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Preconversion Processing of Bituminous Coals

- New Directions to Improved Direct Catalytic Coal Liquefaction -

DOE Contract No. DE-AC22-91PC91041

Final Report
(9/20/91-9/19/93)

Prepared for

U.S. Department of Energy
Pittsburgh Energy Technology Center
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September 1993

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Summary

A comprehensive knowledge of the basic coal structure must be acquired for the effective development of coal liquefaction. The cross-linked macromolecular model has been widely accepted by most researchers, and most current coal liquefaction studies are proceeding under this assumption. Recent studies, however, show that significant portions (far more than generally believed) of coal molecules appear to be physically associated. Since this new structural model has gained more credibility from our latest work, the development of any coal liquefaction processes should at least consider this possibility. If physical association is dominant for cross-links, all properties and reactivities germane to the liquefaction process will be specific functions of intra- and intermolecular (secondary) interactions and molecular weight.

One of the main goals for competitive coal liquefaction is to decrease gas yields to reduce hydrogen consumption. Complexing this element as methane and ethane decreases process efficiency and is less cost effective. To decrease the gas yield and increase the liquid yield, an effective preconversion process has been explored on the basis of the physically associated molecular nature of coal. Activities have been focused on two issues: (1) maximizing the dissolution of associated coal and (2) defining the different reactivity associated with a wide molecular weight distribution.

Two-step soaking at 350°C and 400°C in a recycle oil was found to be very effective for coal solubilization. No additional chemicals, catalysts, and hydrogen are required for this preconversion process. High-volatile bituminous coals tested before liquefaction showed 80-90% conversion with 50-55% oil yields. New preconversion steps suggested are as follows: (1) dissolution of coal with two-step high-temperature soaking, (2) separation into oil and heavy fractions of dissolved coal with vacuum distillation, and (3) selective liquefaction of the separated heavy fractions under relatively mild conditions. Laboratory scale tests of the proposed procedure mode using a small autoclave showed a 30 % increase in the oil yield with a 15-20% decrease in the gas yield. This batch operation projects a substantial reduction in the ultimate cost of coal liquefaction. It is strongly suggested that further testing be done in a continuous mode.

Preface

Coal conversion technology and science is an interdisciplinary area most commonly explored from an engineering point of view. Basic coal chemistry has largely been ignored in these activities, probably due to a poor understanding of coal structure. Scientists have determined that coal is mostly amorphous high-molecular-weight material which makes characterization thereof extremely difficult. The conventional cross-linked structural model has been widely accepted without thorough documentation for the development of coal conversion processes. Significant shortcomings relative to this conventional model, however, are now being observed. Over the past seven years, we have investigated a new structural model for coal. This project reinvestigates effective coal conversion practices based on the new model.

We believe that a significant reduction in the cost of liquefaction will be realized using our proposed procedure. A better understanding of coal structure and reactivity is required, with equal emphasis on coal chemistry and engineering necessary for any future development. Coal is the most abundant fossil fuel and is expected to become even more important in the next century. Any breakthrough realized in this utilization process will come from a better understanding of coal structure. Coal conversion problems, in the light of this new technology, now appear to be surmountable.

This project was awarded to BCR National Laboratory; however, due to the closure of the BCR Laboratory after one year, was transferred and completed under Viking Systems International. We acknowledge and greatly appreciate the assistance of personnel at the former BCR National Laboratory, especially Dr. Yerushalmi, for help in preparing the research proposal. In addition, we wish to thank DOE for giving us the opportunity to conduct this project. Although this work has been carried out at Viking Systems International, the PI (M.N.) accepts full scientific responsibility for opinions expressed.

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Notations

CyS:	Cyclohexane Solubles
CyI:	Cyclohexane Insolubles
ToS:	Toluene Solubles
ToI:	Toluene Insolubles
TS:	Tetrahydrofuran Solubles
TI:	Tetrahydrofuran Insolubles
PS:	Pyridine Solubles
PI:	Pyridine Insolubles
THF:	Tetrahydrofuran
CHP:	Cumene Hydroxyperoxide (80% in cumene)
H ₂ O ₂ :	Hydrogen Peroxide (3% in water)
AKZO:	AKZO AO-60 catalyst
MoS ₂ :	Molybdenum Sulfide obtained from Aldrich Co. (<1μ)
Liquid A:	Coal Liquid derived from Illinois No. 6 Coal in the Wilsonville plant
Liquid B:	Coal Liquid derived from Pittsburgh No. 8 Coal in the Wilsonville plant
CT:	Coal Tar distillate
DECS-2:	Illinois No. 6 coal obtained from the DOE Coal Bank at the Pennsylvania State University
DECS-12:	Pittsburgh No. 8 coal obtained from the DOE Coal Bank at the Pennsylvania State University
DECS-8:	Smith-Roland coal obtained from the DOE Coal Bank at the Pennsylvania State University
DECS-3:	Coal Basin M coal obtained from the DOE Coal Bank at the Pennsylvania State University

Chapter 1 Introduction

This work was designed to evaluate methods for significantly improving the two-stage coal liquefaction process with a focus on preconversion techniques using bituminous coals.

R&D work on direct coal liquefaction has shown a steady evolutionary progress. The overall trend has been towards the use of milder conditions in the process. The development of the two-stage, especially over the past decade, has brought significant improvements in the form of higher yields of liquids having a higher quality. Economic projections, based upon the most recent results, show the cost of hydrotreated oil is competitive with that of sweet crude selling for \$30-\$33 per barrel.

The current two-stage liquefaction process, however, still runs under relatively severe conditions, with the first stage typically operating in a temperature range from 430-450°C under elevated pressures approaching 150 atmospheres. The key to further improvement involves efficient processing of the coal under significantly milder conditions. The purpose of this research was to conduct a series of systematic tests which would potentially delineate a new set of considerably milder conditions for operating the two-stage liquefaction process, without any sacrifice of conversion and/or product quality.

The fundamental concept which underlies this work is the visualization of coal as largely entangled and/or physically associated molecular entities, rather than the three-dimensionally cross-linked model currently in vogue. Indeed, a physically associated model of coal has gained credibility from recent tasks conducted by this investigator¹⁻⁵. To fortify this concept, we proposed soaking the coal in recycle oil derived from the coal at a temperature range from 320 to 380°C. High-temperature soaking tends to weaken and to break up physically associated complexes and efficiently disperse these entities in the oil. This occurs without appreciable scission of chemical bonds. In this state, the molecular entities of coal are more amenable to the actions of a catalyst and to subsequent hydroprocessing.

We proposed the following approach:

1. To soak coal in recycle oil at a temperature from 320 to 380°C, at rather low pressures (hydrogen partial pressure of less than 5 atmospheres). These conditions would

induce a high degree of coal dissolution, even in the absence of a catalyst and hydrogen, and generate high liquid yields on subsequent liquefaction.

2. To study the use of free-radical initiators which could be introduced in small quantities at either the coal dissolution stage or the first liquefaction stage. According to the prevailing view, free radicals may promote retrograde reactions and require capping by hydrogen. We showed that under the conditions imposed, free radical initiators may actually aid in cracking and result in higher liquid yields.

3. The aforementioned steps were expected to produce considerable breakdown and dispersal of the coal constituents and show some cracking of high-molecular-weight molecules. These results would make it possible to run the first liquefaction stage at conditions that are considerably milder than those employed at the present.

Several recent reviews on the commercial status of direct coal liquefaction are available. We cite two references^{6,7}, but do not intend to summarize these surveys here. We did wish to highlight the general trends and showed both the relevance and promise of our proposed work.

From a perspective spanning the time from the first oil crisis (1973) to the late 1980's, the development of direct liquefaction processes appears gradual and evolutionary. It seems ironic that the greatest strides have been made in the past few years during which the interest in coal liquefaction has greatly diminished due to a precipitous drop in oil prices. Over the past decade, processes that were poised for commercial demonstration (H-Coal, SRC-I, SRC-II, and EDS) gave way to the two-stage liquefaction process. In a typical two-stage liquefaction process, separate phases in the dissolution of coal and its subsequent conversion are carried out in different reactors to optimize overall conditions. This concept has been the basis for large-scale developments in Japan, Great Britain, and Australia.

The two-stage approach generated remarkable improvements in the form of higher yields and higher product quality. These, in turn, led to significant improvements in overall economics.

Figures 1.1-1.3⁶ trace some of the recent technical improvements in direct coal liquefaction. *Figure 1.1* shows relative yields from processes using Illinois No. 6 coal. *Figure 1.2* shows the total conversion of coal to liquids, while *Figure 1.3* shows the resultant

Figure 1.1 Yields from Illinois No. 6 coal

Figure 1.2 Liquefaction yields per ton of coal

Figure 1.3 Product quality from Illinois No. 6 coal

Figure 1.4 Coal liquefaction yields and product distributions⁷

product quality. The results labeled "Current" in these figures represent those obtained at the Wilsonville facility in 1985. Since that time, the researchers at Wilsonville as well as Hydrocarbon Research Inc. (HRI) have reported further improvements, some of which are shown in *Figure 1.4*.⁷

A summary of economics with a comparison of figures based upon the Wilsonville 1985 data and those relating to previous processes is shown in *Tables 1.1* and *1.2*. *Table 1.1* shows capital requirements while *Table 1.2* summarizes the annual operating costs. From the aforementioned work, it may be concluded that a high-quality synthetic liquid may be from coal for approximately \$35 per barrel, and that this liquid (owing to some quality advantage) would be competitive with sweet crude oil selling for as low as \$30 per barrel.

It is perhaps worthwhile to put the previous statements in perspective so the potential for further improvement can be understood. The overall yield of liquid from coal has increased dramatically. It is now estimated (for a bituminous coal) at approximately 4-5 barrels per ton which approaches the theoretical limit. Product quality has also improved immensely, as the HRI data shows in *Figure 1.4*.

Hydrogen consumption, however, has not decreased in pace with the developments of the past few years and currently remains around 5-6% of the MAF coal. Hydrogen is a major cost item and to whatever extent its use could be decreased by producing less gas and/or employing less severe conditions would favor improved economics.

Perhaps the greatest opportunity for improving liquefaction processes lies in following a trend already established: namely, using milder operating conditions. This would result in lower capital costs, and inevitably, in lower annual operating and maintenance costs. The work planned was directed toward the possibilities raised above.

This report is composed of 9 chapters. The purpose and scope of the studies reported in each chapter are as follows:

Chapter 1 is the Introduction. *Chapter 2* describes the preparation of two types of reactors as well as coals and coal liquids used in this study.

It is known that coal does interact strongly with selected compounds; however, such interactions between specific molecules and coal have not been fully studied. A knowledge

of both intra- and intermolecular interactions could significantly supplement future coal utilization. Compounds in a recycle oil may be selectively adsorbed on coal and significantly influence coal liquefaction. In *Chapter 3*, selective interactions involving high-volatile bituminous coal are studied.

It is generally understood that most bituminous coal entities can be disintegrated in coal-derived liquids and polycyclic aromatic hydrocarbons at 300-400°C (high-temperature soaking). A better understanding of the coal disintegration mechanism induced by high-temperature soaking is necessary for the development of coal conversion. Insolubles produced by high-temperature soaking are investigated in *Chapter 4* using coal swelling to study the mechanism. The effects of soaking time, soaking temperature, soluble fractions, and coal rank on high-temperature soaking is studied in *Chapter 5*.

Disintegrated coal generated from high-temperature soaking remains high-molecular-weight material. Therefore, an alternative pretreatment to manifest the breakdown of the high-molecular-weight material is desired before liquefaction. While information on their role at this stage of preconversion is limited, breakdown of the high-molecular-weight material by radicals may be possible under certain conditions. In *Chapter 6*, the effect of radicals on preconversion and liquefaction is evaluated as a method for initiating chemical breakdown during or after physical dissolution.

In *Chapter 7*, an improved pretreatment procedure for coal liquefaction is investigated on the basis of the associated molecular nature of coal. Activities are focused on two issues: (1) maximizing the dissolution of associated coal and (2) step-wise conversion of associated coal with a wide molecular weight distribution. An improved preconversion concept is proposed. In *Chapter 8*, the proposed process is tested under various conditions. Second stage liquefaction is also investigated.

Chapter 9 presents the Conclusions derived from this study.

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Table 1.1 Economic comparison (Illinois No. 6 coal, \$1986)

	EDS	H-COAL	ITSL	1986
MF Coal Input, (1000 t/d)				
Liquefaction	30.0	30.0	30.0	30.0
Hydrogen Production	0.0	0.5	0.4	2.4
Steam	2.5	2.5	2.6	7.2
Total	32.5	33.0	33.0	39.6
Output, bbl/d (raw)	79,512	85,117	92,398	116,851
Output, bbl/d (hydrotreated)	79,390	92,316	103,790	127,663
Construction Cost (\$ million)				
Liquefaction	1,372	1,490	1,657	1,643
Hydrogen Production	607	611	627	763
Balance of Plant	550	552	527	521
Total	2,350	2,654	2,812	2,928
Capital Required (\$ million)	4,104	4,291	4,418	4,658

Table 1.2 Annual operating costs (Illinois No. 6 coal, millions @\$1986)

	EDS	H-COAL	ITSL	1986
Operating Costs				
Coal Cost	2710	2750	2700	330
Other	329	337	337	374
Total	601	612	607	704
Byproduct Credits				
Sulfur @ \$100/t	47	48	47	51
Ammonia @ \$150/t	22	22	22	24
SNG @ 5/MMBtu	74	69	10	76
Total	143	139	79	150
Hydrotreating Cost	145	297	227	209

Chapter 2 Preparation of Reactors and Materials

1. Installation of Reactors

Two reactor systems were installed as the experimental apparatus. One was the Model 4576 high-temperature and high-pressure autoclave (Parr Instrument, 500°C and 5000 psi) pictured in *Figure 2.1*. This unit was obtained from the manufacturer and assembled as directed. The other was a 27 ml capacity microreactor. This unit consists of the following main parts:

- a. Structural frame
- b. Microreactor (*Figures 2.2 and 2.3*)
- c. Lift table
- d. Fluidized sand-bath, and
- e. Shaker unit

The fluidized sand-bath (Techne, Model No. SBL-2) is rated for temperatures ranging from 50 - 600°C. The temperature controller (Coleman Instruments, Digi Sense) controls the temperature within $\pm 0.5^\circ\text{C}$ of the set point. The shaker unit, procured from the Burrell Corporation of Pittsburgh, PA was modified by coupling horizontal and vertical bars (fabricated at the University of Pittsburgh) to hold the microreactor and shake it horizontally at 320 rev min^{-1} . The lift table (Model No. SBL 51836E, B&G Industrial Supply, Inc., Irwin, PA) a capacity of 500 lb, and can be raised from 8 - 28" above the floor.

The microreactor and its accessories were fabricated in the machine shop at the University of Pittsburgh. The detailed design of the microreactor is shown in *Figures 2.2 and 2.3*. The horizontally shaken microreactor is made of SS316 and consists of three main parts: (1) a horizontal reactor tube with a screw cap, (2) a vertical extension tube, and (3) a multiport valve. The reactor tube has a pressure rating of ~3,500 psi at 510°C with an internal volume of 27 ml. A pressure gage is fitted to the multiport valve which facilitates charging and releasing of gases. The multiport valve was purchased from Pittsburgh Valve and Fitting Co. in Pittsburgh, PA. This valve has a pressure rating of 6,000 psi at 38°C and 1,700 psi at 650°C. The lift table permits rapid insertion and removal of the microreactor

from the heated sand bath.

Auxiliary lines for hydrogen, nitrogen, air, cooling water, and purging were installed. The microreactor and the autoclave were then tested with a coal and coal liquid combination at temperatures of 350 and 425°C under nitrogen and hydrogen up to 1,000 psi. A combustion gas monitor (Model 2001; Sierra Monitor Corp.) was installed to detect possible reactor leaks.

2. Material

(1) Coal

Coal samples were obtained from the Penn State University (PSU) Coal Bank. Included were the Illinois No. 6 (DECS-2) and the Pittsburgh No. 8 (DECS-12) coals considered to be DOE standards. Elemental analyses provided by PSU are shown in *Table 2.1*.

(2) Coal liquids

Coal liquids were obtained from the Wilsonville liquefaction facility. One was derived from Illinois No. 6 coal (V-178, 2/25/89, Run 257H), while the second was derived from Pittsburgh No. 8 coal (V-178, 3/8/90, Run 2598). The third coal liquid, (a coal tar distillate), was obtained from Aristech Chemical Co. of Pittsburgh, PA. Elemental analyses of these liquids are included in *Table 2.1*. The analytical data characterizing the coal tar distillate are shown in *Table 2.2*.

Table 2.1 Elemental analyses of coals and coal liquids used (wt%)

Symbol	Sample	H ₂ O	Ash	Element (daf)			
				C	H	N	S
DECS-2	Illinois no. 6 (hvb)	10.4	14.5	78.1	5.4	1.3	5.4
DECS-12	Pittsburgh no. 8 (hvb)	2.4	10.0	83.3	5.7	1.4	1.3
Liquid A	Liquid derived from Illinois no. 6 coal	-	-	88.4	11.4	0.2	< 0.1
Liquid B	Liquid derived from Pittsburgh no. 8 coal	-	-	87.1	9.6	0.2	< 0.1
CT	Coal tar distillate	-	-	91.8	6.0	0.7	0.6

Figure 2.1 Autoclave Assembly

Figure 2.3 Reactor Cap Details

Table 2.2 Analytical Data of Coal Tar Distillate

Components		
Indan	1.3	wt%
Indene	1.2	
Naphthalene	7.3-7.9	
Quinoline	0.3-0.8	
Quinoline isomer	0.1-0.3	
2-Methylnaphthalene and Indole	1.5-4.5	
1-Methylnaphthalene and Quinaldine	0.7-2.0	
Biphenyl & 1.3-, 1.6-, and 1.7-Dimethylnaphthalenes	0.4-1.1	
Acenaphthene	4.5-6.1	
Dibenzofuran	2.5-3.7	
Fluorene	3.7-4.7	
Methyldibenzofuran	2.1-2.5	
Methylfluorene	0.5-1.2	
Dibenzothiophene	1.0-1.4	
Phenanthrene	13.5-15.7	
Anthracene	4.0-4.2	
Carbazole	1.5-2.1	
Methylphenanthrene	2.5-3.0	
Fluoranthene	7.1-9.5	
Pyrene	5.1-7.2	
Benzo[fluorene]	4.8-7.0	
Methylfluoranthene	4.0-4.8	
Methylpyrene	2.1-3.3	
1,2-Benzanthracene	1.7-2.1	
Chrysene	1.7-2.1	
Methylbenzanthracene and Methylchrysene	0.9-1.1	
Benzo[<i>b</i>]fluoranthene	0.5-1.1	
Benzo[<i>a</i>]pyrene	0.2-0.7	
Perylene	0.05-0.25	
Methylbenzopyrene	0.2-2.2	
Benzo[<i>ghi</i>]perylene	0.3-0.4	
Density	1.115	
H ₂ O	0.1 %	
Start	131°C	
0 - 132°C	1 %	
0 - 157°C	14 %	
0 - 179°C	52 %	
Residue	45.6 %	
C residue	-	

Chapter 3 Strong interactions between selective compounds and coal

1. Introduction

It is common knowledge that pyridine is retained in both extract and residue following Soxhlet extraction of coal¹⁻⁵. Even after drying at 100°C under high vacuum pyridine is not completely removed. The amount of pyridine retained reaches 1-10 wt%. Since retained pyridine is easily exchangeable with free pyridine¹, this is an example of *physical incorporation* in coal.

