

## LIQUEFACTION OF WYODAK COAL IN INDOLINE\*

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### INTRODUCTION

Several investigators have observed an enhancement of Wyodak coal liquefaction when 1,2,3,4-tetrahydroquinoline (THQ) is used as the solvent (1,2). A difficulty in evaluating the cause of this observed enhancement was that THQ possesses both hydrogen-donor and polar (basic nitrogen) characteristics. We examined the liquefaction behavior of Wyodak coal in a variety of heterocyclic solvents to learn the role of the nitrogen functionality in coal liquefaction (3). We observed high conversion for Wyodak coal in indole, a non-hydrogen-donor, nitrogen-heterocyclic solvent. We found that a large fraction of the Wyodak coal was held together by hydrogen bonds which were disrupted by interaction with the N-H functionality of indole to form associatively bound coal-indole complexes. These coal-indole complexes were THF soluble and accounted for the high conversion observed for Wyodak liquefaction in indole under mild liquefaction conditions. We feel this mechanism would also explain the role of the basic nitrogen functionality in other solvents with the N-H structure, such as THQ.

Having an understanding of the role of the basic nitrogen characteristic of the solvent, we began a study of a solvent possessing both basic-nitrogen and hydrogen-donor characteristics. We chose to investigate indoline (2,3-dihydroindole) because it has both solvent characteristics, has a single dehydrogenated species (indole), which along with the hydrogenated form is readily monitored, and knowledge of the liquefaction behavior of its dehydrogenated form had already been obtained. We have now conducted experiments in indoline to learn if there is a possible further enhancement of the liquefaction reaction in this type of solvent due to an actual complexing of the hydrogen donor molecule to the coal molecule. We have determined that liquefaction in indoline, which can first complex to the coal and then donate its hydrogen, is much more effective than liquefaction in either a pure hydrogen donor (tetralin) or a combination of hydrogen donor + nitrogen heterocyclic (tetralin + indole).

### EXPERIMENTAL

The data reported below were obtained from batch microreactor runs using Wyodak coal (South Pit Mine) and selected model solvents. The 25 cm microreactors were loaded with an 8 gram sample of a 2/1 solvent to coal mixture. They were then pressurized to 1000 psig with nitrogen. The microreactors were heated (13 minutes to reach reaction temperature) in a fluidized sand bath and held at temperature for the specified time. The microreactors were then cooled (30 seconds for a 200°C quench) in a second fluidized sand bath held at room temperature. Conversion to THF soluble products was obtained by subsampling the whole liquid product from the microreactor, sonicating the sample in THF and then pressure filtering through a 0.2 micron Millipore filter. The filter was then analyzed by gel permeation high performance liquid

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chromatography (HPLC) to observe differences in product distribution (4). This technique separates the filtrate into high, intermediate and low molecular weight fractions. These fractions are comparable to the classical preasphaltene (mw  $\sim$  1000), asphaltene (mw  $\sim$  450) and oil (mw  $\sim$  250) fractions obtained by Soxhlet analysis.

## RESULTS AND DISCUSSION

We began our study of the effects of indoline on Wyodak coal conversion by liquefying Wyodak coal at various times and temperatures in indoline, indole and tetralin and measuring the conversion to THF soluble products. Figures 1 and 2 show these results.

We can see from Figure 1 that at 375°C the conversion of Wyodak coal to THF solubles is very high for liquefaction in indoline, even at short reaction times. Comparison of the conversions in tetralin and indoline at 20 minutes shows that in indoline the conversion is more than double that obtained with tetralin (82% to 40%). The conversion in both of these solvents continues to increase with time, suggesting continued reaction between the coal and these hydrogen donors. We also observe in Figure 1 that as a function of time at 375°C, conversion of Wyodak coal in indole levels off. This is attributed to the fact that at a fixed temperature a certain level of coal hydrogen bond disruption will take place after the time necessary for complete interaction of the solvent with the coal structure. Beyond this time, no additional indole-coal reactions can occur in this system.

Figure 2 likewise shows that for all temperatures and a 20-minute reaction time, conversion in indoline is greater than conversion in tetralin. However, we do observe that at high temperatures the two hydrogen donor solvents appear to be approaching the same conversion level. This suggests that at high temperature the hydrogen transfer reactions begin to dominate the reaction mechanism and therefore indoline and tetralin begin to behave similarly.

Further evidence that at high temperatures a hydrogen transfer mechanism begins to dominate the liquefaction chemistry can be seen in Figure 3. In Figure 3, we have plotted the ratio of the indole to indoline concentrations measured in the product material formed in an experiment with Wyodak coal and indoline. These concentrations were measured by HPLC analysis. This ratio is a measure of the degree of indoline dehydrogenation. We can see from Figure 3 that between 375°C and 400°C, a significant increase in the hydrogen transfer rate occurs.

The data in both Figure 1 and Figure 2 confirm that when indoline is used as the solvent for Wyodak liquefaction, there is enhancement of the conversion above that obtained in a good hydrogen donor. We believe that this is due to the interaction of the N-H functionality of indoline with the coal structure. This results in coal-indoline complexes, similar to those observed in our study of Wyodak liquefaction in indole. Figure 4a is the HPLC spectrum that we obtained for products of Wyodak liquefaction in indole. Here we see a large peak in the molecular weight distribution due to the indole-coal complex. Figure 4b is the HPLC spectrum for products obtained from liquefaction of Wyodak coal with indoline as the solvent. We see a peak for indoline and indole (dehydrogenated indoline) and a peak for the coal-indole complex and the coal-indoline complex. The peak for the coal-indoline complex never becomes as large as the complex peak in Figure 4a because the complex undergoes hydrogen transfer resulting in an indole molecule and a non-associative coal molecule. Thus in the indoline system, the complex is an intermediate species as compared to the indole system where the complex is a stable product.

The mechanism discussed above is illustrated in Figure 5. In this proposed liquefaction mechanism, the structure for the hydrogen bonded

coal fragment has not been determined in our work but is merely intended to be representative of possible structures. The heat is apparently needed to fluidize the coal sufficiently for solvent access. This fluidization is actually a weakening of the coal-coal hydrogen bonds.

We have proposed that the hydrogen transfer occurs from the indoline molecule involved in the associatively bound complex rather than from neighboring molecules. Thus, the hydrogen transfer and the disruption of the coal hydrogen-bonded structure do not occur independently. To test our hypothesis, we have performed experiments with Wyodak coal in a mixture of indole and tetralin to simulate the total solvent characteristics of indoline, but with separation of these characteristics into individual molecules. Figure 6 is a comparison of the THF conversions for Wyodak coal in these solvents. The conversion using indole + tetralin is much lower than the conversion in indoline (45% vs 82%). This is consistent with our hypothesis, i.e., that liquefaction of Wyodak coal in indoline, where the solvent first complexes to coal molecule and then transfers its hydrogen, is much more effective than hydrogen transfer from a non-interactive solvent.

The results in Figure 6 were somewhat surprising in that we expected the conversion level in the mixture of indole plus tetralin to be at least as high as the conversion found in indole. In order for the conversion in the mixed solvent system to be lower than the indole conversion, we must have interaction between the solvents or one solvent must interface with the mechanism of the other solvent. If we had had interaction between the tetralin and the indole, we would observe a difference in conversion if we increased the overall solvent to coal ratio. We doubled the solvent to coal ratio, but only increased the conversion by a few percent. Tetralin must interfere with the indole liquefaction mechanism to result in the observed conversion level.

We collected the THF solubles from a liquefaction run of Wyodak coal and indole (mostly coal-indole complex). We then reacted this material with tetralin at 375°C for 20 minutes to determine if there was any degradation of the complex and/or production of insoluble material (insols). There was no production of insols or change in the complex concentration. As far as we were able to determine, the tetralin did nothing to the soluble products from the liquefaction of Wyodak in indole. Therefore, tetralin is unable to interfere in the indole liquefaction mechanism after the coal and indole have reacted.

Although the measured conversion for Wyodak coal in tetralin is only 40% at 375°C, the tetralin may interact with a significantly larger fraction of the coal; just not producing THF soluble products. In addition, the coal itself could undergo condensation reactions at sites which are otherwise stabilized through associative bonding with indole, i.e., two hydrogen bonded hydroxyls may eliminate H<sub>2</sub>O and form an ether linkage. To determine if either of these situations might be occurring, we reacted the THF insols from the liquefaction of Wyodak in tetralin with indole at 375°C for 20 minutes. If these insols were unaltered coal, then we might expect ~33% conversion of the insols during reaction with indole to bring the overall coal conversion to 60%. However, we measured ~10% conversion. This indicates that either condensation reactions are occurring in the coal or that a step in the tetralin liquefaction mechanism results in retrogressive reactions at 375°C. The former seems more probable and would have occurred in our mixed solvent experiment if tetralin blocked indole access to a portion of the coal hydrogen-bonding sites. Additional experiments are being performed to determine if condensation reactions at coal hydrogen bonding sites are the cause of the low conversion observed during liquefaction of Wyodak in indole + tetralin.

## CONCLUSIONS

We have found that indoline is an excellent liquefaction solvent for Wyodak coal, liquefying over 80% of the coal in 20 minutes at 375°C. The indoline system is a good solvent medium for kinetic studies of hydrogen transfer because it has only one, easily monitored, dehydrogenated form. Liquefaction with indoline is much more effective than liquefaction in either a pure hydrogen donor (tetralin) or a combination of hydrogen donor plus nitrogen heterocyclic (tetralin plus indole).

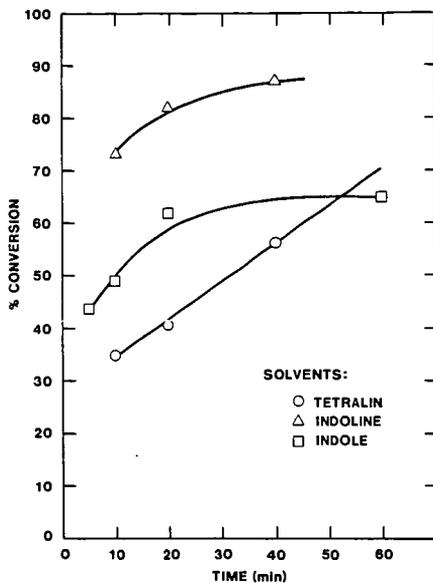
We believe that the effectiveness of indoline is the result of a liquefaction mechanism in which the indoline first functions as a basic nitrogen solvent to disrupt the coal-coal hydrogen bonds and form coal-indoline complexes. The indoline then functions as a hydrogen donor solvent and transfers its hydrogen within the complex to the coal molecule. This mechanism would apply to other similar solvents such as THQ and is much more effective than hydrogen transfer from non-interactive solvents.

We have also determined that if the coal structure is not first interacted with an associative solvent (N-H functionality) to disrupt coal-coal hydrogen bonds, condensation reactions or other retrogressive reactions which make the coal less reactive may occur.

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**FIGURE 1. WYODAK LIQUEFACTION AT 375 C AS A FUNCTION OF TIME**



**FIGURE 2. WYODAK LIQUEFACTION AS A FUNCTION OF TEMPERATURE**

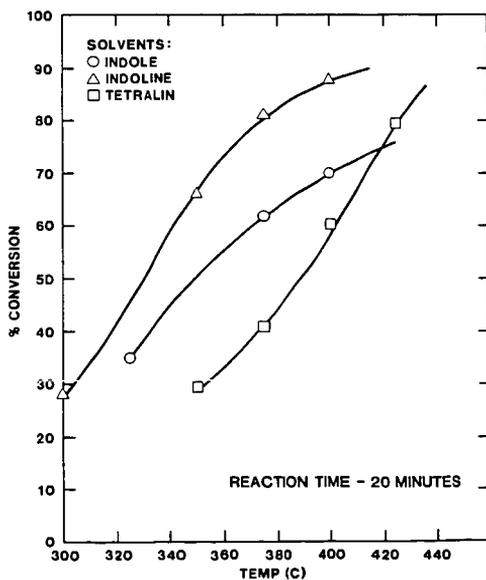


FIGURE 3. PLOT OF INDOLE/INDOLINE RATIO vs TIME FOR WYODAK LIQUEFACTION AT 375 C

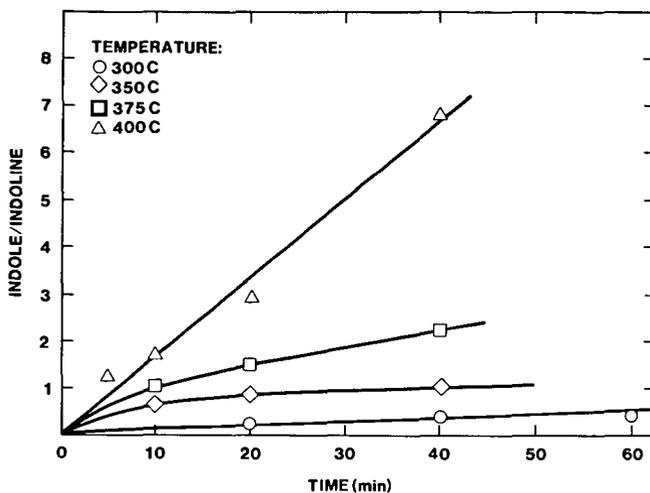
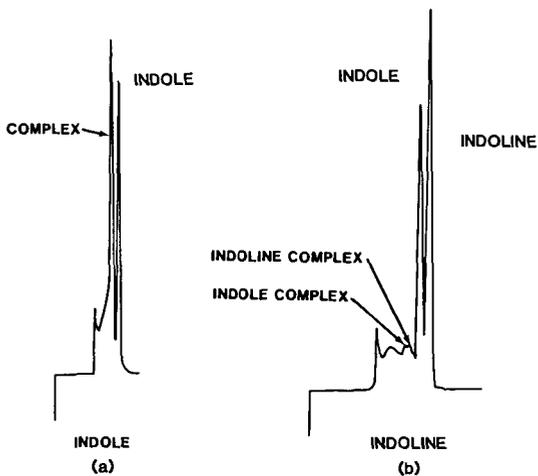


