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**NOVEL PROCESS FOR DEPOLYMERIZATION OF COAL TO C₂-C₄
HYDROCARBONS**

Final Report for the Period September 1, 1989--August 31, 1993

**By
Wendell H. Wiser
Alex G. Oblad**

July 8, 1994

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**By
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FINAL REPORT

Contract Period 1 September, 1989 - 31 August, 1993

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July 8, 1994

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ABSTRACT

A principal objective of this work was to study the conversion of coal to C_2 - C_4 hydrocarbons in a two-stage reactor system. Coal was converted to liquids at 440°C in a stirred batch autoclave using tetralin as the hydrogen donor solvent. The liquids produced were separated from the unreacted coal and ash by filtration. The liquids were then fed into a second stage fixed bed reactor containing sulfided Ni-Mo/ Al_2O_3 and $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst. The liquids were hydrocracked on the dual functional catalyst giving high yields of C_2 - C_4 hydrocarbons. The pressure was 1800 psi and the temperatures were in the range of 425 to 500°C . The kinetic parameters of the conversion of coal liquids to gases were determined. The activation energy was determined to be 23.9 Kcal/mol. Cracking reactions involving C-C bonds appear to be rate-controlling.

Coal-derived liquids essentially free of the original hydrogen donor solvent were produced by recycling the liquids produced in the first stage several times. The liquids thus produced were used in the second stage to compare the conversions obtained from coal-derived liquids with those from coal-derived liquids containing the solvent.

Coal-derived liquids gave higher conversions and higher rate constant.

Experiments were conducted to study the effectiveness of a hydrogen donor solvent (tetralin) in a supercritical phase in controlling agglomeration and adhering tendency of a caking coal. It was observed that supercritical tetralin was as effective as tetralin in the liquid phase in controlling agglomeration and adhering tendency.

Pressure fluctuation measurements were made in a fluidized bed reactor while fluidizing sand particles with nitrogen at atmospheric pressure and 500 psi. By Fast Fourier Transform technique, the pressure fluctuation data were converted to Power Spectral Density Function (PSDF). The variation of PSDF with frequency indicated if the bed is fluidizing.

CHAPTER 1

INTRODUCTION

Coal is the most abundant fossil-fuel resource occurring in the world. In the early part of the twentieth century, coal had emerged as the dominant energy resource used in the industrialized world. However, as petroleum and natural gas resources became available in large quantities, coal was replaced by these two resources. As reserves of petroleum and natural gas decline, coal is expected to return to its position of dominance. Hydrocarbon gases produced from coal may contribute significantly to the replacement of petroleum and natural gas in the future.

In the U.S., more than five percent of petroleum is used to supply C_2 - C_4 hydrocarbons as the feedstock in the petrochemical industry. C_4 hydrocarbons are also useful as motor fuel due to their high octane number and their ability to burn cleanly. This work is concerned about the production of high yields of C_2 - C_4 hydrocarbons from coal.

In 1982, Kithany and Wiser¹ studied a process to convert coal to high yields of C_2 - C_4 hydrocarbons. They conducted experiments in a stirred batch autoclave using a

Haiawatha high volatile bituminous coal and sulfided Ni-Mo/Al₂O₃ and SiO₂-Al₂O₃ catalyst. About 50 weight percent of the coal was converted to C₂-C₄ hydrocarbons at a temperature of 500°C, pressure of 2000 psi and reaction time of 30 minutes.

Later, in 1993, Liu and Wiser² determined the reaction kinetics of coal conversion to C₂-C₄ hydrocarbons in a single stage using the same catalyst as in the previous study. They also conducted some experiments to determine the mechanism of formation of hydrocarbon gases from coal. They observed that coal is converted to gases in two steps. Coal conversion to liquids occurs very rapidly and is completed within 10 minutes. In the second step, the liquids are converted to gases rather slowly and follow first order kinetics with an activation energy of approximately 23 Kcal/mol. From the study of model compounds, it was concluded that the liquids are converted to gases by a carbonium ion mechanism.

When a catalyst is used with coal, the catalyst encounters a severe environment. The catalyst is deactivated not only by sulfur and nitrogen in the coal, but the active sites of the catalyst are poisoned by the metals in the mineral matter of the coal and organometallic structures, making regeneration of the catalyst impractical. From the studies of Liu and Wiser, it was observed that coal conversion to liquids is fast whereas the conversion of liquids to gases is rather slow. So, it is advantageous to

separate the two steps, making it possible to optimize the two steps individually. In the first stage, coal can be converted to liquids using a disposable and/or inexpensive catalyst. The liquids produced in the first stage can then be converted to C_2 - C_4 hydrocarbons in the second stage using a dual functional hydrocracking catalyst, which is relatively more expensive.

The liquids produced in the above two studies are very light. Visual observation of the liquids led to the conclusion that at the reaction conditions employed in these studies, the liquids would probably be in a supercritical phase as the liquids are of molecular sizes with critical temperatures like those of xylenes and toluenes. If the process were to be carried out on a large scale, the coal-derived liquids will be used to facilitate feeding of the coal into the reactor and as the hydrogen donor solvent for converting coal to liquids. Caking coals tend to agglomerate and adhere to the reactor walls causing serious problems of the operability of the process. It is known that hydrogen donor solvents in the liquid phase effectively control agglomeration and adhering tendency of caking coals. However, it is not known if the same hydrogen donor solvent when it is in a supercritical phase would be effective in controlling agglomeration and adhering tendency of caking coals. So, it is important to ensure the effectiveness of the supercritical hydrogen donor solvent in controlling the agglomeration and adhering tendency.

Fluidized bed reactors offer several advantages for a process like this compared to other types of reactors. There are several techniques available to determine the fluidization characteristics of the beds. However, they are, in general, quite expensive and difficult to use. There is a need for a relatively simple technique for determining whether the bed is fluidizing.

The objectives of the present work are:

- (1) To convert coal to liquids in the first stage, using a hydrogen donor solvent, tetralin. The liquids produced in the first stage are to be converted to gases in the second stage using the same dual functional hydrocracking catalyst used in the previous two studies.
- (2) To determine the kinetic parameters for the conversion of liquids to gases in the second stage and compare with the kinetic parameters determined by Liu².
- (3) To produce coal-derived liquids essentially free of the original hydrogen donor solvent by recycling the liquids produced in the first stage and to convert these liquids in the second stage to see if similar conversions are obtained.
- (4) To study whether a hydrogen donor solvent in a supercritical phase is effective in controlling agglomeration and adhering tendency of a caking coal.
- (5) To develop a relatively simple technique for determining whether the bed is fluidizing.

CHAPTER 2

LITERATURE REVIEW

The chemistry underlying the technology involved in this study appears to be quite specific in relation to the structure and other features of the feed material. For this reason these features are discussed in this report.

2.1 Coal Structure

Coal is an aggregate of heterogeneous substances composed of organic and inorganic materials. The organic materials are believed to be predominantly of plant remains. The plant matter deposited in sedimentary strata was subjected to bacterial action and other chemical alterations and geological effects. Through a series of evolutionary changes the decaying matter transformed into humic acid which then converted sequentially into peat, subbituminous coal, bituminous coal, and finally into anthracite.³ Mineral matter in coals resulted from various sources: direct precipitation from solution, precipitation by organic metabolism, transportation by water, secondary precipitation from ground water, etc.⁴

2.1.1 Petrographic composition

As many physical and chemical properties of coal vary with the petrographic composition (type) and rank, coals are classified by their type and rank. The microscopic study of

coal and the relation of its different visible features to the original plant material forms the basis of coal petrography. Petrographic components or macerals are classified into three main groups called vitrinite, exinite, and inertinite, and many individual macerals on the basis of source material (woody versus nonwoody tissues), morphology, nature of formation (biochemical degradation versus charring by fire), similarity in chemical composition, internal structures, level of reflectivity or color, and degree of coalification.⁵ A detailed description and classification of macerals was given in the International Handbook of Coal Petrology (International Committee for Coal Petrology (ICCP), 1963) and its supplements (ICCP, 1971, 1976).

Storch and co-workers⁶ studying the role of petrography in coal liquefaction behavior concluded that two compositional parameters must be considered in coal liquefaction: the petrography and the moisture- and ash-free (MAF) carbon content of the coal. They found that certain macerals were less reactive than others, and for a given maceral type, a minimum in conversion occurred with increasing carbon content. Given and co-workers⁷ found that the conversion to liquids increases with an increase in total reactive macerals. Reactives are defined as the sum of vitrinite, pseudo-vitrinite (a subcategory of vitrinite) and sporinite (a subcategory of liptinite) contents.

2.1.2 Rank

Rank signifies the degree of maturation in the coalification of plant material and is the most important property for classifying coals. Lignite is the lowest ranked coal, followed in increasing rank by subbituminous coal, bituminous coal, and anthracite. The lower the coal rank, the lower is its fixed carbon content and the higher its oxygen and hydrogen content. Generally, the lower the coal rank, the lower also is the calorific value and the higher the fraction of moisture and volatile matter.

Given and co-workers⁸ concluded, based on a series of experiments, that the coals having greater than 90% MAF carbon yielded very low benzene-soluble product. Maximum conversions to benzene-soluble products were for coals having 82-84% MAF carbon.

2.1.3 Coal porosity⁹

Aromatic and hydroaromatic units, the main building blocks of coal, are connected by cross links such as methylene, oxygen, and sulfur. Various heteroatom functionalities are located on the periphery of the aromatic and hydroaromatic units. The extensive porosity of coal results from the poor alignment of these units in three dimensions. Porosity in coal is of great influence, because it is through these very small capillaries that reagents or vapors have to pass during adsorption or chemical reaction processes.

The specific internal surfaces of bituminous coals are in the range of 30-100 m²/g and are situated almost entirely in the ultrafine capillaries. These capillaries have widths below 40 Å and are accessible only through constrictions of width 5 to 8 Å.¹⁰

As coal gasification processes involve chemical reactions between coal surfaces and gases, the overall rates of reactions are determined by the ease of diffusion of reactant molecules into the pores and the product molecules out of the pore system. This is especially true because most of the surface area of coals is located in micropores.⁸ The preservation of microporosity in coals as they are converted to chars and cokes results in high reactivity to gasification reactions.

During coal liquefaction in the presence of a hydrogen donor solvent at 400-450°C, the free radicals formed by the thermal cleavage of covalent bonds are stabilized by hydrogen transfer from the hydrogen donor solvent. If the transfer is not effective the unstabilized free radicals may result in retrogressive polymerization reactions. To avoid this, the donor solvent should be in intimate contact with the free radical species. The donor solvent would be imbibed into the coal structure even if the coal were devoid of porosity. However, the time required for completion of imbibition would be considerably reduced by the presence of porosity within the coal. Appearance of plasticity during coal liquefaction indicates the breakage of cross links in

coal and reduction of molecular weight. However, this involves the disappearance of microporosity in coal. Neavel¹¹ has shown that the loss of plasticity of caking coals brought about by introduction of cross-links through oxidation has a deleterious effect on liquefaction yields.

2.1.4 Structural parameters

Though it is difficult to define the concept of coal structure because of the difficulty of assigning a structure to a mixture, coal can be described in terms of structural parameters leading to an understanding of the "average coal structure" which is useful in understanding and predicting the coal conversion processes. Some of the parameters that are of importance are: size distribution of the macromolecules, degree of cross linking, type of cross links, carbon aromaticity, average size of condensed aromatic units, number of hydroxyl groups, scissile bridging structures.

2.1.4.1 Molecular weight. There are a number of different techniques such as depolymerization,^{12,13} reductive alkylation,^{12,14,15} acyclation,^{12,16} and base/alcohol hydrolysis,^{17,18,19} all of which convert the largely insoluble coal to soluble fragments by breaking the cross-links in the coal. The conversion is carried out under mild conditions to make sure that the coal molecules remain unchanged as far as possible, especially by avoiding the cracking reactions which take place above 350°C. Thus, all of the methods

report the molecular weight of the coal fragments between cross-links. Because of the difficulty in breaking the cross-links in a known way and obtaining number averaged molecular weights instead of weight averaged molecular weights, there are uncertainties about the reported values which range from 300 to 1000.

2.1.4.2 Aromaticity of coal. The carbon aromaticity of coal is defined as the ratio of aromatic carbon to the total carbon. In the oxidative degradation technique the aliphatic portion of the coal is selectively oxidized with oxidants such as HNO_3 , $\text{K}_2\text{Cr}_2\text{O}_7/\text{HNO}_3$, $\text{KMnO}_4/\text{OH}^-$, and peracetic acid. Using these oxidants, some workers have concluded that the coal is predominantly aromatic and contains many condensed rings.^{20,21} Other authors using NaOCl/OH^- have come to the conclusion that coals contain large amounts of quarternary aliphatic carbon and 50% aromatic carbon or less.²² A method pioneered by Deno^{23,24} uses trifluoroacetic acid in combination with hydrogen peroxide to selectively oxidize and destroy the aromatic rings and to preserve most of the aliphatic structures. As the yields obtained were in the range of 60-70%, the technique does not give the values for the percentage contribution of aliphatic structures in coal. Nevertheless, the technique is valuable in characterizing a part of the coal structure which is lost in the other oxidative degradation techniques.

Because of the difficulties involved in selectively oxidizing either aliphatic or aromatic portions, other

direct techniques such as x-ray scattering,^{25,26} ultraviolet technique,²⁷ polarographic reduction,²⁸ FTIR,^{29,30} and C-13 NMR^{31,32} have been used.

The NMR cross-polarization technique developed by Pines et al.³³ overcomes the problems of dipolar line broadening caused by protons in the coals by utilizing high-power proton decoupling. The spectra of whole coals obtained with this technique show two overlapping bands; one due to aromatic carbons, the other due to aliphatic ones. In the spectra the aromatic resonance is asymmetric and somewhat broad because of the large chemical shift anisotropy of the aromatic carbons. The problem is overcome by spinning the coal sample rapidly (3KHz) at the "magic angle" reducing the anisotropic chemical shift contribution to the spectrum to zero so that the aromatic and aliphatic resonances are completely separated.³⁴

Most of the problems that might invalidate the quantitative reliability of the technique have been satisfactorily resolved and the technique is the most reliable available for determining the carbon aromaticity of coals. A number of studies^{35,36,37} were conducted using this technique and it can be concluded that coals are highly aromatic materials, and that their aromaticity increases more or less gradually with coal rank. The aromatic carbon content increases from 50-60% for some subbituminous coals to over 90% for anthracites. In the case of macerals from an

hvAb coal, the carbon aromaticity values decreased in the order fusinite > micrinite/vitrinite > exinite.

The sizes of ring systems have been studied using techniques such as C13 NMR, oxidative degradation, sodium dichromate oxidation, performic acid oxidation, NaOH/alcohol hydrolysis, etc. These values are obtained by deducing ring structures from elemental composition and aromaticity data or by degrading coal and identifying the products. Most recent studies have indicated that the condensed units in coal are fairly small -- often not more than four rings.

Hydroaromatic structures are important in coal conversion processes because of their presence in coal itself. They readily transfer hydrogen required for stabilizing the free radicals produced in the thermal cracking reactions. A number of studies^{38,39,40} have been conducted to estimate the hydroaromaticity in coals and it has been estimated that about 15 to 25% of the total carbon is in the hydroaromatic structures of coals of 70-85% carbon. Hydroaromaticity of coals decreases as rank increases reaching about 10% in coals of 90% carbon and is gradually eliminated in the anthracite range.⁴¹

2.1.4.3 Bridge structures. Coal depolymerization studies conducted with phenol-boron trifluoride at 100°C indicate the presence of methylene bridges and a possibility of the presence of other aliphatic bridges.⁴² Among the aliphatic bridge structures methylene bridges are of

particular importance because of the high probability of these bridges being broken due to the carbon-carbon bonds on both sides of the bridge being activated under the reaction conditions used in coal depolymerization.⁴³ In high volatile bituminous coals the breaking of aliphatic carbon bridges is considered to be the major means of depolymerization. In bituminous coals of higher rank ($C > 83\%$), the depolymerization product yield was observed to decrease sharply with increasing rank. This may be due to the bridge structures being associated with tetralin-like hydroaromatic rings which involves breaking of several bonds between two aromatic groups to effect depolymerization.

Lazarov and Angelova,⁴⁴ by treating coals with sodium in liquid ammonia (Diaryl ethers react easily with this reagent whereas aliphatic ethers do not) found that about 50% of the oxygen in a coking coal (87.6% C, maf) was present in diaryl ether or arylalkyl ether linkages whereas less than 4% of the oxygen in a high volatile bituminous coal was found to be in similar structures. Similar results were obtained by other workers^{45,46} providing strong evidence for the presence of oxygen bridges in coals.

2.1.4.4 Functional groups and heteroatoms. Most studies concerning functional groups in coal were conducted using infrared spectra of solid coals. Functional groups containing oxygen are the most predominant. The groups include alcohols, ethers, carboxylic acids and carbonyls.

Several authors have reviewed the quantitative determination of these groups.^{47,48} Good correlations exist between the rank of the coal and the contents of various functional groups. Bituminous coal is expected to have one ether, one phenol, and slightly more than two aromatic nuclei per molecular unit whereas no carboxylic acids or methoxy groups are expected. Subbituminous coals have one carboxylic acid, one ether, two phenols, and two aromatic nuclei. Lignite is expected to have more than one carboxylic acid, three phenols, one ether and less than two aromatic nuclei.⁴⁹

A number of good reviews were published on the forms of sulfur found in coal.^{50,51} The two major classes of sulfur in coal are inorganic sulfur (mostly pyrite) and organic sulfur. The chemistry of sulfur and oxygen species are very similar in coals because sulfur is introduced via exchange of oxygen functionality. Major sulfur functional groups are thiols, sulfides, and heterocyclic aromatic rings (thiophene derivatives). The content of thiols is substantially larger in lignites and high volatile bituminous coals than in low volatile bituminous coal. The fraction of aliphatic sulfides (R-S-R) remains constant at about 18-25%.⁵²

Nitrogen content of all coals is constant at about 1-2% showing little variation. The major groups are heterocyclic rings such as pyridine or pyrrole derivatives.

2.1.4.5 Mineral matter in coal. The clay minerals are the most abundant mineral assemblages found in coal,

constituting 60-70 wt% of the average low temperature ash. The second most abundant mineral phase in U.S coal is quartz, accounting for 20-30 wt% of the mineral matter assemblage. The minor minerals are carbonates, disulfides, pyrite, marcasite, sulfides, sulfates.⁵³

2.1.5 Average chemical structures

Several investigators have developed illustrative skeletal structures for typical coals or, more correctly, vitrinite or vitrinite rich coals. These structures have been developed by synthesis of information obtained by various techniques such as x-ray diffraction, infrared and nmr spectroscopy, elemental and functional group analysis, molecular weight measurement and chemical degradation of the coal substance. These models help visualize the chemical structure of coal and help predict the chemical behavior of coal under certain circumstances.

There are currently three different types of models proposed to represent the organic structure of coal: aliphatic/polyamantane model,²² aromatic/hydroaromatic model^{54,55,56} and molecular sieve model.⁵⁷ As the aliphatic/polyamantane model and the molecular sieve models do not adequately explain the structure of the coal, only the aromatic/hydroaromatic model is briefly explained below. The aromatic/hydroaromatic model is the generally accepted model.

One of the early aromatic models proposed is shown in Figure 2.1.⁵⁴ The model for an 82% carbon vitrinite corresponding to a high volatile bituminous coal has as basic unit 9,10-dihydroanthracene. It shows highly substituted aromatics, functionalities known to be present in coal and methylene bridges.

The model proposed by Wiser⁵⁶ (Figure 2.2) includes a distribution of aromatic-unit sizes ranging from one to five rings (a portion of which are hydroaromatic), connecting linkages between ring clusters consisting of short aliphatic chains (C_1 - C_3) and ether bridges. The connecting linkages indicated by arrows represent relatively weak bonds which account for the rapid disintegration of coal into smaller soluble fragments. The major strength of this model is its ability to explain the behavior of coal during liquefaction.

Representations of the basic units of coals of different ranks are shown in Figure 2.3.⁵⁸

2.2 Coal liquefaction

2.2.1 Definition of coal liquefaction

The term liquefaction is used to describe conversion of coal in which the major product is a "liquid." The conversion is universally defined as:

Figure 2.1. Molecular structure of coal proposed by Given
Reprinted with permission (ref. 54)

Figure 2.2. Schematic representation of structural groups and connecting bridges in bituminous coal by Wiser

Figure 2.3. Representative partial structures of different ranks of coal proposed by Wender
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$$\% \text{ conversion} = \frac{\text{maf coal in} - \text{maf insoluble residue out}}{\text{maf coal in}} \times 100$$

The definition of maf-insoluble residue is not universally agreed on and different investigators have defined conversion on the basis of product's solubility in different solvents such as benzene, cresol, tetrahydrofuran, quinoline, and pyridine. The conversions with the solvents cresol, tetrahydrofuran, quinoline, and pyridine agree rather closely with one another but are substantially higher than the conversion with the solvent benzene.

2.2.2 Mechanism of coal liquefaction

The reactive macerals of coal are considered to be highly cross linked, amorphous, macromolecular networks consisting of a number of condensed aromatic units joined by relatively weak linkages.⁵⁹ The weak bonds such as hydrogen bonding and charge-transfer complexes are overcome to some extent at temperatures below 250°C, yielding extracts of up to 40-50% of some bituminous coals. As the temperature is increased above 350-375°C, thermal disintegration of the relatively weak bonds consisting of aliphatic and etheric bridges takes place giving rise to reactive fragments of free radicals.^{60,61} If these radicals are stabilized by redistribution of hydrogen in the organic matrix (autostabilization) or by donation by the solvent, they give rise to stable species with molecular weights in the range

of 300 to 1000. If the radical species are not stabilized because of the unavailability of hydrogen or because of the concentration of the radicals becoming excessively large, the fragments recombine or polymerize giving rise to very high molecular weight compounds and coke. In the autostabilization portion of the process the solvent may act as a net shuttler of hydrogen, redistributing hydrogen within the coal matrix.⁵⁹

As the conversion of preasphaltenes and asphaltenes progresses, the hydroaromatic structures in coal are dehydrogenated increasing the aromaticity of the residue substantially.

2.2.3. Effect of coal particle size

Studies indicate that the effect of particle size on solvent extract yield is very small over the normal size of interest (1 to 1200 microns). Careful short reaction time autoclave studies of the particle size range <45, 45-75, 75-425, and 425-600 microns have been carried out using several bituminous and subbituminous coals.⁶² The results show that the particle size effects, if they exist, are within the variation of data due to minor differences in parameters such as time, temperature profile, solvent/coal ratio etc.

2.2.4 Effect of coal surface properties

Porosity and surface area measurements were conducted before and after partial liquefaction of various coals to

evaluate the effect of coal surface properties on liquefaction. The studies show that the coal particle pore structure is not conducive to the intraparticle transport of donor solvent and liquefaction product molecules and therefore does not play a significant role in the dissolution process.⁶³ The coal particles in these studies had very little micropore structure, low total pore volume and had about 5-10% void volume. Total pore volumes were typically in the range 0.08 to 0.16 cm³/g. Of the total pore volume, about a third is too small for organic molecules to gain access. An additional third is capable of diffusion of solvent molecules and low molecular weight liquefaction product molecules. It was observed that during dissolution the void volume fraction of these two size ranges only increases slightly. The remaining third of the pore volume consists of large cavities and cracks, i.e., the macropore structure.

2.2.5 Changes in gross particle morphology during liquefaction

Photomicroscopy studies of coal particles have been conducted to understand the physical processes in coal dissolution.⁶²⁻⁶⁵ Unstirred autoclave experiments conducted at temperatures up to 450°C on West Kentucky bituminous coal and Wyodak subbituminous coal in various solvents indicate that the overall size and shape of the particles were not changed despite a conversion to pyridine solubles of 80-85%

for the West Kentucky coal and about 70% for the Wyodak coal. The Wyodak residue particles were slightly smaller than the parent coal, while the West Kentucky particles were larger. Both residues were fragile and easily shattered.

Photomicrographs of the residue from stirred reactor runs for the same coals showed that the residue particles were extremely small indicating that rapid stirring provides enough stress to completely disintegrate the particles.

The coal particles are relatively featureless initially and will not break up even with stirring at reaction conditions if there is no conversion to soluble form. As the organic material is converted the particle surface is eroded and a macropore system begins to form on the surface eventually extending into the bulk. The micropore system does not seem to be affected significantly. With violent agitation or stirring of the system the particles break up as the dissolution process progresses. In addition to the reaction in the bulk solution, reactions and dissolution occur within the particle further weakening the coal particle. At some point, the particle is broken into pieces due to the external stresses such as stirring, rendering intraparticle diffusion to be completely insignificant. As the reactions occurring within the particle are likely to be different from the reactions occurring in the bulk solution, they contribute differently to the product distribution and composition.⁶⁵

2.2.6 Effect of coal rank on liquefaction

Researchers at Pennsylvania State University and Gulf Research and Development have conducted experiments to correlate coal rank with liquefaction behavior, examining coals from most of the seven major U.S. coal provinces.^{7,8,66}

The highest rank coals were found to be relatively unreactive. Coals of high rank (>88% MAF C) produce negligible CO, CO₂, and H₂O and very little hydrocarbons, and are found to be having low ultimate reactivities and low rates, even if they are rich in vitrinites. These coals have highly aromatic structures with very little reactive hydrogen and few reactive functional groups. The hydrogen consumption of these coals is low and the H/C mole ratios of products and residue are also very low.

The lowest rank coals (<80% MAF C) are very reactive. Their hydrogen consumption is high and they produce substantially large quantities of CO, CO₂ and H₂O, even at short times. Even though they are slow to react they ultimately reach high conversions. The initial products are also very reactive as evidenced by the continuing hydrogen consumption and generation of oxygen-containing products. Rates of conversion are prone to be limited by hydrogen-donor availability and therefore they require good sources of hydrogen. Differences in hydrogen donor capability of the solvents may be the cause for disagreement in the literature over the ultimate conversion of low-rank coals.

Intermediate rank coals reach their ultimate conversions quickly and initial yields that are rich in asphaltols are high but decrease with time. Their ultimate hydrogen consumption and yields of hydrocarbon gases and light liquids are the highest. As time progresses, they produce some H_2O , CO , and CO_2 . However, they appear to be more reactive than lower rank coals because the initial products are soluble in pyridine due to the products being less functional and having lower molecular weight.

2.2.7 Effect of mineral matter on liquefaction

The correlation between mineral-matter abundance and liquefaction efficiency is well known.^{7,8,66} Of all the coal minerals, pyrite appears to have the most positive catalytic effect upon coal liquefaction.⁶⁷ The pyrite is converted to pyrrhotite in the early stages of liquefaction. It is the pyrrhotite that acts as the catalyst to the reaction.⁶⁸ It has been indicated that the actual effectiveness of the pyrrhotite as a catalyst depends upon the iron content and number of lattice vacancies within the pyrrhotite structures. Since pyrite reduces nearly quantitatively to H_2S and FeS during the first two minutes, the increases in rates of solvent-solvent interactions are probably not due to iron sulfides alone; hydrogen sulfide may act as a radical chain-transfer agent. There is also some indication that the clay minerals may act as catalyst in the liquefaction processes.⁶⁹

2.2.8 Effect of solvent properties on liquefaction

Coal liquefaction in a solvent may be considered as a three-step process involving dissolution, hydrogen transfer, and hydrogenation. The chemical composition of the solvent controls the overall liquefaction behavior and can affect each of the above steps.

The free radicals produced by thermal fragmentation of macromolecular structure in the coal can be stabilized in three possible ways.^{70,71} 1) Hydrogen abstraction from the solvent or a hydrogen-rich portion of the coal; 2) either elimination of part of the radical particle with associated group migration, or rearrangement to form another more stable structure, or both; 3) combination reaction such as condensation or alkylation with another molecule in the solvent, which could also be a radical. The path taken is determined by the presence and type of hydrogen donors.

The quality of the solvent which plays a very important role on the mechanism of coal dissolution and subsequent upgrading of coal liquids is determined by four quantities, namely H-donors, phenols, H-shuttlers, and H-abstractors.⁶²

2.2.8.1 Hydrogen donation from the solvent. In a liquefaction process hydrogen can be obtained from hydrogen gas, solvent, coal, and coal-derived materials such as heavy residue and solvent-refined coal.⁶¹ The requirement for hydrogen is greatest during the initial stage of reaction,

when large numbers of free radicals are produced, and decays gradually as the remaining bonds become increasingly more difficult to cleave thermally.

The concentration of tetralin is a good indicator of the hydroaromatic concentration in the solvent for low boiling solvents.⁶³ Researchers at Exxon⁷² have correlated the conversion of coal to cyclohexane-soluble products with a "solvent quality index" which is an indication of the concentration of hydroaromatics. For low quality solvents elemental hydrogen can help increase the degree of conversion.

The principal sources of hydrogen are partially hydrogenated aromatic hydrocarbons: tetralin and its homologs, partially hydrogenated pyrene, phenanthrene, and other polycyclic aromatic compounds.

High concentrations of active hydroaromatics in the solvent also are important in achieving rapid desulfurization and deoxygenation.

2.2.8.2 Effect of polyaromatic hydrocarbons. H-donors are the major controlling species in coal liquefaction. However, there are other important factors involved. It has been reported that coal or coal-derived products can provide significant amounts of hydrogen.. It has been observed that reasonably good coal conversions can be achieved in the absence of hydrogen gas or a hydroaromatic solvent but in the presence of a polyaromatic nondonor solvent such as

naphthalene.^{73,74} The phenomenon by which a polyaromatic nondonor solvent aids in the redistribution of hydrogen among different coal species is termed H-shuttling.

As no net hydrogen is donated no net change in the shuttler or the H/C ratio of the coal occurs. However, the net content of unsaturated carbons in the coal products increases. The usefulness of this type of process is limited because no net hydrogen is donated. The amount of labile hydrogen available from coal itself is limited. For a typical bituminous coal the amount of available hydrogen of this nature is about 1.9 gH/100 g MAF coal.⁷⁴

Among the polyaromatic nondonor solvents the more highly condensed ring systems were effective in promoting coal conversions, with the exception of anthracene. This is in line with the ability of solvents of higher boiling points to increase the conversion efficiency.

Single ring aromatic compounds may not be good H-shuttlers because the molecules are not labile toward acceptance of H from the coal. Though pyridine is an excellent solvent for coal products, it does not promote coal solubilization at either short or long times.

When the content of H-donors is limited in the solvent H-donors and H-shuttlers can work together synergistically.

2.2.8.3 Effect of phenols. Several researchers have reported the beneficial effects of phenols on liquefaction.^{75,76} Phenolic compounds constitute a major

portion of the recycle solvents in liquefaction processes and can be divided into two parts: light phenols (<9 carbons) which represent about 2/3 of the total -OH content per unit weight of the solvent, and heavy phenols (>9 carbons).

The light phenols do not contain hydroaromatics and are not considered as classical hydrogen donors. In liquefaction reactions involving solvents with limited hydroaromatic content, the light phenols can donate hydrogen through alkylation reactions with aromatic rings and the phenols can become incorporated into coal products. Light phenols tend to become incorporated in the coal products even when the hydroaromatic content of the solvent is relatively high.

The heavy phenols too can donate hydrogen through alkylation reactions as in the case of light phenols. Additionally, the heavy phenols have the potential of hydroaromatic structures and could also function as hydrogen donors by dehydrogenation. The hydroaromatic phenols have been found to be excellent H-donors in coal conversion⁷⁴.

2.2.8.4 Effects of H-acceptors. Some solvent components undergo cracking to form hydrocarbon gases, molecular weight reduction and dehydroxylation leading to a demand for hydrogen. Because of the consumption of hydrogen by the solvent components, the overall hydrogen available for reaction with coal is reduced. The H-acceptors promote

char formation from liquefaction products and even solvent components, and lead to reduction in apparent conversions.⁷⁷

2.2.8.5 Char formation from solvent. The organically derived solids, called char or coke, are commonly accounted for with unconverted coal as they are physically inseparable from it. The high chemical functionality in the coal-derived liquids appears to be closely related to the tendency toward char formation from those liquids. Coal dissolution products formed in the early stages of coal liquefaction in a solvent are mostly benzene insoluble, high in molecular weight and phenol content.⁶³ On the other hand, the products formed during the later stages of reaction are less functional and benzene or hexane soluble. Therefore the products from the early stages of reaction are conducive to char formation due to their high functionality.

2.2.8.6 Regeneration of the H-donors in recycle solvents. Hydroaromatics in the solvent are converted to aromatics upon reaction with coal.^{70,71} The solvent can be replenished by conversion of coal to provide new additional solvent, or the hydrogen-depleted solvent can be rehydrogenated by gaseous hydrogen. However, coal-derived liquids of an appropriate nature to serve as solvent reach appreciable quantities only after about 50% of the oxygen has been removed.⁷⁷ Similarly, solvent rehydrogenation is slow compared with H-donation from solvent to coal or coal-derived products. When the hydroaromatics are depleted from

the solvent, side reactions such as phenol condensation, solvent dimerization, or char formation occur. However, mineral matter in coal is known to exhibit hydrogenation activity, the most important being pyrites.⁶⁷⁻⁶⁹ The mineral matter being in a finely divided state can have appreciable surface area. In addition to the mineral matter in coal, reactor solids high in iron content may also be important in catalyzing the hydrogenation reactions.

2.3 Coal gasification

Gaseous fuels produced from coal can be divided into three classes based on the heating value of the fuel produced.⁷⁸ Low-btu gas (heating value 100-200 Btu/scf) is produced by gasifying coal with steam and air. The nitrogen from air acts as a diluent reducing the heating value of the gas produced. Medium-Btu gas (heating value 200-500 Btu/scf) is the product of coal gasification with steam and oxygen. Medium-Btu gas can be upgraded to high-Btu gas (heating value 900 Btu/scf) by catalytic shift conversion and methanation. All these gases are further cleaned to remove particulates, tars, H₂S and CO₂.

Coal gasification to pipeline quality high-Btu or substitute natural gas involves four basic steps.⁷⁹ Coal is first devolatilized to produce char and some methane.

In the second step, the devolatilized coal (char) is reacted with steam and oxygen to produce synthesis gas, a mixture of CO and H₂.

Since the reaction is highly endothermic it requires large amounts of heat which is most commonly supplied by partial combustion of the char.

Oxygen, though much more expensive than air, is desirable to avoid the dilution of the product gas with nitrogen which reduces the heating value of the product gas.

CO₂ produced in the above reaction is converted back to CO by reaction with hot char in the reactor by the Boudouard reaction.

In the third step, the CO reacts with steam to produce more H₂ by the water-gas shift reaction, which is used mainly to adjust the H₂:CO ratio.

This reaction is used to generate additional H₂ within the gasifier to promote direct hydrogasification of char to methane. The hydrogasification reaction is exothermic, and helps provide heat for the steam-carbon reaction.

Alternatively, the shift reaction can be carried out externally to adjust the H₂/CO ratio to a value of 3 for

production of methane by the highly exothermic catalytic methanation reaction. But the heat generated in this reaction can not be effectively utilized as this reaction is carried out at a lower temperature to favor methane formation and in a separate reactor.

Hydrogasification and catalytic methanation are the two basic routes by which methanation can be carried out, which is the final step in the production of high-Btugas.

Hydrogasification:

Catalytic Methanation:

Low-btu gas which is primarily used for electric power generation on site or for heating in industrial plants can be produced using Lurgi and U-gas processes. Medium-Btu gas can be produced by Lurgi medium-Btu, Koppers-Totzek, Winkler, Texaco processes. Lurgi high-Btu, Bi-gas, Synthane, steam-oxygen Hygas are examples of processes for production of high-btu gas.

2.3.1 Hydrogasification

Steam/air or steam/oxygen gasifiers operate at high temperatures (950°C or higher) and pressures to increase reaction rates, throughput, and steam and carbon conversion,

thus decreasing the gasification costs. The off gas contains little or no methane (the higher the temperature, the lower the methane content) and has a low H_2/CO ratio.

Low temperatures, high pressures and a high hydrogen-to-oxidant ratio in the feed increase the concentration of methane in the equilibrium gas mixture. By using pure hydrogen nearly 75% of the carbon is converted directly to methane in the gasifier. Carbon dioxide and steam concentrations in the off gas are low and only a light methanation step is required to produce the final product.

In the Hydrane process,⁸⁰ developed by the U.S. Bureau of mines, only hydrogen and coal are fed into the gasifier. The Hydrogen is produced in a separate unit by steam/oxygen gasification of the unreacted char from the hydrogasifier. The off gas contains about 94% of the methane required for a pipeline quality gas. Consequently, only a light methanation would be required to produce the final product. The experimental gasifier was operated at pressures of 20 Mpa and temperatures up to 750°C.

The Hygas process,⁸¹ developed by the Institute of Gas Technology, was originally designed to operate with a relatively pure hydrogen stream produced in a separate unit. Later, the steam/oxygen process to produce hydrogen has been incorporated directly into the Hygas gasifier, so the carbon oxides from the off gas cannot be removed. Therefore, the process cannot be considered a true hydrogasification

process. The Hygas gasifier, like the Hydrane gasifier, has a first dilute phase stage followed by a second dense-phase fluidized bed stage. Pressures of 6.8 to 10.2 Mpa and moderate temperatures of 930 to 980°C are selected to enhance methane formation. The off gases have 15 to 20% methane which represents about 60% of the methane in the final SNG product.

There are some basic problems associated with the hydrogasification processes. First, at 700-800°C, the temperature range that permits an efficient direct synthesis of methane, the rate of coal conversion is low. Increasing the temperature does increase the rate of conversion, but the equilibrium content of methane decreases with increasing temperature. Secondly, Hydrogasification requires an external hydrogen source to maintain the high hydrogen partial pressures. Finally the heat released in the hydrogenation step cannot be fully utilized.

2.3.2 Catalytic gasification

The overall synthesis of methane can be represented as below

As can be seen the overall reaction is very nearly thermoneutral ($\Delta H = 3.7$ Kcal/mole). The gasification step is highly endothermic and requires a high reaction temperature of about 950°C whereas the methanation step is highly exothermic but requires a much lower reaction temperature of about 430°C. The heat evolved in the methanation step cannot be recycled back to the gasifier which must be maintained at the higher reaction temperature. This leads to poor thermal efficiencies. The major problem with the above ideal gasification route is that the rate of methane formation at low temperatures is slow relative to the other gasification reactions.

It has been known for sometime that alkali metals catalyze the reaction of carbon with steam to form mainly carbon monoxide and hydrogen. More recent studies by Exxon have shown that potassium catalysts also promote the gas phase shift and methanation. Alkali metal catalysts also reduce agglomeration of caking coals.

2.3.3 Exxon process

Exxon Research and engineering Co. has developed a process⁸² based on the ideal gasification route using potassium carbonate catalyst. It was shown that potassium carbonate of from 10 to 20 mass percent of the coal at 700°C results in commercially acceptable rates of gasification. Since the methanation reaction is close to equilibrium there is consequently no buildup of carbon monoxide and hydrogen

as would occur in an uncatalyzed system. So it is possible to recycle carbon monoxide and hydrogen by separating it from the off gas resulting in a product containing mostly methane. Thus water gas shift and methanation steps are avoided in the process.

2.3.4 Two stage coal gasification to high-btu gas⁸³

Li and Wiser studied a process to convert coal to High-Btu gas without oxidation-reduction reactions. Coal is converted to the final product of methane in a two-stage process without changing the reduced form of carbon. The technique has smaller process energy requirement and reduced hydrogen requirement compared to conventional gasification processes.

In the first stage, called a hydrosolvation stage, coal and sulfided Ni-Mo/Al₂O₃ were slurried in tetralin under hydrogen pressure. At 480°C, 2000 psi, and 1 hour reaction time a conversion of 85% was obtained. The heavy liquid product from the first stage was converted in a fixed Ni-Mo catalyst bed at 600°C, 1750 psi hydrogen pressure, and 1 WHSV to 64% gas, 29% liquid and 7% coke. The overall conversion of coal was to 62% gas, 10% gasoline, 7% middle oil, 2% heavy oil and 19% char. Methane was 77 weight% of the total gas and the heating value of the product gas was 1202 Btu/scf.

2.3.5 Single stage coal gasification to low molecular weight hydrocarbon gases¹

Kithany and Wiser investigated a process to convert coal to low molecular weight hydrocarbon gases. Coal was mixed with a dual functional catalyst mixture consisting of sulfided Ni-Mo/Al₂O₃ and 25% SiO₂-75% Al₂O₃ along with tetralin. At a temperature of 500°C, hydrogen pressure of 2000 psi and a reaction time of 30 minutes, coal was converted to 60% by weight to gas, 20% to liquid and 20% to char. C₂-C₄ hydrocarbon components in the gas product represent nearly 50% of the dmmf coal. C₂-C₄ hydrocarbons are particularly important due to their value as petrochemical feed stock.

2.3.6 Kinetics of single stage coal gasification to hydrocarbon gases²

Liu and Wiser determined the kinetics of single stage coal conversion to hydrocarbon gases in a stirred batch autoclave with a feed injector using Ni-Mo/Al₂O₃ mixed with silica-alumina catalyst. The kinetic parameters were determined in the temperature range of 440°C-500°C, reaction time of 0-60 min, and coal to tetralin to catalyst ratio of 1:3:1.25. It was found that coal conversion to liquids was very rapid and that conversion of liquids to gases was the rate-determining step. The apparent activation energy of conversion of liquids to gases was determined to be 23 Kcal/mol. Conversion of liquids to gases was observed to be taking place by carbonium ion mechanism.

2.4 Coal agglomeration

When coal is heated in an inert atmosphere, it decomposes with the evolution of a variety of volatile materials. The thermal decomposition proceeds in three basic stages. In Stage 1 which occurs below 200°F, the principal products are water, carbon dioxide, carbon monoxide, and hydrogen sulfide which arise from a loss of functional groups or through condensation reactions. In stage 2, which occurs between about 350°F to 550°F, the reactions are fast. The principal products are light hydrocarbon gases as well as a variety of organic compounds which condense at room temperature to a tarry mixture. Stage 3 begins above 550°F. The main products are water, carbon monoxide, carbon dioxide, hydrogen, methane, ethane, ethene, acetylene, ammonia, tars and a graphite-like solid of high carbon content. During Stage 2 caking coals pass through a plastic state in which the coal appears to soften, swell, and then resolidify into a porous mass. High volatile A, medium volatile, and low volatile bituminous coals exhibit this strong caking behavior.

Gryaznov et al.⁸⁴ suggested that the main reactions involved are thermal radical polycondensation reactions. During the process of thermal degradation a redistribution of hydrogen takes place resulting in the formation of intermediate metastable liquid and gaseous products enriched with hydrogen.

Several workers have studied the effect of agglomeration on the operation of fluidized beds. Most of the studies were done in relation to coal gasification and combustion in fluidized beds. Stallman and Neavel⁸⁵ found that the agglomerates of fused ash appear to form at temperatures below the initial deformation temperature, as defined by the ASTM fusibility test. Huffman et al.⁸⁶ observed that significant particle melting of the ashes occurred at temperatures as much as 200-400°C below the ASTM initial deformation temperature. Mason and Patel⁸⁷ found that agglomeration depends on fluidized bed temperature, bed ash concentration, average particle size, superficial velocity, and bed height.

No studies have been reported in the literature on the agglomeration of a caking coal in a supercritical hydrogen donor solvent.

2.5 Kinetics and mechanisms of hydrocarbon conversions

2.5.1 Thermal cracking

Hydrocarbons undergo thermal cracking via free-radical mechanisms when they are brought to high temperatures without the presence of catalysts. The initiation step in thermal cracking of a paraffin is the homolysis of a carbon-carbon bond.

The free radicals undergo scission at a bond located to the carbon atom having the unpaired electron. Cracking at the β position gives directly an α -olefin and a primary radical (lacking one hydrogen atom on a primary carbon atom). The primary radical derived from this step may immediately recrack at the β bond to give ethylene and another primary radical. By successive cracking, the radicals ultimately are reduced to methyl or ethyl fragments. These radicals then react with the feed stock molecules to produce new free radicals and are themselves converted to methane or ethane. Thus cracking is propagated as a chain reaction. To start the chain and to compensate for the loss of chain carriers by side reactions, a few highly activated molecules decompose spontaneously or at the wall.

The theory of thermal cracking, called Rich-Kossiakoff theory, satisfactorily predicts the high yields of ethylene, the low yields of methane, and the absence of isomerized products.

2.5.2 Catalytic cracking

Hydrocarbon reactions over acidic cracking catalysts are known to be taking place by carbonium ion mechanism.

The reactions take place in accordance with the general principles of carbonium ion reactions. The stability of carbonium ions decrease in the sequence:⁶⁸

In catalytic cracking the products are formed as a result of both primary and secondary reactions⁶⁹. Primary reactions are those involving the initial carbon-carbon bond scission and the immediate neutralization of the carbonium ion⁹⁰. The primary reactions are as follows:

Carbonium ions are formed initially by thermal cracking of a small amount of n-paraffins to olefins. These olefins form into large carbonium ions by abstracting a proton from the catalyst. The large carbonium ions thus formed crack according to the β rule to form smaller carbonium ions and olefins. The smaller carbonium ions propagate the chain reaction by transferring a hydrogen ion from a n-paraffin to form a small paraffin molecule and a new large carbonium ion, and the chain propagates.

The basic mechanism described above is essentially the same in various hydrocarbon types. However, the manner and extent of cracking differs considerably among the different types of hydrocarbons.

2.5.2.1 Cracking of paraffins. Paraffins undergo cracking to lower paraffins and olefins. The cracked gases

contain a high proportion of C_3 and C_4 hydrocarbons. The products may isomerize to branched structures. Secondary reactions involving olefins form aromatic hydrocarbons⁹¹. The size and structure of the paraffins determine the reaction rates and products formed. The effect of the catalyst is more pronounced as the number of carbon atoms in the molecule increases; the effect is not appreciable until the number of carbon atoms is at least six.

Figure 2.4 shows the comparison of experimental and calculated product distribution from cracking of n-hexadecane. The solid line represents experimentally observed products at 24% conversion in the presence of silica-zirconia-alumina at 500°C and LHSV=10. The calculated values are based on the carbonium ion theory.⁸⁸

2.5.2.2 Cracking of olefins.⁹² Olefins undergo the following main reactions:

- 1) carbon-carbon bond scission
- 2) Isomerization
- 3) Polymerization
- 4) Saturation, aromatization, and carbon formation

Olefins undergo catalytic cracking reactions at a much faster rate than the corresponding paraffins.

The higher velocity of hydrogen transfer reactions for branched olefins results in ratios of iso-to normal paraffins higher than the equilibrium ratios of the parent olefins. Isoparaffins and aromatics are formed in transfer

Figure 2.4. Catalytic cracking of n-hexadecane
Solid line represents experimental values
and dashed line, calculated values.
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reactions of olefins with naphthenes which act as hydrogen donors.

Naphthenes also undergo dehydrogenation to aromatics. Though there is carbon-carbon bond scission in both the ring and attached side chains, the dehydrogenation reactions are considerably greater below 1000°F. Dehydrogenation is very extensive for C₉ and larger naphthenes. The nonring liquid products and cracked gases from naphthenic hydrocarbon cracking are more saturated than those produced from cracking paraffins.

2.5.2.3 Cracking of aromatic hydrocarbons. In the case of aromatics with long alkyl chains the side chains are cracked adjacent to the ring without breaking the ring. Aromatics with alkyl groups containing less than three carbons are not very reactive. Benzene compounds containing alkyl groups are cracked with nearly quantitative recovery of benzene.⁹²

2.5.2.4 Coke formation. When hydrocarbons contact strong acids they undergo side reactions giving rise to high molecular-weight, highly unsaturated material called coke, which remains on the catalyst surface leading to severe loss of catalyst activity. The catalyst can be regenerated by burning off the coke with air. The heat generated by the exothermic regeneration reaction can be used to supply the heat required for the endothermic cracking reaction⁹³.

2.5.3 Hydrocracking

Hydrocracking which is carried out under hydrogen pressure converts high boiling hydrocarbons to lower boiling products with an overall consumption of hydrogen. It is thus a combination of catalytic cracking and hydrogenation. The catalyst used in hydrocracking is dual functional with a hydrogenation component and an acidic cracking component. The chemistry of hydrocracking is that expected from carbonium ion principles along with the chemistry of hydrogenation. The reactions catalyzed by the two components of the catalyst are different in nature. As the strength of the two components can be varied, the balance between the contributions of each component determines the reactions that take place and the products that are formed.

The presence of the acidic component, usually amorphous silica-alumina and/or zeolites, leads to cracking reactions which give rise to a high ratio of branched to straight-chain alkanes. The monocyclic rings are conserved. β -scission leads to substantial skeletal isomerization forming tertiary cations as intermediates. The hydrogenation component prevents the formation of olefins from the cations. If the olefins are formed they are reduced to the corresponding alkanes. Polymerization and consequent coke formation are minimized as a result of the minimization of olefins in the product.

The important components for hydrogenation are platinum, nickel, palladium, molybdenum, and cobalt; for cracking silica-alumina and zeolites.

2.5.3.1 Reactions of paraffins. A number of researchers have studied the reaction mechanisms of paraffin hydrocracking. A number of reactions may occur with varying degrees of importance: dehydrogenation and hydrogenation, isomerization, scission of carbon-carbon bonds, hydrogen transfer, disproportionation, and cyclization.

2.5.3.2 Strongly acidic catalysts with mild hydrogenation activity.⁹⁴ Typical catalysts of this type are metal sulfides such as nickel, tungsten, cobalt on supports such as silica-alumina. The important characteristics of the products of hydrocracking of n-paraffins with this type of catalyst are:

- (1) The product consists mainly of isoparaffins.
- (2) Little or no methane or ethane is formed.
- (3) Only a small amount of the normal paraffin reactant isomerizes without cracking.
- (4) An important side reaction is an apparent disproportionation process.

Figure 2.5 shows the product distribution from hydrocracking of typical normal paraffins with nickel sulfide on silica-alumina catalyst at 290°C and 82 atm.

The mechanism of hydrocracking of paraffin with a strongly acidic catalyst containing a mild hydrogenation

Figure 2.5. Products from hydrocracking of n-hexadecane over nickel sulfide on silica alumina
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component is similar to that for catalytic cracking with hydrogenation and hydroisomerization superimposed.

The following reaction steps are proposed for the hydrocracking of a normal paraffin.⁹⁴

(1) A normal olefin is formed by dehydrogenation of the normal paraffin reactant.

(2) The normal olefin is adsorbed on the acidic sites of the catalyst to form an ionic specie. Ionic intermediates can also be formed by hydride ion exchange.

(3) The carbonium ion thus formed can isomerize to a more stable specie (a tertiary carbonium ion), crack to form a smaller ion and an olefin, or desorb as a normal olefin.

(4) The tertiary carbonium ion formed in the previous step can undergo further isomerization, crack, or desorb.

(5) Olefinic products are saturated by hydrogenation or hydrogen transfer reactions.

The similarity of product distribution in catalytic cracking and hydrocracking of a normal paraffin at a given temperature indicates that a similar mechanism occurs in both processes. The product distribution for catalytic cracking of n-decane with silica-alumina and for hydrocracking of n-decane with nickel sulfide on silica-alumina at 288°C are shown in Figure 2.6.

Isoparaffins undergo reactions analogous to normal paraffins, but the reaction rates of isoparaffins are much

Figure 2.6. Products from hydrocracking n-decane at 288°C and 82 atm.
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faster than those of normal paraffins of the same carbon number. The rate of hydrocracking of n-paraffins increases with increasing molecular weight.

Hydroisomerization of any n-olefins formed in the cracking step to isoparaffins is another reason for the high ratios of isoparaffins to normal paraffins in the products of hydrocracking.

Catalysts of higher hydrogen activity relative to acidity give rise to product distributions different from those of catalysts with strong acidity and weak hydrogenation activity. The reactions of importance are isomerization of the reactant (without cracking), hydrogenolysis and cyclization. Catalysts in this category are unsulfided metal catalysts.

2.5.3.3 Reactions of cycloparaffins.⁹⁵ Egan, Langlois, and White reported the reactions of a number of cycloparaffins over nickel sulfide on silica-alumina catalyst. Methyl groups from cycloparaffins are pared and eliminated as branched paraffins, mainly isobutane, in such a way as to conserve rings. The selectivity of the cracking reaction to form one acyclic product and one cycloparaffin decreases dramatically in going from a reactant with 10 or more carbons atoms to a reactant with only nine carbon atoms. With the latter the ring yield is low; there is almost as much pentane formed as butane, and there is no single predominant cycloparaffin product. The rate of

cracking of the C_{10} cycloparaffin is over 100 times higher than that of C_9 cycloparaffin.

A characteristic of the paring reaction of cycloparaffins is the unusually high ratio of singly branched paraffins to unbranched paraffins in the products.

Extensive isomerization of the reactant precedes the cracking of cycloparaffins. A notable feature of hydrocracking of cycloparaffins is the stability of the cycloparaffin ring. Very little ring cleavage occurs. The bonds in the cycloparaffin ring may crack as readily as those in the side chains. However, because of the favorable circumstances for reversing the reaction, the net loss of ring structures is small, and the side chain cleavage reaction, which is essentially irreversible, predominates.

2.5.3.4 Reactions of alkyl aromatics. Sullivan, Egan, and Langlois^{96,97} studied the reactions of alkyl aromatics over nickel sulfide on silica-alumina. The important reactions taking place are isomerization, dealkylation, alkyl transfer, paring, and cyclization. Compared with cycloparaffins, aromatics show wider variation and greater dependence on the specific structure of the reactant.

Direct dealkylation is the primary cracking reaction in the case of alkylbenzenes containing side chains of three to five carbon atoms. Alkyl group transfer or disproportionation to form benzene and dibutylbenzene is also important. With larger alkyl side chains the reactions

become more complex. In addition, there are many other reactions taking place which include cyclization.

2.5.3.5 Reactions of polycyclic aromatics. Reactions of polycyclic aromatics⁹⁶ over acidic hydrocracking catalysts are very complex. With paraffins, cycloparaffins, and alkyl aromatics hydrocracking products are very similar to those obtained from catalytic cracking. For polycyclic aromatics, however, reaction products from catalytic cracking and hydrocracking are quite different. Catalytic cracking of phenanthrene with silica-alumina produces only coke and small quantities of gases compared with the low molecular weight cyclic products produced in hydrocracking. In hydrocracking, the hydrogenation component serves to convert the refractory polycyclic aromatics into partially hydrogenated species which can then react readily.

Qader et al.⁹⁸ studied the hydrocracking of naphthalene using H-zeolon and oxides and sulfides of Co, Mo, Ni, and W in a batch reactor. The reaction followed first order kinetics and the activation energy was determined to be 25.2 Kcal/mole. The liquid product predominantly consisted of tetralin and indanes, with varying amounts of benzene, toluene and ethyl benzene. The gaseous product consisted mainly of methane, ethane and propane, with propane being the highest. A three step mechanism of hydrogenation, isomerization and cracking was proposed shown in Figure 2.7.

Hydrocracking of anthracene was studied by Qader⁹⁹ using H-zeolon and WS_2 . The reaction was found to be first order with respect to anthracene concentration and the activation energy was 28.6 Kcal/mole. This reaction also proceeded through a three step mechanism of hydrogenation, isomerization and cracking as in the case of naphthalene. During hydrogenation, anthracene was hydrogenated to 9, 10 dihydroanthracene, 1, 2, 3, 4 tetrahydroanthracene, 1, 2, 3, 4, 5, 6, 7, 8 octahydroanthracene, sequentially. In the second step of isomerization of the hydroanthracenes, saturated 6-membered rings were converted to 5-membered rings with a methyl group attached to them. The final step was the hydrocracking of the isomer to lower molecular weight compounds. Dihydroanthracene did not crack under the existing conditions. Tetrahydroanthracene was hydrocracked to naphthalene either directly or through the formation of isomers which subsequently were cracked to C_{13} isomers and naphthalenes. The principal products were C_{13} isomers, naphthalenes, tetralins, indanes, ethyl benzenes, toluenes and benzene as shown in Figure 2.8.

Sullivan et al.⁹⁶ investigated the hydrocracking of phenanthrene. The principal product was tetralin, and the next most important product was methylcyclohexane. Most of the C_{14} products were partially hydrogenated, and a large fraction contained only one aromatic ring.

R, R' = METHYL GROUPS and H-ATOMS

Figure 2.8. Mechanism of anthracene hydrocracking
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There were three types of reactions taking place as indicated by the product distribution. The first was saturation and cleavage of one of the terminal rings to form a paraffin and a bicyclic such as tetralin. This was a minor reaction resulting in the formation of paraffins. The second type of reaction was ring saturation and cleavage of the central ring which accounted for the appreciable amounts of methylcyclohexane and ethylcyclohexane. The final predominant reaction was an unusual cracking reaction that produces bicyclic hydrocarbons, principally tetralin, without producing an equivalent amount of light paraffins.

A mechanism that accounts for the type of products produced is given below.⁶

- (a) Partial hydrogenation of the polycyclic aromatic.
- (b) Opening of one of the cycloparaffin rings to form a butyl side chain.
- (c) Alkyl transfer of the side chain to another reactant molecule.
- (d) Ring closure accompanied by hydrogenation to form a tetracyclic hydrocarbon.
- (e) Cracking of a central cycloparaffin ring to give a tetralin and a cycloparaffin.

Sullivan et al.⁶ also studied the hydrocracking of *n*-butyl benzene, tetralin, anthracene, and pyrene and observed the same general type of products.

2.6 Pressure fluctuation measurements to determine fluidization

In the study of fluidization phenomena, the transition from a fixed bed to a fluidized bed is usually visually determined. In high pressure and temperature systems the visual observation of the fluidization phenomenon requires the use of quartz windows capable of withstanding the high temperatures and pressures, making the mechanical design of fluidized bed reactors very complex. Additionally, the high pressure and temperature systems may require the use of fiber optic systems (for visual observation) from safety considerations. Use of visual observation techniques may not at all be feasible in cases such as coal liquefaction where conversion products are black liquids. Although the use of experimental techniques such as gamma-ray scans, radioactive gas, solid and liquid tracers, or sonic probes may give more information about the fluid properties of fluidized beds, they are in general quite expensive and difficult to use. There have been very few studies found in the literature on the use of power spectra in determining the fluid properties. Glasgow et al.¹⁰⁰ measured the wall pressure fluctuations and bubble size distributions in an Airlift Fermentor. Fan et al.¹⁰¹ attempted to characterize the flow regimes in a gas-liquid-solid fluidized bed by using the power spectral density function and the root mean square of the pressure fluctuations. They found that for the three regimes, dispersed, coalesced and slug flow, the

power spectral density functions appear distinctly different. For each regime, there is a distinct peak between 0 and 2 Hz and a broad peak between 16 and 25 Hz. At frequencies above 30 Hz, the power spectral density function is negligibly small for all three flow regimes. For the dispersed bubble regime, there is almost no contribution of frequencies between 2 and 16 Hz to the power spectrum, whereas for the coalesced bubble regime, the contribution of these frequencies is fairly large and for the slug flow regime it is quite large. They concluded that the contribution of frequencies between 2 and 16 Hz to the power spectral density is somehow related to the bubbling characteristics of the flow regime.

CHAPTER 3

EXPERIMENTAL WORK

The experimental set up consisted of two stages. The first stage was designed for converting coal to liquids using tetralin as hydrogen donor solvent, and hydrogen under pressure. The liquids produced in the first stage were separated from the unreacted coal and char and fed to the second stage, where they were converted into gases.

3.1. First stage

Flow diagram of the first stage is shown in Figure 3.1. An autoclave of one gallon size supplied by Autoclave Engineers was used to convert coal to liquids. The autoclave was of 316 stainless steel and was rated at 5500 psi at 650° F. The autoclave was equipped with a variable speed magnetic drive stirrer, an rpm indicator, a pressure gauge, a safety rupture disc, provision for introducing gases, liquids and solids, a thermocouple well, and a cooling coil inside the autoclave for quenching the reaction mixture. The stirrer was a turbine-type agitator provided with a hollow shaft. The heating assembly was an electric jacket furnace sliding onto the body of the autoclave. The

Figure 3.1. First stage experimental set-up

temperature controller supplied by Autoclave Engineers was a self contained unit. The dual point controller (model KCS0000) had both specimen and over-temperature control functions providing accurate control of the temperature in the autoclave.

There was provision for introducing hydrogen continuously through a micrometering valve and the flow rate was measured by a hydrogen mass flow meter which was connected to the computer data logging system. From the measurement of flow rate and the time, the total hydrogen input could be calculated. The mass flow meter was calibrated using a wet test meter.

The pressure and temperature data were also logged onto the computer by means of a pressure transducer and thermocouples. The pressure transducer was calibrated using a test pressure gauge.

The system pressure was maintained constant by means of a back pressure regulator. The gaseous products leaving the top of the reactor were cooled in a condenser and passed through the back pressure regulator. The liquids leaving along with the gases were cooled in the condenser and were separated in a separator. The gases were then passed through NH_3 and H_2S scrubbers, a wet test meter which measured the total volume of the gases, and were finally vented. There was provision on the autoclave for collecting the gas samples.

The experiments were conducted using 250gms of coal and 750 gms of tetralin at 1800 psi. A tetralin to coal ratio (by weight) of 3:1 was always maintained. To ensure efficient mixing of hydrogen, the stirrer was rotated at a constant speed of 1250 rpm.

Before each run, the autoclave, its fittings, magnetic stirrer and breaker were thoroughly cleaned with acetone. The head bolts were cleaned with a wire brush and a fresh coating of Jet Lube[®], a high temperature anti-seize compound, was applied. The 316 stainless steel gasket and the contact surfaces were thoroughly cleaned to ensure a good seal.

Coal and tetralin were weighed separately, mixed together and introduced into the autoclave. After keeping the gasket in place with its proper orientation, the autoclave head assembly was carefully lowered onto the gasket. The head bolts were uniformly torqued to about 250 ft.lbs.

The system was pressurized with nitrogen to about 1900 psi for leak testing and left at this pressure for several hours. Any significant pressure drop indicated leaks. If the gasket was found to be leaking the bolts were removed, the gasket cleaned and the head assembly retightened.

Water lines for cooling the magnetic stirrer were connected as well as the water lines for quenching the reaction mixture after the experiment. The electric furnace

was slid onto the autoclave. After the system was pressurized with hydrogen to about 1450 psi, the furnace was turned on. The furnace temperature was set at 520°C. It took nearly 2 hours for the autoclave to reach a temperature of 440°C and this time was taken as zero time. The magnetic stirrer was turned on when the temperature in the autoclave started rising and the water flow for cooling the magnetic stirrer was kept on as long as the stirrer was rotating. As the system pressure was set at 1800 psi using the back pressure regulator, the gaseous products and hydrogen flowed out of the autoclave through the back pressure regulator, maintaining the system pressure constant at 1800 psi. The hydrogen flow into the autoclave was regulated using a micrometering valve.

At the termination of the experiment, the heater was turned off and removed, and the cold water was turned on to quench the reaction mixture. The temperature dropped to below 250°C in about 10 minutes. After the autoclave cooled to room temperature the pressure was released through the back pressure regulator. The volume of the gas was measured by the wet test meter. Ammonia and hydrogen sulfide were absorbed in the scrubbers containing sulfuric acid and ammonium hydroxide, respectively. Two gas samples were collected for GC analysis. The head assembly was then removed from the autoclave and the contents were carefully recovered. The solid and liquid residue sticking to the walls of the reactor and the stirrer were recovered by

scraping with a tissue paper. The paper was weighed before and after wiping. The solid product was separated by filtration. The filter cake was collected and dried in a vacuum evaporator. The difference between the wet and dry cake was considered as the liquid product remaining in the cake.

3.1.1. Feed stock

Wyodak subbituminous coal was studied in this work. Coal was pulverized and sieved to -200 Tyler mesh size. Before the experiment coal was dried overnight in a vacuum heater at 80°C. The proximate and ultimate analyses are shown in Table 3.1. The hydrogen donor solvent used was 1,2,3,4-tetrahydronaphthalene of 99% purity supplied by Aldrich Chemical Company. Molecular formula, molecular weight, and normal boiling point of the tetralin are $C_{10}H_{12}$, 132.196 and 207.57°C, respectively. Hydrogen was taken from commercially available 2000 psi gas cylinders.

3.2. Second stage

The second stage is represented schematically in Figure 3.2. The system consists mainly of a liquid feeding system, a preheater, a reactor, and a liquids separating system. The preheater and reactor were incorporated into the same unit. The upper section of a 316 stainless steel tube (length 26 7/16", OD 5/8", wall thickness 0.065", and ID = 0.495") functions as the preheater and the lower section as the reactor. The stainless steel tube had a carbon steel

Table 3.1. Proximate and ultimate analysis of Wyodak coal

<u>Proximate analysis (wt%)</u>	
Moisture	29.34
Ash (dry basis)	10.22
Volatile matter (dry basis)	55.79
Fixed carbon (dry basis)	33.99
<u>Ultimate analysis (wt%, MAF basis)</u>	
Carbon	72.96
Hydrogen	5.69
Nitrogen	1.02
Sulfur	0.97
Oxygen (by difference)	19.36
H/C (atomic ratio)	0.936

1. Feed burette	10. Thermocouple	18. Filter
2. Filter	11. Thermocouple	19. Back pressure regulator
3. Feed pump	12. Temp controller	20. Separator
4. Check valve	13. Temp controller	21. NH_3 scrubber
5. Flow meter	14. Valve	22. H_2S scrubber
6. Metering valve	15. Glass beads	23. Wet test meter
7. Hydrogen cyl	16. Catalyst	24. Gas pump
8. Preheater	17. Condenser	25. Metering valve
9. Reactor		26. Valve manifold

Figure 3.2. Second stage experimental set-up

heat conducting cylinder mounted on it to effect good heat transfer. The preheater and the reactor sections were heated separately. Each section had a cylinder type electric heater around it rated at 1400W at 115 volts. The electric heaters were covered with Fiberfax[®], a high temperature heat insulation material to minimize heat losses. The unit was wrapped with a thick fiber sheet.

A thermocouple was located at the end of the preheater section and another one at the middle of the reactor section. The temperatures of the preheater and the reactor were controlled by two Omega CN 9000 microprocessor-based temperature controllers. The heaters were connected to the temperature controllers via two voltage regulators to vary the electric power input to the reactor and the preheater. The heat conductor and the equal spacing of the spiral heating elements maintained uniform temperature along the length of the preheater and the reactor. The nominal temperature was measured at the center of the catalyst bed. The temperature of the catalyst bed was constant throughout each run. The temperature deviated from the set point by a maximum of 1°C. Thirty-two grams of catalyst were packed between glass beads in the reactor.

The coal-derived liquid was pumped by a Milroyal packed plunger pump (Model 2396-31). The duplex pump had a minimum and maximum pumping capacity of 16 and 320 ml/hour. The pressure rating was 6000 psi. The pump was calibrated at 1800 psi using the coal-derived liquids. The feed flow rate

was measured by a burette of 50 ml capacity with graduations of 0.1 ml. A 7-micron filter was installed on the suction side of the pump to prevent any solids from entering the pump.

As mentioned earlier hydrogen was taken from a 2000 psi cylinder, flowed through a pressure regulator, micrometering valve, mass flow meter, and check valve. The flow rate was measured by the mass flow meter and the data were logged on to the computer.

Coal liquids and hydrogen were mixed together and fed to the top of the preheater. Hydrogen and coal liquid flowed down the preheater into the reactor. The product stream leaving the bottom of the reactor was cooled in a condenser. The pressure was reduced in a back pressure regulator and the liquids and gases were separated in a separator. To prevent any solids from entering the back pressure regulator and thus rendering it ineffective, a 2 micron filter was located between the condenser and the back pressure regulator.

After the gases left the separator a small portion of the gases was drawn by a gas sampling pump and fed to the gas sampling valve manifold. A micrometering valve was located on the discharge side of the gas sampling pump to precisely regulate the flow of the sample. The sample flowing through the valve manifold was measured at regular intervals by a bubble flow meter.

The gas sampling valve manifold was used to collect samples at regular intervals. The manifold contained 9 sampling valves each with a sampling loop of approximately 2 cc. Initially all the valves were closed and the gases flowed out of the manifold, short circuiting the sampling loops. When a particular valve was switched on, the flow passed through the sampling loop of that valve. Each valve was kept open for 20 seconds and then closed. The sample becomes trapped in the loop when the valve is closed. The operation of the valve manifold was controlled by the computer. The valves were opened and closed at regular intervals as programmed. Visual Lab-M, a software package developed by Dr. Yang, was used for logging the data and for operating the valve manifold. The block diagram of the computer system is shown in Appendix A. The operation sequence of the manifold is represented diagrammatically in Appendix B.

The valve manifold was calibrated by collecting a standard gas (methane) of known concentration in the nine sampling loops using the procedure described above. Each sample was then analyzed by the gas chromatograph and compared to a 2 cc sample injected by a syringe into the GC. The areas obtained by integrating the peaks were used to determine the relative volumes of the sampling loops.

A major portion of the gases passed through the NH_3 and H_2S scrubbers, and through the wet test meter which measured the volume of the gases passing through.

3.2.1. Feedstock

The coal-derived liquid used in the second stage was produced in the first stage. The unreacted coal and char were separated by filtration. The density of the liquid was 0.9953 g/cc.

3.2.2. Catalyst

In all the experiments, the catalyst used was a physical mixture of sulfided nickel-molybdenum on alumina, and 25% silica-75% alumina in the weight ratio of 4:1. The properties of the nickel-molybdenum on alumina, supplied by Englehard Corporation, are shown in Table 3.2 and the properties of silica-alumina, supplied by Gulf Research and Development Co., are shown in Table 3.3. Both catalysts were ground and sieved to - 20 + 40 Tyler mesh. The Ni-Mo/ Al_2O_3 catalyst was sulfided in the sulfiding unit and mixed with silica-alumina in the weight ratio of 4:1.

3.3. Sulfiding the catalyst

The catalyst sulfiding unit is shown in Figure 3.3. About 50 gms of the Ni-Mo/ Al_2O_3 catalyst was loaded into the glass tube reactor and both the ends were closed with stop cocks and sealed with stop cock grease. The reactor was purged with nitrogen to remove any traces of oxygen, then heated to 400°C under nitrogen flow. The nitrogen flow was continued for 1 hour. The nitrogen flow was then shut off and a mixture of 10% hydrogen sulfide in hydrogen was passed

Table 3.2. Properties of Ni-Mo/Al₂O₃ catalyst

Size	1/12" extrudate
NiO (wt%)	4.75
MoO ₃ (wt%)	19.75
P ₂ O ₃ (wt%)	4.75
Average micropore radius	48.8

Table 3.3. Properties of 25% SiO₂-75% Al₂O₃ catalyst

Surface area (m ² /gm)	416
Pore volume (ml/gm)	0.65
Pore radius (A°)	35.7

Figure 3.3. Catalyst sulfiding unit

through the catalyst at 400°C for two hours. The heater was then turned off and nitrogen passed through the catalyst to remove any excess hydrogen sulfide. The sulfided catalyst after cooling was removed and stored. After a sufficient quantity of catalyst was sulfided, it was mixed with silica-alumina in the ratio of 4:1 and stored.

3.4. Gas analysis

The hydrocarbon gas composition was determined by analyzing the sample gases in a Shimadzu GC 14A Gas Chromatograph. The column used was 80/100 chromosorb 102 (6'x1/8") supplied by Supelco. The detector was a Flame Ionization Detector (FID) and the carrier gas was helium. Scotty analyzed gases supplied by Scott Company were used as the standard gases. The other GC conditions are shown in Table 3.4.

The gas samples collected in the gas sampling valve manifold were used in the analysis. The manifold was connected to the carrier gas line after the carrier gas pressure regulator. The carrier gas entered the manifold on one end and left on the other end, then entered directly into the column without going to the injector. Before connecting the manifold to the column, the manifold was purged with helium gas for a few minutes. After connecting the manifold to the column a blank run was made to ensure that there were no hydrocarbon gases remaining in the manifold except in the sampling loops. By opening a valve

Table 3.4. Gas analysis by gas chromatograph

Column	Chromosorb 102
Detector	FID
Carrier gas	Helium, 50 cc/min
Detector temperature, °C	250
<u>Column conditions</u>	
Initial temperature, °C	80
Initial hold, min.	1
Rate, °C/min	8
Final temperature, °C	180
Final time, min.	2

with the electric switch provided for each valve separately the carrier gas entered the sampling loop of that valve and carried the sample to the column. Each valve was kept open for about twenty seconds, then closed. The operation was done manually. After a sample was completely analyzed by the GC, the next valve was opened and so on until all the samples were analyzed.

3.5. Experimental procedure for the second stage

Thirty two grams of catalyst were loaded between glass beads of 3 mm diameter. About 52 grams of glass beads were on top of the catalyst bed and about 8 grams below the catalyst bed. The top portion of the glass beads was in the preheater section. A small piece of stainless steel screen of 20 Tyler mesh was inserted in a bottom fitting to keep the glass beads in place. After loading the catalyst and the glass beads the top and bottom fittings were tightened and the reactor was leak tested with nitrogen at 1800 psi. After making sure that there were no leaks the nitrogen pressure was released and the system was pressurized to about 1400 psi with hydrogen. The heaters were then turned on. The reactor pressure increased to 1800 psi. The system pressure remained constant at 1800 psi as the back pressure regulator was set at 1800 psi.

After the temperature stabilized at the set point, the liquid feed pump was switched on. The hydrogen flow was turned on and adjusted to the required flow rate. As soon as

the liquid feed came in contact with the catalyst, due to the exothermic nature of the hydrocracking reactions the temperature rose by about 4 to 9°C. The temperature controllers corrected the temperature overshoot and returned the temperatures to the set point. Once stabilized the temperatures deviated by a maximum of $\pm 1^\circ\text{C}$. The feed rate was monitored by taking readings off the burette at regular intervals. The hydrogen flow rate and the temperatures were continuously logged onto the computer.

After about 20 minutes of the temperature overshoot the gas sampling pump was switched on which pumped the sample to the gas sampling valve manifold. The flow through the manifold was measured at regular intervals to check if the flow rate was constant. About 5 minutes after the gas sampling pump was turned on the gas sampling valve manifold sequence was started by means of a switch designed for this purpose. Once the sequence started the computer automatically turned on and off the valves at 10 minute intervals as programmed. About six samples were collected for each run and each run lasted a total of about 90 minutes.

At the conclusion of the experiment, the pump was turned off and the discharge valve of the pump was shut off. The heaters also were turned off. About 4 minutes after turning off the pump, hydrogen flow and the gas sampling pump were also turned off.

The flow rate through the wet test meter was noted at regular intervals. The liquids in the separator were collected and measured at regular intervals.

After the reactor cooled to room temperature the hydrogen pressure was released and the contents of the reactor carefully removed. The glass beads and the catalyst were easily separated by screening after drying.

3.6. Coal agglomeration studies

3.6.1. Autoclave

The experimental set-up is shown in Figure 3.4. An autoclave of one gallon size supplied by Autoclave Engineers was used to conduct the experiments. The autoclave was equipped with a variable speed magnetic drive stirrer, an rpm indicator, a pressure gauge, a safety rupture disc, a provision for introducing gases, liquids and solids, a thermocouple well, and a cooling coil inside the autoclave for quenching the reaction mixture. The heating assembly on the autoclave was an electric jacket furnace sliding onto the body of the autoclave. The temperature controller supplied by Autoclave Engineers was a self contained unit.

The pressure and temperature data were logged onto the computer by means of a pressure transducer and thermocouples. The pressure transducer was calibrated using a test pressure gauge. The system pressure was maintained constant by means of a back pressure regulator.

Figure 3.4. Experimental set-up for agglomeration studies

The coal slurry was injected into the reactor through a pressurized cylinder as shown in the Figure 3.4.

3.6.2. Fluidized bed reactor

A high pressure fluidized bed reactor fabricated from SS 316 was used in the study. The reactor had two flanges at the ends welded onto the main body of the reactor. The top and bottom were closed by means of two end plates and sealed by metal seals. The reactor was capable of accommodating pressures to 3000 psi and temperatures to 500°C. At the bottom of the reactor in the bottom end plate there was provision for inserting a distributor plate. There were four thermocouples inserted along the length of the reactor as shown in Figure 3.5. As the original reactor diameter of three inches would necessitate a large pump and a preheater, the diameter was reduced in size to about $\frac{3}{4}$ " by inserting a sleeve into the reactor. The top portion of the sleeve was tapered to give a gradually increasing diameter so that the fluidized coal particles disengage in this section. The circulating pump (Milton Roy metering pump model MB1-M13-P071, capacity 5.3 gph at 3000 psi) draws in tetralin at the top of the reactor above the disengaging section. As the pump cannot handle high temperatures, the tetralin was cooled to about 80°C before entering the pump. A 40 cc pulsation dampener was installed on the discharge line of the pump before the preheater to smooth out the

1. N ₂ cylinder	11. Differential pressure gauge
2. Ball valves	12. Circulating pump
3. Check valve	13. Preheater
4. Cylinder	14. Temp controller
5. Condenser	15. Thermocouple
6. Fluidized bed reactor	16. Back pressure regulator
7. Heating furnace	17. NH ₃ scrubber
8. Thermocouple	18. H ₂ S scrubber
9. Temp controller	19. Wet test meter
10. Distributor plate	

Figure 3.5. Fluidized bed reactor for agglomeration studies

pulses from the reciprocating pump utilizing the cushion of air trapped in the upper part of the chamber.

The discharge from the pump was passed through a preheater where the tetralin was heated to about 460°C. The preheater was a $\frac{1}{4}$ inch SS 316 tube heated by Omega high temperature heating tapes. The temperature at the exit of the preheater was controlled by an Omega CN 9000 microprocessor-based temperature controller. The reactor temperature was also controlled by an Omega CN 9000 controller. To minimize heat losses from the large diameter flanges, the same were heated by an auxiliary heater wound around them.

It takes about 3 hours to heat up the reactor to 470°C. If coal and tetralin are in the reactor at the start of the heat up period, most of the reactions will be complete by the time the reactor reaches the set temperature of 470°C during which time coal particles will be in contact with tetralin in a liquid phase. To ensure that coal particles are in contact with tetralin in a supercritical state, the reactor was heated with only tetralin in the reactor. As the temperature reached about 470°C coal and tetralin slurry was injected into the reactor through a pressurized cylinder. In one experiment, immediately after injection of coal paste, nitrogen was bubbled through the bed keeping the coal particles in suspension. In another experiment, the circulating pump was started, immediately after the injection of the coal slurry, fluidizing the coal particles.

3.7. Pressure fluctuation measurements

The fluidized bed reactor used for measuring pressure fluctuation was described in an earlier section. Nitrogen gas was used as the fluidizing medium and was taken from a cylinder at 2300 psi. The gas passed through a pressure regulator, a metering valve and a check valve and entered the bottom of the reactor. Sand particles were sieved to between -65 and +100 mesh (150 μm to 212 μm) and placed inside the reactor. The particles were supported on a distributor plate. The distributor plate was a stainless steel mesh screen of 50 mesh sandwiched between two perforated stainless steel plates. The gas flow was regulated by means of the micrometering valve and the flow was measured after it passed through the bed by a wet test meter. The flow diagram is shown in Figure 3.6. The pressure drop across the bed was measured by a differential pressure transducer model PX 750-DI. The transducer had a range of 0 to 30 in H_2O . The output was 4-20 mA dc. The transducer was connected to a 12 V dc power supply and the output to a 286 computer through an analog to digital converter. The differential pressure transducer produces a current output in the range of 4-20 mA, proportional to the measured differential pressure. The current signal was converted to a voltage signal by means of a fixed resistance. The convertor on the computer converts the analog signal to a digital signal. A software package

1. N₂ cylinder
2. On-off valve
3. Micrometering valve
4. Check valve
5. Fluidized bed reactor
6. Distributor plate
7. Differential pressure gauge
8. Back pressure regulator
9. Wet test meter

Figure 3.6. Experimental set-up for pressure fluctuation measurements

developed by Dr. Yang was used to display and record the data acquired. The software had the capability to collect large amounts of data within a short period of time of about 10 seconds. At each flow rate the data were collected for about 10 seconds and stored. The data thus collected were used to calculate the power spectral density function. The power spectral density function expresses the distribution of energy with frequency and was calculated by the Fast Fourier Transform method using a program written by Dr. Yang.

3.8. Visual observation of fluidization phenomena

The reactor described above had provision for installing quartz windows at the top. In the experiments conducted to visually observe the fluidization phenomena, the quartz windows were installed in place. There were two quartz windows, one of which was used for observing the inside phenomena and incorporating a fiber optic system, and the other was used for illumination purposes. The arrangement of the quartz windows is shown in Figure 3.7. The fiber optic system was hooked to a video camera and a TV, and the fluidization phenomena were recorded. The bed of sand particles was fluidized at atmospheric pressure, at 500 psi and 1000 psi, using nitrogen gas as described in the previous section.

Figure 3.7. The high pressure-high temperature sight glass of the fluidized bed reactor.

Chapter 4

RESULTS AND DISCUSSION

4.1 First stage

The purpose of the first stage was to convert coal to liquids for use in the second stage. Coal and tetralin under hydrogen pressure of 1800 psi were reacted together at a temperature of 440°C and a reaction time of 40 minutes. A coal conversion of 83% was obtained at the reaction conditions. Coal conversion was defined as

$$\text{Coal conversion} = \frac{\text{MAF coal in} - \text{MAF residue out}}{\text{MAF coal in}} \times 100$$

Most of the coal was converted to liquids with a small amount converted to gases. The yield of gases (C_1 - C_4) was 6.2 weight% of the dmmf coal. Of the gases C_1 was 34.4 wt%, C_2 = 29.9 wt%, C_3 = 28.5 wt%, and C_4 = 7.2 wt%. It should be noted that the yield of C_2 - C_4 hydrocarbons, as a weight% of the coal, was still very low.

4.2 Reaction mechanism

Coal conversion in the presence of hydrogen donor solvents has been studied extensively by several investigators.^{1,59,60,70,71} It has been noted that free

radicals play a primary role in the liquefaction behavior of coals.^{70,71} The reactive maceral components of coal are considered to be highly cross linked, amorphous, macromolecular networks consisting of a number of stable cluster units connected by relatively weak linkages.^{59,70,71} In the Wiser model of coal, these linkages are represented by methylene, ether and other bridge structures.⁵⁴ Above about 350°C these linkages rupture, giving rise to free radicals.^{70,71} It was shown from experiments that once the required temperature has been reached, the disintegration is very rapid. The rapidity of disintegration of the coal particles suggests a purely thermal process controlled by heat transfer rate.⁶⁴ The free radicals once formed may stabilize themselves by undergoing a variety of secondary cracking, dehydrogenation and condensation reactions yielding hydrocarbon gases, small amounts of light oils, but mostly high molecular weight carbonaceous solids (char). On the other hand, if molecular hydrogen or a hydrogen donor solvent is present, hydrogen may be added from these sources stabilizing the free radicals.^{70,71} Tetralin or similar molecules are good donors because the free radical intermediate is a relatively stable benzylic type free radical and the product after the loss of four hydrogen atoms is a stable aromatic compound (naphthalene).

Curran et al.⁵⁹ showed that hydrogen transfer by hydrogen donor solvents promotes formation of low molecular

weight compounds at temperatures around 400°C but noted that secondary thermal reactions involving condensation caused the molecular weight of the compounds to increase resulting in the formation of char if the solvent treatment was prolonged. The hydrogen transfer reactions appear to be purely thermal processes. Attempts to accelerate the reaction by the use of catalysts have been largely unsuccessful.⁶¹ The possibility of catalysis during the initial phase of liquefaction is precluded by the fact that coal is not in solution during the initial phase. The donor solvent (or molecular hydrogen) diffuses into the coal particle and the hydrogen transfer reactions take place within the coal particle itself. The rate of hydrogen transfer with the more active donors is about the same regardless of the structure of the coal.⁶¹

Although free radical formation is a thermal process, heat alone is not sufficient to break down the coal to liquid-size molecules.^{64,65} Although all the coal particles disintegrate at 400°C with a hydrogen donor solvent (tetralin), the same coal at the same temperature with a nondonor solvent (paraffin oil) does not show any disintegration, while with decalin, a not very active hydrogen donor solvent, only partial disintegration is observed even after 2 hours.

The sources of hydrogen in coal liquefaction can be hydroaromatic structures in coal, hydrogen donor solvent,

and molecular hydrogen.⁷⁰ Through dehydrogenation studies, hydroaromatic carbon has been estimated to be ranging from 15% to 22% of the total carbon in coals with 70-85% carbon⁴¹ with a few low-rank coals having up to 35% hydroaromatic carbon content. These hydroaromatic structures have been found to be the main source of stabilization of free radicals in coal pyrolysis. Wiser^{70,71} has discussed the similarities between pyrolysis and donor extraction and concluded that both processes are initiated by thermal cracking at temperatures above 350°C, irrespective of whether other reactants are present in the system. This thermal cracking of each covalent bond results in two free radicals. These free radicals can be stabilized via three different routes, depending on the availability of other species and on the free energy of stabilization: (1) addition of atoms or other radical groups to the free radicals; (2) rearrangement of atoms within the free radical; and (3) polymerization of the free radicals. Coal dissolution with a hydrogen donor solvent proceeds via the first route. With no hydrogen donor solvent, rearrangement of the free radical is possible if the latter contains hydroaromatic units. In the third route, the free radicals will polymerize into high molecular weight molecules, if the free radicals have no other means of stabilization.

Heredy and Fugassi¹⁰³ studying the dissolution of coal in phenanthrene, a nondonor solvent, found that the

dissolution yield is very high. By replacing the hydrogen in phenanthrene by tritium, they discovered that during the dissolution process the tritium was transferred to the free radicals. The phenanthrene remained the same except that the tritium was replaced by hydrogen. It was concluded that the free radicals in coal abstract hydrogen from phenanthrene and in turn, the phenanthrene free radicals thus formed abstract hydrogen from the hydroaromatic structures in coal. This process, sometimes called hydrogen shuttling, results in higher aromaticity in the products compared with the original coal. Thus phenanthrene plays the role of a free radical carrier or hydrogen transfer agent instead of a hydrogen donor.

Even a very poor hydrogen donor such as paraffin oil dissolves coal, even though fairly slowly, if molecular hydrogen is present under pressure.^{64,65} Even with hydrogen donor solvents, the presence of hydrogen pressure increases conversion. In general, it has been shown that high coal conversions are more readily obtained when hydrogen pressure is applied. It appears that hydrogen reacts through the donor solvent as an intermediary. However, direct reaction of hydrogen with coal catalyzed by coal ash may be important in some cases.

Wiser et al.^{70,71} noted the similarities among batch hydrogenation, pyrolysis and dissolution. They found that the three processes under the given conditions approach

completion at similar rates. They also involve similar mechanisms involving thermal fragmentation to yield free radicals, followed by radical stabilization as the rate determining step. The activation energy for coal pyrolysis was determined to be 35.6 Kcal/mole. The reaction was second order with respect to the quantity of unreacted but potentially reactive coal. Batch hydrogenation of coal impregnated with ammonium molybdate catalyst had an activation energy of 39Kcal/mole and the reaction order was determined to be 2.

Similarly, coal dissolution in tetralin proceeds by a second order reaction with an activation energy of 29 Kcal/mole. Analysis of the data indicates that the process is first order with respect to unreacted but potentially reactive coal and first order with respect to unreacted Tetralin. Mathematically, this is expressed as^{70,71}

$$\frac{dx}{dt} = K_s (a-x) (b-x)$$

where a is the maximum weight fraction of coal that can be converted at the temperature of reaction, b is the initial weight fraction of Tetralin (b=1.0), K_s is the second order rate constant, x is the weight fraction of reacted coal. This model, which represents the primary reaction step, was found to correlate data well to a temperature of 500°C.

It is important to know the composition and types of compounds present in the coal liquids produced in the first

stage to understand the process of conversion of coal liquids to gases. Though no analysis has been conducted on the coal liquids produced in the present work, there have been several studies conducted to characterize coal-derived liquids produced in other processes. As the liquefaction mechanism is similar in all the thermal processes involving a donor solvent, the same type of compounds are expected to be present in the coal liquids produced in the present work. Though the composition of the coal liquids produced in the present work may not be the same, an understanding of the general nature of the coal liquids will help explain the reactions taking place during the conversion of liquids to gases.

Table 4.1 shows the composition of coal liquefaction products from the Synthoil process¹⁰⁴ and Table 4.2 from the H-coal process.¹⁰⁵ Table 4.3 shows the structure of the major ring systems expected in coal liquefaction products.¹⁰⁴

Anderson et al.¹⁰⁶ characterized the coal-derived liquids obtained by hydrogenating coal in a coiled-tube reactor at 500°C and 1800 psig. The coal was impregnated with 5% by weight of zinc chloride. The yields were 10% gases, 5% light liquids (B.P<250°C), 55% heavy liquids, 15% char and 15% water. After removing the paraffinic material by extraction with ethanol and acetone, the heavy liquids (b.p>250°C) were separated into light, middle and heavy distillable fractions and resid. Fractions separated

Table 4.1. Composition of the liquefaction products from
SYNTHOIL process.¹⁰⁴

Run conditions:		
Feed coal	Kentucky Homestead Mine	
Reactor temperature	450°C	
Preheater temperature	450°C	
Paste composition	35% coal, 65% oil	
Reactor size	2.54cm i.d × 4.27m	
Catalyst	CoMo/SiO ₂ -Al ₂ O ₃	
Hydrogen pressure	13.79 Mpa	

Component	Weight	Percent
Oil	89.65	
Saturates		15.08
Aromatics		59.85
Polars		23.44
Loss		1.63
		100.00
Asphaltenes	3.26	
Preasphaltenes	0.87	
Water	<0.05	
Loss	6.22	
Total	100.00	

Table 4.1. - continued

Saturates	Wt%	Aromatics	Wt%	Polars	Wt%
Paraffins	8.13	1 ring	37.60	Mono-oxygen	52.41
1-ring naphthenes	23.11	2 ring	33.87	Dioxygen	3.71
2-ring naphthenes	27.21	3 ring	13.59	Miscellaneous	0.52
3-ring naphthenes	24.23	4-8 ring	14.94	N-Compounds	23.85
4-ring naphthenes	11.86	Total	100.00	N-O Compounds	0.95
5-ring naphthenes	2.55			Misc. N-Compounds	0.14
6-ring naphthenes	0.00			S-Compounds	0.10
Monoaromatics	2.91			Hydrocarbons	1.71
Total	100.00			Residue	16.61
				Total	100.00

Table 4.2. Composition of H-coal liquids from
Illinois No. 6 seam coal.¹⁰⁵

Component	C ₄ -400°F# Wt%	400-650°F++ Wt%	650-919°F+ Wt%
<u>Saturated hydrocarbons</u>			
Paraffins	11.99	6.5	1.4
Monocycloparaffins	42.64	14.0	3.1
Dicycloparaffins	8.50	7.9	0.6
Tricycloparaffins	0.19	2.6	0.7
Other	-	-	1.0
	63.32	31.0	6.8
<u>Unsaturated naphthenes</u>			
Monocycloolefins	5.32	4.3	0.5
Bicycloolefins	4.98	-	0.3
Tricycloolefins	0.90	-	0.2
Other	-	-	0.6
	11.20	4.3	1.6
<u>Aromatic hydrocarbons</u>			
Alkylbenzenes	17.55	12.6	3.0
Indans and/or	6.44	30.8	0.5
"Tetralins"			
Other aromatics	0.59	16.2	72.8*
	24.58	59.6	76.3

Table 4.2. - continued

Nonhydrocarbons

Phenols	0.90	2.0	-
Other			
nonhydrocarbons	-	3.10	13.8
(S and N			
compounds)			
	0.90	5.10	13.8
	100.0	100.0	100.0

C₄-400°F boiling fraction of the liquids.

++ 400-650°F boiling fraction of the liquids.

+ 650-919°F boiling fraction of the liquids.

* An approximate breakdown of aromatic hydrocarbons is as follows in m moles/100gm: naphthalenes, 93.4; phenanthrenes, 91.9; chrysenes, 21.9; 1,2-benzanthracenes, 3,4-benzphenanthrenes, 14.6; pyrenes, 15.4; 5-ring aromatics, 5.1.

Table 4.3. Major ring systems expected in coal liquids

Formula	Structure	Formula	Structure
C_6H_6		$C_{14}H_{10}$
C_9H_8		$C_{15}H_{10}$
$C_{10}H_8$		$C_{16}H_{10}$
$C_{12}H_8$		$C_{18}H_{12}$
$C_{12}H_{10}$		$C_{18}H_{12}$
$C_{13}H_{10}$		$C_{19}H_{12}$
$C_{14}H_{10}$		$C_{20}H_{12}$

Table 4.3.- Continued

were analyzed and characterized. The results are shown in Table 4.4. The possible structural units expected in the fractions are shown in Figure 4.1. The heavy liquid product was determined to have 2.4 aromatic rings, and 0.8 naphthenic and saturated rings. Aromaticity was .63 and the cluster size was 2.2.

There have been several other studies characterizing coal-derived liquids.¹⁰⁷⁻¹⁰⁹

From these studies it can be concluded that coal-derived liquids consist mostly of aromatic/hydroaromatic structures with ring size varying from 1 to 5, with the average being about 2 to 3. There are also substantial amounts of saturates with the majority being paraffins, and mono and bicycloparaffins. Unsaturated naphthenes with mono and bicycloolefins constitute a small portion of the liquids. The carbon/hydrogen ratio and the concentrations of heteroatoms nitrogen, sulfur and oxygen are generally much higher in coal liquids than in petroleum crudes. Typical elemental compositions are shown in Table 4.5.¹⁰⁹

The molecular weights of coal liquids lie within a narrow range, generally between 300 and 1000.¹⁰⁹

In the present study no catalyst was used in the first stage to produce liquids and hence the liquids are expected to have relatively high molecular weight species compared to the liquids produced using catalysts which promote hydrogenation.

Table 4.4. Analytical data on the heavy liquids

	Yield (wt%)*	Mol. Wt	RA	RN	#cl	fa	RA/#cl
HVL-P	100	258	2.4	0.8	1.1	0.63	2.2
Light	19.2	183	1.2	0.6	1.0	0.55	1.2
Middle	15.7	210	1.6	0.7	1.1	0.58	1.5
Heavy	17.6	272	2.4	1.3	1.0	0.59	2.4
Resid	40.0	396	4.4	1.2	1.3	0.68	

* Weight % of Coal.

Note: RA = Number of Aromatic Rings.

RN = Number of Naphthenic and Saturated Rings.

#cl = Number of Aromatic Clusters.

fa = Fraction of Aromatic Carbons (= Aromaticity)

RA/#cl = Cluster Size.

Figure 4.1. Possible structural units in the heavy liquids¹⁰⁶

Table 4.5. Typical elemental composition of coal liquids
and petroleum fuels

Element, Wt%	SRC	H-Coal	Synthoil	Fuel oil	residuum
C	87.93	89.00	87.62	86.40	83.88
H	5.72	7.94	7.97	11.20	9.97
O	3.50	2.12	2.08	0.30	0.48
N	1.71	0.77	0.97	0.41	0.40
S	0.57	0.42	0.43	1.96	4.19

4.3 Second stage

The second stage was a fixed bed continuous flow system. The catalyst used was a sulfided Ni-Mo/ Al_2O_3 mixed with SiO_2 - Al_2O_3 . All the experiments were conducted at a pressure of 1800 psi. The coal-derived liquids produced in the first stage were hydrocracked to C_1 - C_4 hydrocarbons in the second stage. Coal-derived liquids are complex mixtures of organic compounds containing predominantly aromatic structures. Substantial quantities of aliphatic and naphthenic compounds are also present. The compounds contain significant amounts of sulfur, nitrogen and oxygen.

A number of experiments were conducted at different temperatures and space velocities. Six sets of experiments were conducted at temperatures 425, 440, 455, 470, 485, and 500°C. Weight hourly space velocities (WHSV) ranged from 1 to 0.2. Hydrogen pressure was 1800 psi in all experiments. Hydrogen to feed ratio was 3563 cc/gm. The high hydrogen to feed ratio was selected to ensure a large excess of hydrogen above that required from stoichiometric considerations. Tables 4.6 to 4.11 show the results from these experiments. The data are represented graphically in Figures 4.2 to 4.7. Weight% conversion and weight% of C_1 , C_2 , C_3 , and C_4 hydrocarbons are plotted against WHSV.

Decreasing the space velocity which increases the contact time has a similar effect as increasing the reaction time. The weight hourly space velocity is defined as:

Table 4.6. Effect of space velocity on conversion and product distribution in second stage at 425°C

Preheater temperature, °C	425	425	425	425
Reactor temperature, °C	425	425	425	425
H ₂ pressure, psi	1800	1800	1800	1800
H ₂ /feed ratio(cc/gm)	3563	3563	3563	3563
WHSV	1.0	0.6	0.4	0.28
Conversion, wt%	9.4205	11.2914	20.8870	31.3620
C ₁ , wt%	4.8045	4.2250	3.2838	2.5246
C ₂ , wt%	7.2899	6.7656	4.1455	5.0690
C ₃ , wt%	50.8830	41.5681	37.5660	32.6082
C ₄ , wt%	37.0221	47.4412	55.0050	59.7981

Table 4.7. Effect of space velocity on conversion and product distribution in second stage at 440°C

Preheater temperature, °C	440	440	440	440
Reactor temperature, °C	440	440	440	440
H ₂ pressure, psi	1800	1800	1800	1800
H ₂ /feed ratio(cc/gm)	3563	3563	3563	3563
WHSV	1.0	0.6	0.4	0.28
Conversion, wt%	14.4401	26.8660	34.3548	42.9031
C ₁ , wt%	4.4136	2.6103	3.4432	3.0770
C ₂ , wt%	6.8353	4.0987	6.0403	6.4400
C ₃ , wt%	45.6904	37.8029	36.6014	38.4124
C ₄ , wt%	43.0598	55.4880	53.9150	52.0706

Table 4.8. Effect of space velocity on conversion and product distribution in second stage at 455°C

Preheater temperature, °C	455	455	455	455
Reactor temperature, °C	455	455	455	455
H ₂ pressure, psi	1800	1800	1800	1800
H ₂ /feed ratio(cc/gm)	3563	3563	3563	3563
WHSV	1.0	0.6	0.4	0.28
Conversion, wt%	15.9957	26.7172	42.2850	53.2049
C ₁ , wt%	5.6240	5.7892	4.3012	2.3537
C ₂ , wt%	7.0447	7.8141	6.1514	4.6065
C ₃ , wt%	50.4131	43.7336	37.5560	41.8902
C ₄ , wt%	36.9181	42.6627	51.9910	51.1497

Table 4.9. Effect of space velocity on conversion and product distribution in second stage at 470°C

Preheater temperature, °C	470	470	470	470
Reactor temperature, °C	470	470	470	470
H ₂ pressure, psi	1800	1800	1800	1800
H ₂ /feed ratio(cc/gm)	3563	3563	3563	3563
WHSV	1.0	0.8	0.6	0.4
Conversion, wt%	19.7014	23.4402	34.2370	50.4132
C ₁ , wt%	6.6504	6.1622	6.1762	5.2044
C ₂ , wt%	8.1505	8.4953	9.3892	9.1488
C ₃ , wt%	50.0914	48.3336	41.9016	39.9578
C ₄ , wt%	35.1076	37.0088	42.5329	45.6889

Table 4.10. Effect of space velocity on conversion and product distribution in second stage at 485°C

Preheater temperature, °C	485	485	485	485	485
Reactor temperature, °C	485	485	485	485	485
H ₂ pressure, psi	1800	1800	1800	1800	1800
H ₂ /feed ratio(cc/gm)	3563	3563	3563	3563	3563
WHSV	1.0	0.8	0.6	0.4	0.28
Conversion, wt%	19.0377	30.3334	39.2049	56.6169	72.4492
C ₁ , wt%	7.5855	10.0822	9.0702	7.5826	10.2688
C ₂ , wt%	11.8156	15.5169	17.7688	14.1040	12.7928
C ₃ , wt%	46.9980	41.2010	40.6654	40.2059	41.4289
C ₄ , wt%	33.6010	33.1999	32.4957	38.1074	35.5095

Table 4.11. Effect of space velocity on conversion and product distribution in second stage at 500°C

Preheater temperature, °C	500	500	500	500
Reactor temperature, °C	500	500	500	500
H ₂ pressure, psi	1800	1800	1800	1800
H ₂ /feed Ratio(cc/gm)	3563	3563	3563	3563
WHSV	1.0	0.6	0.4	0.28
Conversion, wt%	21.5230	44.2674	63.6354	83.8311
C ₁ , wt%	13.0716	10.7696	10.7291	12.1524
C ₂ , wt%	18.6874	19.7239	17.2651	18.0468
C ₃ , wt%	43.1644	40.6182	38.9955	39.6859
C ₄ , wt%	25.0765	28.8883	33.0103	30.1149

Figure 4.2. Effect of space velocity on conversion and product distribution (425 deg. C)

Figure 4.3. Effect of space velocity on conversion and product distribution (440 deg. C)

Figure 4.4. Effect of space velocity on conversion and product distribution (455 deg. C)

Figure 4.5. Effect of space velocity on conversion and product distribution (470 deg. C)

Figure 4.6. Effect of space velocity on conversion and product distribution (485 deg. C)

Figure 4.7. Effect of space velocity on conversion and product distribution (500 deg. C)

$$\text{WHSV (hr}^{-1}\text{)} = \frac{\text{weight feed rate of coal-derived liquid (weight/hr)}}{\text{weight of catalyst (weight)}}$$

WHSV gives a relative measurement of contact time.

4.4 Effect of WHSV on conversion and product distribution

As WHSV decreased conversions increased. Conversions increased with increasing temperature, with a maximum conversion of 83.83 weight% at 500°C and .28 WHSV. The increase in conversion is mostly due to the increase in production of C₄ hydrocarbons. Conversion to C₄ hydrocarbons increased with decreasing WHSV at all temperatures. Conversion to C₃ hydrocarbons decreased with decreasing WHSV. The same trend is observed at all temperatures. There is only a slight variation in the yields of C₁ and C₂ hydrocarbons and essentially the yields remained constant with WHSV.

In the raffinate hydrocracking with palladium-nickel containing synthetic mica-montmorillonite catalyst, Giannetti and Fisher¹¹⁰ observed that isobutane yields increased primarily at the expense of propane, with n-butane yields being virtually unchanged as the hydrocracking severity increased. C₁+C₂ yields also remained constant as the severity increased. Kithany¹ also observed an increase in C₄ yields and decrease in C₃ yields as the reaction time increased from 30 minutes to 60 minutes in converting coal to C₂-C₄ hydrocarbons using a sulfided Ni-Mo/Al₂O₃ mixed with

$\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst at 1800 psi and 500°C. Sullivan and Meyer¹¹¹, studying the catalyst effects in hydrocracking hydrotreated gas oils, observed that large quantities of isobutanes are produced selectively from cycloparaffins. Egan et al.⁹⁵ showed that hydrocracking of cycloparaffins with carbon numbers of 10 or more react selectively to give isobutanes plus lower molecular weight cycloparaffins. The reaction was termed a paring reaction. Alkyl aromatics with side chains of three or more carbons crack by dealkylation, with much less isomerization of the alkyl group. Butanes are also produced by cracking reactions other than the ones mentioned above.¹¹¹ For example, substantial quantities are produced by hydrocracking of paraffins.

$\text{C}_1\text{-C}_4$ hydrocarbons (mostly C_1) are also produced by thermal cracking reactions in addition to hydrocracking reaction, because of the high temperatures involved in the present study. In addition, C_3 and C_4 hydrocarbons undergo secondary cracking to lower hydrocarbons. The relative rates of production of C_3 and C_4 hydrocarbons by thermal and hydrocracking reactions, and destruction by secondary cracking reactions, determine whether C_3 and C_4 hydrocarbons increase or decrease with WHSV.

Due to the complex nature of the feed material and the reaction taking place it is difficult to give any precise explanation for the increase or decrease of C_3 and C_4 hydrocarbons with WHSV.

4.5 Effect of temperature on conversion and product distribution

Tables 4.12-4.15 and Figures 4.8-4.11 show the effects of temperature on conversion and product distribution at different space velocities. Conversions to C_1 and C_2 hydrocarbons increased with temperature at all space velocities. Space velocities ranged from 1.0 to 0.28. C_4 hydrocarbons decreased with temperature at all space velocities. C_3 hydrocarbons exhibit a broad maximum in the temperature range 440 to 485. It is likely that C_3 cracks to C_1 and C_2 as temperature increases.

At the lower temperatures, the C_3 produced is higher than the amount cracked to C_1 and C_2 which results in a net increase in the C_3 yield. As the temperature increases, the production of C_3 slows down while its cracking to C_1 and C_2 continues. As temperature increases the cracking of C_4 increases resulting in the decrease of C_4 with temperature. The additional C_1 and C_2 produced from the cracking of C_3 and C_4 is responsible for the increase of C_1 and C_2 with temperature. Total conversion to gases increases with temperature due to the increase in C_3 in the temperature range 425 to 470°C, while the increase comes from the increase in C_1 and C_2 in the temperature range 470 to 500°C. For the same temperature range (425-500°C), the conversion to gases increases rapidly as the WHSV is reduced from 1.0 to 0.28. At the WHSV of 1.0 the increase in conversion was from 9.42 to 21.52 (12.1 weight%). At WHSV 0.6, 0.4 and 0.28

Table 4.12. Effect of temperature on conversion and product distribution (WHSV=1)

Preheater temperature, °C	425	440	455	470	485	500
Reactor temperature, °C	425	440	455	470	485	500
H ₂ pressure, psi	1800	1800	1800	1800	1800	1800
H ₂ /feed ratio, cc/gm	3563	3563	3563	3563	3563	3563
WHSV, wt/wt/hour	1.0	1.0	1.0	1.0	1.0	1.0
Conversion, wt%	9.4205	14.4401	15.9957	19.7014	19.0377	21.5230
C ₁	4.8045	4.4136	5.6240	6.6504	7.5855	13.0716
C ₂	7.2899	6.8363	7.0447	8.1505	11.8156	18.6874
C ₃	50.8830	45.6904	50.4131	50.0914	46.9980	43.1644
C ₄	37.0221	43.0598	36.9181	35.1076	33.6010	25.0765

Table 4.13. Effect of temperature on conversion and product distribution (WHSV=0.6)

Preheater temperature, °C	425	440	455	470	485	500
Reactor temperature, °C	425	440	455	470	485	500
H ₂ pressure, psi	1800	1800	1800	1800	1800	1800
H ₂ /feed ratio, cc/gm	3563	3563	3563	3563	3563	3563
WHSV, wt/wt/hour	0.6	0.6	0.6	0.6	0.6	0.6
Conversion, wt%	11.2914	26.8660	26.7172	34.2370	39.2049	44.2674
C ₁	4.2250	2.6103	5.7892	6.1762	9.0702	10.7696
C ₂	6.7656	4.0987	7.8141	9.3892	17.7688	19.7239
C ₃	41.5681	37.8029	43.7336	41.9016	40.6654	40.6182
C ₄	47.4412	55.4880	42.6627	42.5329	32.4957	28.8883

Table 4.14. Effect of temperature on conversion and product distribution (WHSV=0.4)

Preheater temperature, °C	425	440	455	470	485	500
Reactor temperature, °C	425	440	455	470	485	500
H ₂ pressure, psi	1800	1800	1800	1800	1800	1800
H ₂ /feed ratio, cc/gm	3563	3563	3563	3563	3563	3563
WHSV, wt/wt/hour	0.4	0.4	0.4	0.4	0.4	0.4
Conversion, wt%	20.8870	34.3548	42.2850	50.4132	56.6169	63.6354
C ₁	3.2838	3.4432	4.3012	5.2044	7.5826	10.7291
C ₂	4.1455	6.0403	6.1514	9.1488	14.1040	17.2651
C ₃	37.5660	36.6014	37.5560	39.9578	40.2059	38.9955
C ₄	55.0050	53.9150	51.9910	45.6889	38.1074	33.0103

Table 4.15. Effect of temperature on conversion and product distribution (WHSV=28)

Preheater temperature, °C	425	440	455	485	500
Reactor temperature, °C	425	440	455	485	500
H ₂ pressure, psi	1800	1800	1800	1800	1800
H ₂ /feed ratio, cc/gm	3563	3563	3563	3563	3563
WHSV, wt/wt/hour	0.28	0.28	0.28	0.28	0.28
Conversion, wt%	31.3620	42.9031	53.2049	72.4492	83.8311
C ₁	2.5246	3.0770	2.3537	10.2688	12.1524
C ₂	5.0690	6.4400	4.6065	12.7928	18.0468
C ₃	32.6082	38.4124	41.8902	41.4289	39.6859
C ₄	59.7981	52.0706	51.1497	35.5095	30.1149

Figure 4.8. Effect of temperature on conversion and product distribution (WHSV = 1)

Figure 4.9. Effect of temperature on conversion and product distribution (WHSV = 0.6)

Figure 4.10. Effect of temperature on conversion and product distribution (WHSV = 0.4)

Figure 4.11. Effect of temperature on conversion and product distribution (WHSV = 0.28)

the increase was 33.0, 42.7 and 52.4 weight% respectively.

From the above data it can be seen that high yields of C_4 hydrocarbons are obtained by operating at low temperatures and low WHSV. On the other hand, for maximum C_3 production, operation at the intermediate temperatures of 440-485 at high WHSV of about 1.0 is preferred. C_1 and C_2 production is maximum at high temperatures.

4.6 Mechanism of conversion of coal-derived liquids to hydrocarbon gases

As the major types of products expected to be present in coal liquids are paraffins, cycloparaffins, alkyl aromatics and polycyclic aromatics, the reaction mechanisms to produce light hydrocarbons from these products are considered in some detail below.

Catalytic hydrocracking can be considered as catalytic cracking with hydrogenation superimposed. The hydrocracking catalysts are dual functional catalysts containing both a hydrogenation-dehydrogenation component and an acidic component. The acidic component, usually silica alumina, promotes the cracking and isomerization reactions involving carbonium-ion type intermediates, whereas the hydrogenation component, usually metal sulfides, promotes the hydrogenation-dehydrogenation type reactions.

4.6.1 Hydrocracking of paraffins

The mechanism of hydrocracking is considered similar to that of catalytic cracking with features of hydrogenation and hydroisomerization superimposed. The first step in the hydrocracking reaction is dehydrogenation of an alkane to alkene. The alkene thus formed is then adsorbed on the acidic sites of the catalyst to form a carbonium ion, which then initiates the catalytic chain reaction. The dehydrogenation step seems to be the rate determining step.⁹⁴

The products from hydrocracking n-hexadecane over nickel sulfide on silica-alumina at 290°C, 82 atm, and 51% conversion are shown in Figure 2.5.¹¹² As can be seen most of the products are C₃-C₇ hydrocarbons. Similarly the C₃-C₇ are the primary products of hydrocracking n-decane at 288°C and 82 atm over nickel sulfide on silica-alumina. The similarity between catalytic cracking and hydrocracking can also be seen from the Figure 2.6. The minor differences in product distributions are attributed to differences in reaction conditions.¹¹³

Cracking is essentially the reverse of polymerization, occurring at the bond located β to the carbon atom bearing the positive charge. The continued pattern of cracking of straight chains at the β position leads to formation of propylene, in high yields. On the other hand thermal cracking which proceeds by free-radical mechanism gives high yields of ethylene. Thus high yields of propylene indicate

catalytic cracking whereas high yields of ethylene indicate thermal cracking.⁸⁸

Paraffin molecules first react with a proton or a small carbonium ion at the surface of the catalyst to form larger carbonium ions. Since secondary carbonium ions are more stable than primary carbonium ions, secondary carbonium ions immediately predominate. β -scission of the secondary carbonium ions yields large quantities of propylene. Since a tertiary carbonium ion is even more stable than a secondary carbonium ion, a number of secondary carbonium ions rearrange to tertiary carbonium ions, β -scission of which yields large quantities of isobutylene.¹¹⁴

The rate of hydrocracking of n-paraffins increases with increasing molecular weight. For example, Flinn et al.¹¹⁵ observed that at the same conditions n-hexadecane conversion was 95% whereas the conversion of n-octane was only 53%.

Liu² hydrocracked n-hexadecane at 450°C and 1800 psi over NiMo/Al₂O₃ mixed with SiO₂-Al₂O₃ catalyst (same conditions as in the present study). The product distribution is shown in Figure 4.12 along with the product distribution from hydrocracking of n-hexadecane obtained by Archibald.¹¹⁶ Archibald's experiments showed that n-hexadecane hydrocracking proceeds by carbonium ion mechanism. Due to a similarity of product distributions it was concluded that at the conditions at which the experiment was conducted cracking proceeds by carbonium ion mechanism. The important feature to note in the product distributions

Figure 4.12. Product distribution from hydrocracking of n-hexadecane

is the abundance of C_3 and high hydrocarbons. As mentioned earlier thermal cracking yields high C_2 hydrocarbons. The product distribution obtained by thermal cracking of n-hexadecane at 500°C is shown in Figure 4.13 which clearly shows the abundance of C_2 hydrocarbons.

4.6.2 Hydrocracking of olefins

Olefins hydrocrack more readily than paraffins. It is generally agreed that the first step in the hydrocracking of olefins is the formation of a carbonium ion by the addition of a proton from a Bronsted site to the double bond of the olefin. The carbonium ion thus formed cracks according to the β rule yielding large quantities of propylene and isobutylene. From similarities in product distribution it can be concluded that the hydrocracking of paraffins and olefins proceeds through the same reaction intermediate.¹¹⁷

4.6.3 Hydrocracking of cycloparaffins

The hydrocracking of C_9 to C_{12} methyl cycloparaffins over sulfided nickel on $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst at about $230\text{-}290^\circ\text{C}$ has been studied.⁹⁵ The principal acyclic product is isobutane, and the principal cyclic product contains four carbon atoms less than the original alkylcyclohexane. Very little ring rupture occurs. The amount of methane in the products is very small indicating that the production of cycloalkanes of lower molecular weight is not due to the simple demethanation reaction. It has been suggested that

Figure 4.13. Product distribution from thermal cracking of n-hexadecane

methyl groups are pared from cycloparaffin rings and eliminated as branched paraffins; mainly isobutane, in such a way as to conserve rings. This type of reaction, called a paring reaction, is predominant in cycloparaffins with 10 or more carbon atoms. In cycloparaffins with 9 carbon atoms, the ring yield is low; there is almost as much pentane formed as butane, and there is no single predominant cycloparaffin product. In addition, the rate of cracking of C_9 cycloparaffin is about 100 times smaller than that of C_{10} cycloparaffin.

It has been observed that the ratio of singly branched paraffins to unbranched paraffins is very high in the products of cycloparaffins undergoing paring reaction. The similarity of product distribution in the hydrocracked products of five isomeric cycloparaffins containing 10 carbons indicates that the composition of the product is essentially independent of the reactant structure. It has been observed that extensive isomerization of the reactant precedes the cracking of cycloparaffins.

A mechanism proposed for the paring reaction is shown in Figure 4.14.⁹⁵ Carbonium ion intermediates are formed either by dehydrogenation followed by protonation of the double bond or by hydride ion transfer to another carbonium ion. The adsorbed species then isomerize rapidly on the catalyst surface. This is followed at a slower rate by selective cracking of certain favorable structures. This explains the fact that the product distribution is

Figure 4.14. A proposed mechanism for the paring reaction

essentially independent of the structure of the original cycloparaffin.

The high selectivity of the products indicates that the types of carbonium ions that will crack are restricted. The product composition indicates that the predominant cracking occurs with tertiary ions which can produce another tertiary ion by β -scission. This assumption is consistent with the production of isobutane rather than n-butane and propane. As at least 10 carbon atoms are necessary to form the favorable carbonium ion intermediate, the C₉ cycloparaffins fail to undergo the selective paring reaction.

The hydrocracking of a multiple ring naphthene such as decalin is more rapid than that of the corresponding n-paraffins.¹¹⁸ At milder process conditions hydrocracking of decalin yields light paraffins and single ring naphthenes such as methyl cyclopentane and cyclohexane. In the hydrogenolysis of polymethyl cyclopentanes, demethanation to produce lower polymethyl cyclopentanes, and ring cleavage to produce paraffins are the main reactions.¹¹⁹

It has been observed in connection with the hydrocracking of cycloparaffins at mild temperatures of about 550°F that the cycloparaffin ring is very stable. However, higher temperatures led to increased ring destruction.¹¹⁷ Bond energies of the carbon-carbon bonds in the ring are approximately the same as those in the side chains. A structure such as I can undergo ring cleavage by the favored β -scission of a tertiary ion to produce another

tertiary ion. When ring cleavage of cation I occurs, the initial product is a cation containing an olefinic double bond II. This intermediate, still bound to the catalyst in the activated form, can subsequently desorb and hydrogenate to form a paraffin of the same carbon number as the reactant which is further cracked by carbonium ion chemistry to give

high yields of C_3 hydrocarbons. Alternatively the intermediate can directly crack again to form lighter acyclic products. Either way, there will be high yields of light hydrocarbons from cracking the rings.

4.6.4 Hydrocracking of alkyl aromatics

Hydrocracking of a number of alkyl aromatics over nickel sulfide on silica-alumina catalyst indicate that the alkyl aromatics undergo a number of reactions such as isomerization, dealkylation, alkyl transfer, paring, and cyclization. The wide variation in product distributions suggests a greater dependence on the specific structure of the reactant compared to cycloparaffin reactants.⁹⁴

Hydrocracking of alkylbenzenes containing three to five carbons as alkyl groups is relatively simple involving

direct dealkylation as the primary cracking reaction. For example, tert-amylbenzenes gives benzene and isopentane and n-butylbenzene reacts to form benzene and butane.⁹⁴

As the alkyl side chain size increases, the product distribution becomes more complex involving cyclization reactions. In hydrocracking of n-decylbenzene simple dealkylation to benzene and decane is still the most important reaction, but many other reactions also take place. All the paraffins from C_3 through C_{10} are produced in substantial quantities as well as alkylbenzenes from 7 to 12 carbon number. C_9 - C_{12} polycyclic hydrocarbons, particularly tetralins and indanes, are also formed in considerable quantities by cyclization reactions.⁹⁴

Hydrocracking of polyalkylbenzenes gives light paraffins and C_{10} and C_{11} methylbenzenes as the main products. Ring cleavage is almost absent and hydrogenolysis to form methane is at a minimum. A mechanism similar to the paring reaction was proposed to explain the product distribution.⁹⁶

The larger paraffins formed in these reactions conducted at mild conditions may further be cracked to lighter hydrocarbons as the severity of hydrocracking is increased as in the present study. Other products formed as mentioned above also may undergo further cracking yielding lighter hydrocarbons as the hydrocracking severity is increased.

4.6.5 Hydrocracking of polycyclic aromatics

As most of the coal liquids consist of aromatic/hydroaromatic ring structures, reactions involving these structures are the most important in producing high yields of C_2 - C_4 hydrocarbons. Hydrocracking of a number of polycyclic aromatics has been reported.

Qader¹⁰² studied the hydrocracking of naphthalene, anthracene and pyrene on different catalysts, $CoS/SiO_2-Al_2O_3$, $MoS_2/SiO_2-Al_2O_3$, $NiS/SiO_2-Al_2O_3$ and $WS_2/SiO_2-Al_2O_3$ at 475°C and pressures of about 1900 psi in a stirred autoclave. The reaction time was 30 minutes. The product distributions are shown in Tables 4.16-4.18.

Liu and Wiser² conducted similar experiments at about 1800 psi in a stirred autoclave using sulfided Ni-Mo/ Al_2O_3 mixed with $SiO_2-Al_2O_3$. The compounds studied were tetralin, anthracene and phenanthrene. Though complete product distribution was not given, the analysis of the liquid and gas products by gc-ms and gc indicate similar product distribution as obtained by Qader.¹⁰² Among the gas products C_3 and C_4 are predominant. The gas product distribution was compared to that obtained by Sullivan et al.⁹⁶ and was found to be similar.

Naphthalene hydrocracking data indicate that naphthalene is first hydrogenated to tetralin. The presence of methylindan and indan in the products suggest a sequential isomerization and dealkylation reaction. The butylbenzenes seem to have been formed from tetralin or

Table 4.16. Hydrocracking product distribution
of naphthalene

Cracking catalyst: Silica-(High) Alumina				
Temperature: 475°C				
Pressure: 1000 psi (cold), 1950 psi (hot)				
H ₂ /Naphthalene (Moles): 11.7				
Reaction Time: 30 min.				
Hydrogenation catalyst	CoS	MoS ₂	NiS	WS ₂
Product composition, mol%				
Higher compounds	1.0	0.9	1.0	1.1
Naphthalene	27.1	30.3	28.2	28.1
Tetralin	24.0	24.4	26.7	25.0
Methyl indan	17.3	19.2	18.5	17.1
Indan	5.2	4.1	3.8	4.7
Butylbenzene	1.4	0.3	0.4	0.5
Ethylbenzene	5.5	4.3	4.5	5.1
Toluene	8.5	7.5	8.4	8.1
Benzene	10.0	9.0	8.5	10.3
Butanes	3.2	2.1	2.5	3.4
Propane	20.1	18.5	18.4	19.8
Ethane	3.5	2.8	2.6	3.1
Methane	1.6	1.8	1.7	1.4

Adapted from reference 102.

Table 4.17. Hydrocracking product distribution
of anthracene

Cracking catalyst: Silica- (High) Alumina				
Temperature: 475°C				
Pressure: 1000 psi (cold), 1920 psi (hot)				
H ₂ /Anthracene (Moles): 16.2				
Reaction Time: 30 min.				
Hydrogenation catalyst	CoS	MoS ₂	NiS	WS ₂
Product composition, mol%				
Higher compounds	1.3	1.7	1.2	1.5
Anthracene	12.0	17.2	14.1	11.6
9, 10-Dihydroanthracene	7.5	6.1	6.3	8.0
1, 2, 3, 4-Tetrahydroanthracene	20.2	32.8	27.3	18.3
1, 2, 3, 4, 5, 6, 7, 8-Octahydroanthracene	7.0	5.3	6.5	6.3
Hydroanthracene isomers (C ₁₄)	9.5	6.5	7.3	10.5
Hydroanthracene isomers (C ₁₃)	13.0	8.2	9.4	12.3
Naphthalenes, tetralins and indans	22.0	18.1	23.6	21.4
Benzene and alkylbenzenes	7.5	4.1	4.3	10.1
Butanes	12.3	9.1	11.7	15.2
Propane	18.5	12.4	14.2	19.3
Ethane	10.2	6.6	7.8	10.8
Methane	6.6	4.7	5.5	6.7

Adapted from reference 102.

Table 4.18. Hydrocracking product distribution of pyrene 102

Cracking catalyst: Silica-(High) Alumina				
Temperature: 475°C				
Pressure: 1000 psi (cold), 1910 psi (hot)				
H ₂ /Pyrene (Moles): 18.4				
Reaction Time: 30 min.				
Hydrogenation catalyst	CoS	MoS ₂	NiS	WS ₂
Product composition, mol%				
Pyrene	59.0	70.1	69.5	60.3
Hydropyrenes	22.1	15.9	15.5	21.7
Phenanthrenes & Isomers	8.4	7.1	8.6	8.1
Naphthalenes, tetralins and indans	6.3	5.1	4.3	5.0
Benzenes	4.2	1.8	2.1	4.9
Butanes	0.6	0.7	0.9	1.3
Propane	18.5	11.4	11.5	17.7
Ethane	7.3	4.2	3.9	7.0
Methane	5.1	3.5	3.1	5.1

Adapted from reference 102.

methylandan by ring opening. The presence of C_2 - C_4 hydrocarbons can be explained by the β -scission of the carbonium ions formed. Predominance of C_3 in the gaseous products is consistent with the carbonium ion chemistry. A mechanistic scheme of the formation of C_1 - C_4 hydrocarbons is shown in Figure 4.15.

Anthracene hydrocracking reactions are very complex and the Figure 4.16 shows only the gross pattern of hydrocracking as indicated by the product distributions. As in the case of naphthalene, anthracene hydrocracking also involves a multiple mechanism of hydrogenation, isomerization and cracking. Anthracene is sequentially hydrogenated forming di-, tetra- and octahydroanthracenes. The saturated six member rings of tetra- and octahydroanthracenes isomerize, forming hydroanthracene isomers which subsequently are hydrocracked to naphthalenes. The naphthalenes are converted to tetralins and indans and finally to benzenes. The carbonium ions formed as intermediates during hydrocracking yield substantial quantities of C_2 - C_4 hydrocarbons. Again C_3 's are predominant in the gas products.

Carbonium ions can be formed either by protonation of an aromatic ring or by hydride abstraction from a naphthenic ring. The carbonium ion can form on the benzene ring or on the naphthenic ring. Carbonium ion theory accounts for the high yields of C_3 and C_4 over C_1 and C_2 . The order of stability of carbonium ions is as follows:

Tertiary > Secondary > Primary

The more stable tertiary and secondary carbonium ions predominate over the less stable primary ions. High production of C_3 and C_4 result from the scission of secondary and tertiary carbonium ions. The production of C_1 and C_2 is not favored because it involves break-up of primary carbonium ions.

The product distribution from hydrocracking of pyrene indicates a multistep mechanism of hydrogenation, isomerization and cracking as in the case of naphthalenes and anthracenes. Again, C_3 is the predominant component among gas products.¹⁰²

4.6.6 Thermal cracking and secondary cracking

Even though the present study was conducted at high hydrogen pressure with a dual functional catalyst, certain thermal cracking reactions may also occur due to the high temperatures involved. Thermal cracking reactions involve free-radical mechanisms. The free radicals formed by the homolysis of carbon-carbon bonds can undergo β -scission to give substantial quantities of C_2 hydrocarbons.

The larger gas components C_3 and C_4 can undergo secondary cracking increasing the C_1 and C_2 components in the products. Brooks¹²⁰ studied the hydrogenolysis of low boiling hydrocarbons in a flow reactor in the temperature range 500-600°C. The apparent first order rate constants are shown in Table 4.19. In the presence of hydrogen the rate

Table 4.19. Observed apparent first order rate constants for various 10% hydrocarbon and 90% H₂ mixtures at 600 psi

Hydrocarbon	k, sec ⁻¹	k at 500°C, sec ⁻¹	T _{1/2} (half-life) at 500°C
Ethane	10 ^{17.5} exp (-90,000/RT)	1.1 × 10 ⁻⁸	711 days
i-butane	10 ^{15.2} exp (-64,500/RT)	9.2 × 10 ⁻⁴	12.6 minutes
n-butane	10 ^{17.6} exp (-71,800/RT)	2.0 × 10 ⁻³	5.8 minutes
Neopentane	10 ^{12.3} exp (-50,700/RT)	9.2 × 10 ⁻³	75 seconds

Note: Activation energy in calories/mole

Adapted from reference 120.

Table 4.20. Initial breakdown product at 560°C and 600 psi

Hydrocarbon	Percentage product (on H ₂ -free basis)			
	C ₁	C ₂	C ₃	C ₄
i-butane	35	1	35	28
n-butane	46	35	19	0
Neopentane	48	0	3	49

Adapted from reference 120.

constants were observed to increase by a factor of 2-3 compared to the rate constants in the absence of hydrogen. Product distribution from the cracking of some of the compounds is shown in Table 4.20. As can be seen the cracking is substantial at the reaction condition studied. In the present study, the decrease of C_4 hydrocarbons and increase of C_1 , C_2 and C_3 hydrocarbons with temperature can be attributed to the secondary cracking of C_4 hydrocarbons. Additionally, higher temperatures involve increased thermal cracking giving higher yields of C_1 and C_2 hydrocarbons.

4.7 Kinetics of conversion of coal-derived liquids to C_1 - C_4 hydrocarbons

In this study coal-derived liquids are converted to C_1 - C_4 gases in a fixed bed continuous flow reactor. The reactor is filled with catalyst and the reactants flow down the catalyst bed. The kinetic study is done in the flow system at a constant pressure of 1800 psi and temperature range of 425 to 500°C.

Assuming a reaction weight of dW in the catalyst bed of W_c gm in the reactor, a liquid flow rate of w gm/hr, and the reactant concentration of x moles, the rate of disappearance of the reactants for an n th order reaction can be represented by

$$-dx/dt = Kx^n dW \quad 4.1$$

where K is the rate constant. At steady state, the reactant entering and leaving the catalyst bed in time dt hour will

respectively be $wxdx$ and $w(x-dx)dt$. The reactant disappearing will then be $-Kx^n dWdt$. Therefore,

$$\begin{aligned} wxdt &= w(x-dx)dt - Kx^n dWdt \\ \text{or } -wdxdt &= Kx^n dWdt \\ \text{or } -dx/x^n &= (K/w) dW \end{aligned} \quad 4.2$$

At the entrance to the catalyst bed $W=0$ and $x=x_i$, where x_i is the initial concentration of the reactants (feed material as such, weight). At the exit of the catalyst bed, $W=W_c$ and $x=x_f$ where x_f is the final concentration of the reactants (liquid product, weight). By integration over the entire catalyst weight and concentration of the reactants equation 4.2 becomes

$$\int_{x_i}^{x_f} \frac{1}{x^n} dx = \int_0^{W_c} \frac{K}{w} dW \quad 4.3$$

For a first order reaction, equation 4.3 becomes

$$\begin{aligned} \int_{x_i}^{x_f} \frac{1}{x} dx &= \int_0^{W_c} \frac{K}{w} dW \quad \text{since } n=1 \\ \ln \frac{x_i}{x_f} &= \frac{K}{w} W_c \end{aligned} \quad 4.4$$

Since $w/W_c = \text{WHSV}$ (weight hourly space velocity), equation 4.4 becomes

$$\ln \frac{x_i}{x_f} = \frac{K}{\text{WHSV}} \quad 4.5$$

If conversion is defined as $x = (x_i - x_f)/x_i$

$$\text{then } x_f = x_i (1-x)$$

Substituting the value of x_f in equation 4.5

$$\ln \frac{x_i}{x_i(1-x)} = \frac{K}{\text{WHSV}}$$

$$- \ln (1-x) = \frac{K}{\text{WHSV}} = K\tau$$

where τ is space time $\tau = 1/\text{WHSV}$

Table 4.21 gives the variation of conversion with weight hourly space velocity (WHSV). The $-\ln(1-x)$ values are plotted against WHSV for different temperatures in Figure 4.17. The plots are linear and, thus, the first order rate constant can be represented by

$$\frac{-d(\text{gas})}{dt} = K(\text{coal-derived liquid})$$

where K is the rate constant for hydrocracking coal-derived liquid.

The values of rate constants obtained from the plots are given in Table 4.22. The rate constant varied from 0.00188 min^{-1} at 425°C to 0.01018 min^{-1} at 500°C .

Table 4.21. Variation of conversion with WHSV at
different temperatures

Temperature, °C	WHSV	1/WHSV	Conversion, x	ln(1-x)
425	1.0	1.0	9.4205	-0.09894
425	0.6	1.667	11.2914	-0.1198
425	0.4	2.5	20.8870	-0.2343
425	0.28	3.5714	31.3620	-0.3763
440	1.0	1.0	14.4401	-0.15595
440	0.6	1.667	26.8660	-0.3129
440	0.4	2.5	34.3548	-0.4209
440	0.28	3.5714	42.9031	-0.5604
455	1.0	1.0	15.9957	-0.1743
455	0.6	1.667	26.7172	-0.3108
455	0.4	2.5	42.2850	-0.5497
455	0.28	3.5714	53.2049	-0.7594
470	1.0	1.0	19.7014	-0.2194
470	0.8	1.25	23.4402	-0.2671
470	0.6	1.667	34.2370	-0.4191
470	0.4	2.5	50.4132	-0.7015

Table 4.21. - continued

485	1.0	1.0	19.0377	-0.21119
485	0.8	1.25	30.3334	-0.3615
485	0.6	1.667	39.2049	-0.49766
485	0.4	2.5	56.6169	-0.8351
485	0.28	3.5714	72.4492	-1.2891
500	1.0	1.0	21.5230	-0.2424
500	0.6	1.667	44.2674	-0.5846
500	0.4	2.5	63.6354	-0.0116
500	0.28	3.5714	83.8311	-1.8221

◻	425	deg	C	$y = -0.0390 + 0.1128x$	$r^2 = 0.9647$
■	440	deg	C	$y = 0.0294 + 0.1525x$	$r^2 = 0.9792$
◇	455	deg	C	$y = -0.0903 + 0.2528x$	$r^2 = 0.9974$
◆	470	deg	C	$y = -0.1270 + 0.3296x$	$r^2 = 0.9955$
◻	485	deg	C	$y = -0.1809 + 0.4104x$	$r^2 = 0.9982$
■	500	deg	C	$y = -0.4192 + 0.6108x$	$r^2 = 0.9888$

Figure 4.17. First order plot of the variation of conversion with space velocity

Table 4.22. Rate constants for the conversion
of liquids to gases

Temperature, °C	Rate Constant k, min ⁻¹
425	.0018800
440	.0025417
455	.0042133
470	.005493
485	.0068400
500	.0101800

The rate constants obtained above were used to draw the Arrhenius plot.

$$k = A \exp(-E/RT)$$

$$\ln k = \ln A - (E/R \times 1/T)$$

where A is the preexponential factor

E is the apparent activation energy

R is the gas constant, 1.987 kcal/mole, and

T is the absolute temperature, °K.

The Arrhenius plot is shown in Figure 4.18. Apparent activation energy obtained from the plot is 23.9 Kcal/mole and the preexponential factor 56950 min⁻¹. Therefore the rate constants are represented by the equation.

$$k = 56950 e^{-23,900/RT} \text{ min}^{-1}$$

Liu² studied the kinetics of coal conversion to C₁-C₄ hydrocarbon gases in an autoclave using the similar conditions as in the present study (pressure: 1800 psi, Temperature range: 440-500°C and catalyst: sulfided Ni-Mo/Al₂O₃ mixed with SiO₂-Al₂O₃). However, she reacted coal (5gm) and tetralin (15gm) directly in the presence of a catalyst (6.25gm) in a single stage batch system, converting coal to liquids and then the liquids to gases. She observed that coal conversion to liquids was essentially complete in the first 10 minutes of the reaction. During the first 10 minutes there was some production of gases directly from coal. The liquids produced were also slowly converted to gases. She studied the kinetics of the conversion of the

Figure 4.18. Arrhenius plot for determining the activation energy and preexponential factor

coal liquids to gases by separating, mathematically, the gases produced from the two different sources.

The above described study of Liu assumed an isothermal temperature profile whereas the actual temperature was not constant. Immediately after injection of the coal and tetralin paste into the heated autoclave containing the catalyst, there was an increase in the reaction temperature by about 40-50°C higher than the intended run temperature in about 5 minutes. The increase in temperature resulted from the exothermic coal hydrogenation. The temperature settled back to the set temperature in about 10 minutes. After that time the temperature cycled above and below the set point due to the on-off temperature controller employed in the study. To take into account the temperature variation, Liu conducted a kinetic analysis by non-isothermal mode.

The activation energy values obtained by Liu by isothermal and non-isothermal modes were 22.65 kcal/mole and 26.55 kcal/mole. The value obtained in the present study is 23.9 kcal/mole. The slightly different values obtained by Liu are due to the complexity of determining the kinetics of conversion of coal liquids to gases in a system which converts coal to liquids and gases and then the liquids to gases with all the reaction taking place in a single reactor vessel. In the isothermal mode of analysis that actual average temperature was slightly higher than the nominal temperature resulting in lower activation energy. In the non-isothermal mode of analysis the temperature profile was

closely simulated to the actual temperature profile.

However, the gas products obtained by the simulation method were slightly different at different temperatures, resulting in higher activation energy.

In the previous experiments, the liquids used were from converting coal to liquids in tetralin solvent (tetralin: coal, 3:1 by weight). Therefore, the liquids contained substantial amounts of tetralin and naphthalene from the original solvent, in addition to the tetralins produced from the coal. One of the main purposes of this work is to compare the kinetic parameters determined in a two-stage process with those from the single stage process determined previously. The single stage process was described briefly in an earlier section. Kinetics of conversion of coal to C_1 - C_4 hydrocarbons were determined in a batch system with coal:Tetralin:catalyst weight ratio of 1:3:1.25. The coal-derived liquids along with tetralin were converted to gases in the process. To be able to compare the results from the present work with the results obtained in the above study, the liquid from the first stage was used as it is in the second stage.

4.8 Reactions of the solvent

It was observed that tetralin undergoes little reaction when heated alone to temperatures of about 500°C. Formation of naphthalene and hydrogen is essentially negligible. However, when coal and tetralin are heated together

appreciable quantities of naphthalene and hydrogen are produced, indicating that the process involves release of hydrogen atoms by the tetralin in the immediate vicinity of the thermally ruptured bonds in coal.^{70,71} However, little or no rupture of carbon-carbon bonds within the fused aromatic structures occurs at temperatures below 500°C. Infra-red analysis of the coal and of the extracts indicated that the aromaticity of the products increased when compared to the original coal, the result of aromatization of the hydroaromatic structures present in the coal.^{70,71}

Using deuterium gas and/or tetralin-d₁₂ Skowronski et al.¹²¹ showed that the 1-position of tetralin is most reactive for the hydrogenation of coal, and that the abstraction of hydrogen from tetralin by a coal-derived radical is involved in the rate-determining step of the formation of soluble products. Vliegar et al.¹²² studied reactions of tetralin with different coals. H-NMR spectra of the spent solvent indicated that the solvent consists of tetralin and naphthalene with small amounts of decalins, methylandan and n-butylbenzene. They discussed the formation of methylandan and butylbenzene during the reaction of tetralin with coal.

It can be concluded from the studies referred to above that some of the tetralin undergoes dehydrogenation, isomerization and hydrocracking reactions yielding naphthalene with small amounts of methylandan and n-butylbenzene.

In the second stage, tetralin and its products from the first stage undergo hydrocracking reactions similar to the other aromatic compounds produced from coal. The reactions typically involve hydrogenation, isomerization, disproportionation and catalytic cracking. The mechanisms of conversion of different classes of compounds are discussed in detail later in the chapter. Thus, the hydrocracking of tetralin and its products also produces substantial quantities of C_1 - C_4 hydrocarbons. In the present study, the gases produced from the solvent are also included in determining the kinetic parameters, as it is difficult to determine separately the gases produced from the two different sources. Separation of the solvent alone from the liquids is not feasible, because coal liquefaction products themselves contain significant quantities of tetralins. A blank run of the solvent without coal liquids may not be informative because the reactions the solvent undergoes may be different in the presence of other compounds.

Kithany¹ studying the conversion of coal to C_1 - C_4 hydrocarbons conducted experiments without hydrogen-donor solvent but with hydrogen and sulfided Ni-Mo/ Al_2O_3 mixed with SiO_2 - Al_2O_3 catalyst. He observed that the hydrocarbon composition was similar with and without the solvent indicating a similar reaction mechanism in both cases. However, more severe reaction conditions were required for the case without the solvent.

Liu² observed an increase in conversion to gases in the experiments with recycled liquids compared to coal-derived liquids containing the solvent.

4.9 Experiments with recycled liquid

A few experiments were conducted at a temperature of 485°C to compare the results from converting coal-derived liquids containing the solvent to the recycled coal liquids. Coal-derived liquids contain substantial quantities of tetralins produced from the coal. It is difficult to differentiate between tetralins produced from the coal and the original tetralin used as hydrogen-donor solvent. So it is difficult to separate the solvent alone from the liquids. To ensure that coal-derived liquids are essentially free of the original solvent, several runs were made in the first stage recycling the coal liquids at 1800 psi hydrogen pressure and 440°C. During the first run coal and tetralin were reacted in the ratio of 3:1. The liquids produced in the first run were used as solvent in the second run and so on until the seventh run. However, in the second run there was a decrease in the net liquids produced due to the limited hydrogen-donor capability of coal-derived liquids compared to tetralin. No catalyst was used during the first run. To improve the hydrogen-donor capability of coal-derived liquids for use in the subsequent runs, from the third run onwards sulfided Ni-Mo/Al₂O₃ catalyst was used. The coal:catalyst:coal-derived liquids were in the ratio of

1:1:3 by weight. Presence of the catalyst improved the hydrogen donor capability of the coal-derived liquids resulting from the hydrogenation of the solvent. The coal-derived liquids finally obtained were lighter (density = 0.9606 g/cc) compared to the liquids containing the solvent (density = 0.9953 g/cc).

The plots for recycled coal liquid and the coal liquid containing the solvent are shown in Figure 4.19. The recycled liquids gave higher conversion, and the reaction rate constant is higher (0.01132min^{-1}) than that for coal liquid containing the solvent (0.00684min^{-1}). (For the same pump setting, the pumping rate increased slightly for the recycled liquids due to the liquids being lighter and less viscous. The increased pumping rate resulted in decreased WHSV and increased space-time, as shown in the Figure 4.19).

The coal-derived liquids consist of predominantly aromatic structures with the average ring size being about three. On the other hand, the coal liquids containing solvent have an average ring size smaller than that of coal-derived liquids due to the presence of tetralin, naphthalene, and small amounts of methylindan and n-butylbenzene.

It has been consistently observed that large molecules are inherently less stable at elevated temperatures than smaller molecules of similar composition. Qader et al.¹²³

Figure 4.19. First order plots for recycled coal liquids and the coal liquid containing the solvent.

studying the hydrocracking of pure compounds in a batch autoclave at 475°C temperature and 1000 psi pressure over $\text{MoS}_2/\text{SiO}_2\text{-Al}_2\text{O}_3$ observed that 3-member rings have higher rate constants than 2-member rings.

As can be seen from Table 4.23 hydrocracking of anthracene and phenanthrene (3-member rings) is much faster than naphthalene (2-member ring). Pyrene (4-member ring) was also more reactive than naphthalene. Thus recycled liquids with larger average ring size hydrocrack readily compared to the coal liquids containing the solvent.

Liu² observed that hydrogen-to-carbon ratio of the recycled liquids increased with the number of times the solvent was recycled, indicating efficient hydrogenation of the liquid in the presence of catalyst and hydrogen pressure. The proton NMR spectra of the recycled liquids also showed an increase in aliphatic-to-aromatic hydrogen ratio. The presence of a larger amount of aliphatic

Table 4.23. First order rate constants for different hydrocarbons¹²³

Hydrocarbon	$k_{\text{hydrogenation}} \times 10^4 \text{ min}^{-1}$	$k_{\text{hydrocracking}} \times 10^4 \text{ min}^{-1}$
Naphthalene	93	61
Anthracene	510	136
Phenanthrene	253	90
Pyrene	180	64

hydrocarbons also increases the rate of hydrocracking as aliphatic hydrocarbons readily hydrocrack compared with aromatic structures. Similarly, an increase in the naphthenic structures, which is expected in the recycled liquids, also increases the rate of hydrocracking. Khavkin et al.¹²⁶, studying the hydrocracking of petroleum fractions, observed that the group of hydrocarbons containing polycyclic naphthenes (3 plus rings) undergoes the maximum hydrocracking.

4.10 Kinetic mechanism

In hydrocracking, reaction temperature and the relationship of acidity to the hydrogenating-dehydrogenating activity are primarily responsible in deciding the product distribution. Though the hydrocracking reactions involving feeds like coal-derived liquids are complex in nature, the overall reaction kinetics can be expressed in simple terms. Hydrocracking of coal-derived liquids primarily involve hydrogenation, cracking, and isomerization reactions.

To put the value of activation energy (23.9 kcal/mole) determined in the present study in perspective, some of the activation energy values reported in the literature are given below.

Qader and Hill¹²⁴ obtained activation energies of 14.3 kcal/mole and 15.5 kcal/mole for hydrocracking petroleum and coal oils respectively. The experiments were conducted in a fixed bed reactor with a 6% nickel sulfide and 19% tungsten

disulfide on silica-alumina catalyst at a hydrogen pressure of 2000 psi and in the temperature range of 400°C to 500°C. The hydrocracking process is milder compared to the present study, as reflected in the high yields of liquids produced compared to the high yields of gases in the present work. It was suggested by Qader and Hill that chemical reactions involving the cracking of C-C, C-O, C-S, and C-N bonds control the reaction rate. The hydrocracking reactions followed first-order kinetics as in the present study.

In another study of hydrocracking of polynuclear aromatic hydrocarbons over silica-alumina based dual functional catalysts, Qader¹⁰² found that hydrocracking of polynuclear aromatic hydrocarbons is a bimolecular reaction taking place on the surface of a solid catalyst. He found that hydrocracking of naphthalene, anthracene and pyrene followed first order kinetics and that the kinetic data were compatible with the dual site mechanism of the Langmuir-Hinshellwood model. The rate of hydrocracking of polynuclear aromatic hydrocarbons was represented by the equation.

$$R = \frac{K^* K_A K_H C_A C_H}{(1 + K_A C_A)^2}$$

where K = rate constant

K_A, K_H = Adsorption constant of polynuclear

aromatic hydrocarbon and hydrogen respectively

C_A = Concentration of polynuclear aromatic hydrocarbon

C_H = Concentration of hydrogen

In another study Qader et al.⁹⁹ determined the apparent activation energy of anthracene hydrocracking to be 28.6 and 16.5 kcal/mole at 1000 and 1400 psi respectively with the WS_2 + H-zeolon combination and 22.9 kcal/mole with WS_2 + silica-(low) alumina combination at 1400 psi. Activation energies of 21.7 and 19.5 kcal/mole were obtained in phenanthrene hydrocracking with H-zeolon + WS_2 and silica-(low) alumina + WS_2 systems respectively at 1400 psi.

The activation energy value of 23.9 kcal/mole obtained in the present study suggests that chemical reactions involving the rupture of C-C bonds of the hydrocarbon molecules in the feed determine the rate in the process. The compatibility of the data from hydrocracking of polynuclear hydrocarbons with the dual site mechanism of the Langmuir-Hinshelwood model suggest that hydrocracking of aromatic hydrocarbons is a bimolecular reaction on the surface of the catalyst.¹⁰⁸ Bimolecular surface reactions occur due to the interaction of two reactant molecules adsorbed on neighboring active sites of the catalyst according to the Langmuir-Hinshelwood mechanism.

The catalyst used in this study is a dual-functional catalyst, containing both cracking and hydrogenation components. It is well known that cracking is the rate-controlling step in hydrocracking. Since cracking is the rate-controlling step, the reaction rates and the product

yields are mainly influenced by the activity of the cracking component of the catalyst.

The high yields of C_1 - C_4 hydrocarbons suggest a mechanism involving a combination of cracking, hydrogenation, isomerization, paring and disproportionation reactions.

The cracking of paraffins yield mainly C_3 and C_4 hydrocarbons. Like catalytic cracking, hydrocracking yields very little C_1 and C_2 fractions. However, unlike catalytic cracking, only saturated products are formed in hydrocracking due to the presence of hydrogen and the hydrogenating component of the catalyst. C_4 fractions rich in isobutane are formed because of a great tendency to form tert-butylcarbonium ion.

Hydrocracking of n-paraffins involves dehydrogenation to form olefins, formation of carbonium ion intermediates, isomerization of the carbonium ion intermediates to more stable tertiary carbonium ions, cracking to form mainly C_3 and C_4 hydrocarbons and saturation of olefinic products by hydrogenation.

Hydrocracking of n-paraffins can be represented by

Step (1) represents dehydrogenation to form an olefin. The olefins formed are isomerized via carbonium ion intermediates in step (2). The isomerized products crack in step (3) forming low molecular weight isoparaffins (mainly C_3 and C_4 fractions) and some olefins. The olefins are saturated in step (4) by hydrogenation to give low molecular weight hydrocarbons.

Olefins hydrocrack more readily than paraffins. Olefins and paraffins give similar product distributions suggesting that olefins hydrocrack in a similar manner as described above for paraffins. Multiring naphthenes hydrocrack more readily than the corresponding normal paraffins to give even higher iso/normal ratio of light paraffins. However, the reaction mechanism is similar to that of paraffins and olefins.

Hydrocracking of cycloparaffins involves isomerization, dealkylation and paring reactions.

The main reactions are isomerization and dealkylation. Cracking of cycloparaffins is preceded by rapid isomerization so that the products from cracking depend only on the molecular weight of the reactant and are essentially

independent of its starting structure. Principal products are isobutane and a cycloparaffin containing four fewer carbons. Higher temperatures lead to further destruction of the cycloparaffins formed yielding lighter hydrocarbons. The paraffin fragments formed may undergo secondary cracking yielding lighter paraffins and olefins. Olefins formed may be hydrogenated further to yield paraffins. Step (5) represents isomerization and cracking whereas steps (6), (7), and (8) represent cracking of the rings, secondary cracking of paraffin fragments, and hydrogenation of olefins respectively.

Alkyl aromatics crack before isomerization and the products depend on the structure of the reactant. Skeletal isomerization in the case of alkyl aromatics is appreciably slower relative to the cracking reaction than with the cycloparaffins. As in the case of cycloparaffins the paraffin fragments formed undergo secondary cracking yielding lighter paraffins and olefins. Olefins are further hydrogenated yielding paraffins.

Steps 9, 10, 11, 12 represent cracking, isomerization, secondary cracking, and hydrogenation respectively.

Polycyclic aromatics undergo a multiple mechanism of hydrogenation, isomerization, and cracking until benzene and its homologs are produced as the end product.

Step 13 represents hydrogenation of the polynuclear aromatic. Step 14 represents isomerization of the aromatic ring. Step 15 indicates cracking of the hydrogenated ring yielding an alkyl aromatic by carbonium ion mechanism. The alkyl aromatic may dealkylate yielding an aromatic and a paraffin as indicated by step 16. Step 17 and step 18 represent secondary cracking yielding lighter paraffins and olefins, and hydrogenation of olefins respectively.

Hydrocracking of Polynuclear hydroaromatics proceeds in a similar manner.

The cracking reactions shown above involve the breakage of C-C bonds present in different types of hydrocarbons and the cracking mainly proceeds through a carbonium ion mechanism.

Qader and Hill¹²⁵ studying the hydrocracking of gas oil suggested that desulfurization and denitrogenation reactions involve the breaking of C-S and C-N bonds with subsequent interaction of hydrogen with the fragmented molecules, forming hydrogen sulfide and ammonia, respectively. It was also suggested that sulfur and nitrogen removal may proceed through an accelerated radical mechanism.

The magnitude of activation energy (23.9 kcal/mole) obtained in the study indicate that chemical reactions but not physical processes are rate controlling. In the process there is a large excess of hydrogen. In the presence of excess hydrogen, the reactions between hydrogen and the fragmented molecules occur freely and rapidly. Thus, hydrogenation reactions may not be rate-controlling. Therefore, cracking and isomerization reactions must be rate-controlling, as was also suggested by Weisz and Prater,¹²⁷ Keulemans and Voge,¹²⁸ and Qader and Hill.¹²⁵ Archibald et al.¹¹⁵ and Flinn et al.¹¹⁴ observed that products from hydrocracking contain an excess of branched isomers as dictated by thermodynamic equilibrium considerations. This is possible only if the isomerization and the desorption of the isomerized products from the catalyst surface occur rapidly. Generally large amounts of isoparaffins found in the products suggest that isomerization is fast and cannot control the reaction rate. Therefore, the cracking

reactions involving the C-C bonds must be rate-controlling in hydrocracking of coal-derived liquids.¹²⁵

4.11 Agglomeration control of a caking coal by supercritical tetralin

As discussed in the literature review, the reactive maceral components of coal are highly crosslinked, macromolecular networks consisting of a number of stable cluster units connected by relatively weak linkages. The coal structure for a bituminous coal proposed by Wiser⁵⁶ and shown in Figure 2.2 includes a distribution of aromatic units connected together by relatively weak linkages consisting of short aliphatic chains and ether bridges. As coal is heated to above 350°C the weak linkages thermally disintegrate leading to the formation of free radicals. Several investigators studied the formation of free radicals using Electron Spin Resonance (ESR) spectrometry.¹²⁹⁻¹³² Petrakis and Grandy¹³³ observed that radical concentrations increased with rank. Among the coals studied, high volatile bituminous coals have higher concentrations than subbituminous coals suggesting that thermal disintegration reactions leading to the formation of free radicals are very high in high volatile bituminous coals.

The free radicals formed seek stabilization. If a hydrogen donor solvent such as tetralin is present in the immediate vicinity of the ruptured bond, the free radical may abstract a hydrogen atom from the solvent, thus stabilizing the free radical. In the study of agglomeration

of coal particles the reactions occurring on the surface of the coal particle are of particular importance. In a fluidized bed the formation of such agglomerates may lead to the loss of fluidization. The formation of free radicals on the surface of the coal particles leads to the strong adhering of the particles to the reactor walls, leading to plugging. Thus, the formation of agglomerates and the adhering of the particles to the reactor walls may eventually lead to termination of the process.

It was also observed from coal hydrogenation studies that molecular hydrogen is ineffective, in the absence of an appropriate catalyst, in controlling the agglomeration of caking coals. Processes involving molecular hydrogen and caking coals generally require that the coal be oxidized in controlled conditions to reduce the agglomerating tendency. Excessive oxidation leads to decrease in conversion to liquids. The inability of molecular hydrogen in the absence of a suitable catalyst to increase the volatile product yields above that of pyrolysis also indicates that atoms or free radicals, not molecules, are required for stabilization of the free radicals. A hydrogen donor solvent such as tetralin in the liquid phase is known to provide for abstraction of hydrogen atoms by the free radicals and thus stabilize the free radicals and control agglomeration. However, no studies have been reported in the literature on the agglomeration of a caking coal in a supercritical

hydrogen donor solvent. Homogeneous fluids are normally divided into two classes, liquids and gases. However, the distinction cannot always be sharply drawn, because the two phases become indistinguishable at what is called the critical point. Thus, supercritical fluids are characterized by the indistinguishability of liquid and gas phases. As passing through the critical point does not cause any discontinuity in the properties of the fluid, a hydrogen donor solvent, whether in a liquid state or in a supercritical state should control the agglomeration of a caking coal equally well. However, it is important to demonstrate experimentally that a supercritical fluid can actually control agglomeration before trying to develop a process wherein a supercritical hydrogen donor solvent is used to convert coal to liquids and/or gases.

The experimental set-up was described in the Chapter 3. Two experiments were conducted using the one gallon autoclave. The autoclave was initially heated to about 470°C and a pressure of 600 psi. A coal slurry was injected through a pressurized cylinder into the autoclave at a pressure of 1180 psi. The slurry contained tetralin and coal in the weight ratio of 3:1, and approximately 850 grams of slurry were injected in each of the experiments. Immediately after injection of the slurry there was a sudden drop in temperature to about 460°C. The coal slurry was kept agitated by means of a stirrer rotating at 1500 rpm. About 45 minutes after the injection of the slurry, the

reactor was quenched by circulating water through the autoclave. After the autoclave was cooled to room temperature the head assembly was removed and the contents carefully removed. Coal conversion was about 50%. The coal particles showed little tendency to agglomerate and very little coal was observed to adhere to the reactor walls.

However, as it is not known if the agitation of the coal particles by the stirrer resulted in the breaking up of any coal agglomerates that may have been formed, a few more experiments were conducted in a fluidized bed reactor to study the coal agglomeration phenomenon.

The experimental set-up of the fluidized bed reactor was described in Chapter 3. In one experiment the reactor was heated to about 480°C and the coal slurry was injected into the reactor at about 1000 psi. The coal particles in the supercritical tetralin medium were fluidized continuously by bubbling nitrogen through the bottom distributor. The temperature in the fluidizing section of the reactor was maintained above the critical temperature of tetralin for about 25 minutes. Nitrogen was continuously bubbled through the reactor until the temperature was reduced to below 350°C. The coal particles remained essentially unagglomerated during the run.

In another experiment tetralin was heated in the reactor to about 470°C and tetralin-coal slurry was injected into the reactor at 1000 psi. Tetralin was circulated through the system using the circulating pump which draws in

the tetralin from the top of the bed and discharges into the bottom of the bed through the distributor plate, fluidizing the coal particles. The coal particles were in contact with the supercritical tetralin for about 30 minutes. It took less than a minute to inject the coal slurry into the reactor and less than 5 minutes for the temperature in the reactor to come back to above the supercritical temperature after injection. Tetralin was continuously circulated through the bed using the pump until the temperature in the reactor came down to below 350°C. The coal particles remained essentially unagglomerated during the experiment.

4.12 Pressure fluctuation measurement to determine fluidization

Two sets of data were collected, one at atmospheric pressure and the other at a pressure of 500 psi. In the experiments conducted at atmospheric pressure the back pressure regulator was bypassed and the flow from the reactor went directly to the wet test meter. The flow was gradually increased by means of the micrometering valve and the pressure drop measurements were taken at different flow rates. 85.14 gms of sand particles screened to -65 +100 Tyler mesh (150m to 212 m) were fluidized by nitrogen gas. The pressure drop in centimeters of water is plotted against flow rate in cc/min in Figure 4.20. The fluidization region is also shown in the figure. Figure 4.21 shows the pressure drop versus time. The pressure drop is constant for a flow

Figure 4.20. Variation of pressure drop with flow rate at atmospheric pressure

Figure 4.21. Variation of pressure drop with time

rate of 15 cc/sec. As the flow rate is slowly increased, at a particular flow rate the sand particles are fluidized. The pressure drop profile at a flow rate of 21.5 cc/sec is shown in the figure. The pressure drop is unsteady but shows a definite periodicity, probably resulting from slugging of the bed. The variation of power spectral density function (PSDF) with frequency at different flow rates is shown in Figures 4.22 to 4.32. As can be seen for the flow rates 178.7, 298.4, 417.9, 591.3, 743.6 and 900.6 cc/min, at which the sand particles are in a fixed bed mode, there are no broad peaks. For the flow rates 1287.4, 1404.0, 1795.0, 2457.3 and 3504.7 cc/min, at which the sand particles are in a fluidized bed mode, there is a distinct broad peak in the frequency range 0-4 Hzs. It is important to note that the PSDF function (Y-axis) is in logarithmic scale, and hence the absolute value of the broad peak in the region 0-4 Hzs is much larger than the PSDF value in the rest of the frequency range. Thus the peaks in the frequency range 0-4 Hzs indicate fluidization of the bed.

Similar experiments were conducted at a pressure of 500 psi. Sand particles weighing 78.3 gms were fluidized by nitrogen gas. The system pressure was maintained constant by a back pressure regulator. The pressure drop is plotted against flow rate in Figure 4.33 and the PSDF value is plotted against frequency at different flow rates in Figures 4.34 to 4.49. As in the case of fluidization at atmospheric pressure, there are distinct peaks in the frequency range

Figure 4.22. Variation of PSD with frequency at a flow rate of 178.7 cc/min.

Figure 4.23. Variation of PSDF with frequency at a flow rate of 298.4 cc/min.

Figure 4.24. Variation of PSDF with frequency at a flow rate of 417.9 cc/min.

Figure 4.25. Variation of PSD with frequency at a flow rate of 591.3 cc/min.

Figure 4.26. Variation of PSDF with frequency at a flow rate of 743.6 cc/min.

Figure 4.27. Variation of PSDF with frequency at a flow rate of 900.6 cc/min.

Figure 4.28. Variation of PSDF with frequency at a flow rate of 1287.4 cc/min.

Figure 4.29. Variation of PSDF with frequency at a flow rate of 1404.0 cc/min.

Figure 4.30. Variation of PSDF with frequency at a flow rate of 1795.0 cc/min.

Figure 4.31. Variation of PSDF with frequency
at a flow rate of 2457.3 cc/min.

Figure 4.32. Variation of PSDF with frequency
at a flow rate of 3504.7 cc/min.

Figure 4.33. Variation of pressure drop with flow rate at 500 psi.

Figure 4.34. Variation of PSD with frequency
at a flow rate of 4025 cc/min.

Figure 4.35. Variation of PSDF with frequency
at a flow rate of 7832 cc/min.

Figure 4.36. Variation of PSDF with frequency at a flow rate of 11290 cc/min.

Figure 4.37. Variation of PSDF with frequency at a flow rate of 14497 cc/min.

Figure 4.38. Variation of PSDF with frequency
at a flow rate of 19344 cc/min.

Figure 4.39. Variation of PSDF with frequency at a flow rate of 21903 cc/min.

Figure 4.40. Variation of PSDF with frequency
at a flow rate of 26499 cc/min.

Figure 4.41. Variation of PSDF with frequency at a flow rate of 28224 cc/min.

Figure 4.42. Variation of PSDF with frequency
at a flow rate of 28931 cc/min.

Figure 4.43. Variation of PSD with frequency
at a flow rate of 28970 cc/min.

Figure 4.44. Variation of PSDF with frequency at a flow rate of 32851 cc/min.

Figure 4.45. Variation of PSDF with frequency at a flow rate of 34269 cc/min.

Figure 4.46. Variation of PSD with frequency at a flow rate of 34373 cc/min.

Figure 4.47. Variation of PSDF with frequency at a flow rate of 35480 cc/min.

Figure 4.48. Variation of PSDF with frequency at a flow rate of 36302 cc/min.

Figure 4.49. Variation of PSDF with frequency at a flow rate of 36364 cc/min.

0-4 Hz for the flow rates corresponding to fluidization.

A signal can be viewed from two alternative standpoints. One is the time domain approach wherein the amplitude of the signal $f(t)$ is displayed against the independent time variable t . The second representation is in the frequency domain, where the spectrum $F(j)$ is displayed against an independent frequency variable j . A given signal can be fully represented in either of these two domains, both of them being equivalent. The equivalence is typically expressed by the Fourier transform $\mathcal{F}$ of the signal, which permits a free conversion of the signal from one form to the other, as symbolized below¹³⁴

$$f(t) \xleftrightarrow{\mathcal{F}} F(j\omega)$$

Given two interacting functions, the integral of their product represents energy. For any wave form $f(t)$ with Fourier transform $F(j\omega)$ the total signal energy is as follows:

$$\int_{-\infty}^{\infty} f^2(t) dt$$

The energy spectral density is defined as¹³⁵

$$E(j\omega) = |F(j\omega)|^2$$

$E(j\omega) = |F(j\omega)|^2$ truly represents the distribution of energy with frequency and indicates the relative-frequency content of the waveform $f(t)$ with respect to its energy.

One of the statistical measures in the analysis of signals in time domain is the autocorrelation function

$R_f(\tau)$. The autocorrelation function is defined as¹³⁶

$$R_f(\tau) = \lim_{T \rightarrow \infty} (1/T) \int_{-T/2}^{T/2} f(t) f(t+\tau) dt$$

where $f(t)$ is the magnitude of the signal at an arbitrary instant of time t , and $f(t+\tau)$ designates the magnitude of the same signal observed at a time τ later. When the time interval separating the two measuring points is zero then

$$R_f(\tau=0) = \lim_{T \rightarrow \infty} (1/T) \int_{-T/2}^{T/2} f^2(t) dt$$

and is just equal to the mean-square value of the signal.

Power spectral density function is the Fourier transform of $R_f(\tau)$ and is given by

$$S_F(j\omega) = (1/2\pi) \int_{-\infty}^{\infty} R_f(\tau) e^{-j\omega\tau} d\tau$$

From the properties of the Fourier transform and its inverse, $R_f(\tau)$ can be defined as¹³⁷

$$R_f(\tau) = \int_{-\infty}^{\infty} S_F(j\omega) e^{j\omega\tau} d(j\omega)$$

It can be shown that

$$R_f(\tau=0) = \int_{-\infty}^{\infty} S_F(j\omega) d(j\omega)$$

Comparison of this equation with the earlier equation for $R_f(\tau=0)$ shows that the mean-square value of a signal is given by the area under the graph of spectral density $S_F(j\omega)$ against $j\omega$. The units of $S_F(j\omega)$ are accordingly those of

the mean square per unit of frequency and a more complete name for $S_f(j\omega)$ is the mean-square spectral density. Since the value of $R_f(\gamma=0)$ in the time domain involves squaring of the time function, $S_f(j\omega)$ has been designated as the power spectral density function.¹³⁷ The physical significance of the power spectral density function is that it gives the energy content distributed over the frequency bandwidth. In the present case when the sand particles are fluidized the energy content associated with the movement of the particles shows up at a bandwidth ranging from 0-4 hz.

The visual observation of the fluidization phenomena indicates that fluidization is very smooth at higher pressures compared to fluidization at atmospheric pressure. In the fluidized bed reactor employed in the present study, there was considerable slugging of the bed at atmospheric pressure. However, at elevated pressures the slugging of the bed reduced considerably, resulting in a smoothly fluidized bed as could be observed visually.

CHAPTER 5

CONCLUSIONS

The following conclusions can be drawn from the results obtained from this study.

(1) Coal is converted to liquids in the first stage using tetralin as the hydrogen donor solvent. The liquids produced in the first stage are converted to gases high in C_2 - C_4 hydrocarbons. The conversion of liquids to gases follows first order kinetics with an activation energy of 23.9 kcal/mol. Cracking reactions involving C-C bonds appear to be rate-controlling.

(2) Formation of C_1 and C_2 hydrocarbons increases with temperatures at all space velocities studied, ranging from 1 to 0.28, whereas the formation of C_4 hydrocarbons decreases with temperature. C_3 hydrocarbons seem to be having a broad maximum in the temperature range 440 to 485°C.

(3) As WHSV decreases conversion increases. The increase in conversion is mostly due to the increase in conversion to C_4 hydrocarbons. Conversion to C_4 hydrocarbons increases with decreasing WHSV at all temperatures. Conversion to C_3 hydrocarbons also increases with decreasing

WHSV. The yields of C_1 and C_2 hydrocarbons remains essentially constant with WHSV.

(4) Coal-derived liquids essentially free of the original hydrogen donor solvent (tetralin) give conversions higher than the coal derived liquids containing the tetralin. The reaction rate constant at 485°C is also higher (0.01132 min^{-1}) than that for coal-derived liquids containing the solvent (0.00684 min^{-1}).

(5) Hydrogen donor solvent in supercritical phase is as effective as the hydrogen donor solvent in liquid phase in controlling agglomeration and adhering tendency of a caking coal.

(6) Pressure fluctuation measurements and the variation of power spectral density function with frequency give a good indication of the fluidization.

(7) Bed fluidization at elevated pressure (500 psi) is considerably smoother than fluidization at atmospheric pressure.

APPENDIX A

COMPUTER SYSTEM

A 286 IBM compatible computer was assembled for data acquisition and to implement the controls of the sampling block.

PCL-812PG, a high speed multi function data acquisition card supplied by Cyber Research, Inc. along with the daughter boards PCLD-789, an amplifier/multiplexer board, PCLD-785, a relay output board, and PCLD-780, a screw terminal board were used for this purpose. All the boards were assembled into the system as shown in the block diagram (Figure 4.50). Analog outputs from the flow meter and the pressure gauges were connected to the screw terminal board and the thermocouple outputs to the amplifier/multiplexer board. The A/D card (PCL-812PG) converted the analog signals into digital signals. Visual Lab-M, a software program developed by Dr. Yang, was used to acquire, display, and record the data. The same software was also used to precisely control the timings of the 3-way electric valves of the sampling block by means of the relay output board.

One of the output lines from the relay output board was used to synchronize the timings of GC analysis and data acquisition. VLGC 812, another software program developed by Dr. Yang, was used to start the GC analysis and to acquire and process the GC data.

The same system was used to record the differential pressure data from the differential pressure gauge. The analog output from the gauge was connected to the screw terminal board which was then digitized by the A/D card.

The software program VLH, developed by Dr. Yang, enabled fast sampling of large numbers of data in a short time of about ten seconds.

Figure 4.50. Block diagram of the computer system.

APPENDIX B

OPERATION SEQUENCE OF THE
SAMPLING BLOCK

The sampling block operation sequence is shown diagrammatically in Figure 4.51. The operation sequence is as follows:

A. Sample flow is bypassed through the outer loop to the bubble flow meter.

B. Sample enters the first sampling loop and flows to the bubble flow meter. The opening and closing of the 3-way electric valve and the timing is controlled by the program Visual Lab-M. Up to nine samples can be collected in the nine sampling loops.

C. To purge the outer loop of any trace sample, helium is passed through the outer loop.

D. The individual samples are swept by the carrier gas, helium, to the GC column and are analyzed by the GC. The opening and closing of the 3-way electric valves are controlled by the electric switches provided for the individual valves.

Figure 4.51. Sampling block operation sequence

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