Maleic anhydride is incorporated in high-volatile bituminous coal by heating at 100-200°C in solvents such as benzene and chlorobenzene⁶⁻⁸. A portion of maleic anhydride incorporated is an adduct of the Diels-Alder reaction, but a significant amount of the unreacted maleic anhydride is physically retained⁹. While this compound is easily dissolved in water and methanol, it is difficult to recover the adsorbed maleic anhydride with these solvents.

Hydrogen bonds are known to provide major interactions with coals of lower rank¹⁰⁻¹². Compounds containing functional groups such as -OH and -NH- interact with coal through hydrogen bonds. Since most hydrogen bonds can be broken with pyridine^{13,14}, many compounds would be readily recovered using this solvent. However, if interactions between coal and such compounds are relatively strong, these compounds may resist recovery using pyridine. The charge-transfer phenomenon is one of the stronger interactions involving high-volatile bituminous coal¹⁵. Some portions of the charge-transfer complexes in coal cannot be solvated with pyridine¹⁵, although it is known to be a good electron-donor solvent. These complexes in original coal are readily broken at higher temperature with the formation of more stable charge-transfer complexes. Therefore the strength and abundance of selective interactions or complexes in coal may change dramatically at higher temperature.

These results show that coal does interact strongly with selected compounds; however, such interactions between specific molecules and coal have not been fully studied. A knowledge of both intra- and intermolecular interactions could significantly supplement future coal utilization. Coal is routinely mixed with solvents and oils in processes involving

coal liquefaction and combustion and selective molecular interactions may occur. Compounds in a recycle oil may be selectively adsorbed on coal and significantly influence coal liquefaction. If selective adsorption occurs during combustion with a mixture of heavy oils, this may ultimately affect the overall efficiency of the operation.

In this section, selective interactions involving high-volatile bituminous coal were studied using various types of standard compounds, coal, and a coal liquid. A mixture of a coal residue and standards or coal and a coal liquid were soaked at three different temperatures. Recoveries of the components were determined.

2. Experimental

The Illinois No. 6 coal sample (DECS-2, -20 mesh size) was used. A 10 g sample of this coal was Soxhlet-extracted with pyridine for 72 h, rinsed with methanol for 24 h, and dried under vacuum at 95°C overnight. The residue (PI) was retained for later use in this study. A coal liquid derived from the Illinois No. 6 coal was obtained from the Wilsonville pilot plant¹⁶. Solvents used were all HPLC-grade. Tetrahydrofuran (THF) was distilled before use but remaining reagents were used without further purification.

The following procedures are summarized in *Table 3.1*. Coal samples (5 g) were placed in a 250 ml autoclave with 10 ml of coal liquid and 50 ml of cyclohexane (Runs 8 and 9). The autoclave was evacuated and purged with nitrogen five times, then heated at 5 K min⁻¹ to 200 and 350°C under nitrogen (initial pressure 50 psi), while being agitated with the autoclave stirrer (500 rev min⁻¹). For treatment at room temperature (25°C) (Run 7), the mixtures were agitated with a magnetic stirrer under nitrogen in a 500 ml flask. Similar procedures were used for the treatment of PI residues with coal liquids (Runs 4-6). In addition, PI residues were mixed with a standard compound solution in methylene chloride (Runs 1-3). With these tests, 4 g of residue, 40 ml of cyclohexane and 1 ml of methylene chloride solution (~0.05 g ml⁻¹) were charged. Following each treatment, all mixtures were filtered and Soxhlet-extracted for 24 h.

Coal liquid samples produced in specific runs were fractionated into chemical classes using column adsorption chromatography on neutral alumina¹⁷. These fractions and the standard compounds were analyzed by gas chromatograph (g.c.) with the flame ionization detector. Samples were injected in split mode (~1:20) using a hydrogen carrier gas set at

Table 3.1 Run numbers for treatments

Run No.	Treatment
1	Residue + a standard mixture: soaked in cyclohexane at 25°C for 2 h, followed by Soxhlet extraction with cyclohexane, THF and pyridine for 24 h, respectively
2	Residue + a standard mixture: soaked in cyclohexane at 200°C for 2 h, followed by Soxhlet extraction with cyclohexane, THF and pyridine for 24 h, respectively
3	Residue + a standard mixture: soaked in cyclohexane at 350°C for 2 h, followed by Soxhlet extraction with cyclohexane, THF and pyridine for 24 h, respectively
4	Residue + a coal liquid: soaked in cyclohexane at 25°C for 2 h, followed by Soxhlet extraction with cyclohexane, and THF for 24 h, respectively
5	Residue + a coal liquid: soaked in cyclohexane at 200°C for 2 h, followed by Soxhlet extraction with cyclohexane, and THF for 24 h, respectively
6	Residue + a coal liquid: soaked in cyclohexane at 350°C for 2 h, followed by Soxhlet extraction with cyclohexane, and THF for 24 h, respectively
7	Coal + a coal liquid: soaked in cyclohexane at 25°C for 2 h, followed by filtration and evaporation of the solvent
8	Coal + a coal liquid: soaked in cyclohexane at 200°C for 2 h, followed by filtration and evaporation of the solvent
9	Coal + a coal liquid: soaked in cyclohexane at 350°C for 2 h, followed by filtration and evaporation of the solvent

a flow rate of 80 cm s⁻¹. A fused silica capillary column (15 m × 0.25 mm i.d.) coated with SE-54 (film thickness 0.25 µm) was used. Elemental analyses of the coal liquids were conducted by Geochemical Testing of Somerset, PA.

3. Results and Discussion

Four types of standard compounds were mixed with PI in cyclohexane at 25, 200 and 350°C for 2h. These compounds were (1) the neutral compounds eicosane and phenanthrene, (2) the electron-acceptor compound anthraquinone, (3) the electron-donor and basic compounds carbazole and acridine, and (4) the hydroxyl and weakly acidic compounds tetrahydronaphthol, naphthol and 4-phenylphenol. Approximate recoveries using cyclohexane, THF and pyridine were determined using g.c. as shown in *Table 3.2*.

Nearly 100 % of the neutral compounds eicosane and phenanthrene were recovered with cyclohexane after all treatments. Recovery of phenanthrene was > 100 % after the treatments at 200 and 350°C, presumably as a consequence of additional generation from

Table 3.2 Approximate recoveries (wt%) of standard compounds after treatments in cyclohexane

Compound	Structure	25°C (run 2)			200°C (run 3)			350°C (run 4)		
		Cy ^a	THF ^a	Py ^a	Cy	THF	Py	Cy	THF	Py
Eicosane	$n\text{-C}_{20}\text{H}_{42}$	100	0 ^b	0	100	0	0	100	0	0
Phenanthrene		100	0	0	100	5	0	110	0	0
Anthraquinone		100	0	0	10	90	0	0	60	0
Carbazole		60	5	0	1	10	0	0	0	0
Acridine		40	0	0	0	5	0	0	0	0
1,2,3,4-Tetrahydro-1-naphthol		30	0	0	0	10	0	0	0	0
2-Naphthol		2	10	0	0	10	0	0	0	0
4-Phenylphenol		5	95	0	0	5	0	0	0	1

^aRecovery solvent: Cy, cyclohexane; THF, tetrahydrofuran; Py, pyridine ^bRecovery <1% was regarded as 0 PI¹⁸. Although nearly 100 % of the anthraquinone was recovered with cyclohexane after treatment at 25°C, only 10 % was recovered after the treatment at 200°C. The remaining anthraquinone adsorbed on the PI was recovered with THF. No anthraquinone was recovered with cyclohexane after treatment at 350°C, and only 60 % was recovered with THF. It is not known whether the remaining 40 % of anthraquinone was very strongly adsorbed or had reacted with the PI, but this result clearly demonstrates a strong mutual interaction.

Maleic anhydride has a similar structure to anthraquinone, in that both compounds have two carbonyls conjugated with the carbon double bond. The Diels-Alder reaction was initiated by soaking coal with maleic anhydride in chlorobenzene at 115°C for 7 days⁹. A significant amount of unreacted maleic anhydride was subsequently recovered by extraction with THF after thorough washing of the reacted coals with water or methanol⁹. The strong adsorption of both anthraquinone and maleic anhydride in such soakings is consistent.

As shown in *Table 3.2*, a strong adsorption of basic and weakly acidic compounds on the coal residue (PI) is evident. After extraction with cyclohexane at 25°C, the 4-phenylphenol was recovered with THF; however, the remaining acidic compounds were not recovered with either THF or pyridine. In most cases, recoveries of the weakly acidic compounds were smaller than those of the basic compounds. Compounds carbazole, acridine and naphthol are presumably not so labile at 350°C, since these are known to be major constituents in coal liquid and coal tars¹⁹. It is, therefore, unlikely that all of the unrecovered compounds reacted with the coal. These results suggest that these compounds are strongly adsorbed on the coal, and that the interaction between coal and the weakly acidic compounds is stronger than that involving the basic compounds. The data also suggest that the interaction or apparent adsorption became stronger with increasing temperature of treatment, since < 10 % of these compounds were recovered with the good solvents THF and pyridine after treatment at > 200°C.

Relative adsorption was further investigated with the coal liquid. Runs 4-6 (see *Table 3.1*) were conducted paralleling the procedure set up for the above procedure. Recovery with THF after extraction with cyclohexane was regarded as adsorbed coal liquid fractions. The amounts of adsorbed coal liquids from the 10 g sample were 0.03, 1.5 and 1.9 g at 25, 200, 350°C respectively; increasing with increasing treatment temperatures. This result is consistent with the trend observed using standard compounds.

The original and adsorbed coal liquids were fractionated into chemical classes, and the yield of each fraction was investigated. As shown in *Table 3.3*, the A-1 to A-4 fractions are composed of neutral aliphatics, neutral aromatics, basic aromatics and weakly acidic aromatics, respectively¹⁷. Total recoveries obtained using adsorption chromatography ranged from 85-95 %. Normalized values are shown in *Table 3.3*. The adsorbed coal liquids from Runs 4, 5, and 6 are composed predominantly of A-3 and A-4 fractions with the ratio of A-3 to A-4 decreasing with increasing temperatures of treatment.

Changes in the chemical composition of the coal liquid during the treatment were also examined. The original coal and the coal liquids representing Runs 7, 8, and 9 were treated under the same conditions used for the residue (PI). Yields determined using adsorption chromatography from these treated coal liquids are also listed in *Table 3.3*. While the A-1 fraction decreased and the A-2 fraction increased with an increase in the

Table 3.3 Recovery and normalized yields of each fraction by neutral alumina fractionation

Sample	Recovery (g)	Fraction (wt%)			
		A-1 Aliphatics	A-2 Neutral aromatics	A-3 Basic aromatics	A-4 Acidic aromatics
1 Original coal liquid	-	73	22	4	1
2 Adsorbed coal liquid from run 4	0.03	7	6	48	39
3 Adsorbed coal liquid from run 5	0.5	5	13	32	49
4 Adsorbed coal liquid from run 6	1.9	15	21	18	46
5 Recovered coal liquid from run 7	-	81	12	3	3
6 Recovered coal liquid from run 8	-	58	40	2	0
7 Recovered coal liquid from run 9	-	38	49	12	2

temperature of treatment, the A-3 and A-4 fractions did not change enough to explain their higher yields for the adsorbed coal liquids shown above. This result, therefore, supports the premise that basic and weakly acidic aromatics in the coal liquid were strongly adsorbed on the coal, and that the weakly acidic aromatics were adsorbed more strongly than the basic aromatics. Such findings are consistent with the results obtained using the standard compounds.

The elemental analysis of the adsorbed coal liquid at 350°C (Sample 4 in *Table 3.3*) was compared with that of the original coal liquid. Data in *Table 3.4* indicate that the adsorbed coal liquid had much higher contents of N, S, and O heteroatoms. Although this fraction may contain some adsorbed THF-solubles produced from the PI at 350°C, the results imply that strong interactions occur between basic and weakly acidic compounds and the coal. In addition, the H/C atomic ratios that this adsorbed fraction is more aromatic

Table 3.4 Elemental analyses of original and adsorbed coal liquids

Sample ^a	Element					H/C atomic ratio
	C	H	N	S	O ^b	
1	88.4	11.4	0.2	<0.1	<0.1	1.5
4	81.7	6.8	1.4	1.1	9.0	1.0

^aSample no. as in *Table 3.3*

^bBy difference

than the original coal liquid.

Each fraction shown in *Table 3.3* was analyzed using g.c. No significant differences were seen in g.c. chromatograms for the neutral aliphatic and aromatic fractions (A-1 and A-2). However, compounds elutable in the A-3 and A-4 fractions from the adsorbed coal liquids significantly decreased in number with an increase in temperature of treatment. *Figure 3.1* compares the chromatograms of the A-3 fractions from Samples 1, 4 and 7 (see *Table 3.3*). Amount of A-3 fraction injected were ~50 ng from Sample 1 and ~500 ng from Samples 4 and 7. As shown in chromatogram B, the A-3 fraction of Sample 4 did not contain significant amounts of the basic aromatics with low molecular weight. These are also less abundant in the A-3 fraction from Sample 7, as shown in chromatogram C. (Later testing showed that the A-4 fraction of Sample 4 also did not contain a significant amount of the weakly acidic aromatics with low molecular weight.) Detailed identification of compounds in the A-3 and A-4 fractions was difficult, but the results show that the basic and weakly acidic aromatics were not recovered with THF after treatment at 200 and 350°C. It appears that the basicity and acidity of the major constituent in these A-3 and A-4 fractions from adsorbed coal liquids would not be as strong as that of acridine, carbazole and naphthol, and that these constituents may be more aromatic and high-molecular-weight material.

The above results using standard compounds and a coal liquid show that interactions between certain compounds and coal are quite strong. These compounds include basic and weakly acidic aromatics. Even at room temperature (25°C) strong adsorption was noted, with said compounds not easily recovered with good solvents such as THF and pyridine. Adsorption is enhanced by heat treatment as evidenced by higher temperatures inducing stronger adsorption. This is presumably a consequence of the change in equilibrium between coal and molecules adsorbed at high temperature. Complete recovery of compounds strongly adsorbed on coal was very difficult, even when using pyridine.

A solvent-induced association is initiated by selective soaking of high-volatile bituminous coal^{20,21}. The degree of association is highly dependent on solvents used and temperature. This suggests that coal molecules change their conformation on soaking and tend to attain more stable and associated states. That response is attributed to a change in equilibrium between the associated and dissociated coal molecules. Complete solvation

Figure 3.1 Gas chromatograms of basic aromatic fractions (A-3) of (A) Sample 1, (B) Sample 4 and (C) Sample 7 (see *Table 3.3*). Conditions are as follows: 40-120°C at 10°C min⁻¹ and 120-250°C at 4°C min⁻¹ after an initial 2-min isothermal period

of the complexes formed is very difficult with Soxhlet pyridine extraction. This probably results in a decrease in pyridine extractability of the coal. The strong adsorption of selective molecules on coal and the solvent-induced association are presumably similar physical phenomena. Differences would be related to molecular size. Total adsorption, therefore, would be dependent on coal rank, solvent used, and temperature, due to the high dependence of the solvent-induced association on these factors.

4. Summary

Interactions between coal and a coal liquid (Runs 7, 8, 9) and coal residue and various standard compounds (Runs 1, 2, 3) were investigated. These mixtures were soaked in cyclohexane under nitrogen at 25, 200 and 350°C for 2 h, and recoveries of the coal liquid and standard compounds determined by solvent extraction. Nearly 100% of the neutral compounds were recovered after the treatment. On the other hand, weakly acidic aromatics containing a hydroxyl group and basic aromatics containing nitrogen were selectively adsorbed on coal as low as 25°C. Complete recovery was extremely difficult even with tetrahydrofuran (THF) and pyridine. The adsorption of weakly acidic compounds was stronger than that of basic compounds and further enhanced when soaked at higher temperatures. Similar results were also observed for selective interactions between the residue and the coal liquid as observed in Runs 4, 5, and 6.

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Chapter 4 Mechanism of Coal Solubilization from High-Temperature Soaking: Investigation by Coal Swelling

1. Introduction

A better understanding of the coal disintegration mechanism induced by high-temperature soaking is important for the development of coal conversion. Extracts from Illinois No. 6 (DECS-2) coal were treated in toluene at three separate temperatures. The treated samples were analyzed by respective coal swelling using a recently developed method. Studies evaluating the effect of soaking time, soaking temperature, soluble portions, and coal rank will be reported in the next chapter.

A cross-linked, three-dimensional macromolecular model has been widely accepted as depicting the structure of coal. Recent reports¹, however, show that significant portions (far more generally believed) of coal molecules are physically associated. It is common knowledge, as shown in this paper¹, that most bituminous coal entities can be disintegrated in coal-derived liquids and polycyclic aromatic hydrocarbons at 300-400°C (high-temperature soaking). The author proposes that electron donors and acceptors of low molecular weight contained in these materials substitute coal-coal complexes with charge-transfer interactions. This is physical dissociation of associated coal molecules. Chemical reactions, however, may also occur at these temperatures.