FIGURE 4. HPLC SPECTRA OF WYODAK LIQUEFACTION PRODUCTS



LIQUEFACTION CONDITION: 375C, 20min

FIGURE 5. PROPOSED MODEL FOR THE INDOLINE LIQUEFACTION MECHANISM OF WYODAK COAL

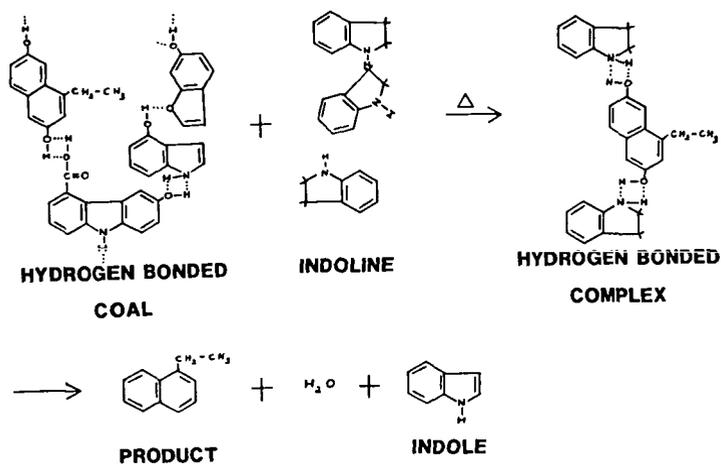
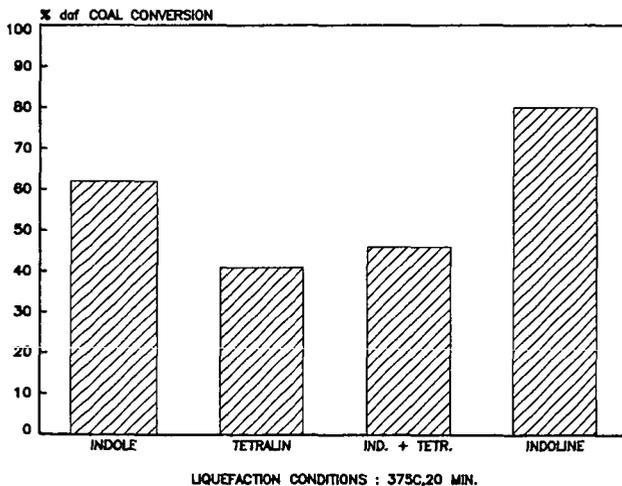


FIGURE 6. THF CONVERSIONS FOR WYODAK COAL IN MODEL SOLVENTS



## THE FATE OF NITROGENOUS MODEL PROCESS SOLVENTS IN COAL LIQUEFACTION

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### INTRODUCTION

The nature and role of the liquefaction solvent are the keys to understanding liquefaction chemistry. Solvent apparently serves many purposes during the dissolution of coal but two of the most significant roles have been suggested to be as a hydrogen transfer mechanism and as a catalyst (1). In this regard recent work with 1,2,3,4-tetrahydroquinoline (THQ) as a model liquefaction solvent has demonstrated its ability to convert a variety of coals, both bituminous and subbituminous, to pyridine and toluene solubles in a rapid and nearly complete fashion (2-4). While high conversions to soluble products have been realized, the ultimate goal of conversion to distillate materials in high yields remains to be attained. It is now apparent that during liquefaction, significant portions of THQ are adducted to the dissolving coal to give a non-distillable yet toluene/pyridine soluble material. The purpose of the present work is to quantify this adduction with respect to product distribution and to discern the possible modes of solvent nitrogen loss either through adduction into the coal-derived product or through thermal cracking of the solvent. Products from an in-house tubing bomb reactor and from Kerr McGee Corp. are examined. In addition a series of THQ-related model solvents will be examined in order to ascertain the effect of slight changes in solvent basicity, nitrogen atom substituent and nitrogen atom ring position upon the extent of coal conversion to soluble and distillable material.

### EXPERIMENTAL

Liquefaction experiments on a Wyodak #3 western subbituminous coal were performed both in-house and at Kerr McGee Corp. (Crescent, OK). The in-house experiments involved preparation of the feed coal by drying at 293°K, 12 hours under a stream of dry nitrogen and then grinding to less than 60 mesh particle size. The Kerr McGee sample was prepared in a different manner which involved drying under vacuum at room temperature for 24 hours followed by grinding to 60 mesh particle size. The proximate and ultimate analysis (MF basis) for both samples are presented in Table I.

TABLE I

	Proximate Analyses		Ultimate Analyses		
	% Wt. <sup>a</sup>	% Wt. <sup>b</sup>	% Wt. <sup>a</sup>	% Wt. <sup>b</sup>	
			Carbon	56.1	57.2
			Hydrogen	3.2	4.6
			Nitrogen	0.8	0.8
			Oxygen	11.8	15.6
			Sulfur	7.6	3.02
Ash	17.5	18.7			
Volatiles	58.4	47.9			
Fixed Carbon	24.1	33.4			

<sup>a</sup>In-house Sample (19.2% H<sub>2</sub>O); <sup>b</sup>Kerr McGee Sample (24.1% H<sub>2</sub>O)

Liquefaction of the feed coal proceeded under the general conditions of 2:1 solvent:coal, 691°K reaction temperature, 30 minutes reaction time and 7.5 MPa hydrogen atmosphere (cold charge). Experiments performed in-house were conducted in 40 mL microautoclave vessels with 4 grams of coal. The Kerr McGee experiment involved a 1 liter autoclave vessel and 100 grams of coal. Sample workup for the in-house samples involved extraction with toluene and pyridine to obtain a conversion based on solubility and through distillation to a 1050°F endpoint (300°C, 1.3 Pa). The Kerr McGee product work-up involved distillation of the products to a 850°F endpoint at atmospheric pressure (400°F, 13.3 Pa). Nitrogen determinations of these products were obtained from Galbraith Laboratories (Knoxville, TN).

## RESULTS AND DISCUSSION

The model compounds used as process solvents in the liquefaction runs were 1-methylnaphthalene (MN), tetralin (TET), 1,2,3,4-THQ, 2,3-cyclohexenopyridine (CHP), 1,2,3,4-tetrahydroisoquinoline (THIQ), 1-methyl-2,3,4-trihydroquinoline (MTHQ) and quinoline (QU). We determined (1) the extent of conversion to both solvent soluble and distillate material and (2) the level of solvent incorporation into the residuum in terms of solvent basicity, position and presence of donatable hydrogen, substituent interference (MTHQ) and presence of nitrogen in the ring (THQ vs. CHP).

A comparison of the toluene and pyridine conversions obtained for these runs is described in Figure 1. With respect to these conversions, the solubilities reported were obtained in the presence of the process solvent. Therefore, co-solvency effects may be involved. For example, as expected percent pyridine conversions are consistently higher than percent toluene conversions regardless of the model process solvent. For MN, TET and QU, the differences average more than 25%; whereas, with THQ, THIQ, MTHQ and CHP the differences are 6% or less. Co-solvency rather than depolymerization to smaller fragments may account for the relatively high toluene solubilities observed with most of the nitrogen-containing solvents. From these data conversion to pyridine solubles appears to be solely dependent upon the presence of readily donatable hydrogen as evidenced by comparing MN/TET (69.9% vs 96.8%) and QU/THQ (76.8% vs 95.5%). A dependence of toluene soluble conversion on the presence of nitrogen in the ring system is not very striking, MN/QU (51.1% vs 54.2%); whereas, if the nitrogen is accompanied by donatable hydrogen the dependence is great, TET/QU (71.4% vs 89.5%). Dependence of conversion to toluene or pyridine soluble products on the position of nitrogen in the ring, the basicity of the model solvent and the positional relationship of nitrogen to the donatable hydrogen in the ring structure was not found.

The product mass balances for the samples obtained through distillation are shown in Figure 2. Inspection of the figure demonstrates several points. First, the only run to demonstrate a net increase in distillate recovery was that of MN. In the TET case there was a net conversion of the insoluble MF coal. However, a recovery of volatile products demonstrated a conversion to light ends and gases rather than to slightly less volatile material. In all of the nitrogen heterocyclic cases, a net gain in residuum mass was found. In general, the distillate recoveries were greater than that in the tetralin case but they were still less than that predicted by the starting solvent mass. The reduction in distillate recovery correlates with incorporation of solvent into the residuum or a cracking of distillate to light ends of approximately 10-15% of the starting solvent mass. The exception found here was THIQ where even a larger amount of process solvent was lost to the light ends material.

The nitrogen content distributions for the products recovered in these runs are displayed in Figure 3. The nitrogen analyses were obtained from Galbraith Laboratories with use of the Kjeldahl method. In the cases of MN and tetralin, the sole source of nitrogen within the run was the coal itself. In both these products a shift of nitrogen content to the distillate mass was found. Under these conditions, approximately 20% of the nitrogen content in the coal is dynamic. When nitrogen heterocyclic compounds were employed a considerable amount of the nitrogen base was found to have adducted into the residuum or lost to the light ends. The percent nitrogen increase in the residuum reflects an incorporation of between 8 and 15% of the starting solvent mass. Steric interference was not found for MTHQ since the expected reduction in adduction did not occur. Distillate analysis via GC-FTIR demonstrated that a rapid dissociation of MTHQ to THQ had occurred resulting in a similar quantity of adduction.

To further delineate and quantify the coal-solvent interaction, nitrogen and mass balance data have been obtained on the products produced from a liquefaction run performed by Kerr McGee. The results of this investigation are presented in Table II. Upon inspection of these data, it is apparent that the nitrogen content of the initial solvent (THQ) is highly mobile. Approximately 8.0% of the original THQ material is lost to light ends, gas product and residuum material. The major portion of this loss was to the residuum (67.5% of N loss from solvent). This adduction was further found to be restricted to the solvent (THF) soluble material. The remainder of the loss was to ammonia and small chain alkyl amines located in the gas product and light end. See Figure 4.

It is apparent from these data that adduction of process solvent to non-distillate and high boiling distillate materials is significant. Though some breakdown of process solvent was found, its contribution to the loss of the dynamic nitrogen component is minimal in comparison to the problem of adduction.

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TABLE II  
MASS BALANCE AND NITROGEN CONTENT DATA

<u>Starting Material</u>			
Mass		Total Wt. Nitrogen	21.66 g
THQ	200 g	% contribution	
Tetralin	--	by solvent	97.14%
Solvent	200 g		(21.06 g)
Coal	100 g	by coal	2.86%
MF Coal	75.9 g		(0.62 g)
<u>Recovered Products</u>			
Distillate Wt.	203.19 g	Residuum Wt.	55.23 g
%N	9.55%	%N	3.18%
Wt. N	19.40 g	Wt. N	1.74 g
% Total N	89.48%	% Total N	8.03%
Retained		Retained	
Net Gain or Loss		Net Gain or Loss	
From solvent		from Moisture free	
(initial weight)		Coal (initial weight)	
Mass	+3.19 g	Mass	-20.67 g
	(1.6%)		(-27.2%)
Nitrogen	-1.66 g	Nitrogen	+1.12 g
	(-7.88%)		(181%)
<u>Product Distributions</u>			
% Total Mass	86.14%	% Total Mass as	13.86%
Recovered as		Light Ends and Gas	
Distillate and		Product (by	
Residuum		difference)	
% Total Nitrogen	97.51%	% Total Nitrogen	2.49%
Retained in Residuum		in Gas Product	
and Distillate		and Light Ends	
		(by difference)	

# CONVERSION OF WYODAK #3 TO SOLUBLE PRODUCTS

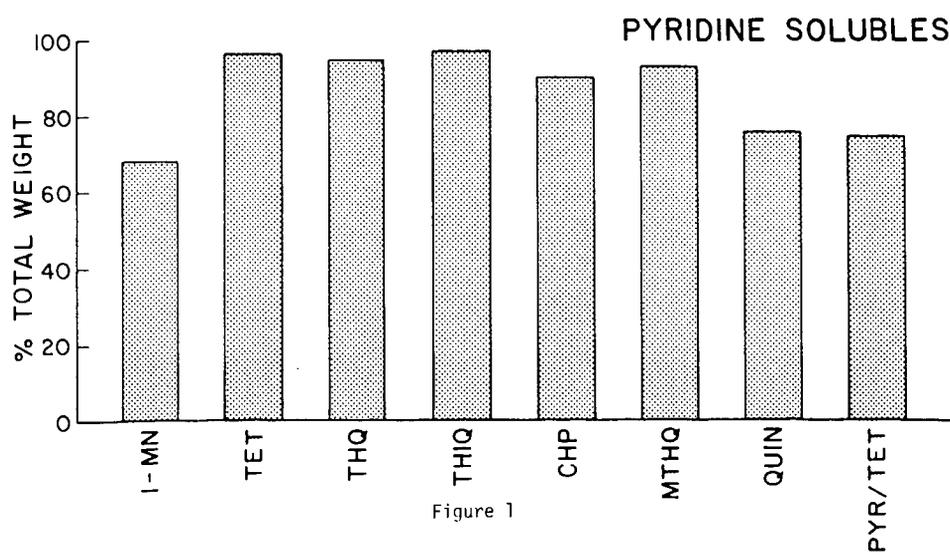
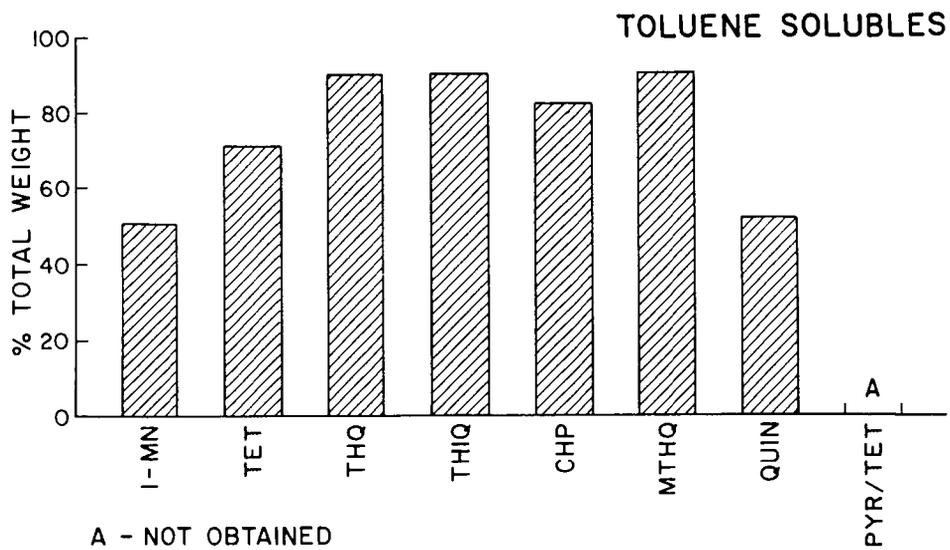


Figure 1

### PRODUCT DISTRIBUTIONS

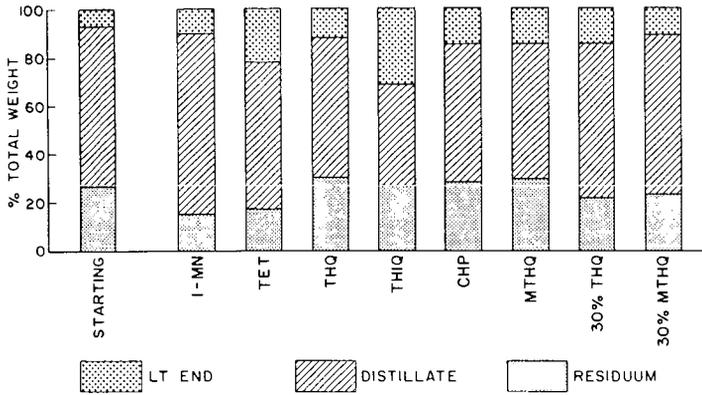


Figure 2

### PRODUCT DISTRIBUTIONS

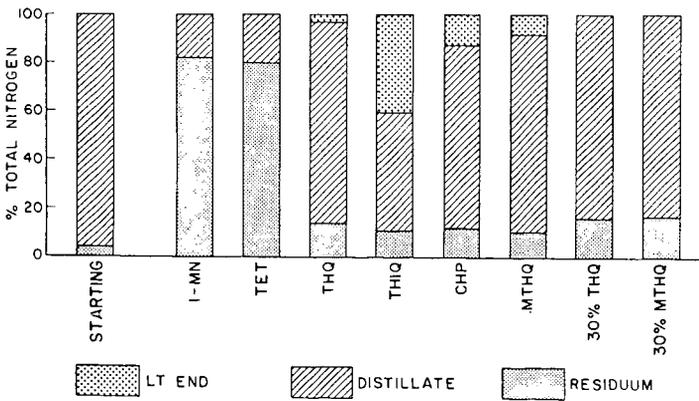


Figure 3

# KERR MCGEE RUN P-24 MASS AND NITROGEN DISTRIBUTIONS

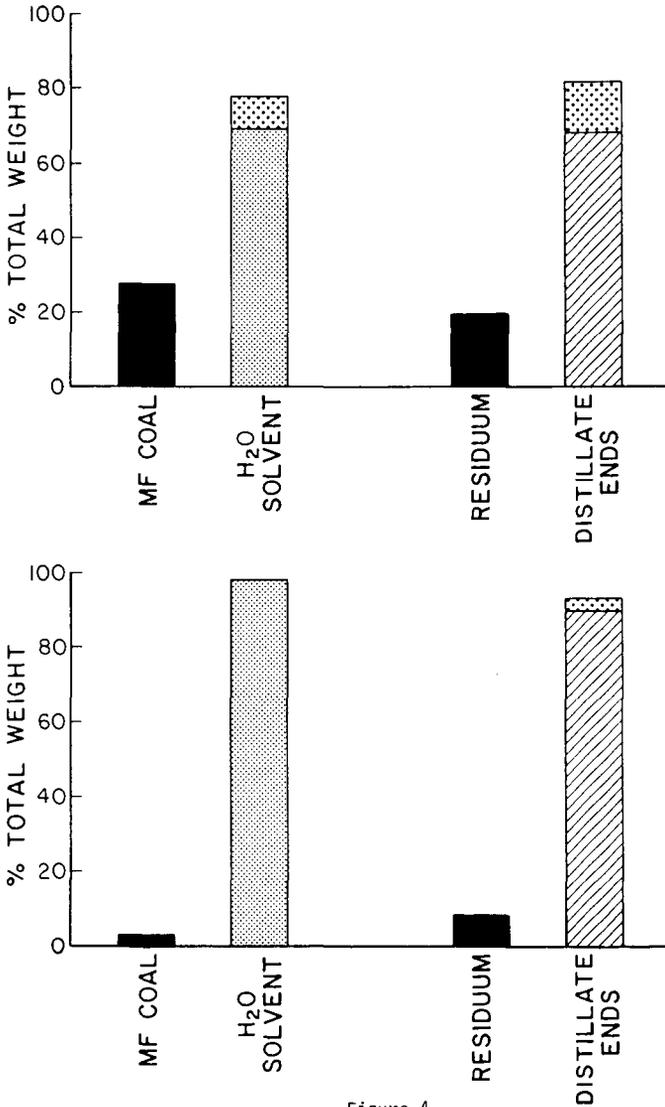


Figure 4

## EFFECTS OF START-UP SOLVENT ON COMPOSITION OF RECYCLE LIQUEFACTION PRODUCT SLURRY FROM LOW-RANK COALS

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### Introduction

As part of the on-going research in the liquefaction of low-rank coal, the University of North Dakota Energy Research Center (UNDERC) carried out two bottoms recycle runs. The purpose of these 40 pass runs was to investigate the effect of two different start-up solvents on the composition of the product from pass to pass, especially the bottoms portion used as recycle solvent, and the final lined-out composition of the product.

Runs 101 and 103 were carried out in the bottoms recycle mode in the Continuous Processing Unit (CPU) (1). Zap, North Dakota lignite from the Indian Head mine was introduced at 5 lbs/hr as a 30% slurry (wt % as-received coal) in recycle feed with H<sub>2</sub>S addition in both runs. The nominal temperature was 440°C and the nominal pressure was 4000 psig H<sub>2</sub>/CO (95/5). The startup solvent for Run 101 was a typical anthracene oil, A04, purchased from Crowley Tar Products, NY, previously described (2,3). Run 103 was started up with a Process Development Unit (PDU) recycle solvent obtained from the University of North Dakota Chemical Engineering Department's Project Lignite (4). The PDU solvent was derived from Zap, North Dakota Indian Head lignite. It has been characterized in detail (3). A short summary of the relevant properties of the two startup solvents appears in Table I. Both solvents provided adequate operability of the CPU and were greater than 95% distillable. These two startup solvents were chosen because they differ in several important ways. The PDU solvent contained about seven times more total alkanes and ten times more n-alkanes than the A04 solvent (Table I). The PDU solvent also contained a higher concentration of methylated and other alkylated aromatic hydrocarbons than A04. For example, 2- and 3-methylphenanthrene are present in the PDU solvent at 4.6 and 3.0 times their concentrations in A04. The PDU solvent also contains hydroaromatics (such as dihydro-, tetrahydro- and octahydro-phenanthrene, dihydropyrene, and tetrahydrofluoranthene) and phenols (6.2%). A04, deficient in both hydroaromatics and phenols, is composed mainly of unsubstituted aromatic hydrocarbons including larger amounts of aromatic compounds with more than three fused rings (i.e., chrysene and benz(a)anthracene) than the PDU solvent. These differences in composition are expected to affect the solvating power of the solvent toward coal and coal-derived products. The difference in reactive nature of the solvents at high temperature and pressure is expected to lead to different initial products.

The liquefaction products were examined from pass to pass in order to follow the compositional changes as the reaction proceeded toward steady-state composition (lineout) and to determine whether the products were chemically the same for both runs after 40 reactor passes.

Table I. Properties of Startup Solvents A04 and UND PDU Solvent Used In CPU Runs 101 and 103

	A04	PDU
<u>Elemental Analysis:</u>		
% C	90.33	82.36
H	6.54	7.89
N	0.83	0.21
S	0.57	1.19
O (by difference)	1.73	2.49
Ash, %	0.03	1.43
Water, %	0.20	4.43
<u>Selected Organic Component Analysis, wt %:</u>		
n-alkanes	0.6	6.8
total alkanes	2.2	13.9
<u>Selected Hydrocarbons and Ethers:</u>		
naphthalene	0.75	0
2-methylnaphthalene	1.44	0.14
acenaphthene	9.54	0.08
phenanthrene	16.6	6.99
dibenzofuran	6.67	0.39
3-methylphenanthrene	0.66	3.06
2-methylphenanthrene	0.84	2.55
fluoranthene	0.52	0.82
pyrene	6.87	0.46
fluorene	6.67	0.36
benzo(a)anthracene	0.26	0.06
chrysene	0.27	0.16
9,10-dihydrophenanthrene	0	0.23
octahydrophenanthrene	0	0.02
1,2,3,4-tetrahydrophenanthrene	0	0.18
4,5-dihdropyrene	0	0.44
1,2,3,4-tetrahydrofluoranthene	0.01	0.06
polars (phenols, base and polar aromatics)	18.4	21.4
phenols	0	6.2

Our previous efforts were concentrated on analysis of distillable portions of the products from earlier runs which averaged approximately 13 passes (5). When we investigated these runs we noticed that some irreversible changes caused by heating had occurred to the vacuum bottoms during the ASTM D-1160 distillation. We carried out several preliminary separations using Soxhlet extraction, sonication and sonication with heat, none of which proved satisfactory for this study. A method was then selected for separation of the slurry that excluded all severe handling of the product to avoid changes in the heavy product composition during separation.

The preliminary characterization of the separated heavy products and their composition as compared with the composition of the oils are the focus of this report. Changes in the startup solvent as it reacts with coal and is diluted by coal-derived products are discussed with emphasis on the heavy components. Differences between the two runs started up with different solvents are described.

### Experimental

The method chosen to separate the product slurry is based on solubilities at room temperature (Figure 1). This separation yielded a pentane soluble, volatile oil fraction (oil), a pentane insoluble, methylene chloride soluble heavy fraction (soluble heavy ends), and a methylene chloride insoluble fraction (insoluble heavy ends), Table II. Further fractionation of the oils and soluble heavy ends from pass 40 was carried out by silica gel open column chromatography. Three fractions were collected: alkanes (eluted with pentane, isooctane, pentane), aromatics (eluted with methylene chloride), and polars (eluted with methanol) (Table III). The chromatographic method involved 100 g Aldrich Grade 12 28-200 mesh silica gel activated at 250°C for 24 hours packed dry between two glass wool plugs in a Pyrex column that had a 75-100  $\mu$  fritted glass plate. The silica gel was wetted with HPLC grade pentane and then loaded with ~1 gram of sample. Elution was in the following sequence with HPLC grade solvents: 150 ml pentane, 100 ml isooctane, 50 ml pentane, 250 ml methylene chloride, and 100 ml methanol. The first three listed elute alkanes, the fourth elutes aromatics and the polar compounds are eluted with the fifth.

Characterization studies were carried out on the fractions using elemental analysis, tetrahydrofuran (THF) solubility, thermogravimetric analysis (TGA), size exclusion high performance liquid chromatography (mobile phase THF, UV and refractive index detection), IR spectrometry, 200 MHz  $^1\text{H}$  NMR and 50 MHz  $^{13}\text{C}$  NMR spectrometry, capillary GC/MS and direct probe MS.

### Results and Discussion

The variation in composition of the product slurries from Runs 101 and 103 during 40 recycle passes is shown in Figure 2 and Table II.

Insoluble Heavy Ends. The insoluble heavy ends increased during both runs. A steadier, earlier increase was seen during Run 101 (Figure 2), coinciding with the increasing viscosity. During Run 101 the reactor was "blown down" only once (pass 25) to remove accumulated reactor solids resulting in a rapid drop in viscosity. The viscosity then rose slowly until pass 40 where a rapid increase was seen (3). The insoluble heavy ends increased more slowly during Run 103. This slower increase may be related to the much lower viscosity observed

Table II. Composition of Recycle Slurries (Wt %) During CPU Runs 101 and 103

Fractions	Pass No.				
	0	7	19	30 (31)	40
Oil:					
101	94.5	70.9	50.2	54.7	48.4
103	88.3	67.0	59.0	46.3	46.1
Soluble Heavy Ends:					
101	4.1	14.3	19.9	16.4	16.1
103	2.7	18.9	19.6	16.2	19.7
Insoluble Heavy Ends:*					
101	0.04	8.6	19.1	27.6	29.8
103	<u>3.1</u>	<u>9.9</u>	<u>12.7</u>	<u>24.4</u>	<u>25.6</u>
Total % Recovery:					
101	98.6	93.8	89.2	98.7	94.3
103	94.1	95.8	91.3	86.9	91.4
Ash:					
101	0.03	6.6	10.8	11.2	11.4
103	4.4	6.9	9.8	13.0	11.5

\*Includes mineral matter.

Table III. Silica Gel Column Fractionation of CPU Runs 101 and 103 Pass 40 Oils and Soluble Heavy Ends (Wt %)

	101 Pass 40		103 Pass 40	
	Soluble Heavy Ends	Oil	Soluble Heavy Ends	Oil
Alkanes	0.1	5.6	0.6	8.0
Aromatics	56.2	59.1	45.0	58.6
Polars	<u>35.3</u>	<u>28.1</u>	<u>36.6</u>	<u>31.2</u>
% Recovery	92.6	92.8	82.2	97.8

during Run 103. The viscosity was controlled during Run 103 by scheduling reactor blowdown every twelfth pass. Direct insertion probe MS heating profiles of the insoluble heavy ends from Runs 101 and 103 gave non-quantitative profiles of the small percentage of the material that could be analyzed by this method. The insoluble heavy ends sample from Run 101 gave a prominent peak that volatilized early in the run. This peak gave a mass spectrum that appeared to be identical with that of 1,2'-binaphthyl. This component was not present in the insoluble heavy ends from Run 103. It was not a prominent component of the soluble heavy ends from either run. After subtracting the ash content and the THF soluble portion of the heavy ends, 7.5% of Run 101 and 6.7% of Run 103 is intractable THF insoluble organic matter (Table IV).

Soluble Heavy Ends. The soluble heavy ends also increased gradually from pass to pass during both Runs 101 and 103 as the coal-derived materials began to replace the >91% soluble startup solvents (Figure 2 and Table II) until pass 40 where the sum of the insoluble and soluble heavy ends reached about 45% to 46%. This leaves 48.4% (Run 101) and 46.1% (Run 103) oils as products at pass 40 (Figure 2 and Table II).

Characterization of the soluble heavy ends is much more difficult than the characterization of distillable oils which can be easily separated by capillary GC and identified by GC, GC/MS and NMR comparisons with known standard compounds. However the soluble heavy ends resemble the oils in some very important ways. They can be separated by simple column chromatography on silica gel into fractions easily identified as alkanes ( $\delta$ 0.5-1.4), aromatics ( $\delta$ 7.2-8.7), and polars ( $\delta$ 6.2-7.2) by 200 MHz  $^1\text{H}$  NMR (Figure 3) and 50 MHz  $^{13}\text{C}$  NMR spectrometry. The soluble heavy ends from Runs 101 and 103 partitioned differently with our separation (Table III). Run 103 produced more C-9 and larger alkanes in the heavy and oil fractions than Run 101. Small contamination of both alkane fractions by phthalates occurred (note extraneous peaks on Figure 3, top right). Small amounts of phthalate contaminants were accidentally introduced into the slurry. They appear in all three column fractions, but mainly in the heavy ends polar fraction of Run 101. Run 103 also produced more polars in the oil and heavy fractions than Run 101 (Table III). Run 101 produced slightly more aromatic hydrocarbons than Run 103.

Soluble Heavy Ends-Aromatic Fractions. Differences between aromatic fractions of the soluble heavy ends of Runs 101 and 103 may be seen by inspection of the elemental analyses (Table V), the  $^1\text{H}$  NMR spectra (Figure 3, middle), the IR spectra (not shown), TGA volatiles, and the average molecular weight maxima (Table IV). Direct insertion probe MS heating profiles from 30° to 350°C at 5°/min obtained at 10 ev and 70 ev were compared for samples of aromatic fractions of the soluble heavy ends Run 101 and 103. During the first part of the heating profiles small amounts of materials with masses recognizable as common hydrocarbons were noted. These included such masses as 128,142 (probable naphthalenes), 178,192 (phenanthrenes) and 202,216 (pyrenes) which were seen in the heavy aromatic fractions of both Runs 101 and 103. Masses 168,182 and 196 (probable dibenzofurans) were much more prominent in the heavy aromatics from Run 103 than Run 101. These parent ions, present in both high- and low-voltage mass spectra, are probably small hydrocarbons and ethers partitioned into the heavy fraction during our initial solubility separation. As the heating progressed a large number of masses giving the maximum ion current

Table IV. Properties of Oils, Soluble Heavy Ends, and Insoluble Heavy End Fractions of CPU Runs 101 and 103, Pass 40

<u>Sample</u>	<u>THF Insoluble (wt %)</u>	<u>Nonvolatiles (TGA) (wt %) (T<sub>max</sub>)</u>	<u>Average MW Maxima (Size Exclusions HPLC)</u>
<b>Total Samples:</b>			
101 Sol.	0.00	32.52 (800C)	10,000, 1200, 475
Heavy Ends			
103 Sol.	0.00	31.62 (800C)	10,000, 1200, 475, 280, 240
Heavy Ends			
101 Oil	0.00		1200, 540, 420, 360
103 Oil	0.00		620, 505, 360, 210, 340, 290, 260
<b>Silica Gel Column Fractions 3 (aromatics):</b>			
101 Sol.	0.00	42.69 (500C)	1200, 1000, 550
Heavy Ends			
103 Sol.	0.00	36.25 (500C)	10,000, 1200, 600, 450, 320
Heavy Ends			
101 Oil	0.00	2.83 (500C)	610, 385, 345, 320, 220, 160
103 Oil	0.00	1.75 (500C)	330, 310, 220, 210, 170, 150
<b>Silica Gel Column Fractions 4 (polars):</b>			
101 Sol.	1.97	31.98 (500C)	13,000, 1350, 520, 450
Heavy Ends			
103 Sol.	4.61	17.75 (500C)	1200, 480, 430, 380
Heavy Ends			
101 Oil	0.00	11.31 (500C)	15,000, 1100, 680, 540, 450, 360, 330, 150
103 Oil	4.46	13.53 (500C)	16,000, 1000, 520, 380, 360, 250, 200
<b>Insoluble Heavy Ends:</b>			
101		63.5 (18.9% of slurry)	
103		71.0 (18.2% of slurry)	

Table V. Elemental Analyses of Products from CPU Runs 101 and 103, Pass 40

Sample	Column Fraction	Elemental Analysis				O	C-100 Formula
		C	H	N	O		
101 Oils	Aromatics	85.06	7.34	0.28	7.32		C <sub>100</sub> H <sub>102.82</sub> N <sub>0.28</sub> O <sub>6.46</sub>
101 Sol. Heavy Ends	Aromatics	88.89	5.77	1.43	3.91		C <sub>100</sub> H <sub>77.30</sub> N <sub>1.38</sub> O <sub>3.30</sub>
103 Oils	Aromatics	88.56	7.66	1.67	2.11		C <sub>100</sub> H <sub>103.11</sub> N <sub>1.61</sub> O <sub>1.79</sub>
103 Sol. Heavy Ends	Aromatics	90.44	5.81	1.21	2.54		C <sub>100</sub> H <sub>103.11</sub> N <sub>1.61</sub> O <sub>1.79</sub>
101 Oils	Polar	77.96	7.66	1.33	13.05		C <sub>100</sub> H <sub>117.09</sub> N <sub>1.46</sub> O <sub>12.57</sub>
101 Sol. Heavy Ends	Polar	70.63	4.94	2.36	22.07*		C <sub>100</sub> H <sub>83.33</sub> N <sub>2.86</sub> O <sub>23.46</sub> *
103 Oils	Polar	77.12	7.88	1.06	13.94		C <sub>100</sub> H <sub>121.74</sub> N <sub>1.18</sub> O <sub>13.57</sub>
103 Sol. Heavy Ends	Polar	80.76	6.61	1.86	10.77		C <sub>100</sub> H <sub>97.62</sub> N <sub>1.98</sub> O <sub>10.02</sub>
101 Oils	Total	85.31	8.31	0.58	5.80		C <sub>100</sub> H <sub>116.06</sub> N <sub>0.58</sub> O <sub>5.10</sub>
101 Sol. Heavy Ends	Total	85.87	5.88	1.65	6.60		C <sub>100</sub> H <sub>81.54</sub> N <sub>1.65</sub> O <sub>5.77</sub>
103 Oils	Total	82.23	7.98	0.78	8.01		C <sub>100</sub> H <sub>114.29</sub> N <sub>0.81</sub> O <sub>7.22</sub>
103 Sol. Heavy Ends	Total	85.98	6.05	1.75	6.22		C <sub>100</sub> H <sub>83.80</sub> N <sub>1.75</sub> O <sub>5.44</sub>

\*Contaminated by phthalate plasticizer.

around mass 500 were observed. This result agrees with the maxima of mass 550 and 450 in the size exclusion chromatographic HPLC average molecular weight profiles from both Runs 101 and 103 (Table IV). There were a large number of both even and odd masses represented in profiles from both runs. Run 103 had a particularly prominent odd mass homologous series of 381, 395, 409, 423, 439, 453, and 467. The unit resolution of our quadrupole MS did not permit confirmation of these masses as aromatic nitrogen compounds, however they were tentatively assigned to neutral aromatic nitrogen compounds after considering the N/C ratios (Table V) and the separations used to obtain the fractions.

Soluble Heavy Ends-Polar Fractions.  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectroscopy (Figure 3, bottom) show a predominance of phenolic oxygen functionality in the soluble heavy ends polar fractions from both Runs 101 and 103. Although the total polar nitrogen content in the two runs was almost the same, the distribution of nitrogen compounds differed. The polar compounds from Runs 101 have a higher N/C ratio than those from Run 103 (Table V). Direct insertion probe MS heating profiles comparing the polar fractions from Runs 101 and 103 indicated a lower molecular weight range than that of the aromatic fractions, thus supporting the size exclusion chromatographic HPLC distribution (Table IV). Even and odd masses were plentiful within the molecular weight range found for heavy samples from Runs 101 and 103. A strong correlation between oxygen content (mostly phenolic) and viscosity for solvent-refined coals was noted in our laboratory but the same study failed to find a correlation between total nitrogen content and viscosity (6). At the present time it is not clear whether the differences found in nitrogen compound type distribution in the present study have any effect on viscosity.

Oils. Analysis of the oils from pass 40 of Runs 101 and 103 were carried out in order to provide comparison with the soluble heavy ends and to supply mass balance for the slurry separation analysis. A much more detailed characterization of the oils throughout the entire run is being prepared. The percentage of oils decreases from >85% in the solvents at the beginning of the runs to 45-58% at the last pass. Differences in composition of the oils from Runs 101 and 103, pass 40, were assessed using the analytical procedures already described and solvent extraction (7). Base extraction of the phenols gave the same percent phenols for both Runs 101 and 103. The amounts of methylated phenanthrenes in the aromatic fraction of Run 103 were larger than in Run 101. The difference in the phenanthrene composition between Runs 101 and 103 pass 40 oils may be seen by observing the region between the resonances for unsubstituted phenanthrene hydrogens at 8.71 and 8.68  $\delta$  and the pyrene peak at 8.20 $\delta$  in the 200 MHz  $^1\text{H}$  NMR spectra at the bottom of Figure 4. The peaks between these values are characteristic of substituted phenanthrenes. The unsubstituted aromatic hydrocarbons, phenanthrene (8.71, 8.68  $\delta$ ), fluorene (3.98 $\delta$ ), and acenaphthene (3.39 $\delta$ ) are more plentiful in Run 101 pass 40 oils than in Run 103 oils.

Pass to pass composition changes during the two recycle runs were observed (Table II, Figure 4). These changes are graphically displayed in Figure 4 which shows 200 MHz  $^1\text{H}$  NMR spectra of some of the product oils as they change in composition from pass to pass. These changes are more evident during the initial dilution of startup solvent with product and become more subtle between the 30th and 40th

pass. The composition of product oil from both Runs 101 and 103 still appear to be changing slowly at pass 40.

### Summary

A room temperature solubility separation method was used to separate the products of two 40 pass CPU runs that used different startup solvents. Although the composition was not investigated in detail, the insoluble heavy ends fraction from Run 101 appeared to contain binaphthyl while Run 103 did not. The oils and soluble heavy ends portions from the 40th pass were fractionated by silica gel column chromatography. The separation into alkanes, aromatics, and polars gave clean fractions based on NMR spectral data. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the corresponding oil and heavy fractions within a slurry sample resembled each other with oil polars (known to be mainly phenolic) resembling heavy polars and oil aromatics resembling heavy aromatics. The difference between oil and heavy polar fractions that causes them to be separated by solubility appears to be polarity rather than molecular weight differences. However, the major difference between oil and heavy aromatic fractions causing solubility separation is apparently due to molecular weight differences.

The success of these separations with materials of moderately high molecular weight makes possible a survey of a larger percentage of the liquefaction product slurry. The characterization of the fractions by a combination of techniques is now possible. A lack of high molecular weight model compounds to serve as knowns for further analysis presents a problem; however, additional work is in progress.

The products from Runs 101 and 103 after 40 passes were chemically dissimilar. Both the oils and the heavy ends showed a number of differences. It was of interest to note that the run started up with the PDU recycle solvent that contained more alkanes (13.9%) still yielded a product with more alkanes after 40 passes but the total amount was only 8% of the oil, 3.8% of the product slurry. The percent phenols in the oil (by extraction) was very close to equal for pass 40 from Runs 101 and 103 but the aromatic hydrocarbon character of the startup solvent appeared to be recognizable after 40 passes in both Runs 101 and 103. Run 103 still contains more alkylated and methylated aromatic hydrocarbons like the PDU solvent while Run 101 contained more unsubstituted aromatic hydrocarbons such as phenanthrene, acenaphthene, and fluorene like A04. There was an unequal distribution of nitrogen within the products from the two runs.

Various composition data were examined in an attempt to find a correlation with the much higher viscosity of Run 101. There did not seem to be much difference in the size of any heavy fraction when Runs 101 and 103 were compared, although the insoluble heavy ends were somewhat larger in Run 101 (29.8% of the slurry compared with Run 103 25.6%). The portion of the slurry that represents THF insoluble very heavy intractable organic matter was 7.5% for Run 101 and 6.7% for Run 103. The composition of the soluble heavy ends with respect to amounts of phenols and aromatics did not appear to be the cause of the viscosity. Only one difference was noted and that was Run 101 heavy ends polar fraction showed a higher N/C ratio indicating a different compound type distribution than Run 103. The viscosity difference could not be explained based on the oil composition. The percent phenols in the oil was the same in both Runs 101 and 103 although the polar (mainly phenolic) fraction of Run 101 also showed the higher N/C ratio indicating different compound types are present than in Run 103.

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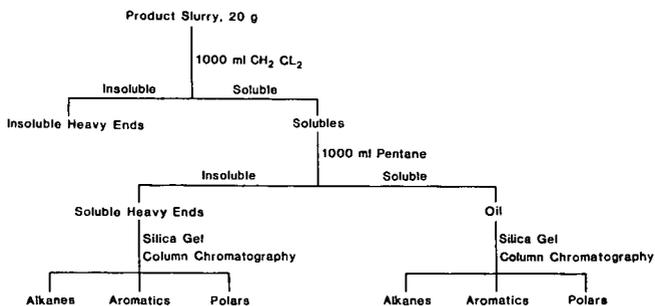
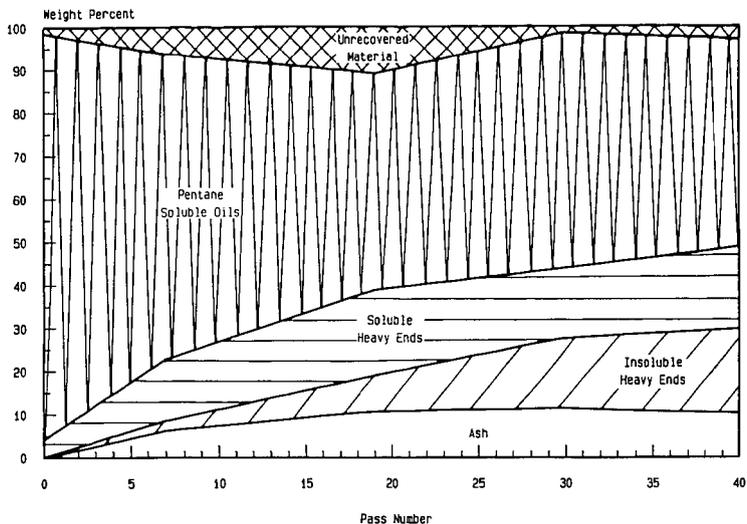


Figure 1. Separation of CPU product slurry by solubility and silica gel column chromatography.

## SLURRY PRODUCT DISTRIBUTION

CPU RUN 101



## SLURRY PRODUCT DISTRIBUTION

CPU RUN 103

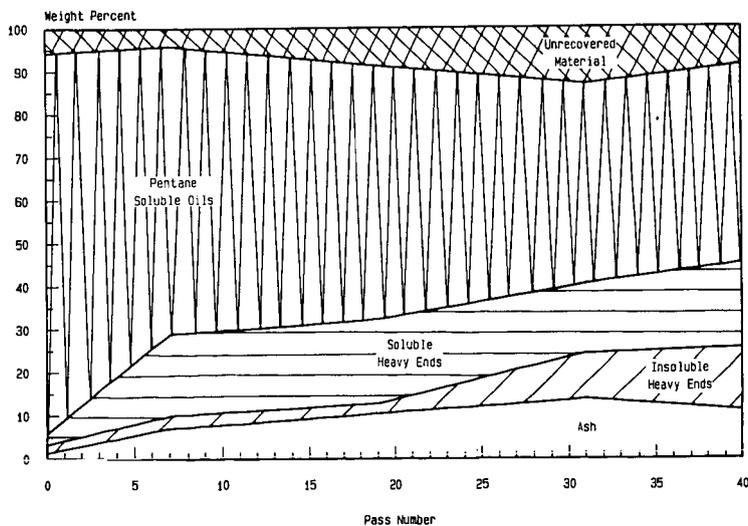


Figure 2. Product distribution as determined by solubility separation and ash analysis for CPU product slurries from Runs 101 and 103.

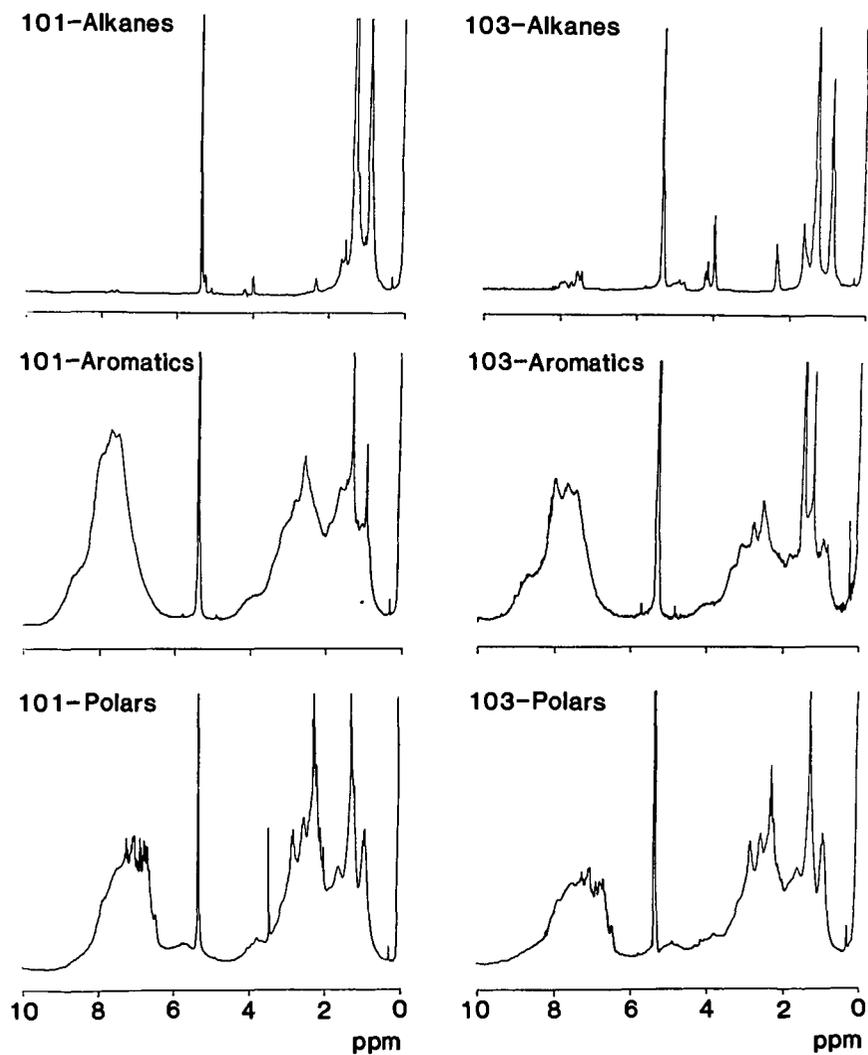


Figure 3. 200 MHz  $^1\text{H}$  NMR spectra of silica gel column chromatographic fractions from soluble heavy ends, CPU Runs 101 and 103.

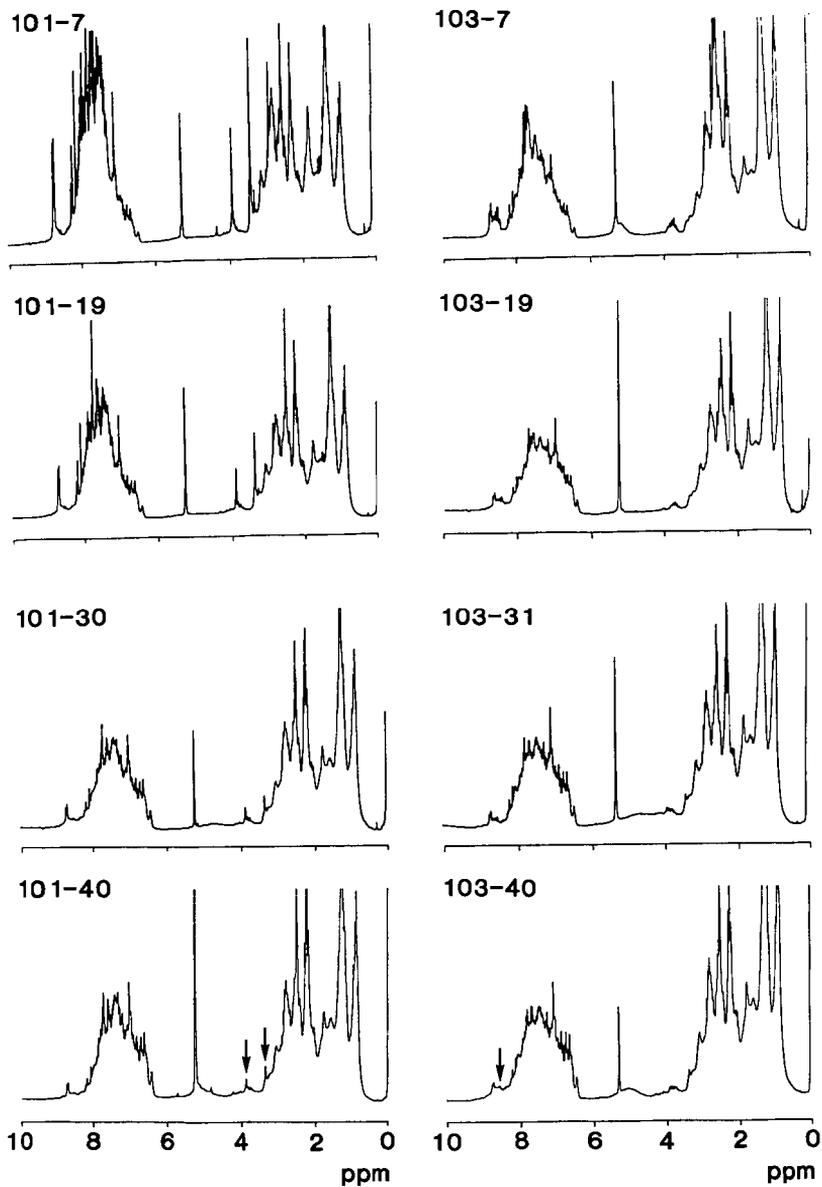


Figure 4. Changes in the oils during CPU Runs 101 and 103 as shown by 200 MHz  $^1\text{H}$  NMR spectroscopy.

## Chemical Interactions Between Heavy Solvent Components and Coal During Coal Liquefaction

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### Introduction

Interest in the heavy components in recycle solvents from direct coal liquefaction processes was generated when Kerr-McGee and Conoco reported that the addition of light SRC, a fraction from the critical solvent deashing step in the SRC Process, to the recycle solvent greatly improved overall solvent quality.<sup>(1)</sup> However, some heavy components are not beneficial and can lead to coke formation. Clearly, recycling some high molecular weight solvent components is beneficial to direct coal liquefaction processes while recycling others is not. The objective of this study has been to look at the chemical reactions of the heavier materials from an actual recycle solvent during the dissolving step of two-stage coal liquefaction.

### Experimental Approach

The experimental approach has been to (1) obtain a recycle solvent from the Lummus integrated two-stage liquefaction (ITSL) process pilot plant, (2) distill the solvent to 454°C, (3) separate each distillation cut into fractions of chemically similar compounds, (4) characterize the separated fractions in detail, and (5) study the effects on liquefaction when each solvent fraction is used as a heavy recycle solvent additive in a microautoclave liquefaction experiment.

### Coal and Solvent

Illinois #6 bituminous coal (Burning Star) which had been ground to 80 percent -200 mesh and dried to 4 percent moisture for use in the Lummus ITSL pilot plant was used for this work. An analysis is shown in Table 1. This coal was ground in Alabama and shipped to New Jersey so it may have experienced some oxidation, but it is probably typical of the coals which would actually be used in direct liquefaction processes. The coal was stored under nitrogen in glass jars after it was received in an attempt to minimize additional oxidation during storage.

Recycle solvent from the Lummus ITSL pilot plant was used as the solvent. This solvent is a +343°C distillation residue which had been partially hydrogenated in the process. The recycle solvent was distilled under vacuum to 427°C and a -427°C distillate and a +427°C residue were obtained and analyzed. Analysis of the starting recycle solvent and the two distillation fractions are listed in Table 2. Of the total solvent, 36 percent boiled below 427°C and 64 percent boiled above 427°C. The residue contained most of the heteroatoms; 80 percent of the nitrogen, 84 percent of the sulfur and 76 percent of the oxygen.

### Solvent Separation

Separations of the solvent fractions obtained by distillation to 454°C were carried out as shown in Figure 1 using a column chromatography method developed by Later and Lee<sup>(2)</sup>. The sample (10 g) was coated on Brockman Activity 1 neutral alumina (200 g) and eluted with hexane, benzene, chloroform, and tetrahydrofuran. The chemical types eluted were non-aromatic hydrocarbons, aromatic hydrocarbons, N-aromatics, and O-aromatics, respectively. Some polar material was retained on the column.

TABLE 1. ANALYSES OF ILLINOIS #6 COAL FROM THE LUMMUS ITSL PROCESS PILOT PLANT

Proximate Analyses, Wt %	As-Received	Dry
Moisture	3.99	-
Ash	9.72	10.12
Elemental Analyses, Wt %		
Carbon	69.73	72.63
Hydrogen	4.93	4.67
Nitrogen	1.18	1.23
Sulfur	2.88	3.00
Oxygen (by difference)		8.35
H/C		0.77
Particle Size Distribution, Wt %		
+70 mesh	0.07	
-70 +120	3.64	
-120 +200	18.90	
-200 +325	14.84	
-325	62.55	

TABLE 2. ANALYSES OF RECYCLE SOLVENT FROM THE LUMMUS ITSL PROCESS PILOT PLANT

Sample	SCT Recycle Solvent (2SCT16-1122)		-427°C	+427°C
Elemental Analyses, Wt %		MAF		MAF
Ash	1.30	-	<0.01	2.00
Carbon	86.77	87.91	90.96	87.88
Hydrogen	6.88	6.97	7.12	6.18
Nitrogen	0.94	0.95	0.57	1.30
Sulfur	0.53	0.54	0.23	0.69
Oxygen (by difference)	3.6	3.63	1.12	1.95
H/C	0.95		0.94	0.84
Distillation Data, Wt %				
-427°C	35.6			
+427°C	64.4			
Molecular Weight, g/mole	477		257	456

A second separation was carried out on partially deactivated silicic acid (3 g water/100 g silicic acid) by coating it with the N-aromatic fraction (3.35 g) and eluting with carbon tetrachloride, benzene and tetrahydrofuran. These single solvents were used instead of the two-component solvents described by Later and Lee(2) so that they could be recycled in the large scale column chromatography equipment. Only the +454 C N-aromatic fraction was separated on silicic acid.

The results of the first column chromatography separation are shown in Figure 2. Of the -454 C fraction, 9.6 percent is non-aromatic hydrocarbons, 72.9 percent is aromatic hydrocarbons, 5.6 percent is N-aromatics and 0.4 percent is O-aromatics. Only 3.8 percent is polar material which did not elute from the column. Overall, 82.5 percent of the -454°C solvent fraction are heteroatom-free hydrocarbons.

The +454°C fraction consists of only 1.3 percent non-aromatic hydrocarbons, 27.0 percent aromatic hydrocarbons, 4.8 percent N-aromatics and 33.3 percent O-aromatics. A large amount of polar material, 29.1 percent, is also present and does not elute from the column. The heteroatom-free hydrocarbons total only 28.3 percent of the +454°C recycle solvent fraction.

Several separations of the +454°C N-aromatic fraction on silicic acid gave yields of 13-26 percent primary nitrogen compound (aromatic amines), probably contaminated with tertiary nitrogen compounds in which the basic nitrogen is sterically "protected". The yield of acidic secondary nitrogen compounds (pyrroles, etc.) was 20-30 percent and the yield of basic tertiary nitrogen compound (pyridine derivatives) was 30-45 percent. Total recoveries ranged from 75-85 percent.

### Results and Discussion

The separated fractions were characterized by measuring molecular weight (by Vapor Phase Osmometry using THF as the solvent), elemental analyses and  $H^1$ -NMR. This data was used to obtain average structural parameters by application of the Brown-Ladner equations,(3) Titrations of basic nitrogen were done using perchloric acid in acetic acid.(4) Titrations of acidic hydrogen were done by refluxing with metallic sodium in tetrahydrofuran, adding water after removing excess sodium, and back titrating the sodium hydroxide formed with standard HCl.(5) The analytical results are summarized in Table 3.

All of the coal liquefaction experiments were done in a microautoclave liquefaction apparatus using 5 minutes reaction time at 427°C under 1000 psi hydrogen (room temperature) with a solvent/coal/additive ratio of 2:1:0.5.

A diagram of the microautoclave reactor is shown in Figure 3. It consists of a 3/4-inch union-tee microreactor which has a volume of 22.4 cc, a valve to add and release gases, a thermocouple which extends into the microautoclave to monitor temperature, and a pressure transducer to monitor pressure during each experiment. The microautoclave is heated in a sand bath and shaken horizontally. A 3/8-inch ball bearing is added to facilitate mixing.

The product gases were analyzed by GC and the liquids and solids were fractionated by their solubilities in THF, toluene and heptane into insoluble organic material (IOM) plus ash, preasphaltenes, asphaltenes and oils. Yields were calculated and a complete mass balance was done for each experiment. Mass balances averaged 99.2 percent, excluding water and gases.

### Non-Aromatic Hydrocarbons

The non-aromatic hydrocarbon fractions are complex mixtures of paraffins, olefins and naphthenes. The -454°C fraction has an average molecular formula of  $C_{21}H_{32}$  (5 unsaturations or rings) and the +454°C fraction has an average molecular formula of  $C_{26}H_{45}$  (3.5 unsaturations or rings). Comparison of the conversions to THF solubles (Table 4) shows that the heavier fraction is a better solvent. The non-aromatic hydrocarbons are expected to act only as a physical solvent since they contain few or no hydroaromatics which can lose hydrogen readily. The heavier material therefore appears to be better able to dissolve the products of liquefaction, possibly because more of the heavier fraction is in the liquid state and less in the vapor phase due to the higher boiling point range.

TABLE 3. ANALYSES OF -454 C AND +454 C RECYCLE SOLVENT FRACTIONS SEPARATED BY COLUMN CHROMATOGRAPHY

Fraction Temp Solvent	Non-aromatic Hydrocarbons -454 C +454 C		Aromatic Hydrocarbons -454 C +454 C		N-Aromatics -454 C +454 C		Secondary-N Carbon tetrachloride		+454 C, N-Aromatic Fractions		OH-Aromatics -454 C +454 C	
	Hydrocarbons Benzene	Hydrocarbons Benzene	Hydrocarbons Benzene	Hydrocarbons Benzene	Hydrocarbons Chloroform	Hydrocarbons Chloroform	Hydrocarbons Benzene	Hydrocarbons Chloroform	Hydrocarbons Benzene	Hydrocarbons Chloroform	Hydrocarbons Benzene	Hydrocarbons THF/Ethanol
Elemental Analyses, wt % HAF												
Carbon	88.03	87.26	92.40	93.18	86.30	87.14	88.83		88.12	86.89	76.50	73.02
Hydrogen	10.97	12.70	7.59	6.88	6.82	6.51	7.05		6.33	6.33	7.20	7.21
Nitrogen	0.00	0.00	0.00	0.00	4.81	2.57	1.64		2.03	2.03	1.86	1.37
Sulfur	0.00	0.00	0.00	0.00	0.69	0.69	0.69		0.69	0.69	0.69	0.69
Oxygen (diff.)	1.48	1.75	0.99	0.84	0.95	0.90	0.95		0.86	0.97	1.13	1.18
H/C												
Molecular Weight, g/mole	289	352	247	300	230	347	398		381	396	217	325
Hydrogen Distribution, % of Total Hydrogen												
Aliphatic	74.2	100.0	31.0	25.9	20.4	23.3	34.8		31.1	26.9	28.2	24.1
Aromatic	22.0	0.0	41.0	35.4	42.5	30.8	26.2		29.8	35.0	45.5	54.4
Phenolic (1)	3.8	0.0	28.0	38.7	37.0	44.7	36.8		38.3	35.3	25.9	20.0
Phenolic (2)	0.0	0.0	0.0	0.0	0	1.3	0.21		.76	2.9	1.8	1.5
Donatable H, wt % of Sample	-	-	1.52	1.42	1.43	0.88	1.31		0.93	1.17	1.53	1.77
Structural Parameters (4)												
$f_a$ - aromaticity	0.29	-	0.65	0.74	0.70	0.76	0.70		0.77	0.70	0.58	0.54
$R_A$ - number of aromatic rings	-	-	2.6	4.1	2.1	3.6	3.8		4.7	3.7	0.48	0.84
$R_{gr}/C_{ar}$ - substitutable aromatic	-	-	0.74	0.65	0.1	0.73	0.72		0.64	0.73	1.	1.
edge atoms/total aromatic atoms	-	-	0.42	0.31	0.38	0.30	0.30		0.32	0.38	0.59	0.70
$\alpha$ - fraction aromatic edge atoms	-	-	12.3	17.2	11.6	19.0	20.6		20.7	20.1	8.0	10.5
$C_a$ - total no. aromatic C atoms	-	-	3.9	3.5	3.6	4.2	4.4		4.2	5.6	4.7	7.3
$R_a$ - substituted aromatic ring	-	-	1.8	1.7	1.5	1.8	2.2		2.0	1.8	1.6	1.5
$n$ - carbon atoms/saturated sub-	-	-	-	-	-	-	-		-	-	-	-
stituent	-	-	-	-	-	-	-		-	-	-	-
Molecular Formula												
C	21	26	19	23	17	25	29.		28.	29.	14	20
H	32	45	19	20	16	23	18.		24.	28.	16.	23.
N	-	-	0.7	0.7	0.7	0.7	0.7		0.7	0.6	0.6	0.6
S	-	-	0.04	0.06	0.04	0.06	0.04		0.05	0.03	0.07	0.06
O	-	-	0.3	0.7	0.2	0.7	0.2		0.6	0.7	1.8	3.6
Nitrogen types, wt % HAF												
Basic nitrogen	-	-	2.08	0.84	2.33	1.63	0.09		0.52	1.58	0.69	0.54
Non-basic nitrogen (diff.)	-	-	-	-	-	-	1.55		2.01	0.45	1.17	0.83
Oxygen types, wt % HAF												
Acidic oxygen	-	-	-	-	-	-	0.24		0.77	3.27	2.07	1.73
Non-acidic oxygen (diff.)	-	-	-	-	-	-	1.95		1.81	0.31	11.35	16.09

- (1) Corrected for phenolic hydrogen
- (2) Assumes all acidic hydrogen is phenolic
- (3) Measured by titration of NaOH from refluxing in Na/THF followed by addition of H<sub>2</sub>O
- (4) From application of Brown-Ladner parameters to NMR data
- (5) Aliphatics contaminated with some aromatics

### Aromatic Hydrocarbons

The molecular formulas are  $C_{19}H_{19}$  for the  $-454^{\circ}C$  material and  $C_{23}H_{20}$  for the  $+454^{\circ}C$  fraction. The aromaticities ( $f_a$ ) are 0.65 and 0.74 for the two fractions. These are hydrogenated materials and there are significant amounts of aliphatic rings (hydroaromatics) present. The molecular weights of the two fractions differ by only 53 g/mole.

Comparison of the liquefaction results (Table 4) shows that the lower boiling range fraction is the better solvent. The major reaction of these fractions is expected to be hydrogen transfer. The  $-454^{\circ}C$  fraction has a higher H/C ratio (0.99 vs 0.84), is less aromatic ( $f_a$  0.65 vs 0.74) and contains more hydroaromatic hydrogens (1.52 vs 1.42 wt %), as measured by assigning portions of the  $H^1$ -NMR spectrum to hydrogens in cyclic structures  $\alpha$  and  $\beta$  to an aromatic ring. Another factor, which has not been measured, is molecular size, which may also have an impact on the relative ability of the smaller and larger molecules to get close enough to the dissolving coal to transfer hydrogen. Only the larger size and boiling point of the  $+454^{\circ}C$  molecules, which should make those molecules more able to physically support the dissolving coal, favor the heavier material.

### N-Containing Aromatics

The difference in molecular weight between the N-aromatic fractions is large, 117 g/mole. The molecular formula of the  $+454^{\circ}C$  fraction indicates that there is also one atom of oxygen present in each molecule. These fractions are polar but are also made up of condensed hydroaromatic structures, so they should be able to act both as hydrogen donors and as physical solvents. The H/C ratios are similar for the  $-454^{\circ}C$  and  $+454^{\circ}C$  fractions, 0.95 and 0.90 respectively, but estimation of donatable hydrogen by  $H^1$ -NMR<sup>(6)</sup> indicates that the lighter fraction should be a much better hydrogen donor, 1.43 weight percent donatable hydrogen vs 0.88 for the  $+454^{\circ}C$  fraction.

The differences in hetero atoms types between the  $-454^{\circ}C$  and  $+454^{\circ}C$  fractions are significant. All of the oxygen in the  $-454^{\circ}C$  fraction is non-acidic while only about 60 percent of the oxygen in the  $+454^{\circ}C$  fraction is non-acidic. Of the nitrogen in the  $-454^{\circ}C$  fraction 47 percent is basic (tertiary) but only 34 percent is basic in the  $+454^{\circ}C$  fraction. The N/C mole ratio is also twice as large (.041 vs .024) in the lighter fraction.

The liquefaction results are compared in Table 4. Both N-aromatic solvent additives result in lower conversions, although the  $-454^{\circ}C$  material is by far the more effective solvent. The hydrogen donation potential of the lighter N-aromatic fraction may be able to overcome most of the negative reactions which occur as a result of the increased polarity of the N-aromatics, compared to the aromatic hydrocarbons. A major reaction of these fractions is adduction of solvent to the dissolving coal to produce large yields of asphaltenes. This is also more pronounced in the  $+454^{\circ}C$  fraction and may be due to the higher amount of acidic (phenolic) oxygen.

### Primary, Secondary and Tertiary $+454^{\circ}C$ N-Aromatics

The  $+454^{\circ}C$  aromatic fraction was split into three fractions by nitrogen type, as shown below:

<u>N-Type</u>	<u>Primary</u>	<u>Secondary</u>	<u>Tertiary</u>
Compound Type			
<u>% of Total N</u>			
Basic	24	5	78
Non-basic (diff.)	76	95	22
<u>% of Total O</u>			
Acidic	30	11	100
Non-acidic (diff.)	70	89	0

TABLE 4. COMPARISON OF EFFECTS OF -454 C AND +454 C SOLVENT FRACTIONS ON COAL LIQUEFACTION (427 C, 5 min, 1000 psi (cold) hydrogen, 3 g Illinois #6 coal, 6.0 g -454 C recycle solvent, 1.5 g solvent fraction)

Added Solvent Fraction	Temp. °C	Net Change (MAF basis) % of MAF Coal		Hydrogen Balance		
		THF Insolubles	Preasphaltenes			
None	-	-80.4	34.3	13.7	20.5	-0.12
Aliphatic	-454	-81.2	33.3	33.7	5.4	-0.15
Hydrocarbons	+454	-84.1	27.9	35.0	-2.8	.48
Aromatic	-454	-87.6	33.1	27.2	15.5	.090
Hydrocarbons	+454	-83.4	33.8	28.9	9.4	-0.14
N-Containing	-454	-79.5	25.6	40.6	7.3	-0.065
Aromatics	+454	-67.1	30.3	47.6	-6.4	-0.060
Primary Nitrogen Aromatic	+454	-79.5 (1)	29.4	42.0	-8.2	+0.05
Secondary Nitrogen Aromatic	+454	-81.0 (1)	29.8	28.8	-15.2	-0.06
Tertiary Nitrogen Aromatic	+454	-71.7 (1)	19.7	48.6	-14.0	0.00
O-Containing	-454	(-58.3) (2)	24.6	38.9	-18.1	-0.030
Aromatics	+454	-71.1	30.8	26.9	0.6	-0.050

(1) All N-aromatic fraction data are based on single liquefaction experiments

(2) Incomplete THF insolubles recovery

The purity of nitrogen types in each fraction can be estimated from the ratios of basic to nonbasic nitrogen present. The primary nitrogen fraction is expected to be contaminated with significant amounts of tertiary nitrogen compounds in which the nitrogen is sterically protected<sup>(2)</sup>. About 24 percent of the nitrogen in this fraction is basic (tertiary) and the other 76 percent is assumed to be the desired primary nitrogen compounds. The secondary (acidic) nitrogen fraction is expected to be the most pure and it is 95 percent nonbasic nitrogen. The tertiary (basic) nitrogen fraction is 78 percent basic nitrogen.

Acidic (phenolic) oxygen is associated primarily with the basic nitrogen, probably in hydrogen bonds. The oxygen associated with secondary (acidic) nitrogen is primarily non-acidic, possibly substituted furans, also in hydrogen bonds. The same oxygen-nitrogen pairs also appear to be present in the contaminated primary nitrogen fraction. Although the primary nitrogen is neutral it should also be able to form hydrogen bonds with non-acidic oxygen.

All of the individual N-aromatic fractions are better solvents than the combined N-aromatics fraction as shown in Table 4. The tertiary nitrogen N-aromatics give the lowest conversions of the three fractions and the most asphaltenes. Based on net hydrogen used, the tertiary nitrogen compounds do not shuttle hydrogen. They may strongly bond with solvent and dissolving coal.

The secondary N-aromatics give the highest conversions and significantly lower asphaltene yields. They result in the largest net loss of oil which indicates that they are also adducted to the dissolving coal and solvent. They show some indication of shuttling hydrogen.

Although the nitrogen compounds have been reported to be good solvents for coal liquefaction, particularly if they are present when the coal moisture is released during drying and can replace the moisture in the coal pores before liquefaction temperatures are reached<sup>(7)</sup>, under the conditions used in these experiments they are relatively poor liquefaction solvents, particularly the tertiary-N fraction.

#### O-Containing Aromatics

The final fraction studied is an oxygen-containing aromatic fraction which eluted from the column chromatography separation. Although much of the oxygen in the coal liquefaction solvents is probably phenolic, titration of acidic hydrogen showed that 90-96 percent of the oxygen on the molecules that eluted was non-acidic, probably in functional groups such as substituted benzofurans. These materials have lower aromaticities than the other fractions and are highly substituted. The -454°C fraction contains an average of 2 oxygens per molecule and the +454°C fraction contains an average of 4 oxygens per molecule. The H/C ratios are high, 1.13 and 1.18, respectively, as are the weight percentages of donatable hydrogen, 1.53 and 1.77, respectively, however, as shown in Table 4, these fractions are very poor solvents. Apparently, the major reaction of this class of compounds is not hydrogen transfer. This may be because the "donatable" hydrogens are not really hydro-aromatic but are  $\alpha$  to oxygen atoms. They seem to adduct in large amounts to solvent, as shown by the negative oil yields. They apparently are also poor physical solvents, possibly due to their low aromaticities and relatively large steric size, caused by the large number of substituents.

#### Conclusions

The hydrocarbon fractions in the recycle solvent have a positive effect on liquefaction while the heteroatom containing fractions have a negative effect. Since the combined amount of non-aromatic and aromatic hydrocarbons is about 82.5 weight percent of the -454°C recycle solvent and only 28.3 weight percent of the +454°C recycle solvent, it is not surprising that the overall effect of adding more -454°C solvent is positive and the overall effect of adding more +454°C solvent is negative (Table 5).

Among the opposing properties of higher molecules weight solvent components which can affect their efficiency as liquefaction solvents are improved

TABLE 5. COMPARISON OF EFFECTS OF +454°C AND -454°C RECYCLE SOLVENTS ON COAL LIQUEFACTION (427°C 5 min, 1000 psi (room temperature) hydrogen, 3 g Illinois #6 coal, 6 g -454°C recycle solvent)

Added Solvent Fraction	Total Solvent/Coal	Net Change (MAF basis), % of MAF Coal (1)				Hydrogen Balance
		THF Insolubles	Preasphaltenes (2)	Asphaltenes (3)	Oils (4)	
None	2.0:1	-80.4	34.3	13.7	20.5	-.12
-454°C/1.5	2.5:1	-86.1	42.9	25.3	19.5	-.063
+454°C/1.5	2.5:1	-77.2	29.2	34.6	12.4	-.36

(1) Net change =  $\frac{\text{Final weight (MAF)} - \text{Initial weight coal} + \text{solvent (MAF)}}{\text{WT MAF coal}} \times 100$   
Initial weights measured by extraction

(2) Preasphaltenes = THF soluble-toluene insolubles

(3) Asphaltenes = Toluene soluble-heptane insolubles

(4) Oils = Heptane solubles

facility for hydrogenation reactions, but lower amount of donatable hydrogen present, lower vapor pressure at elevated temperature but the possibility that their increased size has a negative steric effect on their ability to transfer hydrogen. Comparisons of solvent fractions of differing molecular weights gives mixed results. Of the solvent components which are expected to react primarily by H-transfer (N-aromatics and aromatic hydrocarbons) the heavier fractions are less effective, possibly because of steric hindrance to hydrogen transfer and less available hydrogen to transfer, but of the solvent components expected to act only as physical solvents (non-aromatic hydrocarbons and O-containing aromatics) the heavier components are more effective than the corresponding lower molecular weight fractions.

There appears to be a relationship between the type of heteroatoms present in the recycle solvent fraction which is based on hydrogen bonding. These relationships appear to be an area where additional research may increase understanding of the weak bonds which are made and broken during liquefaction which result in net solvent loss and improved coal solubility. Another area where further research is needed is on the effect of steric size of the solvent components on coal liquefaction.

The overall effect of recycling heavy ends in the ITSL process is positive because it results in the production of a single, higher-value liquid product with low carcinogenicity, in higher yields than would otherwise be possible. The hydrocarbons, about 25 percent of the heavy ends, are productive liquefaction solvent components as well.

#### Acknowledgements

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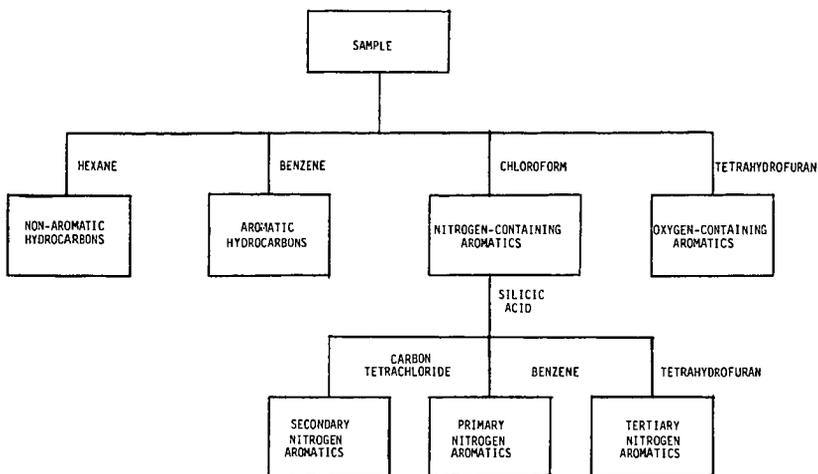


FIGURE 1. METHOD FOR SEPARATION OF FRACTIONS INTO CHEMICAL CLASSES BY COLUMN CHROMATOGRAPHY

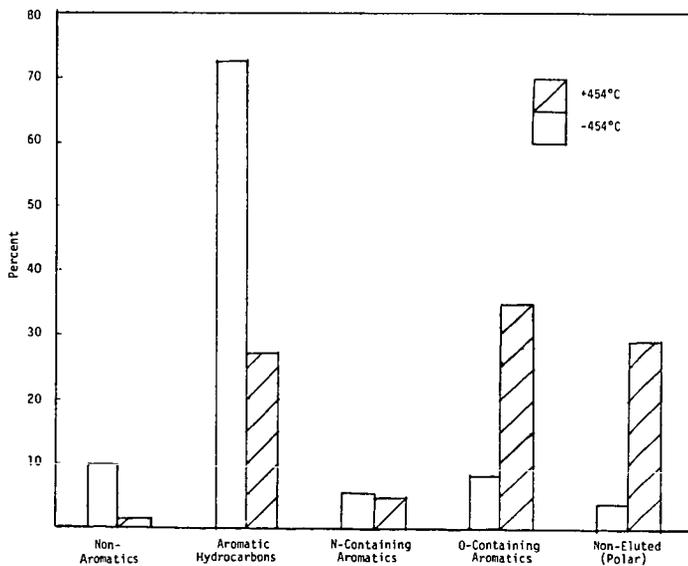


FIGURE 2. DISTRIBUTION OF CHEMICAL TYPES IN -454°C AND +454°C RECYCLE SOLVENT

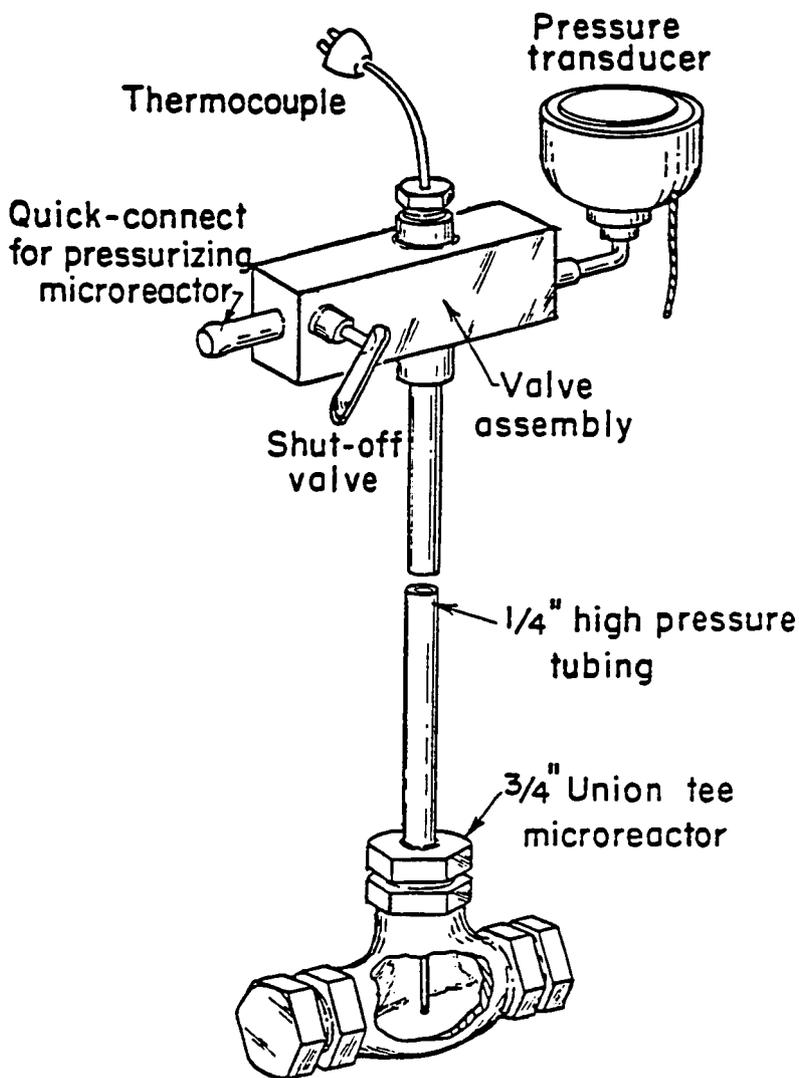


FIGURE 3. MICROAUTOCLAVE REACTOR

BEHAVIOR OF PHENOLICS IN COAL LIQUEFACTION:  
SAMPLE CHARACTERIZATION AND EFFECT ON COAL CONVERSION IN A CSTR UNIT

by

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INTRODUCTION

Phenolic components of coal liquefaction solvents have been considered to be beneficial for conversion of coal (1,2). Orchin and Storch (2), for example, reported that the addition of small amounts of cresol to tetralin increased the conversion of coal compared with the yield observed with tetralin alone. Kamiya and co-workers (3) observed a similar effect with phenol or cresol added to a solvent composed of tetralin and 1-methylnaphthalene; the magnitude of the increase was dependent upon the coal used. The reported effect has been ascribed to a variety of factors, one of which is a hydrogen-bonding interaction between the phenolic species and ethers in the coal (2,3), leading to increased cleavage of various ethers.

Awadalla and Smith (4) observed an increase in conversion with p-cresol but suggested that the effect was an artifact of the extraction process, a co-solvent effect arising from lack of prior removal of the phenolic material. Larsen et al. (5), investigating the use of phenol as a solvent for liquefaction of Bruceton Pittsburgh Seam coal, found that a solvent/coal ratio of 1.5 and reaction temperature of 460°C led to a weight increase of the coal of 9% after a 15-min reaction. This large amount of adduction with only a 10% conversion to pyridine-soluble material indicates that phenol is a very poor solvent under these conditions. Runs made at 482°C resulted in an increase in conversion, up to 82% for a 10/1 phenol/coal feed. However, the liquid product contained 14% by weight phenol of which 6% was attached to the coal by other than hydrogen-bonding interactions. An additional 8% was exchangeable with unlabeled material.

Our (6) past work with naphthols, phenol, and cresols using a micro-autoclave unit indicated that phenol and naphthols were poor solvents for coal liquefaction due to high levels of adduction. However, less adduction was observed with the addition of cresols to the solvents. Therefore, a series of runs were made in a CSTR unit to evaluate the effect of adding phenol and cresols to anthracene oil (AO) and SRC-II derived solvents. In addition, an "OH-reduced" solvent and a solvent mixture of AO plus OH-concentrate were tested.

## EXPERIMENTAL

The coal was Powhatan No. 5 Mine (Pittsburgh No. 8 Seam) ground to pass at least 98% through 100 mesh screen. Analyses of the coal and solvents are given in Table 1.

The bench-scale liquefaction runs were made in a continuous feed stirred-tank reactor (CSTR) system. A flow diagram of the coal liquefaction unit is shown in Figure 1; its operation has been previously described (7). Samples of the reactor slurry were first stripped with nitrogen, and they were then subjected to sequential Soxhlet extraction using pentane, toluene, and tetrahydrofuran (THF), respectively. Fractions were defined as follows, using as a basis MAF coal feed:

wt% oils = {(MAF coal-pentane insolubles)/MAF coal} x 100  
wt% asphaltenes = {pentane insoluble, toluene soluble/MAF coal} x 100  
wt% preasphaltenes (PA) = {toluene insoluble, THF soluble/MAF coal} x 100  
wt% THF insolubles = {THF insoluble material/MAF coal} x 100

## RESULTS AND DISCUSSION

Characterization of the OH-Concentrate: The OH-concentrate (OH-CONC) was isolated by contacting SRC-II solvent with activated Rohm and Haas Co. IRA-904 resin. The OH-CONC was then freed by washes of CO<sub>2</sub>/methanol acid and HCO<sub>2</sub>H/methanol followed by solvent stripping.

The hydroxyl concentrate of SRC-II solvent was added to a small amount of methylene chloride and analyzed by capillary GC/MS. The greatest portion (56%) of the chromatographic peaks other than solvent was phenol (10%) or alkyl-substituted phenols (46%). Methyl phenols (23%) account for approximately half of the alkyl-substituted phenols with the remainder (23%) being C<sub>2</sub> to C<sub>5</sub> phenols. Other peaks include C<sub>9</sub>H<sub>10</sub>O isomers (10%) and C<sub>10</sub>H<sub>12</sub>O isomers (9%) which are probably indanols and methylindanols. Hydroxybiphenyl (1%) and carbazole (3%) were identified. Polynuclear aromatic hydrocarbons accounted for 16% of the peaks. The largest of these was methylphenanthrene (4%). The remainder of the peaks (5%) were small and unidentified.

The <sup>1</sup>H spectrum of the OH-CONC fraction is shown in Figure 2, and the results are summarized in Table 2. This fraction has aromatic, hydroxyl, hydroaromatic, and alkyl substituent functionality. The aromatic region spans from 6 ppm to 8.6 ppm. These aromatic hydrogens represent 39.7% of the total hydrogen. Even though the nitrogen content is relatively low (1.1%), the small amount of intensity between 8.4 ppm and 8.6 ppm in the aromatic region can be assigned to protons ortho to the nitrogen in pyridine-type structures. These protons represent less than 0.3% of the hydrogen. There is a broad resonance at 5.4 ppm which can be assigned to hydroxyl hydrogen. This accounts for 11.3% of the hydrogen in the spectrum. In the region around 3.4 ppm are several smaller signals which can be assigned to methylene bridges between aromatic rings. These methylene bridge hydrogens represent 0.9% of the hydrogen present.

The main type of aliphatic substituent is methyl groups on aromatic rings as evidenced by the sharp signals at 2.2, 2.5, and 2.8 ppm. These signals account for 25.7% of the hydrogen present. There are also some (16.7% of hydrogen) long-chain aliphatic substituents with an average chain length of five carbons. Combining a broad signal at 1.7 ppm, together with an equivalent amount of intensity from the signal at 2.8 ppm, about 5.6% of the hydrogen is hydroaromatic.

The  $^{13}\text{C}$  NMR spectrum, given in Figure 3, shows the OH-CONC to have an aromaticity of 77.4%. The ratio of aromatic carbons to hydroxyl-bearing carbons is 8.5:1. The ratio of total carbon to oxygen is 10.9:1, which is reasonably consistent with that of the elemental carbon-to-oxygen analysis of 12.3:1.

The amount of ortho substitution is determined as the difference between the area of the region from 152 ppm to 156 ppm and one-half of the area between 110 ppm and 117 ppm. The amount of meta substitution is determined from the signals at 154-155 ppm, and the difference between the amount of hydroxyl-bearing carbon and the amounts of ortho and meta substitution is para substitution. The results are given in Table 3.

Since the observed ratio of aromatic carbons to hydroxyl-bearing carbons is 8.5:1 and every molecule theoretically has an acidic hydroxyl group, the OH-CONC consists of a mixture of one- and two-ring systems. Because only a small amount of the concentrate has been identified as naphthols, the remainder of two-ring systems should be comprised of single rings joined by short alkyl bridges. There is evidence for both methylene and ethyl bridges in the carbon spectrum. The distribution is shown in Table 3.

The total alkyl-substituted aromatic carbon is 12.8%. This was determined by summing the methylene bridge area times 2, the ethyl bridge area, one half the hydroaromatic area, and the methyl groups on aromatic rings area. The total nonprotonated aromatic carbon is difficult to determine from the normal spectral regions due to the presence of hydroxyl groups which induce an upfield shift to the carbons ortho and para to it. To study this, a NORD-CDRE (noise off-resonance decoupled convolution difference resolution enhancement) experiment was run. The signals upfield of 129.5 ppm are due to bridge carbons in 1- and 2-naphthols. The total bridge carbon is 15.5% as determined from the difference between the total nonprotonated carbon and the alkyl-substituted carbon plus hydroxyl-bearing carbon (11.8%). Therefore, the level of protonated aromatic carbon is 58.5% of the aromatic carbon.

CSTR Experiments: The results of the CSTR runs are summarized in Table 4. As anticipated, SRC-II distillate is a better solvent than A0 at short reaction times (4 min) as indicated by higher overall coal conversion, a lower level of preasphaltenes, and lower hydrogen consumption. With both solvents the yields of oils were negative. With an increase in space time to 15-19 minutes, overall conversions increased to about the same level (72-75%). The recoveries of preasphaltenes were essentially the same at about 5%, and the hydrogen consumptions were equal at 3.5 g/100 g MAF coal. However, a

sizable negative yield of oils was observed in the AO run at 15 minutes. This was apparently due to a high yield of asphaltenes. While this observation appears to be anomalous, the product slurry was extracted a total of five times with essentially the same results.

The direct addition of phenol to AO (4-min space time) was detrimental. While % solvation increased marginally, the yield of asphaltenes increased greatly over that of the run with AO alone. The product slurry was also very sticky and difficult to handle; therefore, pentane may have had some difficulty penetrating into the slurry sample and then extracting the oils. The yields of preasphaltenes were essentially the same for the runs with AO and AO plus phenol.

The addition of OH-concentrate, recovered from an ion exchange resin treatment (Rohm and Haas IRA-904) of SRC-II solvent, to AO had little effect on the distribution of products. Considering the OH-concentrate had a moderate level of hydroaromaticity while that of AO was low, and that the OH-concentrate had already effectively passed through a liquefaction reactor, the OH-concentrate may not react sufficiently with coal radicals to form additional asphaltenes.

The addition of m-cresol appeared to be of particular benefit to the AO runs. This addition resulted in an increase in the yield of oils along with a marginal increase in % solvation. In the case of m-cresol addition to SRC-II solvent at a 15-minute reaction time, there was a small increase in % solvation with nominal increases in each of the product fractions.

Due to a limited amount of available feed sample, only a single CSTR run was made with the solvent recovered after treatment with IRA-904 resin. This solvent contained 1.9% oxygen, while the as-received SRC-II solvent contained 2.8% oxygen. Even this partial removal of hydroxyls appears to be of benefit, as observed by an increase in oil yield, a decrease in asphaltenes yield, and a marginal increase in % solvation (THF solubles).

#### SUMMARY

Coal liquefaction experiments were carried out at 450°C in a continuous feed stirred-tank reactor (CSTR) to observe the effect of adding phenolics to anthracene oil (AO) and SRC-II recycle solvents. At nominal space times of 4 and 15 minutes, the levels of conversion (THF solubles) were significantly higher with SRC-II recycle solvent than with anthracene oil. The addition of phenol to AO at a ratio of 5/65 resulted in a nominal increase in coal conversion to THF solubles, but the amount of asphaltenes more than doubled resulting in a sizable net loss of solvent. The addition of m-cresol to both AO and SRC-II solvents had a positive effect on coal conversion to both THF and pentane solubles (oils). The partial removal of an OH-concentrate from SRC-II solvent was carried out using Amberlyst IRA-904 ion exchange resin. The "OH-reduced" oil was only marginally better than raw SRC-II recycle solvent for coal liquefaction. A characterization of the OH-concentrate by  $^{13}\text{C}$  and  $^1\text{H}$  NMR and FTIR indicated a moderate level of aromaticity (77%), a

sizable amount of short-chain aliphatic substitution, and also a sizable amount of hydroaromaticity. GC/MS characterization pointed out a high concentration of one- and two-ring substituted phenolics.

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Table 1  
Analyses of Solvents and Coal

<u>Chemical Analysis (wt%)</u>	<u>Raw A0</u>	<u>Raw SRC-II</u>	<u>OH-CONC</u>	<u>OH Reduced</u>	<u>Coal*</u>
Carbon	91.2	87.2	82.0	88.4	72.3
Hydrogen	5.9	8.7	7.8	8.5	5.1
Nitrogen	1.0	0.9	1.1	0.9	1.5
Oxygen	1.3	2.8	8.9	1.9	7.9
Sulfur	0.6	0.4	0.2	0.3	0.6
Ash	-	-	-	-	9.7
	100.0	100.0	100.0	100.0	100.0

\*Powhatan No. 5 Mine (Pittsburgh Seam) coal.

Table 2  
<sup>1</sup>H NMR Analysis of SRC-II Hydroxyl Concentrate

Aliphatic Hydrogens

Methylene bridge	0.9%
Methyl	25.6
Hydroaromatic	5.6
Long alkyl chain (i.e., C <sub>5</sub> )	<u>16.7</u>
Total aliphatic	48.7

Hydroxyl Hydrogens

11.3

Aromatic Hydrogens

Aromatic hydrogen ortho to N	0.3
Others	<u>39.7</u>
Total aromatic	<u>40.0</u>

Total

100.0%

Table 3

<sup>13</sup>C NMR Analysis of SRC-II Hydroxyl ConcentrateAliphatic Carbons

Methylene bridges between rings	1.4%
Other carbons $\alpha$ to aromatic rings	2.0
Methyl groups attached to rings	5.7
Hydroaromatic carbons	7.3
Long-chain alkyls (from <sup>1</sup> H) (est.)	<u>6.2</u>
Total aliphatic carbons	22.6%

Aromatic Carbons (Ar-C)

Ortho methyl groups (to OH)	3.0
Naphthols	1.0
Unknown ortho substituents	<u>0.9</u>
Total substituted Ar-C's ortho to OH groups	4.9
Substituted Ar-C's meta to OH groups	9.9
Substituted Ar-C's para to OH groups	<u>7.4</u>
	22.2*
Hydroxyl substituted Ar-C	9.3
Protonated Ar-C	<u>45.9</u>
Total	100.0

\*This is also subdivided as follows:

Alkyl-substituted Ar-C	10.0
Aromatic bridge carbons	<u>12.2</u>
Total	22.2

Table 4  
Summary of CSTR Runs with Phenolic Additives

Solvent/Additive	Space Time (min)	% