane. In his work at 800°C and a pressure of 100 atmospheres, essentially all of the liquids had already evolved in two seconds, while the yield of methane continued to increase for much longer times.

In the work performed here, as the reaction time was increased, more HC gases were formed resulting in lower ratios of liquids/HC gases. It is believed the saturated portions of the hydroaromatic structures in the liquids can thermally crack to produce HC gases. It appears clear that the rate of cracking of these structures to produce HC gases is substantially slower than the rate of cracking of the connecting bridges between clusters in the coal. It therefore becomes possible, at the appropriate temperature, to convert nearly all of the coal to liquids, at the same time nearly avoiding formation of HC gases. These conclusions are confirmed by the data presented in Figure 4-3, in which is reported a ratio of liquids/HC gases of 30 in a contact time of 3 seconds.

4.1.4.3. Two pass process. In this work, liquids are the desired products. The formation of gaseous hydrocarbons results in high consumption of hydrogen, an expensive material, and hence is undesirable.

In these experiments, coal screened to pass through 200 mesh (Standard Tyler Series) was used. However under the

static conditions in the microreactor, the coal particles did not achieve centerline particle temperatures of 500°C in the short times of 3 to 5 seconds, where the highest ratios of liquids to HC gases were observed. At longer times, cracking of liquids to produce HC gases became excessive. Experiments were then conducted wherein the conversion of coal to liquids was of the order of 50 to 60% in the short times. The solid residue, consisting mostly of unreacted coal, was extracted to remove the liquids, catalyst again applied, and this unreacted coal reacted in a "second pass." An additional 25 to 30% conversion was obtained (see Table 4-6). When the products from the two passes were combined, it was observed that overall conversions of 80% or greater had been obtained in times per "pass" as short as 3 seconds, with combined ratio of liquids/HC gases as high as 30. These data indicate that a multi-pass system may be advantageous in a continuous reactor system for obtaining the highest values of both conversion to liquids and ratios of liquids/HC gases. Such multi-pass operation would normally be achieved by recycle of unreacted solids.

A further observation may be made concerning the formation of HC gases. At the same time of reaction in each of two passes, the yield of HC gases was much smaller in the second pass than in the first. Most of the HC gases produced in times of a few seconds seem to be formed from short aliphatic side chains on the coal structures, but not by rupture of the saturated portions of the hydroaromatic

units. Essentially all of these side chains were removed during the first pass, in the times of 3-5 seconds. Thus in the second pass there did not remain any of these units which could easily produce gases.

It seems clear from the data presented that the rupture of bonds between clusters may be nearly completed in times as short as 3 seconds, after the particles achieve a reaction temperature of 500°C, thereby achieving high conversions to liquids. There exists a time of a few seconds following conversion to liquids in which to remove the liquids from the hot zone before a significant amount of cracking occurs in those liquids to form HC gases. This time difference may be adequate to permit operation of a continuous reactor system at a large scale, with recycle of solids, yielding conversions greater than 70%, with ratios of liquids/HC gases greater than 20. This compares with ratios of liquids/HC gases of the order of 4 to 6 in direct coal liquefaction systems under development at the present time.

4.1.4.4. Catalytic activity. The economic viability and operability of processes to convert coals to useful liquid products could greatly depend upon the successful development and application of suitable catalysts.

Catalyst activity is determined principally by the degree of dispersion and the composition of the catalyst under a given reaction condition. Dispersion is understood

to describe the extent to which the catalyst is distributed over the coal surface area. The degree of coal-catalyst contact is intrinsically related to the catalyst activity, since the catalyst particles will only be able to influence reactions within their immediate vicinity. In most cases, the composition of the catalyst precursor will not be the same as that produced during liquefaction and neither of these will necessarily be the most active phase.

A more efficient process would use highly dispersed catalysts that have intimate contact with the coal molecules, would aid directly in the hydrogenation reaction of coal molecules, and ideally would be active in hydrogenolysis reactions. Apart from the unquantified degree of dispersion, the catalyst activity is also dependent upon the catalyst being able to attain its active form. The rate of conversion of the catalyst precursor to the active phase is a matter of some importance for iron and other catalysts. It is because the thermally-initiated reactions of coal can take place very rapidly and, especially for low-rank coals, can occur at low temperature (about 350°C). If there is some delay in converting the catalyst to its active form, the initial and most crucial reactions will be thermally controlled despite the presence of added catalyst. It seems important to compare the catalytic activity of various catalysts, as only an effective catalyst shows a high coal conversion.

Zinc chloride is known to be an effective catalyst for coal liquefaction which has been explored extensively, so it will not be discussed here.

Examination of the results of various catalysts indicates that coal conversion is dependent on the catalyst or active metal employed. Molybdenum catalysts have been well known to be most effective for promoting hydrogenolysis and heteroatomic bond cleavage reactions. More recent work (Derbyshire, et al., 1988) has demonstrated that dispersed sulfided Mo is effective under mild conditions. The chemical form of the catalyst precursor could have a decisive role. It is generally considered that the ammonium tetrathiomolybdate as precursor is transformed into MoS_2 at higher temperature ($\geq 350^\circ\text{C}$), that serves as the active catalytic species.

Because of obvious economic and environmental benefits (Fe is cheap and presents no environmental hazards), iron-based catalysts can be used in a disposable mode. FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ are understood to be Lewis acids when dry, and are transformed into strong Brönsted acids in the presence of small amounts of water. The active forms of Lewis acid catalysts in coal liquefaction are not known and it is possible that more than one form is active. The most commonly advocated active species is Lewis acid itself, or a Brönsted acid formed by reaction of a Lewis acid with water or with the corresponding hydrogen halide (Derbyshire, 1988). Evidence from many studies suggests that Lewis acids

must first be converted to Brönsted acids, to be active. The rate of alkyl-aryl bond breakage depends on the Brönsted acidity of the active catalyst.

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is a soluble catalyst and the pre-formed aqua complex ion form is $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, which acts as a protonic acid-generating species. Among the more economical catalysts, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ have achieved better performance in terms of overall coal conversion as catalysts for the short-contact-time liquefaction.

The physical properties of catalysts are listed in Table 4-18. As can be seen, the boiling point of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is 280-285°C, which is below the reaction temperature of 500°C. Therefore, it is probable that $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ could diffuse rapidly into the small coal particle during coal liquefaction. It could also display gas-solid contact of catalyst to coal under a reaction temperature of 500°C. The dispersion effect is apparently due to the intimacy of catalyst-coal contact. It is expected to provide advantageously-high dispersion within the coal macromolecule. Moreover, the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ could be in a strong Brönsted acid form ($\text{H}^+[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^-$) around a temperature of 500°C. Or iron sulphide could be formed by reaction with the sulphur in the coal.

The bulk of the available evidence indicates that pyrrhotite is the active form of the iron catalyst under liquefaction conditions. Abe et al. (1938) studied the catalytic behaviour of various inorganic and organic salts

Table 4-18

The Physical Property of Catalysts^a

Catalyst	Melting Point	Boiling Point
	°C	°C
ZnCl ₂	283	732
FeCl ₃ ·6H ₂ O	37	280-285
Ir ₂ O ₃	-	1565
Fe ₂ (SO ₄) ₃ ·5H ₂ O	-	480(d) ^b
(NH ₄) ₂ MoS ₄	-	≥350(d) ^c

^a Data came from Handbook of Chemistry and Physics, 73rd Edition 1992-1993.

^b d: Decomposition.

^c (NH₄)₂MoS₄ decompose to MoS₂.

of iron and reported that ferric chloride is not a good catalyst for liquefaction of Chinese subbituminous coal at a low level of catalyst concentration. However, high values of coal conversion were obtained in the present work by the use of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ impregnated into coal from acetone solution. Its high catalytic activity can be attributed to its acidity and its fluidity at the liquefaction temperature. Thus this catalyst could penetrate into the pores of coal, facilitating strong interaction between the coal and the catalyst. Also, the SIMD analysis data indicate that the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ has a high cracking ability. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ mixed physically with coal showed that it can produce almost the same yield as the impregnated method. This is attributed to $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ physical property. Therefore, impregnation of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is not necessary under the condition of short contact time.

X-ray and chemical evidence show that reaction of FeCl_3 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with coal results in the reduction of some Fe(III) to Fe(II) (Beall, 1980). He found that the samples were observed immediately to become liquid and the occurrence of a chemical reaction was indicated by bubbling which occurred for about one minute, when $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was reacted with coal at 250°C . Mössbauer study results suggest the divalent iron species may be responsible for the stabilization of coal radicals during the initial thermal disintegration, and that elemental iron is the most probable promoter of coal conversion in more prolonged liquefaction

(Peter, 1987). The Cassidy, et al. (1983) model compound studies indicated that iron catalyzes cleavage of the C-O bonds in dibenzyl and aliphatic ethers leading to an increase in concentration of the propagating radicals and thus an increase in reaction rate. Also, hydrogenolysis of isopentane on iron shows that the unique characteristics of iron as a hydrogenolysis catalyst seem largely related to the splitting of carbon-carbon bonds being more rapid than the desorption of hydrocarbons (Monnier, 1984).

$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ will decompose at about 480°C , which probably produces fine particles of iron or iron sulphide which are well-dispersed through the coal during liquefaction. The high catalytic activity of $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ in short time liquefaction, as well as its hydrogenation-hydrogenolysis ability, may partly be due to the well-dispersed fine particles of metallic iron or sulphided iron formed by the thermal decomposition of $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ around 500°C , followed by reaction with sulphur compounds in the coal.

An attempt was made to improve the activity of ferric chloride by incorporation of $(\text{NH}_4)_2\text{MoS}_4$, but it appears that ferric chloride alone has the same effect as the combination.

The catalytic activity of the dry $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ was not very good, because the nature of the catalyst-coal contact type was solid-solid contact under the reaction conditions (poor contact in very short time). Decomposition of the

sulfate group could only start above 600°C, and the melting point of Fe_2O_3 is as high as 1565°C. It appeared to be thermally stable and give catalytically inactive species. $\text{Fe}_2\text{O}_3/\text{SO}_4^-$ particles only can be able to influence reactions in their immediate vicinity. The Farcasiu, et al. (1991) experimental data indicated that the sulfated iron oxide catalyst gives a very active catalyst in the presence of small amounts of water (rehumidification for an hour). Therefore, Fe_2O_3 is not suitable for this short contact time liquefaction procedure. A small amount of water may be required for the formation of active species.

Because of the intimate degree of association between catalyst and coal, dissolution catalysts are difficult to separate and recover for reuse.

The iron concentration in the charge was higher than that of molybdenum. This relatively higher metal concentration was considered to be within practical and economic limits. According to Hiteshue (1962), the relative costs of catalysts in liquid phase hydrogenation, based on 1% metal on coal (maf) are 36 cents and 0.8 cent per gallon of gasoline for Mo and Fe respectively.

These results clearly indicate that $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ are good catalysts for short time coal liquefaction.

Although the exact catalyst mechanisms in our experiments are not known, the catalyst mechanism of ZnCl_2 has been extensively studied. Mobley and Bell (1979)

studied the catalyst mechanism by illustrating the benzylphenylether cleavage. They suggested that the Lewis acid form of ZnCl_2 acts as an electron acceptor, forming a complex with the oxygen. The complex then cleaves to produce a carbonium ion, which can proceed to react by the pathways described in Figure 4-21 (a), and ZnCl_2 is regenerated by the reaction (a)-2. The prevailing opinion advocated Brönsted acid being the active species. Frederick and Bell (1984a) found that the addition of water to ZnCl_2 promoted the cleavage of diphenylmethanes. The Brönsted acid catalyses the cleavage of connecting linkages by proton addition followed by scission to produce a carbonium ion and a smaller hydrocarbon (Figure 4-21, b). These results help us to understand the catalyst mechanism of the acid catalyst in coal liquefaction.

4.1.4.5. Minimum of FeCl_3 concentration. Experiments were conducted to determine the minimum amount of active metal required to achieve high yields. Results of experiments performed by varying the concentration of the Fe showed that doubling the concentration of the active metal had an insignificant effect on the conversion. When the concentration of Fe was reduced to 1% by wt, the conversion was decreased. Therefore, Fe 1.72% by wt can be used without sacrificing conversion.

a.

b.

Figure 4-21 Catalyst mechanisms of ZnCl_2 as catalyst
 a. Lewis acid catalyst mechanisms.
 b. Bronsted acid catalyst mechanisms

4.1.5. Possible Chemical Components in Liquid (THF-soluble) Products. The liquids (THF-soluble) obtained under short-contact-time conditions (5 seconds, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were analyzed by a combination of GC/MS, ^1NMR , ^{13}NMR , FTIR, and elemental analysis. The short contact time procedure employed proceeds with preservation of most of the original aromatic-hydroaromatic units of the coal network, and causes changes in the intercluster linkages resulting from hydrogenolytic and hydrolytic cleavage reactions. These analytical data indicate the types and relative concentrations of oxygen-containing functional groups. It was also possible to identify probable components in the liquid products (THF-soluble).

The coal liquefaction experiments in short contact time were conducted with a high ratio of atomic H/C. Therefore, it would be expected that hydroaromatics did not dehydrogenate during coal liquefaction. It means that hydrogen was directly (catalytically) interacting with reactive coal fragments, and the hydroaromatics were not being used as a source of hydrogen during short contact time reaction. The SIMD result provided a clear illustration of the high efficiency of the short contact time procedure for converting coal into high quality coal liquids.

The mass spectrometric detection of almost exclusively chemical ions of thermally extracted coal products enables one to study the change of molecular weight distribution as a function of reaction time. The spectrum gives a

qualitative picture of the molecular size distribution. The main portions of the product, obtained in the 5-seconds experiment, exhibit molecular weights between 100 to 300. The molecular weight of the product decreases with increasing contact time. The summed mass spectrum of liquid product from Wyodak coal indicates that shorter time leads to a higher molecular weight distribution, and longer time yields a lighter molecular weight distribution. It is consistent with theoretical analysis. The molecular weight distribution suggests that the tar from Wyodak coal contains greater fractions of smaller molecular weight units.

GC/MS results indicate that the remaining stable compounds must exist in forms resembling diarylsulphides and dibenzothiophenes. The identification of the major peak shows that the bond cleavage is very rapid between C-C, C-O, C-N and C-S. Subbituminous coal contains high levels of oxygen. Extensive structure reactivity studies (Mahendra, et al. 1991) of Wyodak coal have revealed that carboxyl groups and ether are the predominant oxygen functionalities of this coal (Figure 4-23, a). Also, the coal oligomer chains are not very long. It can be seen that the much higher concentration of oxygen compounds in the liquid product was obviously the result of hydrogenolysis reaction in the short time, without removing the oxygen atom. This is in agreement with the elemental analysis. Montano (1986) has reported that iron sulfide surfaces are involved in the cleavage of oxygen bonds in coals and coal-derived products.

Figure 4-22. Possible chemical components in SRT liquid

Figure 4-23 Schematic representation of coal liquefaction. a. Salient structural features of Wyodak coal. b. Reaction scheme for short-contact-time coal liquefaction.

Therefore, Fe catalyst used in short contact liquefaction of Wyodak coal may play an important role in C-O bond cleavage and result in rapid conversion of coal to liquid products.

^1H and ^{13}C NMR analyses were performed on the liquid products. The aromaticity of the conversion product (f_a), that is, the fraction of total carbon which is aromatic carbon, calculated from the ^1H NMR spectrum, is 0.72. It was determined using the Brown and Ladner method (Brown and Ladner, 1960) by measuring the proportion of aromatic and aliphatic protons and assuming a hydrogen to carbon mole ratio of 2 for the aliphatic protons. The original coal aromaticity is 0.81. The results suggest that cleavage reaction in short time coal liquefaction only occurs between C-C, C-S, C-O and C-N bonds. The aromatic carbon content in the products from hydrogenolysis and alkyl bond scission is generally the same as that of the original coal (Miknis, et al., 1993). The proton NMR spectrum shows the distribution of hydrogen. The H_a (attached to an aromatic ring in an α position) is about 28% and, the H_β and H_γ are about 57%. The high value for β - and γ -hydrogen is consistent with the presence of long alkyl chains or free paraffins. This is inconsistent with this liquid. These paraffins probably exist as free paraffins in the liquid. The aromaticity cannot be calculated from the ^{13}C NMR spectrum because of variable nuclear overhauser effects and relaxation factors. However, the spectrum indicates the presence of a variety of aromatic carbons, including

oxygenated aromatic carbons (ether, phenolic and benzofuran carbons).

To evaluate the structural integrity of the products obtained from the short contact time liquefaction process, the FTIR analysis was performed on the 5-seconds liquid product. The FTIR spectra of the starting coal and THF soluble liquids are given in Figure 4-19 and Figure 4-20. The aliphatic C-H stretch absorption band ($2800-3000\text{ cm}^{-1}$) is more pronounced in the spectrum of the THF soluble liquids than in the starting coal, which is in agreement with the elemental analysis which indicates a higher H/C ratio. The FTIR spectrum of short-contact-time liquid (THF soluble) product from the Wyodak coal shows some pronounced differences compared with the spectrum of the starting coal. Nonassociated OH groups (sharp band near 3640 cm^{-1}) appear, the intensity of aliphatic CH stretching frequencies between $2830-2980\text{ cm}^{-1}$ increases and the broad band between $1340-1470\text{ cm}^{-1}$ (CH deformations of CH_2 and CH_3 groups) increases in intensity, indicating the probable occurrence of some hydrogenolysis and hydrogenation reactions during short-contact-time coal liquefaction.

For instance, the increase in the concentration of CH_3 groups could result from hydrogenolysis of alkylene linkages between aromatics (e.g., $\text{ArCH}_2 \rightarrow \text{ArH} + \text{ArCH}_3$), CH_3 , CH_2 and CH groups in alkyl substituents, and CH_2 and CH groups in naphthenic rings. At least three CH stretching bands occur in the $2830-2980\text{ cm}^{-1}$ region.

Likewise, a very high content in oxygen functional groups can be deduced in the liquid. The OH stretching band near 3641 cm^{-1} (free OH groups in phenols, alcohols and carboxylic acids), the C=O stretching bands near 1731 and 1767 cm^{-1} and the aryl etheric C-O stretching bands between 1150 - 1310 cm^{-1} of the soluble products are much more pronounced than the corresponding bands in the coal feed spectrum. This may be due in part to the complexing of carbonyl-containing and etheric functional groups with other components in the original coal framework. The aromatic ring breathing band near 1600 cm^{-1} is substantially weaker. The relative intensity of aromatic CH out-of-plane bands between 690 - 900 cm^{-1} increases. This can be ascribed to (aromatic) C-O hydrogenolysis reactions in ethers and phenols. Further, it was observed that the intensity of the band near 862 cm^{-1} increases sharply relative to that of the other two bands in the region (at 810 cm^{-1} and 767 cm^{-1}). This can be ascribed to hydrogenolysis of (aromatic) C-O bonds in aromatics and in phenols having two ortho substituents around the oxygen-containing functional group. Absorptions from 751 to 743 cm^{-1} were assigned to aromatic γ -CH (4 adjacent CH). The IR results are in agreement with those found by GC/MS and NMR analyses. Thus, short-contact-time catalytic liquefaction results in the cleavage of alkylene linkages in the coal, and cleavage of etheric linkages which formed phenolic derivatives.

Probable components in these liquid products are indicated in Figure 4-22. These structural types are considered most likely, based on the analytical results and steric and stability considerations.

4.1.6. Reaction Scheme. Coal liquefaction in this temperature range is believed to follow a mechanism in which free-radicals are formed by thermal bond cleavage and stabilized by hydrogen addition. The hydrogen is provided from molecular hydrogen aided by a catalyst, or from organic donor molecular units. The basic structural units in sub-bituminous coal are condensed units of slightly smaller size, on average, than in bituminous coal. The linkages include C₁-C₃ aliphatic bridges, ethers etc. At the experimental temperature and hydrogen pressure, 500°C and 1500 psig, the rate of coal conversion is very rapid and coal is almost converted completely to liquid and gas within a few seconds.

When coal is heated to above 350°C, thermal bond cleavage occurs. Wiser's coal structure model in Figure 2.1 indicates by arrows the kinds of linkages susceptible to thermal cleavage viz., C-C, C-O, C-N and C-S bond cleavage. Precedence for the rapid thermal cleavage of structures such as tetraaryl, and especially hexaaryl, substituted ethanes is well known (Morrison et al. 1973). This type of bond cleavage is clearly a free-radical process. The breaking of carbon-to-sulphur and carbon-to-nitrogen bonds occurs

through hydrogenolysis. These free radicals are very reactive species which can be stabilized by hydrogen to form products of low molecular weight, or become large molecules by condensation and retrogressive reactions. The catalyst may assist in the cleavage of these bonds to convert coal to liquid products in such short times. The catalyst limits retrogressive reactions, promoting cleavage reactions probably by hydrogen-radical-mediated hydrogenolysis (Schobert, 1991). The radicals are saturated by hydrogen to form liquid and gaseous products (Figure 4-23 b).

In our experimental system the thermal cleavage and hydrogen capping of the free radicals is finished in a few seconds. The radicals are not recombined to form higher molecular-weight products, and are not further broken down to form gas molecules. The consumption of hydrogen by reactive coal fragments is minimal. Inasmuch as the saturated portions of the hydroaromatic units in the coal are not ruptured, hydrocarbon gas formation is very small, and hydrogen consumption is low. Consequently the hydrogen content of the liquids is much higher (H/C ratio of about 1.5) than in conventional raw coal liquids (H/C ratio about 1.1). Li, et al. (1993) experimental results indicate that both total volatile products and tar yields increase rapidly between 400 and 550°C. Recent work by Graff et al. with bituminous coal (Illinois No.6) indicated that residence time of products in the hot reaction zone was of very great importance in minimizing tar formation and maximizing yield

of aromatic liquids. The point of interest is that almost all of the liquid products are formed and removed very rapidly, and heating for longer than a few seconds at the same temperature is unproductive.

The chemical reactions in coal liquefaction are reactions of hydrogen. There are a number of ways in which hydrogen participates in the direct liquefaction of coal. Only hydrogenolysis and alkyl bond scission occur in our short contact time liquefaction.

4.2. The Continuous-flow Reactor System

An additional objective of this research work was to design, construct and operate a continuous-flow reactor under conditions which would give high yields of liquids, with high ratios of liquids/HC gases. A preliminary goal was a liquid yield greater than 50% by weight of the coal, with a ratio of liquids/HC gases of 8/1 or greater. This objective was realized, and the goal which had been set was surpassed. In the course of achieving this objective, several significant achievements were realized, including trouble-free solid feeding of dry coal of particle sizes smaller than 100 mesh (Standard Tyler Screen Series) at pressures of 1500 psia, and efficient use of hydrogen at very low quantities.

4.2.1. Research Scheme. In order to obtain high ratios of liquids/HC gases at high yields, it was necessary to limit the time of reactants and products in the hot zone to times less than 20 seconds, and preferably nearer 10 seconds. In order to achieve high liquid yields, while thus limiting the time in the hot zone for the liquid products, unreacted solids were recycled, in a manner to simulate recycle in a scaled-up version of the process. This was done by using a two-pass scheme. The reasons for this mode of operation are fully discussed in the previous section for the micro-reactor system.

As previously discussed, in order to achieve high conversions in times measured in a few seconds, it is necessary to feed the coal in a finely-divided state. Ideally for this process, it is desirable to achieve a particle center-line temperature in one-to-two seconds equal to the set temperature for the reactor. This feature indicated particle size less than 200 mesh. Great difficulties were encountered in the lock hopper and star feeder when the particles were -200 mesh. In order to achieve stable feeding of the coal, the coal was crushed and screened to yield a fraction with particles smaller than 65 mesh and larger than 100 mesh, which fraction was used for producing the data presented below. Wyodak sub-bituminous coal (the same coal identified for the micro-reactor experiments) was used for all of the work in the continuous reactor.

To achieve particle center-line temperatures of the order of 500 °C in one or two seconds, in a flow system, hot hydrogen gas in turbulent flow was identified as an ideal heat-transfer medium for this system. However, feeding hydrogen gas to the system was restricted feeding from gas cylinders with maximum cylinder pressures of 2200 psi. In the experiments reported here, it was never possible to achieve flow velocities high enough to provide for turbulent flow. Hence, particle heat-up rates were lower than desired, and lower than would be provided under turbulent-flow conditions.

4.2.2. Experimental Results. Due to the limited length of laboratory space, a single length of reactor tube, without bends, did not exceed 13 feet. Within that length, the residence time in the reactor was adjusted by adjusting the flow rate of the gases through the reactor. In order to accomodate greater times that were practical in one 13-foot length of tube, additional 13-foot lengths were added, each joined to the preceding one by a hair-pin turn. With these combinations, residence times from about nine seconds to 50 seconds were examined. Product residence times were calculated from measured gas flow rates through the reactor. Solid residence times were not measured.

Experiments in the 13-foot reactor were conducted at three gas residence times, namely 9, 13, and 16 seconds, accomplished by reducing the gas flow rate through the

reactor. The length of the reactor tube was then increased to 40 feet by the addition of two hair-pin turns. Using gas flow velocities the same as in two of the experiments in the shorter reactor, namely 0.8 and 1.0 feet/second, gas residence times of 40 and 50 seconds, respectively, were achieved.

Inasmuch as it was simpler to conduct an experiment in the micro-reactor than in the continuous-flow reactor, it was decided to screen several catalysts in the micro-reactor, then to use only the most promising of the catalysts for experiments in the continuous reactor. One of the most promising, in terms of conversion and ratio of liquids/HC gases, was ferric chloride hexahydrate. This catalyst was used for the experiments reported in Table 4-19.

4.2.3. Discussion. In the table, two passes are reported as explained above. One noted a steady increase in conversion per pass as the time in the reactor is increased. When one compares these conversion values with values from the micro-reactor, it must be remembered that the coal particles are larger in these experiments, resulting in a larger fraction of the coal within these particles of larger diameters which did not reach the temperature set for the experiment. Further, the particle heat-up rate is slower than desired because the flow through the reactor was laminar, rather than turbulent.

Table 4-19

Coal Feed: Wyodak sub-bituminous, -65, +100 mesh

Temperature, 450 °C; Pressure, 1500 psig

Catalyst: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, impregnated from acetone solution

Gas Residence Time, secs (Gas Flow Rate, ft/sec)		9 (1.5)	13 (1.0)	16 (0.8)	40 (1.0)	50 (0.8)
1st Pass	Conversion, wt. %	37.4	44.7	49.9	64.5	68.5
	Ratio, Liq/HC Gas, by wt.	7.3	8.6	8.3	7.3	6.5
2nd Pass	Conversion, wt. %	34.8	40.9	56.0		
	Ratio Liq/HC Gas, by wt	17.2	16.9	13.7		
Cumulative	Conversion, wt. %	59.2	67.3	78.0		
	Ratio Liq/HC Gas, by wt	10.9	11.4	10.2		

For the first pass, the ratio of liquids/HC gases increased slightly at 13 seconds compared with 9 seconds. In the short times of a few seconds, it appears most of the HC gases are produced from short side chains in the coal structure. As residence time increases, a larger fraction of the coal achieves a temperature at which these side chains will crack from the structure, hence more HC gases are produced. As the residence time increases further, there is a decrease in the ratio of liquids/HC gases. This is due to cracking within the hydroaromatic structures of the coal and of the liquid products, which cracking is very small at the shorter times, resulting in an increase in HC gas yield as residence times increase, hence a decrease in the ratio liquids/HC gases. This observation illustrates clearly the reason why residence times in the hot zone shorter than 10 seconds for the liquid products are desired. It may be noted here that the experiments in the micro-reactor indicate that, whereas the bonds in the connecting bridges between clusters rupture rapidly, and may be complete in 3-5 seconds for -200 mesh particles, the times required for appreciable rupture of bonds in the saturated portions of the hydroaromatic units appear to be about 10 seconds and longer.

Following recovery of the solids and liquids from the first pass, the liquids were removed from the solids, catalyst again applied to the solids, and these solids returned as feed to the reactor for the second pass. The

conversions listed in the Table for the second pass are percentages of the solids recycled. When these liquid amounts are added to the liquid amounts from the first pass, and the total liquids calculated as a percentage of the coal feed to the first pass, the cumulative conversions for the two-pass process are given in the Table. The ratios of liquids/HC gases, for the second pass and for the total process, are calculated in like manner.

It is significant to note that, for the same length of time of the materials in the reactor for the two passes, the ratio of liquids/HC gases for the second pass is considerably larger than for the first pass, and this difference is much greater for the shorter time of 9 seconds. This is a further manifestation of the realities of the chemistry involved, as described in the above paragraph.

A set of experiments was conducted with ferric sulfate pentahydrate as catalyst, at 500 °C and a reactor time of 15 seconds. As was observed in the extensive catalyst screening work with the micro-reactor, the yields were about 5% lower than with the ferric chloride hexahydrate catalyst, and with liquids/HC gases ratios of about 25/1. A set of experiments was also conducted with ferric chloride hexahydrate promoted with molybdenum. The yields were slightly higher than with the ferric chloride hexahydrate alone, and with similar ratios of liquids/HC gases.

It is again noted that it is believed achievable to feed coal dry, with particle sizes of -200 mesh, with modifications to the feed hopper. It is also believed that, with hydrogen in turbulent flow, heat-up rates of the smaller coal particles may permit heating the particle to a center-line temperature of the order of 500 C in times of about one second. If these values are achieved, the conversions in a suitable continuous-flow reactor may approach those observed in the micro-reactor, namely liquid yields, with recycle, greater than 80% by weight of the coal in 3-5 seconds, with ratios of liquids/HC gases of the order of 30/1. It should also be noted that the performance in a two-pass process is intended to simulate recycle in a continuous system, and is believed to be realistic.

It is useful to recall that, in a completely self-sustained coal liquefaction system, it has been reported by Exxon that the maximum net product yield, in the form of a liquid product, is 46% by weight of the coal fed. By this measure some of the single-pass conversions already achieved, in the less-than-ideal conditions of these experiments, represent a considerable improvement in reduction of HC gases produced, and hydrogen consumed, over those found in current state-of-the-art technologies.

4.2.4. Liquid Product Analysis. The liquid products from the continuous flow experiments were subjected to analysis by the same techniques discussed in the prior

section for the micro-reactor system, with results very nearly the same as those results. The techniques used, and the results obtained, will not be discussed again here.

CHAPTER 5

CONCLUSIONS

The principal conclusions resulting from this work are:

1. In a batch micro-reactor, designed specifically for this purpose, investigations were conducted relative to conversion of coal to liquids in high yields, in times measured in seconds. It has been demonstrated that liquid yields in excess of 50% by weight of the coal can be obtained in a single pass, in times as short as three seconds, and in excess of 80% by weight of the coal with recycle of unreacted solids, also in times as short as three seconds per pass.

2. In the same micro-reactor, it has been demonstrated that, in these short times of a few seconds, very small amounts of hydrocarbon (HC) gases are produced (about 3% by weight of the coal), as indicated by the high ratios of liquids/HC gases as high as 30/1 by weight, accompanied by very low consumption of hydrogen. These values are to be compared with current advanced coal liquefaction technologies, which are of the order of 4/1 to 5/1, representing HC gas yields of 15-20% by weight of the coal.

3. These high ratios of liquids/HC gases are obtained by achieving very rapid particle heat-up in times not to exceed one or two seconds, and limiting the residence time of the coal and liquid products in the hot zone to very short times of only a few seconds. As the residence time increases

beyond about 10 seconds, the yield of HC gases increases, accompanied by an increased consumption of hydrogen.

4. The required rapid particle heat-up can best be achieved by feeding the coal dry to the reactor, and feeding small particles, preferably -200 mesh. It is necessary that a liquid phase must not be present, surrounding the coal particles and within the pores of the particles, during particle heat-up, in order that the heat-up process may be accomplished in times of one or two seconds, or less.

5. The results from both the micro-reactor and the continuous-flow reactor indicate that rupture of the connecting bridges can be essentially completed in times as short as three seconds or less, while times of the order of ten seconds or more are required to produce significant cracking of the saturated portions of the hydroaromatic structures in the coal and the liquids. The data indicate that the HC gases are generated principally by thermal cracking within the hydroaromatic units. This time difference provides opportunity to remove the liquids from the hot zone, thereby preserving the liquids and restricting the formation of HC gases.

6. Simulated distillation applied to the liquids indicated that with liquid yields of about 80% by wt of the coal, 86% of those liquids would boil below 538 °C, and 70% would lie in the boiling range of gasoline, kerosene and gas oil (boiling point up to 325 °C).

7. These yields, with low production of HC gases, can be achieved with inexpensive iron catalysts. Two such catalysts have been demonstrated in this work, particularly ferric chloride hexahydrate and ferric sulfate pentahydrate.

8. The data presented herein were obtained at pressures of 1500 psi, which is considerably lower than current advanced technologies. Theoretical considerations based upon the data indicate that much lower pressures, even 500 psi or lower, may yield results near those presented herein.

9. The combination of low hydrogen consumption, much smaller reactor for a given coal feed rate because of the very short residence times, and lower pressures, indicate the probability of a considerable savings in the cost of producing a primary liquid product from coal, when compared with current state-of-the-art technologies.

10. Considering the desirability of using iso-paraffins rather than aromatics for octane improvement in gasoline, it becomes beneficial to preserve the hydroaromatic units in the liquids formed from coal, rather than to permit these units to be cracked to yield unwanted HC gases, which normally are mostly methane.

11. It is believed that when a continuous system is operated on coals crushed and screened to -200 mesh, and the system operated in the turbulent-flow regime, results from such a system will approach the values achieved in the micro-reactor.

LIST OF ABBREVIATIONS

GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
¹H NMR	Proton Nuclear Magnetic Resonance
¹³C NMR	Carbon Nuclear Magnetic Resonance
FTIR	Fourier Transform Infrared
THF	Tetrahydrofuran
EDS	Exxon Donor Solvent
SRC	Solvent Refined Coal
SCT	Short Contact Time

REFERENCES

- Abe, R., Fujikawa, H., Kadotani, C., Okamura, T. and Sugiyama, K. Kogyo Kagaku Zasshi, 1938, **41**, 862
- Abichandani, J.S., Weiland, J.H., Shah, Y.T. and Cronauer, D.C., Am. Inst. Chem. Eng. J. 1984, **30**, p295,
- Anthony, D.B., Howard, J.B., Meissner, H.P. and Hottel, H.C., "Apparatus for determining high pressure coal-hydrogen reaction kinetics under rapid heating conditions", Rev. Sci. Instrum., Vol. **45**, No. 8, August 1974, pp 992.
- Beall, H. (1980) Reactions coal with the chlorides of iron, chromium and copper, Fuel, **59**, 1980, p. 140.
- Bockrath, Bradley, Illig, Eugene, Keller, Murphy, III, and Hough, Marjorie, "Low Temperature Liquefaction Catalysis". Direct Liquefaction Contractors' Review Meeting. p201, 1990
- Brown, J.K. and Ladner, W.R. (1960) Fuel 1960, **39**, 87.
- Cassidy, J.P., Jackson, R.W. and Larkins P.F.
"Hydrogenation of brown coal : IV. model compound studies and mechanistic considerations" Fuel, 1983, **62**, 1409.
- Derbyshire F J, Davis A, Lin R, Stansberry P G, Terrer M-T., (1986) Fuel Processing Technology, **12**, p127-141, 1986.
- Derbyshire F.J., Terrer M-T., Davis A. and lin R., (1988a) Dry catalytic liquefaction of a subbituminous coal: structural inferences, Fuel, 1988, Vol. **67**, August p1029.
- Derbyshire Frank J, (1988b) Catalysis in coal liquefaction, 1988.
- Feldkirchner, H.L., and H.R. Linden, (1963) "Reactivity of coals in High-pressure Gasification", Ind. ENG. Chem. Process Design Develop., **2**, 153, 1963.
- Feldkirchner, H.L., and J.L. Johnson, (1968) "high-pressure Thermo-balance," Rev. Sci. Instr., **39**, 1227, 1968.
- Foster, N.R., Weiss, R.G., Young, M.M. and Clark, K.N., (1984a) Fuel, 1984a. **63**, p66
- Foster, N.R., Young, M.M., Clark, K.N. and Weiss, R.G., (1984b) Fuel, 1984b, **63**, p716.

- Frederick T.J., Bell A.T., (1984a) Journal of Catalysis; **87**; pp196-209.
- Gibbins Jon R. and Kandiyoti Rafael, (1991) 'Liquefaction of coal in a flowing-solvent reactor', Fuel, 1991, Vol. **70**, August, p912.
- Gorbaty, M.L. and Maa, P.S., in "Coal Characterization for Conversion Processes", (Ed., Jacob and Freek), (1986), p91
- Gorin E., (1981) Fundamentals of coal liquefaction in: M.A. Elliott(Ed.), Chemistry of coal utilization. Second Supplementary Volume, John Wiley, New York, 1981, pp1845-1918.
- Heredy, L.A., Stevens, C.M. and Neuworth, M.B., (1965) Fuel, **44**, 1965, pp125-133.
- Hill, G.R., Hairiri, H., Reed, R. and Anderson, L.L., (1966) Am. Chem. Soc. Adv. Chem. Ser. 1966, **55**, p427.
- Hiteshue, R.W., Friedman, S. and Madden, (1962) R. U.S. Bur. Mines Rep. Invest. 6027, 1962.
- Huffman, G.P. et. al., (1992) Structure and Dispersion of Fe-Based Catalysts for Direct Coal Liquefaction. Preprint paper, 1992.
- Lazarov, L. and Angelov, G., (1968) Fuel, **47**, 1968, pp333.
- Li, C.Z., et al. (1993) "Characterization of tars from variable heating rate pyrolysis of maceral concentrates" Fuel, 1993, **72**, 3.
- Mahendra K.J., Deborah B. and Ramani N. (1991) Anaerobic bioprocessing of Wyodak coal Fuel, vol **70**, Fuel, 573.
- Miknis, P.F., et al. (1993) "N.m.r. determination of aromatic carbon balances and hydrogen utilization in direct coal liquefaction" Fuel, 1993, **72**, 217.
- Mitchell, G.D., Davis, A., and Derbyshire, F.J., (1989) In: Proceeding, 1989 International Conference on Coal Science, Tokyo, Japan, Volume II, pp.751-754
- Mobley D.P., Bell A.T., (1979) Effects of zinc chloride on the cleavage of ether structures present in coal. Fuel; **58**; 661-666. 1979.
- Monnier, J., Denes, G and Anderson B.R., (1984) "In Influence of carbon on iron in the hydrogenolysis of isopentane" The Canadian Journal of Chemical Engineering, **62**, 1984, 424.

- Montano, P.A., (1986) American Chemical Society, Division of Fuel Chemistry, Preprints, 31, (2), 1986, 226.
- Moroni, E.C., Fischer, R.H., (1980) Disposal catalysts for coal liquefaction. Presented at the 179th National meeting American Chemical Society, Houston, Texas, March, 1980.
- Moseley, F., and D. Paterson, (1965) "Rapid-temperature Hydrogenation of coal Char, Part 1," J. Inst. Fuel, 38, 13, 1965.
- Oblad, H.B., (1982) Ph.D. Dissertation, University of Utah, Dec. 1982.
- Peter S.C. and John D.C (1987) Mössbauer study of iron catalysis in Victorian brown coal liquefaction, Vol 66, Fuel, 1987, 669.
- Peterson, W.J./ Hamshar, J.A. and Oko, U.M., (1982) City Services R&D Co., Paper pres. to the Symp. on Sci. and Technol. of Synfuels, Colorado Springs, CO, Mar. 1-3, 1982.
- Pradhan, V., Tierney, J., Wender, I., and Huffman, G., Energy and Fuels, 5, 1991, p. 497.
- Sass, Alan, (1972) "The Garrett R&D Company Process for Conversion of Coal to Liquid Fuels," Pres. to 65th Ann. Meeting of AIChE, New York, Nov. 29, 1972.
- Schobert H.H. (1991) Coal Science II, 1991.
- Shah Y.T., (1981) Reaction engineering in direct coal liquefaction, Addison - Wesley, Reading, Massachusetts, 1981.
- Shroeder, W.C., (1961) Pat. No. 3,152,063, Apr. 21, 1961.
- Skulthai, T., (1987) "Low-Temperature Coal Depolymerization and Liquefaction", Ph.D. Dissertation, University of Utah, Salt Lake City, Utah, Dec. 1987.
- Tsai, C.H., "Reaction Kinetics and Mechanisms of Hydropyrolysis Processing of Tar Sand Bitumen and Related Materials" M.S Dissertation, University of Utah, Salt Lake City, Utah, 1987.
- Weisz P.B. (1982) The science of the possible: resource stoichiometry-the widening gap. Chemtech; 12; 114-115, 1982.
- Weller, S. and Pelipetz, M.G., (1951a) Proc. of Third World Petroleum Congress, Sec. IV, Subsect. I., 1951a, p91.

Weller, S. and Pelipetz, M.G., (1951b) Ind. Eng. Chem., **43**, 1951b, p1243.

Weller S W. (1982) Fourth international conference on the chemistry and uses of molybdenum, Golden, Colorado, USA, Climax Molybdenum Company of Michigan, pp179-186, 1982.

Whitehurst, D.D. and Mitchell, T.O. (1977) in 'Liquid Fuels from Coal'. (Ed. R.T. Ellington), Academic Press, NY, 1977, p153.

Whitehurst D. Duayne, Mitchell Thomas O. and Farcasiu Malvina , (1980) <<Coal Liquefaction, -The chemistry and Technology of Thermal Processes>>, 1980, p14

Whitehurst D.D., Mitchell T.O. and Farcasiu M., (1980) Coal liquefaction : technology of thermal processes, Academic, New York, 1980.

Wiser, W.H., (1968) Fuel 1968, **47**, p475.

Wiser W.H., (1975) preprints Fuel Division ACS Meeting, **20** (2), 122, 1975.

Wiser W.H., Shabtai J., Yang Q. and Yang Z., (1992) High conversion in coal liquefaction with low HC gas production. Preprints Fuel Division ACS Meeting, p456-463, 1992.

Zielke C W, Struck R T, Evans J M, Costanza C P, Corin E, (1966a) Molten catalysts for hydrocracking of polynuclear hydrocarbon. Industrial and Engineering Chemistry Process Design & Development, **5**(2); p151-157, 1966a.

Zielke C W, Struck R T, Evans J M, Costanza C P, Corin E, (1966b) Molten zinc halide catalysts for hydrocracking coal extract and coal. Industrial and Engineering Chemistry Process Design & Development, **5**(2); p158-164, 1966b.

DATE

FILMED

11 / 3 / 94

END