Some researchers²⁻⁴ have rationalized the extensive solubility by arguing that hydrogen shuttling provides the primary effect at 300-400°C. This is questionable for the following reasons:

1. The concentration of hydroaromatics is low in anthracene oil, which has often been used in high-temperature soaking studies. The potential for hydrogen donation is poor⁵.

2. Although tetralin is a hydrogen donor, it is not as effective as coal liquids and polycyclic aromatics over the temperature range in question⁶.

3. Polycyclic aromatic hydrocarbons are very effective for dissolution of coal at these temperatures⁷.

4. Coal conversion in polycyclic aromatic hydrocarbons at these temperatures is

proportional to the electron donor capability of these hydrocarbons^{7,8}. This supports the proposition that dissolution is due to breaking charge-transfer complexes.

5. Extractive disintegration can be expressed by a first order process based on equilibria in anthracene oil and aromatic compounds between 250-350°C⁹. If chemical reactions were the main factor, a first order process would not be applicable.

Reduction in extractability after high-temperature soaking is occasionally observed. This has been regarded as a retrograde reaction^{6,10,11}. The extractability, however, may be controlled by associative equilibria after coal has disintegrated to some degree, because coal-coal complexes may dissociate and more stable new complexes form. The differentiation between associative equilibria and retrograde reactions is important.

Associations within high volatile bituminous coals are formed by solvent soaking^{12,13}. These associations are highly dependent on the nature of the solvent and temperature. Dissociated coal molecules are reassociated by soaking in weaker solvents. A pyridine extract from Pittsburgh No. 8 was changed to pyridine insolubles by soaking in chlorobenzene at 115°C for a week^{12,14}. Although a large portion of bituminous coal is broken down in coal-derived liquids and polycyclic aromatic hydrocarbons by high-temperature soaking, the coal may reassociate in weaker solvents when exposed to high-temperature soaking for a short treatment time. Significant changes relative to the enhancement and reduction of coal solubilization by high-temperature soaking may both be controlled by the same mechanism.

It is a difficult task to quantitatively determine whether high-temperature soaking is a physical phenomenon (dissociative or associative equilibria) or a chemical phenomenon (bond breakage or cross-linking). In this chapter, insolubles produced by high-temperature soaking were investigated using coal swelling.

2. Experimental

Ten grams of the Illinois No. 6 coal was Soxhlet-extracted with pyridine for 72 h, rinsed with methanol for 2-3 h and dried under vacuum at 95°C overnight. The extract (PS) and residue (PI) were both used in this study. HPLC-grade solvents were obtained directly from Fisher Scientific (Pittsburgh, PA), and used without purification.

PS extract samples (2.5 g) were charged to the 250 ml autoclave. After adding

toluene (50 ml), evacuating, and purging with nitrogen five times, the autoclave was heated at $\sim 5^{\circ}\text{C min}^{-1}$ to 200 and 350°C under nitrogen (initial pressure: 50 psi, final pressure: 120 psi @ 200°C , 600 psi @ 350°C). The mixtures were heated for 24 and 2 h respectively, while undergoing agitation with the autoclave stirrer (500 rev min^{-1}). After this treatment, the solvent was evaporated and dried under vacuum at 95°C for 2-3 h. The samples were Soxhlet-extracted with pyridine for 24 h then Soxhlet-rinsed with methanol and dried under the above conditions.

The experimental procedure of coal swelling is based upon the earlier reported method^{15,16}. The measurements were performed in disposable Wintrobe Tubes from Fisher Scientific (3 mm inner diameter and 115 mm in length) with graduation in 1 mm divisions. After placing weighed coal samples into the glass tubes, a known volume of solvent was added and the content vigorously stirred with a thin rod. The tubes were centrifuged for 5 min at $3600 \text{ rev min}^{-1}$ and heights of swollen samples promptly read. Separate samples were used to determine the extent of swelling as a function of coal concentration. The specific swelling ratio¹⁵ (Q' ; ml g^{-1}) was calculated by heights and mass of samples.

3. Results and Discussion

Solvents must be isolated from coal after high-temperature soaking to evaluate its mechanism. When a coal liquid and polycyclic aromatic hydrocarbons are used for high-temperature soaking, these solvents largely remain with the coal as a consequence of their high-boiling points; therefore, solvents with low-boiling points are desired. The change in solubility induced by high-temperature soaking is highly dependent upon solvents, but those stable at 350°C are generally poorer for coal. Poorer solvents such as cyclohexane and toluene do not effectively solubilize coal under many conditions. It was observed that a large portion of PS extract obtained from the DECS-2 coal by high-temperature soaking in a coal liquid was changed to PI residue by high-temperature soaking in cyclohexane and toluene. Based on this preliminary observation, the PS from the original DECS-2 coal was treated by high-temperature soaking in toluene. The treated sample was Soxhlet-extracted with pyridine, and the PS and PI analyzed by solvent swelling. One advantage gained by using the PS extract is that a remarkable change in total extractability resulting from high-temperature soaking was indicated. Since the PS is not a three-dimensionally cross-linked

network, analysis after treatment is not as complicated as it would be when using a whole coal.

Swelling ratios were found to be highly dependent on coal concentration^{1,15}. Coal swelling was significantly enhanced at concentrations < 5 wt%. Results indicated that (1) intra- and intermolecular interactions were more solvated at lower concentrations, (2) associated coal dissociates more, and (3) coal was more swollen. A covalently cross-linked network model for coal would not show this direct dependence of concentration on swelling. The relationship was compared for PS and PI¹⁶. The dependence on concentration using tetrahydrofuran (THF) and toluene was similar for PS and PI fractions, but solvent swelling of PS was smaller than that of PI. These results would be expected for a physically associated model of coal, since the average molecular size of the PI residue is larger than that of the PS extract. Predicted coal swelling behaviors for the network and associated models are compared in *Table 4.1*¹⁶. The previous findings all support the foundation for a physically associated model. Further details appear in our paper¹⁶. The similar methodology is used for the PS and PI obtained from these treatments to help determine if PI was formed by association or cross-linking reactions.

Table 4.1 Comparison of predicted solvent swelling for the network (Model A) and the associated (Model B) models of coal

Solvent swelling	Model A	Model B
1 Reswelling	reversible	irreversible
2 Dependence of coal concentration	none or small	significant
3 Dependence of coal concentration for fractionated samples	significantly different	similar
4 Dependence of fractionation on swelling ratio (Q)	$Q_{\text{solubles}} > Q_{\text{insolubles}}$	$Q_{\text{solubles}} < Q_{\text{insolubles}}$
5 Dependence of solvent for fractionated samples	larger for solubles than insolubles	larger for insolubles than solubles

The PS extract was soaked in toluene at 350°C for 2 h, followed by removal of the solvent. The treated PS (PS₃₅₀) was then Soxhlet-extracted with pyridine. Pyridine extractability was only 19 wt%, although the sample was originally pyridine soluble. Two mechanisms suggested for the formation of the PI (PS₃₅₀:PI, 79 wt% of the original PS) are cross-linking reactions or physical associations. If PS₃₅₀:PI is formed by cross-linking, solvent swelling should be smaller than that of the original PS. The pyridine extractable portion after treatment (PS₃₅₀:PS) may contain depolymerized coal, if chemical reactions are dominant; therefore, solvent swelling of the PS₃₅₀:PS may be larger than those of PS and PS₃₅₀:PI. If physical associations are dominant for formation of PS₃₅₀:PI, solvent swelling of PS₃₅₀:PI should be larger than those of PS and PS₃₅₀:PS, because of larger molecular weight between physical cross-links. Swelling behaviors are summarized as follows:

Solvent swelling of these samples was measured in THF with coal/solvent of 4.8 ± 0.4 w/w %. Specific swelling ratios of PS, PS₃₅₀:PS and PS₃₅₀:PI were 1.7, 1.3 and 2.5, respectively ((2) in *Figure 4.1*). These results appear to favor the associative equilibria order shown in above as (1). The same treatment was carried out at 200°C¹³. After the sample was soaked for 24 h, 52 wt% of the treated sample was extracted with pyridine. Specific swelling ratios determined from these samples again supported the model (1) predicted for associative equilibria ((3) in *Figure 4.1*). The conclusion, therefore, is that high-temperature soaking in toluene is primarily controlled by associative equilibria and that the pyridine insolubles (PI) are not the result of a retrograde reaction.

THF-swelling of PI residue treated under similar conditions was also examined ((4) & (5) in *Figure 4.1*). Since relatively insignificant portions of pyridine solubles were formed after treatment, their swelling ratios were not measured. PI₂₀₀ and PI₃₅₀ soaked at 200 and 350°C both exhibited smaller swelling ratios than shown by the original PI. Even considering minimal pyridine extractability, swelling ratios of PI₂₀₀:PI and PI₃₅₀:PI were larger than those of PI₂₀₀ and PI₃₅₀. These results also support an associated equilibria

(1)	Coal 1.8	<u>Pyridine</u> Soxhlet	PS 1.7 (28%) ^a PI 2.3		
(2)	PS 1.7	<u>toluene</u> 350°C, 2h	PS ₃₅₀ 1.4	<u>Pyridine</u> Soxhlet	PS ₃₅₀ :PS 1.3 (19%) PS ₃₅₀ :PI 2.5
(3)	PS 1.7	<u>toluene</u> 200°C, 24h	PS ₂₀₀ 1.6	<u>Pyridine</u> Soxhlet	PS ₂₀₀ :PS 1.4 (52%) PS ₂₀₀ :PI 3.3
(4)	PI 2.3	<u>toluene</u> 350°C, 2h	PI ₃₅₀ 1.3	<u>Pyridine</u> Soxhlet	PI ₃₅₀ :PS - (1%) PI ₃₅₀ :PI 1.7
(5)	PI 2.3	<u>toluene</u> 200°C, 24h	PI ₂₀₀ 1.6	<u>Pyridine</u> Soxhlet	PI ₂₀₀ :PS - (<1%) PI ₂₀₀ :PI 1.7

^aNumbers in parentheses are extraction yields with pyridine

Figure 4.1 Specific swelling ratios with THF for PS and PI obtained from the treatments
(Coal/solvent = 4.8 ± 0.4 w/w %)

model.

The mechanism of high-temperature soaking was investigated using toluene. During this treatment, the pyridine extractability of coal (PS) significantly decreased. This was attributed to associations rather than retrograde reactions. Due to problems encountered during removal of coal liquids and polycyclic aromatic hydrocarbons from soaked coal, the standard procedure was not used with these solvents. High-temperature soaking appears, however, to be controlled primarily by dissociative/associative equilibria.

4. Summary

Pyridine insolubles were obtained from extracts of Illinois No. 6 coal by soaking in toluene at 200 and 350°C. These samples were analyzed by coal swelling to investigate the mechanism controlling the change in coal solubility at these temperatures. Swelling ratios of residues from the raw coal and samples treated at both temperatures proved significantly larger than those obtained from their extracts. Reductions in coal extractability after

soaking in organic solvents and in coal liquids at 200-400°C has been regarded as retrograde reactions. The results of these tests, however, suggest that the ultimate extractability under high-temperature soaking is primarily controlled by associative equilibria.

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Chapter 5 Mechanism of Coal Solubilization from High-Temperature Soaking: Investigation by extractability

1. Introduction

Since a major portion of high volatile bituminous coal can be disintegrated in coal-derived liquids and polycyclic aromatic hydrocarbons at 300 to 400°C¹, heat soaking in coal-derived liquids at high temperatures below the point where liquefaction is to be carried out, (high-temperature soaking) is one method for pretreating or preparing it for further processing. Therefore, a better understanding of the heat soaking mechanism is important for any development of coal preconversion.

A cross-linked, three-dimensional macromolecular model has been widely accepted for the structure of coal. It has previously been reported, however, that significant portions of coal molecules are physically associated¹. Support for the cross-linked model apparently comes from the difficult solubilization of relatively strong intra- and intermolecular interactions under conditions used for normal coal extraction. One example of relatively strong intermolecular activity is the charge-transfer interaction of bituminous coal². It was herein proposed that electron donors and acceptors of low molecular weight in coal liquids substitute coal-coal complexes for the charge-transfer interaction at high temperatures³. Since polycyclic aromatic hydrocarbons are generally good electron donors and are also effective in breaking the charge-transfer complexes, it now seems that *physical dissolution* must be one of the major factors in high-temperature soaking.

It is difficult to distinguish between physical and chemical phenomena involved in high-temperature soaking. As described in the previous chapter, pyridine insolubles were formed from pyridine solubles of a high volatile bituminous coal by soaking in toluene at 200 and 350°C. These materials were analyzed by coal swelling methods to investigate the mechanism of high-temperature soaking. Swelling ratios of pyridine solubles and insolubles suggested that the change in extractability by high-temperature soaking was primarily controlled by associative equilibria (physical phenomena).

In this chapter, a systematic work using actual coal liquids is reported. Various coals and coal liquids are tested under various conditions and extractabilities with three separate

solvents measured. Based on these extractabilities, the proposed mechanism for the disintegration of coal by high-temperature soaking was investigated.

2. Experimental

Coal samples were obtained from the DOE Coal Bank at the Pennsylvania State University and the Premium Sample Program at Argonne National Laboratory⁴. Their elemental analyses are shown in *Table 5.1*. Three coal liquids were obtained from the Wilsonville pilot plant⁵ and Aristech Chemical Co. (see Chapter 2). Elemental analyses of these coal liquids are also shown in *Table 5.1*. The pyridine-refluxed Illinois No. 6 coal was prepared following the previously described procedure⁶. HPLC-grade solvents were obtained from Fisher Scientific Co. (Pittsburgh, PA) and were used without further purification.

Microreactors were used for all experiments. The fluidized sand bath used was controlled within $\pm 1.0^\circ\text{C}$ of the set point. Mixtures in the reactor attained the set point within 5 min after the reactor had been immersed in the sand bath.

Coal (5 g) and coal liquid (15 ml) were charged to the reactor which was purged with nitrogen three times. After high temperature soaking, the reactor was cooled to room temperature under air from a fan. Reactor contents were washed out with pyridine and filtered through an extraction thimble. Sample was then Soxhlet-extracted under nitrogen with pyridine until the solution draining from the thimble became colorless. The residue

Table 5.1 Elemental analyses of coals and coal liquids used (wt%)

Symbol	Sample	H ₂ O	Ash	Element (daf)			
				C	H	N	S
DECS-2	Illinois no. 6 (hvb)	10.4	14.5	78.1	5.4	1.3	5.4
DECS-3	Coal Basin M (mvb)	1.1	5.3	87.4	5.9	1.7	0.7
DECS-8	Smith-Roland (subb)	28.4	9.9	74.4	5.2	1.0	0.9
DECS-12	Pittsburgh no. 8 (hvb)	2.4	10.0	83.3	5.7	1.4	1.3
UF	Upper Freeport (mvb)	1.1	13.0	85.5	4.7	1.6	2.7
Liquid A	Liquid derived from Illinois no. 6 coal	-	-	88.4	11.4	0.2	< 0.1
Liquid B	Liquid derived from Pittsburgh no. 8 coal	-	-	87.1	9.6	0.2	< 0.1
CT	Coal tar distillate	-	-	91.8	6.0	0.7	0.6

was Soxhlet-rinsed with methanol for 6 h and then dried under vacuum at 95°C overnight. Pyridine in the extract was evaporated using a rotary evaporator. Tetrahydrofuran (THF) was then added to the extract in 300-400 ml quantities. This mix was filtered and Soxhlet-extracted with THF. Residue from this sample was treated following the procedure described above for pyridine extraction. The THF extract itself was treated with toluene in a similar fashion.

Amounts of pyridine solubles (PS), THF solubles (TS), and toluene solubles (ToS) were determined as a function of the overall quantity of the respective insolubles.

3. Results and Discussion

(1) Extractability and selectivity

Two high volatile bituminous coals (DECS-2 and 12) were soaked under nitrogen in three different coal-derived liquids at 350°C for 2 h. *Figure 5.1* shows the extractability of these treated coals. The highest PS yields and the lowest ToS yields were obtained by soaking both coals in coal tar distillates (CT). The influence of coal rank on high-temperature soaking was indicated using this CT. *Figure 5.2* shows the extractability of five coals soaked in CT for 1.5 h. The highest PS yields (75 - 80%) and the lowest ToS yields (10 - 15%) were obtained from the two high volatile bituminous coals among the different ranks of coal tested.

If *bond cleavages* were significant for high-temperature soaking, ToS yields should be higher when higher yields of PS are obtained and should be equally effective on different ranks of coal. These results, however, showed that lower PS yields of only 30 - 50% were obtained from the subbituminous and the medium volatile coals used. On the other hand, if the dissolution of coal molecules is primarily controlled by *physical phenomena*, disintegrated molecules would probably exhibit high molecular weight and result in a low yield of ToS even when a high yield of PS is provided. Coal tar distillate, in the form of anthracene oil, has been used for high-temperature soaking studies⁷⁻⁹. When using this coal liquid, significantly extensive coal disintegration has been noted. Additional evidence of physical dissolution found in these studies was discussed in the previous chapter. This lends weight to the argument that the disintegration of high volatile bituminous coal by high-temperature soaking is mainly controlled by physical dissolution.

Figure 5.1 Effect of coal liquid on extractability (soaking condition: 350°C, 50 psi N₂, 2 h)

Figure 5.2 Effect of coal rank on extractability (soaking condition: CT, 350°C, 50 psi N₂, 1.5 h)

(2) Dependence of Time

Raw DECS-2 coal and its PI (73 wt% daf of the raw coal) were soaked in Liquid B at 350°C for different time intervals. *Figures 5.3 and 5.4* show results of these tests. As indicated, PS yield for the raw sample reached a maximum of 90 wt% after 1.5 h then decreased to 84 wt% after 2 h. PS yields for the PI, however, increased with soaking time up to 2 h. Similar results were reported when using tetralin for the dried Illinois No. 6 coal and its PI¹⁰.

In the previous chapter, it was suggested that the association and dissociation of coal took place concurrently during high-temperature soaking, and that total extractability was determined as a function of associative equilibria. Since the degree of association or dissociation depends on the extent of coal disintegration, this may result in a point of minimum or maximum extractability. The result for the raw coal shown in *Figure 5.3* is rationalized by associative equilibria. Such association may be overwhelming after attainment of the maximum extent of dissolution. Conversely, as shown with the PI sample detailed as *Figure 5.4*, less chance for association is expected and no maxima up to 2 h soaking time shown. This tends to support physical dissociation.

Larsen *et al.*¹⁰ attribute the decrease in extractability to retrograde reactions. One would expect that retrograde reactions would occur in a similar fashion for raw, PS, and PI samples and that a point of maximum extractability would be observed for all these samples. In these tests, however, a point of maximum extractability was observed for only the raw portion of the coal while the solvent-induced coal, prepared by treatment with chlorobenzene, did not show maxima. As the treated coal does associate to some degree, the extent during high-temperature soaking would be small and would probably show no point of maximum extractability. These results are consistent with the proposition suggested.

Figure 5.3 Effect of soaking time on extractability for raw coal (soaking condition: DECS-2 + Liquid B, 350°C, 50 psi N₂)

Figure 5.4 Effect of soaking time on extractability for PI (soaking condition: DECS-2 + Liquid B, 350°C, 50 psi N₂)

(3) Dependence of Temperature

Raw DECS-2 coal and its PI were soaked in Liquid B at different temperatures for 1.5 h. As shown in *Figures 5.5 and 5.6*, the PS yield for the raw coal sample reached a maximum of 90 wt% at 350°C and then decreased to 82 wt% at 375°C. PS yield from the PI, however, increased with the soaking temperature up to 375°C. A point of maximum extractability for a whole portion of coal relative to soaking temperature has also been reported by other researchers¹¹⁻¹³. Association and dissociation occur concurrently during high-temperature soaking, and total dissolution is determined as a result of associative equilibria. Association is presumably dominant after attainment of the maximum extent of dissolution. With the larger opportunity for association with the PS fraction in the raw coal, it appears that its extractability exhibits maxima from compensation by association. Alternatively, the yield for the PI sample after soaking was larger at 375°C than at 350°C and, therefore, did not show maxima.

(4) Effect of Solubles

As previously discussed, electron donors and acceptors of low molecular weight in coal liquids substitute coal-coal complexes for charge-transfer interactions during high-temperature soaking. Solvent solubles are thought to have a "solvent" property although their molecular weight is larger than that of the coal liquids. For this reason, dissolution of PI by high-temperature soaking is probably more difficult than dissolution of the raw coal. The PS and PI fractions of the DECS-2 coal were separately soaked in Liquid B at 350°C and total extractability calculated from their weight fractions in the original coal. For comparison, the whole coal was refluxed in pyridine for 72 h. The pyridine was removed and the treated coal soaked under similar conditions. Results of these tests are shown in *Figure 5.7* where total extractability of the separately soaked samples is lower than that of the whole coal. This result supports the "solvent" property of the PS during high-temperature soaking. It tends to refute the network model which infers that diffusion of the coal liquid inside the PI should be faster than that in the whole coal.

Larsen *et al.*¹⁰ compared effects before and after pyridine extraction using Illinois No. 6 coal. Removal of the extract caused a striking reduction in the soluble material produced

Figure 5.5 Effect of soaking temperature on extractability (soaking condition: DECS-2 + Liquid B, 50 psi N₂, 1.5 h)

Figure 5.6 Effect of soaking temperature on extractability for PI (soaking condition: DECS-2 + Liquid B, 50 psi N₂, 1.5 h)

by high-temperature soaking. The rearrangement of PS and PI resulting from exposure to pyridine was assumed to be a major factor¹⁴, however, since the results were compared to the dried whole coal and not to the whole coal exposed to pyridine, they could not properly assess the effects of solubles from those produced by a solvent-induced molecular change. Results showed a 15 wt% reduction in the PS yield after exposure to pyridine and subsequent removal of the solvent. Separate soaking of PS and PI further decreased the PS yield by 8 wt%. This infers that both soluble fractions and solvent-induced molecular changes affect high-temperature soaking. Since solvent-induced associations reduce PS by 10 wt% using Illinois No. 6 coal, these factors would seem to be related.

Figure 5.7 Effect of pyridine solubles on extractability for DECS-2 (soaking condition: 350°C, 50 psi N₂, 1.5 h in Liquid B, (PS + PI) was calculated from $(0.27 \times \text{PS}) + (0.73 \times \text{PI})$)

4. Summary

Soaking high volatile bituminous coal in a coal liquid at 300 to 400°C provides a very effective disintegration of the coal molecules. The procedure, therefore, could be widely used for pretreating coal in the current two stage coal liquefaction process. An understanding of this soaking mechanism is necessary for any further development of this method. A study of coal swelling in the previous chapter has implied that physical associative/dissociative equilibria are the major factors in high-temperature soaking. Associated samples soaked in toluene were used in the study. Further justification of this theory was sought with actual coal liquids. While it was somewhat difficult to differentiate between chemical and physical phenomena during high-temperature soaking, the following results support the associative equilibria theory:

1. Coal tar distillates provided the highest PS yield and the lowest ToS yield.
2. High volatile bituminous coals produced the highest PS yields but the lowest ToS yields on conversion.
3. Whole coals showed a point of maximum PS yield versus both time and temperature which the PI residue did not exhibit.
4. Soaking the whole coals produced a higher conversion than soaking the PS extract and the PI residue separately.

The soaking mechanism is strongly related to the basic structure of coal. The mechanism essentially verified by this study is consistent with a physically associated molecular structure of coal rather than the conventional cross-linked, three-dimensional network model.

5. References

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Chapter 6 Effect of Radical Initiators on Coal Conversion

1. Introduction

Free radicals are present in native coal and are also produced during coal liquefaction^{1,2}. They play an important role in liquefaction³. According to the currently accepted concept, free radicals inhibit preconversion steps in the liquefaction process. Popular theory proposes that coal radicals on adjacent molecules tend to combine, forming more stable, higher molecular weight materials⁴. This is termed a "retrograde" reaction (Equations (1) and (2)), and should be avoided to maximize ultimate yields of coal liquids.

Hydrogen-donor materials such as tetralin or hydrogenated coal liquids are generally used to prevent the "retrograde" reaction. They stabilize radicals by hydrogen transfer^{5,6} (Equation (3)).

Current knowledge states that any polymerization induced with radicals involves four elementary reactions: (1) initiation, (2) propagation, (3) termination, and (4) transfer⁷. The degree of polymerization is determined by these competitive reactions. Depending on specific conditions and the relative rate of each reaction, free radicals can either induce polymerization or initiate the opposite effect; namely, depolymerization. Hydrocarbon polymers with lower molecular weight are formed at higher temperatures by reactions between radicals. Temperature dependence on molecular weight can be explained by equations derived from each reaction rate⁷. The elementary reactions would be applicable to coal radicals⁸:

Initiation:

Equation (1) etc.

Propagation:

Termination:

Equation (2) etc.

Transfer:

Also important for coal radicals are scission reactions such as that for β -scission⁵.

It has been reported that the radical hydrogen transfer reaction (Equation (8)) is an important pathway for selective bond cleavages in coal liquefaction⁹⁻¹².

Hydrogen transfer may be involved in the initiation and scission reactions of coal; however, to our knowledge, no systematic study of radical kinetics has been made. Therefore, it is not possible to predict if the presence of radicals has a positive or a negative effect on coal preconversion and/or liquefaction.

It has been reported that light fractions were formed from coal and petroleum-derived heavy ends from reactions using radical initiators such as hydrogen peroxide (H_2O_2)¹³ and cumene hydroperoxide (CHP)¹⁴ at temperatures between 120-350°C. The tetrahydrofuran (THF) extract of the *n*-butylamine-treated Illinois No. 6 coal was heated in cyclohexane at 350°C in the presence of H_2O_2 (0.3 %)¹³. The sample before and after heating was analyzed using gas chromatography, which showed that 10-20 times more *n*-alkanes and polycyclic aromatic hydrocarbons were newly produced over those found in the original sample. The atmospheric residue of crude oil was heated at 120 and 300°C in the presence of CHP (2%)¹⁴. This heating generated ~16% increase in the fraction coming off in the 100-540°C range, offering proof that free-radical initiators may, under certain conditions, have a positive effect on the conversion of hydrocarbons.

In some liquefaction processes, coal is mixed with a recycle oil before being fed to the reactor^{4,15}. For maximum efficiency, the coal should be largely dissolved prior to liquefaction¹⁶. Since a relatively low temperature (~200°C) has generally been used for the mixing¹⁷, preconversion has not been fully utilized. High volatile bituminous coal, however, have been effectively dissolved by soaking in a coal liquid or recycle oil at 300-400°C (high-temperature soaking)¹⁸.

Berkowitz *et al.*¹⁹⁻²¹ demonstrated that substantial changes in preasphaltene and

asphaltene contents occur at temperature as low as 250°C. They interpreted these results as functions of time- and temperature-dependent pseudo-equilibria between preasphaltene and residue and preasphaltene/asphaltene. Studies²² in the previous chapters showed that solubility induced by high-temperature soaking is primarily controlled by dissociative-/associative equilibria. The solubility mechanism is consistent with the recently proposed structural model of coal that concludes that significant portions (far more than generally believed) of coal molecules are physically associated¹⁸. Therefore, even if substantial chemical bonds are not cleaved, a large portion of the coal may be dissolved by weakening intra- and intermolecular interactions (physical dissolution).

Wham²³ studied the effect of coal pretreatment on subsequent liquefaction. A dramatic increase in conversion at 427°C was observed when a coal/coal-liquid mixture was maintained at temperatures from 277-322°C for 10 min prior to liquefaction. Derbyshire *et al.*²⁴ studied the influence of pretreatment conditions on the product distribution. Coals were pretreated for 1 h in naphthalene at 350°C, and the reacting mixture was subsequently heated to 425°C for 10 min. A high ratio of oil to asphaltene resulted from this pretreatment. Solomon *et al.*²⁵ conducted similar experiments and obtained similar results. These results suggest that high-temperature soaking of coal in a recycle oil could be an ideal method for the physical dissolution of coal or to prepare it for further processing.

The disintegrated coal generated from high-temperature soaking is still high-molecular-weight material and extractability with poorer solvents such as toluene and cyclohexane remains low²². Therefore, an alternative pretreatment to manifest the breakdown of the high-molecular-weight material is desired before liquefaction. While information on their role at this stage of preconversion is limited, breakdown of the high-molecular-weight material by radicals may be possible under certain conditions. In this chapter, the effect of radicals on preconversion and liquefaction is evaluated as a method for initiating chemical breakdown during or after physical dissolution. While any quantitative estimation of the specific role of radicals is very difficult, positive or negative effects on conversion from the addition of radical initiators has been determined.

2. Experimental

Coal samples were obtained from the DOE Coal Bank maintained at the Pennsylvania State University. Elemental analyses characterizing these coal are presented as *Table 6.1*. Wyoming subbituminous coal (DECS-8) was washed with 2N HCl for 24 h then dried following the previously described procedure²⁶. This dried product was used for the tests while the Illinois coal (DECS-2) was used as received. A coal liquid derived from Illinois No. 6 coal (Liquid A) was obtained from the Wilsonville pilot plant²⁷. Reagents and solvents obtained from Aldrich Chemical Co. (Milwaukee, WI) and Fisher Scientific (Pittsburgh, PA) were HPLC-grade and used without further purification. H₂O₂ (3% in water) and CHP (80% in cumene) were also used.

Coal samples (5 g) were charged to a 250 ml autoclave. After adding tetralin or the coal liquid (50 ml) with additives, the autoclave was evacuated and purged with nitrogen five times then heated at $\sim 5^{\circ}\text{C min}^{-1}$ to the required temperature under either a nitrogen or hydrogen atmosphere (initial pressures: 100-200 psi). The mixtures were heated at designated rates ($\sim 5^{\circ}\text{C min}^{-1}$) for 0.5-2 h while maintaining agitation with the autoclave stirrer (500 rev min⁻¹). After treatment, samples were cooled to 200°C in the autoclave then in air to room temperature. The product was filtered and transferred to an extraction thimble then Soxhlet-extracted under nitrogen using cyclohexane, toluene, tetrahydrofuran (THF), and pyridine solvents for 24 h, respectively. Extracts after evaporation of solvents and residues were dried under vacuum at 95°C overnight. Cyclohexane solubles (CyS), toluene solubles (ToS), THF solubles (TS), pyridine solubles (PS), THF insolubles (TI), and pyridine insolubles (PI) were calculated from the weights of their respective residues.

Table 6.1 Elemental analyses of coals used (wt%)

Coal symbol	Coal	H ₂ O	Ash	Element (daf)			
				C	H	N	S
DECS-2	Illinois no. 6 (hvb)	10.4	14.5	78.1	5.4	1.3	5.4
DECS-8	Smith-Roland (subb)	28.4	9.9	74.4	5.2	1.0	0.9

3. Results and Discussion

In Runs 1-19, DECS-2 (Illinois No. 6) coal was soaked in either tetralin or the coal liquid at 350 or 400°C for 0.5 h. In Runs 21-35, DECS-2 or DECS-8 (Wyoming) coal was soaked in the coal liquid at 350°C for 1 h then liquefied at given temperatures for 1 h. These experimental conditions are summarized as *Tables 6.2 and 6.3*, with conversion results shown in *Figures 6.1 and 6.2*, respectively. Runs 2 and 21 were repeated and subsequent yields shown to be reproducible within ± 3 wt%. The dried DECS-2 coal was used for Run 1 while acid-washed and dried DECS-8 coal provided the feed material for Runs 31-35. Raw DECS-2 coal was used for the other experiments.

(1) Effect of hydrogen peroxide (H_2O_2)

The DECS-2 coal was heated under nitrogen in tetralin at 350°C for 0.5 h (Run 2). About 66 wt% of coal was extracted with pyridine after this high-temperature soaking. The yields of PS increased to 77 wt% after adding H_2O_2 which represented 3000 ppm in the solvent (Run 6). Concurrently, the yield of ToS decreased from 42 to 32 wt%, resulting in an increase in the TS•ToI (THF soluble and toluene insoluble) fractions. The same effect was observed using the coal liquid under similar conditions (Runs 16 and 17). When high-temperature soaking time was expanded to 2 h, yields of ToS, TS, and PS increased more than 10 % (Run 14). The same effects from the longer soaking time using H_2O_2 were also observed (Run 15).

(2) Effect of cumene hydroperoxide (CHP)

This organic radical initiator was evaluated in the same fashion as the H_2O_2 . When added as ~1.6 % in tetralin (Run 3) the yields of ToS, TS, and PS increased 2-5 wt% over those shown in Run 2 using H_2O_2 . When CHP was increased to ~8 % in tetralin (Run 4), the yields of TS and PS further increased 2-4 %, but the yield of ToS decreased. Although the changes in these yields were small for Run 3, the effect of CHP shown by Run 4 was significant and consistent with the results obtained from experiments using H_2O_2 .

From these tests, it is concluded that radicals produced from these compounds promote reactions of other radicals under the conditions imposed. The effect of these radical initiators in the total conversion (PS) is positive for high-temperature soaking and

Table 6.2 Run numbers and experimental conditions for high-temperature soaking of DECS-2 coal

Run no.	Condition							
	Temp.	Time	Solvent	Atmosphere			Additive	
	(°C)	(h)	(50 ml)	Gas	Pres. ^a (initial) (psi)	Pres. ^b (actual) (psi)	Compound	Amount (ml)
1 ^c	350	0.5	Tetralin	N ₂	100	280	---	---
2	"	"	"	"	"	310	---	---
3	"	"	"	"	"	340	CHF ¹	1
4	"	"	"	"	"	400	"	5
5	"	"	"	"	"	730	H ₂ O	"
6	"	"	"	"	"	720	H ₂ O ₂ ^e	"
7	300	"	"	"	"	630	H ₂ O	"
8	"	"	"	"	"	640	H ₂ O ₂	"
9	400	"	"	"	"	880	H ₂ O	"
10	"	"	"	"	"	920	H ₂ O ₂	"
11	350	"	"	H ₂	"	310	---	---
12	"	"	"	"	"	700	H ₂ O ₂	5
13	"	"	"	"	"	970	"	10
14	"	2.0	"	"	"	300	---	---
15	"	"	"	"	"	660	H ₂ O ₂	5
16	"	0.5	Liq. A	N ₂	"	260	---	---
17	"	"	"	"	"	720	H ₂ O ₂	5
18	"	"	"	H ₂	"	270	---	---
19	"	"	"	"	"	570	H ₂ O ₂	5

^a@25°C

^bActual pressure under conditions

^cThe dried coal was used for Run 1

^dCHP: Cumene hydroperoxide, 80% in cumene

^e3% in water

Table 6.3 Run numbers and experimental conditions for soaking and liquefaction

Run no.	Condition										
	Coal	Temp.		Time		Atmosphere				Additive	
		Soaking (°C)	Lique. (°C)	Soaking (h)	Lique. (h)	Gas	Pres. ^a (initial) (psi)	Pres. ^b Soaking (psi)	Lique. (psi)	Compound	Amount (ml)
21	DECS-2	350	430	1.0	1.0	N ₂	200	430	810	---	---
22	"	"	"	"	"	"	"	960	1210	H ₂ O ₂ ^c	5
23	"	"	"	"	"	H ₂	"	420	690	---	---
24	"	"	"	"	"	"	"	840	1460	H ₂ O ₂	5
25	"	"	400	"	"	N ₂	"	440	580	---	---
26	"	"	"	"	"	"	"	960	1110	H ₂ O ₂	5
27	"	"	"	"	"	H ₂	"	440	530	---	---
28	"	"	"	"	"	"	"	860	1160	H ₂ O ₂	5
29	"	"	460	"	"	N ₂	200	840	2100	H ₂ O ₂	5
30	"	"	"	"	"	H ₂	"	840	2080	"	"
31	DECS-8	"	440	"	"	H ₂	"	380	880	---	---
32	"	"	"	"	"	"	"	890	1460	H ₂ O ₂	5
33	"	"	"	"	"	"	"	900	1350	H ₂ O	"
34	"	"	"	"	"	N ₂	"	890	1540	H ₂ O ₂	"
35	"	"	430	"	"	"	"	850	1350	"	"

^a@25°C

^bActual pressure under conditions

^c3% in water

Figure 6.1 Yields of toluene solubles (ToS), tetrahydrofuran solubles (TS) and pyridine solubles (PS) and pyridine insolubles (PI) of products (wt%, daf) obtained from high-temperature soaking at 350°C

Figure 6.2 Yields of cyclohexane solubles (Cys), toluene solubles (Tos), tetrahydrofuran solubles (TS) and tetrahydrofuran insolubles (TI) of products (wt%, daf) obtained from soaking and liquefaction (Cyclohexane solubles could not be determined because of the incorporation of the coal liquid into the products)

tends to refute the widely accepted concept which states that coal radicals have a negative effect on coal liquefaction. Scission reactions (Equations (9) and (10)) presumably contribute to coal conversion in the following manner:

As these reactions resulted in a decrease in the ToS fraction and an increase in the TS•ToI fraction, other competitive reactions (Equations (4)-(6)) may be involved.

(3) Effect of water

Since the effect of H_2O_2 was greater than that of CHP, the effect of water used with H_2O_2 was evaluated. The same amount of water used for Run 6 was added (Run 5). Results (Runs 5 and 6) agreed within the experimental error, showing that the addition of water caused the same change in coal conversion as the addition of the H_2O_2 solution; namely, the PS fraction increased, the ToS fraction decreased, and the TS•ToI fraction increased. Since the moisture content of the native raw coal was 10.4 wt%, the dried coal was tested to investigate the effect of water (Run 1). The differences in the ToS, TS, and PS yields between Runs 1 and 2 presumably stem from the difference in the moisture content of the two samples. Results support the effects of water shown above. The effect of the addition of water and H_2O_2 was compared at 300°C (Runs 7 and 8) and 400°C (Runs 9 and 10). The difference was small with Runs 7 and 8 but larger with Runs 9 and 10. The yield of the low-molecular-weight fraction (ToS) was higher at higher temperatures in the presence of H_2O_2 . This is the same trend observed for radical-induced polymerizations³. From these results, the effect of the addition of H_2O_2 is more prominent at higher temperatures. It is notable that more than 90 wt% of PS and more than 70 wt% of ToS were produced from this high volatile bituminous coal by soaking in tetralin at 400°C for 0.5 h with the addition of H_2O_2 without hydrogen (Run 10).

Water pretreatment of coal has been studied as a means to increase the yields of liquid products from pyrolysis and liquefaction. A brief review appears in a recent paper²⁸. Coal was exposed to steam at 200-360°C, followed by flash pyrolysis and liquefaction²⁹⁻³², or was treated in water at 200-400°C before liquefaction³³⁻³⁵. These experimental conditions vary among different researchers making the specific effect of water difficult to evaluate.

Various factors including temperature, coal rank, water under pressure or steam, removal or presence of water during or after treatments all seem to significantly affect conversion. Graff and Brandes³¹ obtained higher yields on flash pyrolysis and total extractability using steam treatments for Illinois No. 6 coal. Ross and Hirschon³³ treated this coal with water at 200°C and liquefied at 400°C. Little obvious change in the yields of ToS were obtained. Serio *et al.*³⁵ reported only a modest benefit from using the water treatment (up to 400°C) for Illinois No. 6 coal. Although structural changes were reported using coal³⁴⁻³⁷ and model compounds³⁸, the mechanisms of water and steam treatments are still not clear. In our work, we show that the addition of relatively small amounts of water produce the same change in coal conversion as does the addition of radical initiators; namely, an increase in the PS fraction, a decrease in the ToS fraction, and an increase in the TS•ToI fraction.

(4) Effect of hydrogen

The effect of hydrogen under low pressure (100 psi) was evaluated with additions to tetralin (Runs 11-13) and to the coal liquid (Runs 18 and 19). The yield of PS was the same or slightly increased under hydrogen without H₂O₂ (Runs 11 and 18), but the yield of ToS significantly decreased 10-20 wt% and TS•ToI fractions increased. The change is of the same magnitude as that realized from the addition of radical initiators and water and implied that hydrogen is involved in radical reactions.

The effect of hydrogen on thermolysis was studied by using model compounds at 450-960°C. Hydrogen extraction by coal radicals from hydrogen was proposed as follows:

Coal radicals may be present in the original coal or may be produced by thermolysis. Although it is thought that radicals are not abundant, radical-induced reactions may be facilitated by hydrogen extraction. If hydrogen extraction does occur under the conditions imposed, the effect would be larger in hydrogen donor solvents.

The yield of ToS decreased ~20 wt% in tetralin (Runs 2 and 11), but only ~10 wt% in the coal liquid (Runs 16 and 18). The larger change observed using the donor solvent (tetralin) supports the hydrogen extraction theory.

If the suggested hydrogen extraction followed by radical-induced reactions is significant, the change in the yields by the addition of radical initiators should be smaller under hydrogen than under nitrogen. Yield changes in tetralin were smaller between Runs 11 and 12 (under hydrogen) than those between Runs 2 and 6 (under nitrogen). The difference between Runs 18 and 19 made under nitrogen using the coal liquid was also smaller than that between Runs 16 and 17 (under hydrogen). These results are consistent with the proposed mechanism involving hydrogen.

(5) Effect of temperature

The DECS-2 coal/coal-liquid mixture was soaked under nitrogen at 350°C for 1 h, then liquified at 430 or 400°C for 1 h (Runs 21 and 25). This same blend (Runs 23 and 27) was soaked under hydrogen (200 psi @25°C) under similar conditions. Hydrogen effects were insignificant. Hydrogen peroxide (5 ml) was added to the mixture and the effect of this radical initiator on coal liquefaction evaluated (Runs 22 and 24). The addition of hydrogen peroxide had a slightly negative effect on conversion under nitrogen at 430°C (Run 22), where the TS and ToS yields decreased 2 and 6 %, respectively. This negative effect was enhanced under hydrogen at 430°C (Run 24) as the TS, ToS, and CyS yields decreased 7, 14, and 15 %, respectively. The same experiments were carried out at 400°C (Runs 26 and 28). In contrast with the negative effect exhibited at 430°C, a slightly positive effect on conversion under nitrogen was observed, where the TS and ToS yields increased 4 and 2%, respectively (Run 26). This positive effect was enhanced under hydrogen (Run 28) as the TS, ToS, and CyS yields increased 2, 2, and 4%, respectively.

Hydrogen peroxide and cumene hydroperoxide did not induce retrograde reactions at 350°C, and had a slightly positive effect on preconversion. Therefore, the overall effect of the radical initiator on coal conversion appears dependent upon temperature. The effect is positive at lower temperatures (350 and 400°C), but negative at higher temperatures (>430°C). These effects are enhanced under hydrogen. To confirm this temperature dependency, the same experiments were carried out under both nitrogen (Run 29) and hydrogen (Run 30) at 460°C. Both reactions generated total yields in excess of 100 wt% (Run 29; 187 wt%, Run 30; 181 wt%), presumably due to the incorporation of the coal liquid into the products. Although the CyS yield was not obtainable from the mass balance,

the ToS yields were only 20-30 wt%. Any significant incorporation of the coal liquid into products can be considered incomplete coal conversion since the ToS and TS yields were lower under hydrogen. These results, therefore, support the dependence of temperature on the influence of radical initiators.

The preceding results were tested using DECS-8 coal. The coal was pretreated under hydrogen (200 psi @25°C) at 350°C for 1 h, then liquefied at 440°C for 1 h with (Run 32) and without (Run 31) hydrogen peroxide. Hydrogen peroxide generated a significantly negative effect. The total recovery of the product was more than 100 wt%, as a result of incorporation of the coal liquid into the product. A comparable amount of water was used (Run 33) under the same conditions. As the yields observed in Runs 31 and 33 are essentially identical, the negative effect observed in Run 32 can be attributed to radical-induced reactions. Hydrogen peroxide was used under nitrogen instead of hydrogen maintaining standard test conditions (Run 24). While the TS yield decreased, the ToS yield greatly increased. For Run 35, the coal was reacted under the same conditions used for Run 32, but at 430°C. The yields of ToS and CyS were much higher than those obtained from Run 31; therefore, the effect of H₂O₂ was obviously positive. These results obtained using the DECS-8 coal are consistent with those obtained from the DECS-2 coal, but the temperatures required to induce the negative effect was higher than that for the DECS-2 coal.

4 Summary

It appears that the effect of hydrogen peroxide on coal conversion is dependent upon temperature. The effect is positive at lower temperatures (<430°C), but negative at higher temperatures (>430°C). These effects are enhanced under hydrogen. The temperatures noted may also change according to the rank of the coal. As a detailed liquefaction mechanism has not been proposed, the reaction mechanism of the radical initiator H₂O₂ during coal conversion is unknown. It is suggested that the reaction mechanism involved in coal liquefaction is different below 430°C than above it. Below 430°C, physical dissolution is presumably dominant^{13,14}, where radical-induced reactions positively affect coal conversion. Above 430°C, chemical reactions dominate where radical-induced reactions are associated with complex chemical reactions and negatively affect coal

conversion. The adverse effect from radical initiators was not as strong as expected, leading one to believe that other radical-induced competitive reactions may be involved. The key to efficient coal conversion is understanding the reaction mechanism of coal radicals.

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Chapter 7 New direction to preconversion processing of coal

1. Introduction

A comprehensive knowledge of basic coal structure must be acquired for the effective development of coal liquefaction. The cross-linked, macromolecular model has been widely accepted by most researchers, and current coal liquefaction studies are proceeding under this assumption. Recent studies, however, show that significant portions (far more than generally believed) of coal molecules appear to be physically associated¹; therefore, the development of any coal liquefaction processes should consider this possibility. If physical association is dominant for cross-links, all properties and reactivities in the liquefaction process must be specific functions of intra- and intermolecular (secondary) interactions as well as molecular weight.

Recent work²⁻⁷ showed the significance and importance of relatively strong secondary interactions for all ranks of coal. These interactions include ionic forces, the charge-transfer interaction, and the so-called π - π interaction⁸. Dissolution of these interactions is believed to be an essential step required before breaking the covalent bonds in coal liquefaction. Some portions of these specific associations, however, are not solvated under normal extraction conditions, even with good solvents such as pyridine^{2,3}. Therefore, dissolution becomes a very difficult task.

It is known from the literature¹, that a substantial amount of high-volatile bituminous coal can be disintegrated in coal-derived liquids and polycyclic aromatic hydrocarbons at 300-400°C (high temperature soaking). These temperatures are well below those maintained during coal liquefaction or other coal decomposition processes. It is proposed that electron donors and acceptors with low molecular weight substitute coal-coal complexes with charge-transfer interactions (physical dissolution), understanding that some chemical bond cleavage may occur concurrently at these temperatures¹.

High-volatile bituminous coal molecules may associate when soaked at temperatures <300°C^{2,3}. This mechanism probably involves the severance of relatively weak secondary interactions concurrent with the formation of stronger secondary interactions (solvent-induced associations)³. The reduction in dissolution observed when soaking coal in a coal

liquid at 200-300°C has been regarded as a retrograde reaction^{9,10}. These temperatures, however, are used in many processes¹¹ for the mixing and preconversion of coal in recycle oils. Hydroaromatics and hydrogenated solvents have been used in the past to prevent retrograde reactions¹². Bond cleavage and stabilization of labile intermediates during preconversion based on the network model are major concerns for current liquefaction processes. Because of the associated nature of coal¹, it is important to carefully select optimal temperatures during pretreatment operations.

One of the main goals in coal liquefaction is to decrease gas yields to reduce hydrogen consumption. Costly hydrogen is lost in the production of gases such as methane and ethane. More gases are generated from severe reactions with undissolved coal which is not as reactive as coal in solution. Therefore, higher reactivity will result in a decrease in gas yield. Since high-temperature soaking in a coal liquid is an effective method for the physical dissolution of coal in the absence of additional chemicals and hydrogen, the subsequent generation of gases should be minimized.

Based on the associated molecular nature of coal, another important factor is suggested to decrease the gas yield. While severe conditions are obviously required for the decomposition of higher-molecular-weight fractions, a larger amount of gas will be produced from associated lower-molecular-weight fractions under these conditions. To optimize the process, coal fractions with different molecular weights should, if possible, be liquefied separately.

Treatment of coal under mild conditions has been studied for years^{13,14}. Pretreatment procedures involving chemical reactions such as alkylation, oxidation, and hydrolysis have been attempted¹⁵. Other methods include treatments in the presence of CO/H₂O¹⁵⁻¹⁸, CH₃OH¹⁵, nitrogen-containing compounds^{19,20}, etc. at temperatures of 300-350°C. From an economic point of view, process conditions involving high pressures of H₂, H₂O and CO and the addition of chemicals are not recommended.

In this chapter, an improved pretreatment procedure for coal liquefaction is investigated on the basis of the associated molecular nature of coal. Activities are focused on two issues mentioned above: (1) maximizing the dissolution of associated coal and (2) step-wise conversion of associated coal with a wide molecular weight distribution. An improved preconversion concept is proposed and tested with autoclave reactors.

2. Experimental

Coal samples were obtained from the DOE Coal Bank at the Pennsylvania State University. Elemental analyses are presented as *Table 7.1*. The Illinois coal (DECS-2) was used as received while the Smith Roland coal (DECS-8) was washed with 2N HCl⁵ and dried before use. Two coal liquids derived from the Illinois No. 6 coal (Liquid A) and Pittsburgh No. 8 coal (Liquid B) were obtained from the Wilsonville pilot plant²¹. Elemental analyses of these coal liquids are also shown in *Table 7.1*. Reagents and solvents (HPLC-grade) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and Fisher Scientific (Pittsburgh, PA) and used without further purification.

A large 250 ml autoclave and small 27 ml microreactors²² were used. These reactors were evacuated and purged with nitrogen five times after charging coals, MoS₂ (Aldrich, <1 μ), and solvents. The autoclave samples were heated at $\sim 8^\circ\text{C min}^{-1}$ to the required temperature, then controlled to $\pm 3^\circ\text{C}$ while being agitated with the autoclave stirrer (500 rev min⁻¹). The microreactor was heated in a fluidized sand bath which was controlled to $\pm 1.0^\circ\text{C}$ of the set point. Mixtures in the microreactor attained the set point within 5 min from the time of immersion into the sand bath. Conditions and results for all experimental runs are summarized in *Tables 7.2* and *7.3*. Liquid A from the Illinois No. 6 coal was generally used, but Liquid B was used for Runs 5-9.

After reactions, the mixtures were filtered and Soxhlet-extracted with cyclohexane, toluene and tetrahydrofuran (THF) for 24 h at each stage. The individual fractions were then dried under vacuum at 95°C overnight. Amounts of cyclohexane solubles (CyS), toluene (ToS), THF solubles (TS), and pyridine solubles (PS) were determined from the weights of their respective insolubles. Gas yields were generally included in CyS yields.

Table 7.1 Elemental Analyses of Coals and Coal Liquids Used (wt%)

symbol	sample	H ₂ O	Ash	element (daf)			
				C	H	N	S
DECS-2	Illinois No. 6 (hvb)	10.4	14.5	78.1	5.4	1.3	5.4
DECS-8	Smith-Roland (subb)	28.4	9.9	74.4	5.2	1.0	0.9
Liquid A	coal liquid derived from Illinois No. 6 coal	--	--	88.4	11.4	0.2	< 0.1
Liquid B	coal liquid derived from Pittsburgh No. 8 coal	--	--	87.1	9.6	0.2	< 0.1

Table 7.2 Experimental Conditions of Preconversion and First Stage Liquefaction Runs (see Table 7.3 for results)

run no.	condition																	
	coal		soaking-1				soaking-2				liquefaction				solvent		cat.	
	code	amount (g)	temp. (°C)	time (h)	gas	pres. ^a (psi)	temp. (°C)	time (h)	gas	pres. ^a (psi)	temp. (°C)	time (h)	gas	pres. ^a (psi)	code	amount (ml)	code	amount (mg)
<u>Effect of Soaking (@250 ml Autoclave) (see Figure 7.1)</u>																		
1	DECS-2	5	200	1.0	N ₂	200	-	-	-	-	430	1.0	N ₂	200	Liq. A	50	-	-
2	"	"	350	"	"	"	-	-	-	-	"	"	"	"	"	"	-	-
3	"	"	-	-	-	-	-	-	-	-	"	"	N ₂ /H ₂	100/400	"	"	MoS ₂	50
4	DECS-2 ^b	"	-	-	-	-	-	-	-	-	"	"	"	"	"	"	"	"
<u>Effect of Soaking Temperature (@27 ml Microreactor) (see Figure 7.2)</u>																		
5	DECS-2	5	275	1.5	N ₂	50	-	-	-	-	-	-	-	-	Liq. B	15	-	-
6	"	"	300	"	"	"	-	-	-	-	-	-	-	-	"	"	-	-
7	"	"	325	"	"	"	-	-	-	-	-	-	-	-	"	"	-	-
8	"	"	350	"	"	"	-	-	-	-	-	-	-	-	"	"	-	-
9	"	"	375	"	"	"	-	-	-	-	-	-	-	-	"	"	-	-
<u>Effect of Step-Wise Soaking (@250 ml Autoclave) (see Figure 7.3)</u>																		
10	DECS-2	5	350	1.0	N ₂	200	400	1.0	N ₂	200	-	-	-	-	Liq. A	50	-	-
11	"	"	200	"	"	"	"	"	"	"	-	-	-	-	"	"	-	-
<u>Effect of Step-Wise Soaking (@27 ml Microreactor) (see Figure 7.3)</u>																		
12	DECS-2	3.5	-	-	-	-	-	-	-	-	430	2.0	N ₂	50	Liq. A	14	-	-
13	"	"	350	0.5	N ₂	50	400	0.5	N ₂	50	"	1.0	"	"	"	"	-	-
14	"	"	(130°C---240°C---350°C---400°C---430°C) 28min 30min 21min 11min								"	"	"	"	"	"	-	-

^a@25°C

^bCoal refluxed in pyridine, followed by the removal of pyridine

Table 7.2 (Continued)

run no.	condition																	
	coal		soaking-1				soaking-2				liquefaction				solvent		cat.	
	code	amount (g)	temp. (°C)	time (h)	gas (psi)	pres. ^a (psi)	temp. (°C)	time (h)	gas (psi)	pres. ^a (psi)	temp. (°C)	time (h)	gas (psi)	pres. ^a (psi)	code	amount (ml)	code	amount (mg)
<u>Effect of Coal Fractions (@250 ml Autoclave) (see Figure 7.4)</u>																		
15	DECS-2	5	-	-	-	-	-	-	-	-	430	1.0	N ₂ /H ₂ 100/400	Liq. A	50	MoS ₂	50	
	/PS ^c																	
16	DECS-2	"	-	-	-	-	-	-	-	-	"	"	"	"	"	"	"	"
	/PI ^c																	
17	DECS-2	"	-	-	-	-	-	-	-	-	"	"	"	"	"	"	"	"
	/Cyl ^d																	
<u>Test of the Proposed Procedure (@250 ml Autoclave) (see Figure 7.6)</u>																		
18	DECS-2	5	200	1.0	N ₂ /H ₂ 100/400	-	-	-	-	-	430	2.0	N ₂ /H ₂ 100/400	Liq. A	50	MoS ₂	50	
19	(Yield Calculated from Runs 10 + 17)																	
20	DECS-8	5	200	1.0	N ₂ /H ₂ 100/400	-	-	-	-	-	430	2.0	N ₂ /H ₂ 100/400	Liq. A	50	MoS ₂	50	
21	DECS-8 ^e	"	350	"	"	"	400	1.0	N ₂ /H ₂ 100/400	430 ^f	1.0	"	"	"	"	"	"	"

^a@25°C^cPS: pyridine solubles, PI: pyridine insolubles^dCyclohexane insolubles from Run 10^e2N HCl-washed and dried coal^fCyclohexane insolubles was liquefied after soaking at 350/400°C

Table 7.3 Results of Preconversion and First Liquefaction Runs (see Table 7.2 for conditions)

run no.	results																	
	heating	soaking-1		heating	soaking-2		heating	liquefaction		recovery				conversion				
	time (min)	temp. (°C)	pres. (psi)	time (min)	temp. (°C)	pres. (psi)	time (min)	temp. (°C)	pres. (psi)	ToS•CyI	TS•ToI	PS•TI	Res.	Gas	CyS	ToS (wt%)	TS	PS
<u>Effect of Soaking (@250 ml Autoclave) (see Figure 7.1)</u>																		
1	27	200	320	-	-	-	36	430	890	0.43	0.51	-	1.28	-	60.3	71.7	85.2	-
2	45	350	430	-	-	-	18	430	810	0.42	0.32	-	1.30	-	65.0	76.2	84.7	-
3	-	-	-	-	-	-	57	430	1370	0.53	0.34	-	1.25	-	62.8	76.9	85.9	-
4	-	-	-	-	-	-	58	430	1400	0.42	0.38	-	1.29	-	69.5	79.5	88.5	-
<u>Effect of Soaking Temperature (@27 ml Microreactor) (see Figure 7.2)</u>																		
5	-5	275	NA*	-	-	-	-	-	-	-	0.45	0.54	3.44	-	-	1.5	13.5	27.8
6	-5	300	NA	-	-	-	-	-	-	-	0.52	0.41	3.29	-	-	6.8	20.6	31.7
7	-5	325	NA	-	-	-	-	-	-	-	0.78	0.75	2.65	-	-	7.8	28.7	48.7
8	-5	350	NA	-	-	-	-	-	-	-	0.98	1.01	1.10	-	-	37.1	63.1	90.0
9	-5	375	NA	-	-	-	-	-	-	-	1.03	0.59	1.39	-	-	39.1	66.6	82.2
<u>Effect of Step-Wise Soaking (@250 ml Autoclave) (see Figure 7.3)</u>																		
10	49	350	440	16	400	580	-	-	-	0.67	0.63	-	1.31	-	49.7	67.6	84.4	-
11	29	200	320	50	400	NA	-	-	-	1.35	0.91	-	3.61	-	NA	NA	NA	-
<u>Effect of Step-Wise Soaking (@27 ml Microreactor) (see Figure 7.3)</u>																		
12	-	-	-	-	-	-	30	430	NA	0.61	0.23	-	1.09	-	46.0	69.1	77.7	-
13	15	350	NA	8	400	NA	7	430	NA	0.41	0.26	-	0.99	-	56.4	72.0	81.7	-
14	(130°C----240°C----350°C----400°C----430°C)									0.41	0.27	-	0.97	-	56.7	72.3	82.5	-
				28min	30min	21min	11min											

*NA: not available

Table 7.3 (Continued)

run no.	results																	
	heating	soaking-1		heating	soaking-2		heating	liquefaction		recovery				conversion				
	time	temp.	pres.	time	temp.	pres.	time	temp.	pres.	ToS•Cyl	TS•Tol	PS•TI	Res.	Gas	CyS	ToS	TS	PS
	(min)	(°C)	(psi)	(min)	(°C)	(psi)	(min)	(°C)	(psi)	(g)				(wt%)				
<u>Effect of Coal Fractions (@250 ml Autoclave) (see Figure 7.4)</u>																		
15	-	-	-	-	-	-	60	430	1350	0.62	0.42	-	0.50	-	69.3	81.7	90.1	-
16	-	-	-	-	-	-	59	430	1320	0.41	0.15	-	1.81	-	66.7	77.1	80.9	-
17	-	-	-	-	-	-	60	430	1340	0.47	0.56	-	2.17	-	50.9	64.2	79.9	-
<u>Test of the Proposed Procedure (@250 ml Autoclave) (see Figure 7.6)</u>																		
18	29	200	750	-	-	-	35	430	1500	0.52	0.42	-	1.29	18.5	41.7	74.0	85.0	-
19	(Yield Calculated from Runs 10 + 17)																	
20	30	200	760	-	-	-	34	430	1530	0.60	0.25	-	1.40	23.0	40.9	77.9	83.6	-
21	(CyI obtained from soaking at 350°/400°C)						57	430	1290	0.70	0.34	-	2.00	1.0	51.9	72.0	81.2	-

Gases were collected for analysis in a sample bag after cooling the autoclave, then analyzed using gas chromatography by the University of Pittsburgh Applied Research Center (Pittsburgh, PA). Approximate gas yields were calculated assuming no change in the amount of nitrogen before and after the reactions.

2. Results and Discussion

(1) Coal Dissolution and Liquefaction

Weakening secondary interactions in coal may aid in increasing its conversion. In this study, the effect of solvation on liquefaction due to soaking was evaluated. Illinois No. 6 coal was liquefied at 430°C for 1 h after soaking at 200°C and 350°C (Runs 1 and 2 in *Figure 7.1*). The yields of TS were the same for both tests, but the yields of ToS and CyS were ~5% higher for the sample soaked at 350°C. For Run 4, the coal was refluxed in pyridine (~115°C) for 24 h instead of undergoing high-temperature soaking. After removal of the pyridine, the sample was liquefied at 430°C. Comparing the total conversion to the conversion of the raw coal liquefied under the same conditions (Run 3), showed the yield of CyS increased ~10% after refluxing in pyridine. These results indicate that solvated coal can be readily converted, and that higher temperatures are needed to solvate coal when soaking in poorer solvents. Alternatively, even low temperatures are effective for solvating coal when soaking in better solvents. Reported results support this interpretation. In one case, an increase in conversion at 427°C was observed when a coal/coal liquid mixture was soaked at 277-322°C for 10 min²³. In another case, swelling with THF and tetraammonium-hydroxide at room temperature, followed by removal of the solvents, was shown to enhance hydroliquefaction yields at 400°C^{24,25}.

As reported in the previous chapter²², the optimum range for high-temperature soaking in coal liquids was ~350°C (Runs 5-9 in *Figure 7.2*). The CyS (or oil) yield, however, was low (35%) even at optimum temperatures. A second soaking of the product from the 350°C treatment (two-step soaking) was tested to determine any differences in oil yield. Two-step soaking at 350°C and 400°C generated a 50% oil yield (Run 10 in *Figure 7.3*)²⁷. Soaking at 200°C, however, followed by soaking at 400°C, produced an apparent yield in excess of 100% due to incorporation of the coal liquid into the product (Run 11). Therefore, two-step high-temperature soaking is proven effective for dissolving coal, but

Figure 7.1 Effect of soaking before liquefaction on coal conversion
(Conditions are listed in Table 7.2)

Figure 7.2 Effect of soaking temperature on extractability²²
(Conditions are listed in Table 7.2)

temperatures above 200°C are required for the first step.

Since two-step high-temperature soaking at 350°C and 400°C generated 50% cyclohexane solubles, slow or programmed heating seems more efficient than fast heating for enhancing coal conversion. In practice, the autoclave was slowly heated with the autoclave heater. The effect of variable heating rates was investigated using the microreactor, which was controlled with the sand bath. For Run 12, the reactor was rapidly heated in one step from room temperature to 430°C in 0.5 h and held at 430°C for 2 h. For Run 13, the mixture was liquefied under the same conditions, but heated in two steps (350°C for 0.5 h and 400°C for 1 h) then held at 430°C for 1 h. The total heatup time from room temperature to 350°C, from 350°C to 400°C, and from 400°C to 430°C was 0.5 h. Therefore, the total residence time including heatup was 2.5 h. In Run 14, the mixture was slowly heated from 130°C to 430°C and held at 430°C for 1 h. Total duration of heatup and reaction times was maintained at 2.5 h. The lowest coal conversion resulted from conditions set forth in Run 12, which reacted the coal for the longest time but used one-step heating. In comparison, oil yields were enhanced ~10% using the programmed heating methods. These results infer that programmed heating and step-wise high-temperature soaking are important factors for increasing coal conversion. Song *et al.*²⁹ recently reported the effect of temperature-programmed liquefaction for low rank coals. In their work, Montana subbituminous coal produced 5-10% more THF solubles by slow heating than rapid heating. These results support the present work.

(2) Coal Fractions and Liquefaction

A wide molecular weight distribution is another feature of associated coal¹. Realizing that a higher gas yield should be obtained by pyrolysis from a fraction with low molecular weight, the dissolved coal may be fractionated into light and heavy fractions and the heavy fraction with high molecular weight selectively liquefied. In this study, pyridine solubles and insolubles were liquefied to compare conversions under similar conditions (Runs 15 and 16). Approximately the same oil yield was obtained from both fractions (Figure 7.4). Liquefaction of cyclohexane insolubles from Run 10 was also examined. Even from this heavy fraction, a 50% oil yield was obtained.

Dissolution and hydrogen consumption rates of PI and coal were found to be similar

Figure 7.3 Effect of step-wise soaking on extractability
(Conditions are listed in Table 7.2)

Figure 7.4 Coal fractions and their conversion
(Conditions are listed in Table 7.2)

using West Kentucky coal (80% carbon, daf)²⁷; however, a significant decrease in conversion was observed when Illinois No. 6 coal was extracted with pyridine²⁸. Warzinski and Holder²⁹ also observed this retrogressive behavior in conversion using pyridine as a characteristic of Illinois No. 6 coal. Although the effect of the soluble and insoluble components on coal conversion is difficult to conclude from these results, it appears that the reactivity of residues or high molecular weight components is better than previously thought when compared with that of the low molecular weight components.

(3) The Associated Molecular Nature and Liquefaction

It has been shown that a significant portion of coal can be dissolved by high-temperature soaking in coal liquids and, that programmed or step-wise heating is preferred to enhance oil yields. Highly dissolved coal has also produced greater liquefaction yields. Test results further suggested that coals, which have a wide molecular weight distribution, should be separated into light and heavy fractions after dissolution with only the heavy fraction liquefied in the next step. From these results, a procedure designed to increase the oil yield and decrease the gas yield is presented in a block diagram as *Figure 7.5*. As described, coal is soaked in a recycle oil at 350°C and 400°C. Gas and oil fractions are isolated using vacuum distillation, and the heavy fraction liquefied under low hydrogen pressure at relatively low operating temperatures.

This procedure was tested in the autoclave. The DECS-2 coal was soaked in the coal liquid under nitrogen at 350°C and 400°C, respectively. The oil fraction was extracted with cyclohexane and the cyclohexane insoluble portion liquefied under low hydrogen pressures (400 psi) at 430°C for 1 h (Run 19). For comparison, the coal was soaked in the coal liquid at 200°C for 1 h and the mixture liquefied under the same conditions for 2 h (Run 18). Gas yields from these tests were determined (*Figure 7.6*). Scheme 1 presents the mass balance for Run 19, which shows that the CyS (or oil) yield increased 30% and the gas yield decreased 15% when compared with yields from Run 18.

DECS-8 (subbituminous) coal was tested using the same procedure. As ionic forces are more significant in lower rank coals⁵, these forces must be weakened prior to high-temperature soaking. Although acid washing has been known to enhance the conversion of lower rank coal³⁰⁻³³, details of this treatment have not been clearly explained. Washing

Figure 7.5 Block diagram of the proposed coal liquefaction procedure

Figure 7.6 Coal conversion by the proposed procedure for a high-volatile bituminous coal and a subbituminous coal (Conditions are listed in Table 7.2, CyS yield from soaking is included for Run 21)

in 2N HCl was used to weaken the ionic forces in the coal before high-temperature soaking. The sample was soaked in the coal liquid at 350°C and 400°C for 1 h, respectively. Cyclohexane insolubles from the soaked coal were similarly liquefied at 430°C for 1 h (Run 21). Since the dried acid-washed coal was used, the dried DECS-8 coal was soaked at 200°C for 1 h then liquefied at 430°C for 2 h (Run 20). Results showed more than 30% increase in the oil yield and 20% decrease in the gas yield (*Figure 7.6* and *Scheme 7.1*).

In a controlled experiment made without using coal, about 2% of the gas was produced from the coal liquid under conditions existing at 430°C; therefore, total gas yields in the previous Runs were compensated by this amount. Since the change in the amount of gas produced from the coal liquid was greater than that of gas produced in the liquefaction step (CyI at 430°C), only semi-quantitative yields were obtained. *Table 7.3* shows the composition of the gases generated at 430°C. The residue (CyI) from high-temperature soaking produced a small amount of CO, CO₂, and methane with a large amount of olefin gases.

4 Summary

Suggested improvements in the coal liquefaction process were tested using the current two-stage process assuming an associated molecular structure for coal. Considering that significant portions of coal molecules are physically associated, it is suggested that physical dissolution should be carried out prior to liquefaction. Step-wise high-temperature soaking is a simple and effective method for coal dissolution in the absence of additional chemicals and hydrogen. A greater degree of dissolution requires less severe conditions during liquefaction. A wide molecular weight distribution of the associated coal is another important factor to be considered for coal conversion. Liquefaction of high-molecular weight fractions isolated after high-temperature soaking produced higher oil yields and lower gas yields. Tests made using autoclave reactors tend to verify the concept proposed in *Figure 7.5* and show it to be a superior coal conversion procedure. Use of this concept resulted in 30% more oil and 15-20% less gas, which projects a substantial reduction in the ultimate cost of coal liquefaction.

Run 19 (DECS-2 Coal) (wt%)

Run 21 (DECS-6 Coal) (wt%)

Scheme 7.1 Mass balance for Runs 19 and 21

Table 7.4 Gas Composition Obtained from Liquefaction^a

gas	(Vol %)			
	run 18	run 19 ^b	run 20 (CyI)	Run 21 ^b (CyI)
Hydrogen	61.53	68.05	62.61	70.76
CO	0.15	0.09	0.45	0.14
CO ₂	0.21	0.07	1.41	0.14
Methane	9.32	5.03	9.23	4.84
Ethane	4.19	2.55	4.15	2.44
Ethylene	0.04	0.05	0.04	0.05
Propane	2.21	1.44	2.15	1.38
Propylene	0.09	0.11	neg	0.10
n-Butane	0.51	0.40	0.48	0.36
i-Butane	0.16	0.12	0.16	0.11
Butene	0.02	0.04	neg	0.02

^aGas samples include gas produced from coal liquid,

Coal/coal liquid = 5 g/50 ml

^bGas obtained after the second step at 430°C

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Chapter 8 Some investigation of the proposed coal liquefaction process

1. Introduction

This project has been focussed on the effective preconversion and liquefaction of coal. One of the main goals was to reduce hydrogen consumption by decreasing the gas yield and increasing the oil yield based on the response expected from a new structural model of coal. This new model proposes that significant portions of coal molecules are physically associated¹ in contrast with the widely accepted conventional model that projects coal as three-dimensional cross-linked macromolecules. A physically associated model has gained credibility from recent tasks conducted by this investigator^{2,3}. Two factors were critically evaluated in previous chapters: (1) maximizing dissolution of associated coal and (2) defining the different reactivity of fractions with different molecular weight.

A summary of the results obtained from previous tasks showed:

- (1) High-temperature soaking at ~ 350°C in a coal liquid (recycle oil) was an effective method for dissolution not requiring additional chemicals and/or hydrogen.
- (2) Two-step soaking at 350°C and 400°C was more effective for maximum dissolution.
- (3) The addition of a relatively small amount of hydrogen peroxide during soaking slightly enhanced preconversion.
- (4) Separation of dissolved coal into light and heavy fractions, followed by liquefaction of the heavy fraction, was effective as a means to improve the product selectivity.
- (5) Vacuum distillation was projected for the simple separation method.
- (6) Cyclohexane extraction was used instead of vacuum distillation since cyclohexane solubles closely resemble the distillable oil fraction.
- (7) Tests of the suggested procedure inferred a 30% increase in the oil yield and a 15-20% decrease in the gas yield.

The proposed procedure was studied in detail in two types of reactors, autoclave (250 ml) and microreactor (27 ml). Low coal to liquid ratios were generally employed. It was

necessary to test under more realistic conditions to assess the proposed procedure. In this chapter, the process was tested at high coal to liquid ratios followed up with vacuum distillation of the liquefied products. Second stage liquefaction was also investigated. While radical initiators showed a positive effect on preconversion during high-temperature soaking, they showed a slightly negative effect at $> 430^{\circ}\text{C}$. Therefore, radical initiators were not used because of the apparent complexity of the reaction.

2. Experimental

The Illinois No. 6 coal and the coal liquid derived from the Illinois No. 6 coal from the Wilsonville pilot plant⁶ were used for this work. Reagents and solvents (HPLC-grade) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and Fisher Scientific (Pittsburgh, PA), and used without further purification. Catalysts used included MoS_2 ($< 1\ \mu$) from Aldrich Chemical Co. and AKZO AO-60 (-100 mech) obtained from Hydrocarbon Research Inc., Lawrenceville, NJ. The analysis of AKZO AO-60 is shown in *Table 8.1*.

The 250 ml autoclave was prepared for this work. Conditions and results for individual runs are summarized in *Tables 8.2* and *8.3*.

After reaction, the mixtures were filtered and Soxhlet-extracted with cyclohexane, toluene and tetrahydrofuran (THF) for 24 h, then dried under vacuum at 95°C overnight. The amounts of THF solubles (TS), toluene solubles (ToS) and cyclohexane solubles (CyS) were determined from the weights of the respective insolubles. For Runs 21-28, gas yields were included in the CyS yields. For gas analysis, samples were collected after cooling in the autoclave, then analyzed with gas chromatography by the University of Pittsburgh Applied Research Center (Pittsburgh, PA). Approximate gas yields were calculated assuming no change in the amount of nitrogen before and after the reactions. Elemental analyses of process products were conducted by Geochemical Testing (Somerset, PA).

3. Results and Discussion

(1) Test at higher coal to liquid ratio (C/L)

A lower weight ratio of coal to liquid ($\text{C/L} = 1/10$) was used in the previous work. Since a higher C/L value (typically $1/3$ to $1/2$) has been used in the conventional processes,

Table 8.1 Properties of AKZO AO-60 catalyst

Nominal Size	1/16"
Chemical Analysis	
Molybdenum (%)	12.25
Nickel (%)	2.6
Physical Properties	
Bulk density, Compacted (g/cc)	0.557
Particle Dens, 10 psi Hg (g/cc)	0.872
Skeletal Dens, 60,000 psi Hg (g/cc)	3.547
Surface Area, calc. (m ² /g)	286
(m ² /cc particle)	249
Pore Volume (cc/g)	0.874
(cc/particle)	0.762
Average Crush Strength (lb/mm)	2.67
Average Diameter (mm)	1.59
Pore Size Distribution (cc/g)	
Diameter > 30 .	0.873
Diameter > 100 .	0.54
Diameter > 250 .	0.24
Diameter > 500 .	0.12
Diameter > 1500 .	0.008
Diameter > 4000 .	0.008
Pore Diameter (.)	
At Median Pore Volume	125

75

@25°C

Three runs were conducted under the same conditions (Run 8(1) to 8(3))

^dThe reactor was cooled down after the first stage reaction

Table 8.2 (Continued)

run no.	condition																					
	coal		soaking-1				soaking-2				liquefaction-1				liquefaction-2				solvent		cat.	
	code	amount (g)	temp. (°C)	time (h)	gas	pres. ^a (psi)	temp. (°C)	time (h)	gas	pres. ^a (psi)	temp. (°C)	time (h)	gas	pres. ^a (psi)	temp. (°C)	time (h)	gas	pres. ^a (psi)	code	amount (ml)	code	amount (mg)
<u>Study of Second Stage Liquefaction (@250 ml Autoclave) (see Figure 8.4)</u>																						
21	DECS-2	10	200	1.0	H ₂	400	-	-	-	-	430	1.0	H ₂	400	410	1.0	H ₂	400	Liq. A	30	MoS ₂	200 ^b
22	"	"	350	"	"	"	-	-	-	-	"	"	"	"	"	"	"	"	"	"	"	100
23	"	"	"	"	"	800	-	-	-	-	"	"	"	800	"	"	"	800	"	"	"	200
24	"	"	"	"	"	400	-	-	-	-	"	"	"	400	420	"	"	400	"	"	"	"
25	"	"	"	"	"	800	-	-	-	-	"	"	"	800	"	"	"	800	"	"	"	"
26	"	"	"	"	"	1110	-	-	-	-	"	"	"	1110	"	"	"	1110	"	"	"	"
27	"	"	"	0.5	"	400	400	0.5	H ₂	400	"	"	"	400	"	"	"	400	"	"	"	"
28	"	"	"	1.0	"	"	-	-	-	-	"	"	"	"	"	"	"	"	"	"	AKZO	200 ^c
<u>Study of Second Stage Liquefaction (@250 ml Autoclave) (see Figure 8.5)</u>																						
29	DECS-2	30	350	1.0	N ₂	100	400	1.0	N ₂	100	-	-	-	-	-	-	-	-	Liq. A	90	-	-
30	DECS-2	10	-	-	-	-	-	-	-	-	430	"	H ₂ /N ₂	800/100	410	1.0	H ₂ /N ₂	800/100	"	30	MoS ₂	200
	/Cyl ^d																					
31	DECS-2	"	200	1.0	H ₂ /N ₂	800/100	-	-	-	-	"	2.0	"	"	"	"	"	"	"	"	"	"
32	"	"	350	"	"	"	400	1.0	H ₂ /N ₂	800/100	"	1.0	"	"	"	"	"	"	"	"	"	"
33	-	-	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"
34	DECS-2	10	"	"	"	"	"	"	"	"	"	"	"	"	400	"	"	"	"	"	"	"
35	"	"	"	"	"	"	"	"	"	"	"	"	"	"	410	"	"	"	"	"	AKZO	"
36	"	"	"	"	"	"	"	"	"	"	"	"	"	"	400	"	"	"	"	"	"	"
37	DECS-2	10	-	-	-	-	-	-	-	-	"	"	"	"	400	1.0	H ₂ /N ₂	800/100	"	"	"	"
	/Cyl ^d																					

^a@25°C^b-3,500 ppm as Mo in the mixture^c-600 ppm as Mo in the mixture^dCyl: Cyclohexane Insolubles after soaking at 350°C/400°C (1h/1h) (see Run 10 in Table 7.2)

Table 8.3 Results of Further Studies of the Proposed Procedure (see Table 8.2 for experimental conditions)

run no.	results																								
	heating		soaking-1		heating		soaking-2		heating		1st stage		heating		2nd stage		recovery				conversion				
	time (min)	temp. (°C)	pres. (psi)	time (min)	temp. (°C)	pres. (psi)	time (min)	temp. (°C)	pres. (psi)	time (min)	temp. (°C)	pres. (psi)	time (min)	temp. (°C)	pres. (psi)	ToS•Cyl	TS•Tol (g)	PS•TI	Res.	Gas	CyS	ToS	TS	PS (wt%)	
<u>Effect of High Coal/Solvent Ratio (@250 ml Autoclave)</u>																									
1	46	350	440	14	400	690	-	-	-	-	-	-	-	-	-	-	-	-	6.78	-	59.1	-	-	-	-
2	50	350	580	14	400	880	-	-	-	-	-	-	-	-	-	-	-	-	14.66	-	41.1	-	-	-	-
3	53	350	630	13	400	920	-	-	-	-	-	-	-	-	-	-	-	-	17.77	-	40.4	-	-	-	-
<u>Effect of High Coal/Solvent Ratio (@250 ml Autoclave) (see Figure 8.1)</u>																									
4	30	200	660	-	-	-	38	430	1380	-	-	-	-	-	-	1.66	1.21	-	5.87	-	41.7	56.4	67.2	-	-
5	45	350	920	-	-	-	18	430	1420	-	-	-	-	-	-	1.86	0.24	-	5.74	-	49.6	66.2	68.3	-	-
6	46	350	920	24	400	1060	9	430	1340	-	-	-	-	-	-	2.22	1.21	-	5.52	-	39.7	59.5	70.3	-	-
7	-	-	-	-	-	-	NA	430	NA	-	-	-	-	-	-	1.05	0.52	-	4.88	-	36.9	53.8	62.2	-	-
<u>Study of Vacuum Distillation (@250 ml Autoclave) (see Figure 8.2)</u>																									
8 ^c	50	350	490	13	400	850	70	430	1980	-	-	-	-	-	-	2.22	1.21	-	5.52	-	39.7	59.5	70.3	-	-
<u>Study of Second Stage Liquefaction (@250 ml Autoclave) (see Figure 8.3)</u>																									
9	33	200	620	-	-	-	38	430	1370	60	410	1460	1.28	0.65	-	5.06	-	-	5.06	-	26.2	43.2	48.1	-	-
10	31	200	660	-	-	-	37	430	1330	53	410	1760	1.27	0.71	-	3.58	-	-	3.58	-	45.2	62.1	71.6	-	-
11	46	350	840	13	400	1000	9	430	1160	59	410	1170	1.31	0.55	-	2.87	-	-	2.87	-	56.3	73.8	81.1	-	-
12	46	350	850	-	-	-	18	430	1240	56	410	1820	1.11	0.78	-	3.05	-	-	3.05	-	53.6	68.3	78.7	-	-
13	-	-	-	-	-	-	62	430	1380	55	410	1430	1.44	0.74	-	5.96	-	-	5.96	-	26.1	46.4	56.8	-	-

Table 8.3 (Continued)

run no.	results																					
	heating	soaking-1		heating	soaking-2		heating	1st stage		cooling	2nd stage		recovery				conversion					
	time	temp.	pres.	time	temp.	pres.	time	temp.	pres.	time	temp.	pres.	ToS•CyI	TS•ToI	PS•TI	Res.	Gas	CyS	ToS	TS	PS	
	(min)	(°C)	(psi)	(min)	(°C)	(psi)	(min)	(°C)	(psi)	(min)	(°C)	(psi)	(g)				(wt%)					
<u>Study of Second Stage Liquefaction (@250 ml Autoclave) (see Figure 8.4)</u>																						
21	31	200	650	-	-	-	41	430	1300	2	410	1250	1.22	0.18	-	3.65	-	52.2	68.4	70.7	-	
22	50	350	840	-	-	-	14	430	1230	6	410	1190	1.16	1.01	-	3.20	-	47.7	63.2	76.6	-	
23	48	350	1510	-	-	-	18	430	1800	2	410	1720	0.97	0.67	-	2.56	-	63.4	76.3	85.2	-	
24	46	350	850	-	-	-	13	430	1210	1	420	1210	1.34	0.81	-	3.20	-	48.0	65.9	76.7	-	
25	51	350	1500	-	-	-	16	430	1770	1	420	1720	1.09	0.66	-	2.60	-	61.2	75.8	84.6	-	
26	51	350	2040	-	-	-	18	430	2290	7	420	2240	0.67	0.71	-	2.35	-	69.7	78.6	88.1	-	
27	47	350	840	12	400	1010	8	430	1250	3	420	1240	1.17	0.73	-	3.66	-	45.2	60.8	70.5	-	
28	49	350	860	-	-	-	18	430	1170	1	420	1140	0.94	0.56	-	3.21	-	56.5	69.0	76.5	-	
<u>Study of Second Stage Liquefaction (@250 ml Autoclave) (see Figure 8.5)</u>																						
29	58	350	680	16	400	990	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
30	-	-	-	-	-	-	66	430	1950	3	410	1850	1.29	0.67	-	4.60	-	48.6	66.7	76.1	-	
31	32	200	1360	-	-	-	40	430	2050	2	410	1940	1.07	0.47	-	2.89	11.0	49.3	74.6	80.9	-	
32	48	350	1740	11	400	1860	6	430	1940	2	410	1870	0.89	0.61	-	2.52	6.0	59.8	77.6	85.7	-	
33	50	350	1570	13	400	1700	7	430	1820	6	410	1760	-	-	-	-	-	-	-	-	-	
34	52	350	1730	14	400	1870	5	430	1950	7	400	1860	0.86	0.42	-	2.60	1.0	66.6	79.1	84.6	-	
35	53	350	1690	14	400	1820	11	430	1870	12	410	1780	0.55	0.45	-	2.45	2.0	71.5	80.8	86.7	-	
36	51	350	1720	9	400	1830	12	430	1910	12	400	1790	0.69	0.34	-	2.45	-	73.0	82.2	86.7	-	
37	-	-	-	-	-	-	63	430	1900	12	400	1820	1.04	0.38	-	4.83	-	52.9	67.5	72.9	-	

the effect of the higher C/L ratio on high temperature soaking and liquefaction was examined. Step-wise high-temperature soaking experiment at 350°C and 400°C were carried out with C/L ratios of 1/3 and 1/2 (Runs 1, 2, and 3). For Run 3, 30 g coal was taken instead of 15 g with C/L ratio of 1/3, while keeping the other process parameters consistent with those used in experiments 1 and 2. Yields of CyS from these experiments ranged from 40-60 wt%. Reproducibility, however, was poor, since handling the very sticky material was difficult. It should be noted that for lower C/L ratio of 1/10, the yield of CyS averaged 50%. These results, therefore, showed that higher C/L ratios (1/3 to 1/2) did not appear to affect the yield of CyS during step-wise high-temperature soaking.

In the next set of experiment, Runs 4-6, the effect of soaking temperature on first stage liquefaction (which follows high temperature soaking) was investigated. A higher C/L ratio of 1/2 was used for these experiments. For Runs 4 and 5, one-step soaking experiments were carried out at 200°C and 350°C, respectively, followed by liquefaction at 430°C under the same condition. The total conversions (TS) were approximately the same for both Runs; however, as shown in *Figure 8.1*, the yield of CyS for Run 3 was higher than that for Run 4. Therefore, a higher soaking temperature of 350°C is more favorable to solubilize coal than is the lower temperature of 200°C. For Run 4, two-step high-temperature soaking was carried out at 350 and 400°C. This was followed by liquefaction at 430°C. The yield of CyS for Run 6 was less than that for Run 5 although TS yields were comparable. These results showed that two-step high-temperature soaking, when combined with liquefaction, was less effective than one-step soaking at 350°C followed by first stage liquefaction. It is important to note that the previous set of experiments involving only high-temperature soaking (i.e., in the absence of liquefaction) showed that two-step soaking was more favorable for coal dissolution than one-step high-temperature soaking. These experiments suggest that for two-step high-temperature soaking to be effective, it is essential to separate the low-molecular-weight fraction (formed due to coal dissolution) before liquefaction of high-molecular-weight material. Carrying out liquefaction without separating the low-molecular-weight material, formed more ToS under the above conditions.

For Run 7, CyI was separated after two-step high-temperature soaking, and was then liquefied under the same conditions. It may be noted that the process conditions used in

Figure 8.1 Effect of higher coal to liquid ratios on soaking and liquefaction (Conditions are listed in *Table 8.2*; Yields for Run 7 show for the original coal; Key, CyS: cyclohexane solubles, ToS: toluene solubles, TS: tetrahydrofuran solubles, TI: tetrahydrofuran insolubles)

Figure 8.2 The yields of coal liquefaction after vacuum distillation (Conditions are listed in *Table 8.2*; base represents the yield for Run 19 in *Chapter 7*, Key, CyS: cyclohexane solubles, ToS: toluene solubles, TS: tetrahydrofuran solubles, TI: tetrahydrofuran insolubles)

Run 7 are similar to those proposed in the previous chapter, but conducted at a higher C/L ratio of 1/3. *Figure 8.1* shows the total yield calculated for the original coal. The yields of CyS, ToS, and TS were much higher than those obtained from Run 4 which is regarded as the base case. Therefore, the effectiveness of the procedure proposed in the previous chapter has been confirmed, even for a higher C/L ratio of 1/3.

(2) Liquefaction of vacuum distilled residue

Vacuum distillation was proposed to isolate light fractions after coal dissolution by two-step high-temperature soaking of coal. In the previous chapter, cyclohexane extraction was used instead of vacuum distillation, because cyclohexane solubles approximately correspond to liquefied fractions distillable under vacuum. The aim of this task was to compare yields of products liquefied under more realistic conditions.

Two-step high-temperature soaked coal was distilled under vacuum. The remaining bottoms were liquefied at 430°C (Run 8). This Run was repeated three times which are denoted as 8(1), 8(2) and 8(3). In Run 8(1), the mixture after two-step high-temperature soaking was completely distilled up to 250°C under vacuum. Precise pressure was not measured. The fraction remaining at the bottom was hard solid material. THF was added to dissolve and remove it from the flask. The dissolved material was transferred to the autoclave and THF was evaporated. The coal liquid was added to the evaporated fraction, but the fraction was not dispersed in the coal liquid at 100°C. Although a significant portion of the fraction was in the form of a solid lump, the mixture was liquefied at 430°C. The TI yield was more than 100% due to the incorporation of the coal liquid into the product. Hence it was not possible to determine the yields of ToS and CyS fractions. In Run 8(2), precautions were taken to prevent the bottoms fraction from forming hard material. This was accomplished by adding coal liquid to the bottoms fraction while maintaining temperatures over 100°C. Temperature greater than 100°C was necessary to maintain the low viscosity of the bottoms fraction. This mixture was then transferred to the autoclave. The bottoms fraction was dispersed to some extent in the coal liquid, but significant lump material was still seen. Yields are presented in *Figure 8.2*. In Run 8(3), vacuum distillation was carried out until approximately half of the lighter fraction was distilled. The coal liquid was then added, followed by liquefaction. A dispersed mixture

was obtained with total conversion (TS) better than that for Run 8(2), but lower than that obtained from the CyI fraction (the base case, see *Figure 8.2*). It was noted that the CyI obtained in the base case was in the form of a fine powder which was efficiently dispersed in the coal liquid before liquefaction. Therefore, better dispersion is presumably required for better conversion. Since it was not possible to obtain good dispersion using glassware in this batch operation, it is recommended that the proposed procedure be tested in a continuous mode. This is needed to prevent formation of the solid mass of the bottoms product.

(3) Second stage liquefaction

Second stage liquefaction was next evaluated. After first stage liquefaction at 430°C, the reactor was cooled to room temperature then repressurized with hydrogen to the level desired for second stage liquefaction. The reactor was then heated to the desired second stage liquefaction temperature of 410°C. For Runs 9 and 10, the coal was soaked at 200°C prior to liquefaction, while for Runs 11 and 12, the coal was soaked at 350°C and 350/400°C (two-step soaking) prior to liquefaction. CyI was liquefied under the same conditions for comparison. Total conversion was calculated based on the original coal (Run 13). As shown in *Figure 8.3*, the effect of hydrogen pressure on second stage liquefaction was more pronounced for high-temperature soaking (350°C). Two-step soaking at high temperatures enhanced overall conversion but not to the extent expected.

In the preceding experiments, the reactor was cooled to room temperature after first stage liquefaction, then repressurized with hydrogen to the pressure desired for second stage liquefaction. The reactor was then reheated to the desired second stage liquefaction temperature. It was thought that the uniformity of the mixture could change after first stage liquefaction if the mixture was cooled. This would significantly affect conversion at the second stage. Therefore, for the following experiments, second stage liquefaction was carried out continuously *without cooling* after first stage liquefaction. Catalysts and hydrogen were added before soaking and coal was continuously liquefied.

A catalyst (200 mg), MoS₂ or AKZO AO-60, was used. The MoS₂ catalyst represented 3,500 ppm as the Mo base in the coal/coal liquid mixture while the AKZO

Figure 8.3 The product yield from second stage liquefaction (No.1) (Conditions are listed in Table 8.2; Yields for Run 13 show for the original coal; Key, CyS: cyclohexane solubles, ToS: toluene solubles, TS: tetrahydrofuran solubles, TI: tetrahydrofuran insolubles)

Figure 8.4 The product yield from second stage liquefaction (No.2) (Conditions are listed in Table 8.2, Key, CyS: cyclohexane solubles, ToS: toluene solubles, TS: tetrahydrofuran solubles, TI: tetrahydrofuran insolubles)

catalyst represented 600 ppm as the Mo base in the mixture. Coal to coal liquid ratio was 1/3 (wt/vol), and residence time was 1 h for each step. For Run 27, the coal was soaked at 350 and 400°C for 0.5 h, respectively; therefore, the residence time remained constant (3 h) among the Runs. Hydrogen pressure was changed between 400 psi and 1200 psi (@25°C) at 420°C in the second stage for Runs 24-26. As shown in *Figure 8.4*, incremental increases in the oil (CyS) and total (TS) yields paralleled this increase in hydrogen pressure. The same effects were obtained at 410°C in the second stage (Runs 22 and 23) as a response to pressure differences. No significant effects of temperature, however, were evident between 410 and 420°C under these conditions. Effects related to high-temperature soaking were compared under 400 psi of hydrogen pressure (Runs 21, 22, and 27). The TS yield held steady or increased, but the CyS yield decreased as a function of soaking temperature. Therefore, the effect of high-temperature soaking at 350 and 400°C was small or slightly negative under 400 psi of hydrogen. This hydrogen pressure is presumably too low for second stage liquefaction.

(4) Product selectivity

Based on the previous results, 800 psi of hydrogen pressure and 410°C of second stage temperature were used for the study of product selectivity (Runs 30-32). In Run 31, as shown in *Figure 8.5*, the DECS-2 coal was soaked at 200°C then liquefied at 430 and 410°C. The coal for Run 32 was soaked at 350 and 400° for 1 h each, then liquefied at 430 and 410°C for 1 h. (Total residence time was adjusted to 4 h for Runs 31-36). As displayed in *Figure 8.5*, the gas yield between these Runs decreased ~ 5% while the CyS and total (TS) yields increased ~ 10%. The difference, therefore, can be considered a function of the two-step high-temperature soaking. For Run 30, the mixture was extracted with cyclohexane after high-temperature soaking and the recovered cyclohexane insolubles (CyI) fraction liquefied under the same conditions. The gas yield (~ 1%) was very low. The total yield increased only 2%, but the increase in the CyS yield was remarkable compared to that noted from Run 32. The oil (CyS) yield increased > 20% over that from Run 31 (the base condition). For Run 34, the coal was liquefied in a continuous operation mode as with Run 32, but at 400°C in the second stage operation. Although CyI was not separated after high-temperature soaking, the gas yield was very low (< 2%), and the CyS

Figure 8.5 The product yield from second stage liquefaction (No.3) (Conditions are listed in Table 8.2; Yields for Runs 30 and 37 show for the original coals; Key, CyS: cyclohexane solubles, ToS: toluene solubles, TS: tetrahydrofuran solubles, TI: tetrahydrofuran insolubles)

yield was > 65%. From a comparison of the results from Runs 32 and 34, the optimum temperature of the second stage may be ~ 400°C. Therefore, milder conditions of the second stage are attainable by two-step high-temperature soaking and precipitate low gas and high oil yields. If soaked coal is separated into light and heavy fractions with only the heavy fraction liquefied, much better product selectivity is attainable.

(5) Effect of catalyst

Although this project does not encompass development of the optimum catalyst for coal conversion, the AKZO AO-60 catalyst was suggested by the DOE project manager. For Run 28 this catalyst was used under the same conditions used for Run 24. Hydrogen pressure effects were not seen under 400 psi for Run 24 (MoS_2), but were noted using the AKZO AO-60. As shown in Figure 8.4, the CyS yield increased ~ 10%. For Runs 35, 36, and 37, this catalyst was examined under 800 psi of hydrogen. The conditions for Run 125 were the same as those for Run 32. The gas yield decreased ~ 5% while the CyS yield increased ~ 5%. The temperature of the second stage was further lowered to 400°C. The catalyst effect was again significant at 400°C of the second stage (compare Runs 34 and 36)

while the gas yield was the same as that for Run 30. Therefore, the effect of this catalyst is significant, particularly under mild conditions.

(6) Characteristics of products

The coal liquid and the CyS (oil) fraction converted from the coal cannot be separated because of the similar physico-chemical nature of the fractions. To obtain the oil fraction, the original coal liquid must be replaced with the oil fraction produced from coal in a continuous operation mode. Assuming all coal liquids are recovered in the CyS fraction, the weight % of the CyS fractions for Runs 30-32 ranges from 11 to 14%. Therefore, the detailed characterization of the CyS (oil) fraction is not required. In this work, elements of fractions from Runs 30-32 were analyzed for information only.

Run 31 was soaked at 200°C, followed by liquefaction and is regarded as the base operation. Run 32 was soaked at 350 and 400°C, followed by liquefaction. Run 30 was also conducted following the proposed procedure. Elemental analyses are shown in *Table 8.3*. The products (CyS, ToS•CyI, and TS•ToI) from Run 30 are less aliphatic than those from Run 31, as seen from H/C ratios in these fractions. Heteroatom contents in the fractions from Run 30 are approximately the same as those in fractions from Run 31, or slightly lower. Therefore, specific properties of the products from the proposed procedure may be better than projected.

(7) Estimated mass balance

Figure 8.6 and *Table 8.4* compare mass balances among the base (conventional) and proposed procedures. These are calculated based on results from Runs 30 and 31. Gas yields are different from those obtained in the previous chapter due to the different conditions. The following assumptions were made for the calculation: (1) all of the cyclohexane soluble fractions are distillable under vacuum, corresponding to naphtha and gas oil fractions, (2) the weight ratio of naphtha to gas oil is 24 to 76, which is based on the average yield obtained from the Wilsonville Run 261 (Illinois No. 6 coal), (3) yields during high-temperature soaking are based on those from Run 19 in the previous chapter (see *Scheme 7.1*), (4) the dilution oil ratio in the recycle oil is 15 wt%, (5) the feed coal to recycle oil ratio is 1/3, and (6) the ratio of the recycle heavy oil in the proposed procedure

Table 8.4 Elemental analyses of products liquefied DECS-2 coal

Sample	Element (daf wt%)					H/C $\frac{\text{atom}}{\text{atom}}$	Ash (wt%)
	C	H	N	S	O (diff.)		
IL Coal Liq.	88.4	11.4	0.2	neg.	neg.	1.55	-
Run-31 ^a CyS ^b	87.2	9.1	0.3	0.1	3.4	1.25	-
Run-32 CyS	87.1	9.4	0.3	0.1	3.2	1.30	-
Run-30 CyS	87.8	9.7	0.3	neg.	2.1	1.33	-
Run-31 ToS•CyI	87.4	5.2	2.1	0.4	4.9	0.71	-
Run-32 ToS•CyI	81.6	5.4	2.2	0.5	0.3	0.79	-
Run-30 ToS•CyI	90.8	5.6	2.7	0.4	0.5	0.74	-
Run-31 TS•ToI	88.6	5.0	2.2	0.5	3.7	0.68	-
Run-32 TS•ToI	87.3	5.1	2.2	0.5	4.9	0.70	-
Run-30 TS•ToI	90.2	5.2	2.3	0.4	2.0	0.69	-
Run-31 TI	81.8	3.5	1.6	14.5	neg.	0.51	57.2
Run-32 TI	66.9	3.0	1.5	17.9	10.7	0.54	59.8
Run-30 TI	83.1	3.6	1.7	10.3	1.3	0.52	52.2
DECS-16 CyI	87.3	5.5	1.9	5.0	0.3	0.76	25.4

^aConditions:

Run-31: 200/430/410°C (1/2/1 h)

Run-32: 350/400/430/410°C (1/1/1/1 h)

Run-30: 350/400 → 430/410°C (1/1 → 1/1 h)

CyI

^bKey:

CyS; Cyclohexane solubles

ToS•CyI; Toluene soluble/cyclohexane insolubles

TS•ToI; Tetrahydrofuran soluble/toluene insolubles

TI; Tetrahydrofuran insolubles

CyI; Cyclohexane insolubles

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Assumption: Cyclohexane solubles correspond to cracked naphtha and gas oil fractions.
 The yield ratio of naphtha to gas oil is 24 to 76 (based on the Wilsonville Run 261).
 Yields from high-temperature soaking is based on those in *Scheme 7.1*.
 The dilution oil ratio is 15 % in the recycle oil.
 The coal to recycle oil ratio is 1 to 3.
 The ratio of the recycle heavy fraction in (b) is 50% in the bottoms.

Figure 8.6 Estimated mass balance for (a) base (based on Run 31) and (b) proposed procedures (based on Run 30) (unit: arbitrary, see Table 8.4)

Table 8.5 Estimated mass balance for (a) base (based on Run 31) and (b) proposed procedures (based on Run 30) (unit: arbitrary, see Figure 8.6)

Base Procedure (based on Run 31)

Stream	1	2	3	4	5	6	7
	coal	gas	naphtha	gas oil	residue	feed	soaked c.
Coal(daf)	84	0	0	0	0	84	84
Gas	0	10	0	0	0	0	0
Naphtha	0	0	10	0	0	0	0
Gas oil	0	0	0	31	0	45	45
Residue	0	0	0	0	33	192	192
Ash	16	0	0	0	16	79	79
Total	100	10	10	31	49	400	400

Stream	8	9	10	11
	product	bottoms	recycle oil	dilute oil
Coal(daf)	0	0	0	0
Gas	10	0	0	0
Naphtha	10	0	0	0
Gas oil	76	0	45	45
Residue	225	225	192	0
Ash	79	79	63	0
Total	400	304	300	45

Proposed Procedure (based on Run 30)

Stream	1	2	3	4	5	6	7
	coal	gas	naphtha	gas oil	residue	feed	soaked c.
Coal(daf)	84	0	0	0	0	84	0
Gas	0	1	0	0	0	0	0
Naphtha	0	0	14	0	0	0	11
Gas oil	0	0	0	45	0	45	79
Residue	0	0	0	0	23	181	220
Ash	16	0	0	0	16	90	90
Total	100	1	14	45	39	400	400

Stream	8	9	10	11	12
	product	bottoms	recycle oil	dilute oil	mixture
Coal(daf)	0	0	0	0	0
Gas	1	0	0	0	1
Naphtha	14	0	0	0	25
Gas oil	45	0	45	45	125
Residue	35	96	181	0	255
Ash	24	24	74	0	114
Total	120	120	300	45	520

is 50 wt% in the bottoms. The high oil yield and the low gas and bottoms yields are noted in the proposed procedure.

4. Summary

Nearly equal conversions were obtained even with high coal/liquid ratio (1/3-1/2) for two-step high-temperature soaking followed by first stage liquefaction. Expected conversions were not realized when the reaction products were vacuum distilled in place of cyclohexane extraction following high-temperature soaking. This is presumably due to inefficient redispersion of vacuum distilled bottoms in the coal liquid during liquefaction which is unavoidable in a batch process. It is suggested that the proposed procedure in the previous chapter be tested in a continuous mode without cooling the bottoms product. This would help prevent the formation of the highly viscous material.

Second stage liquefaction was also evaluated. It was shown that milder conditions of the second stage were attainable by two-step high-temperature soaking. When soaked coal was separated into light and heavy fractions with only the heavy fraction liquefied (the proposed process), much better product selectivity was attainable. This provided confirmation that the proposed procedure was truly effective for two stage liquefaction.

5. References

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Chapter 9 Conclusions

A comprehensive knowledge of basic coal structure must be acquired for the effective development of coal liquefaction. The cross-linked macromolecular model has been widely accepted by most researchers, and current coal liquefaction studies are proceeding under this assumption. Recent studies, however, show that significant portions (far more than generally believed) of coal molecules appear to be physically associated. This new structural model has gained credibility from our latest work; therefore, any development of coal liquefaction processes should consider this possibility. If physical association is dominant for cross-links, all properties and reactivities in the liquefaction process must be specific functions of intra- and intermolecular (secondary) interactions as well as molecular weight.

One of the main goals for competitive coal liquefaction is to decrease gas yields to reduce hydrogen consumption. Complexing this element in light gases decreases process efficiency and is less cost effective. To decrease the gas yield and increase the liquid yield, an effective preconversion process has been explored on the basis of the physically associated molecular nature of coal. Activities have been focused on two issues: (1) maximizing the dissolution of associated coal and (2) defining the different reactivity associated with a wide molecular weight distribution.

Two-step soaking at 350°C and 400°C in a recycle oil was found to be very effective for coal solubilization. No additional chemicals, catalysts, and/or hydrogen are required for this preconversion process. High-volatile bituminous coals pretreated before liquefaction showed 80-90% conversion with 50-55% of oil yields. New preconversion steps suggested are as follows: (1) dissolution of coal with two-step high-temperature soaking, (2) separation into oil and heavy fractions of dissolved coal with vacuum distillation, and (3) selective liquefaction of the separated heavy fractions under relatively mild conditions. Laboratory-scale tests of the proposed procedure using a small autoclave showed a 30 % increase in the oil yield and a 15-20% decrease in the gas yield. This batch operation projects a substantial reduction in the ultimate cost of coal liquefaction. It is strongly suggested that further testing be done in *a continuous mode*.

Several other subjects related to the development of effective preconversion methods

have been studied during the course of this project: (1) selective interactions between coal liquid and coal, (2) dissolution mechanism during high-temperature soaking, (3) the effect of radical initiators during coal conversion.

Interactions between coal and a coal liquid and interactions between coal residue and various standard compounds were investigated in chapter 3. These mixtures were soaked in cyclohexane under nitrogen at 25, 200 and 350°C for 2 h. Recoveries of the coal liquid and standard compounds were determined by solvent extraction. Nearly 100% of the neutral compounds were recovered after the treatment. On the other hand, weakly acidic aromatics containing a hydroxyl group and basic aromatics containing nitrogen were selectively adsorbed on coal at temperatures as low as 25°C. Complete recovery was extremely difficult even with good solvents such as tetrahydrofuran (THF) and pyridine. The adsorption of weakly acidic compounds was stronger than that of basic compounds and was further enhanced when soaked at higher temperatures. Similar results were also observed for selective interactions between the residue and a coal liquid.

Soaking high volatile bituminous coal in a coal liquid at 300 to 400°C causes very effective disintegration of the coal molecules. An understanding of this soaking mechanism is necessary for any further development of the process. The dissolution mechanism has been studied by two methods: (1) coal swelling and (2) extractability after soaking under various conditions.

Pyridine insolubles were obtained from extracts of Illinois No. 6 coal by soaking in toluene at 200 and 350°C. These pyridine insolubles were analyzed by resultant coal swelling to investigate the mechanism controlling the change in coal solubility at these temperatures (see chapter 4). Swelling ratios of residues derived from the raw coal and samples treated at both temperatures proved significantly larger than those obtained from their extracts. Reductions in coal extractability after soaking in organic solvents and in coal liquids at 200-400°C has previously been regarded as retrograde (retrogressive) reactions. The results of these tests, however, suggest that the ultimate extractability under high-temperature soaking is primarily controlled by associative equilibria.

Further justification of the above theory was sought using actual coal liquids. While it was somewhat difficult to differentiate between chemical and physical phenomena during high-temperature soaking, the following results support the associative equilibria theory:

1. Coal tar distillates provided the highest pyridine solubles (PS) yield and the lowest toluene solubles (ToS) yield.
2. High volatile bituminous coals produced the highest PS yields but the lowest ToS yields on conversion.
3. Whole coals showed a point of maximum PS yield versus both time and temperature which the pyridine insolubles (PI) did not exhibit.
4. Soaking the whole coals produced a higher conversion than soaking the PS extract and the PI residue separately.

The soaking mechanism is strongly related to the basic structure of coal. The mechanism essentially verified by this study is consistent with a physically associated molecular structure of coal rather than the conventional cross-linked, three-dimensional network model.

It appears that the effect of hydrogen peroxide on coal conversion is dependent upon temperature. The effect is positive at lower temperatures ($<430^{\circ}\text{C}$), but negative at higher temperatures ($>430^{\circ}\text{C}$). These effects are enhanced under hydrogen. The temperatures noted may also change according to the rank of the coal. As a detailed liquefaction mechanism has not been extrapolated, the reaction mechanism of the radical initiator H_2O_2 during coal conversion is unknown. It is suggested that the reaction mechanism involved in coal liquefaction is different below 430°C than above it. Below 430°C , physical dissolution is presumably dominant, where radical-induced reactions *positively* affect coal conversion. Above 430°C , chemical reactions dominate where radical-induced reactions are associated with complex chemical reactions and *negatively* affect coal conversion. The adverse effect from radical initiators was not as strong as expected, leading one to believe that other radical-induced competitive reactions may be involved. The key to efficient coal conversion is understanding the reaction mechanism of coal radicals.

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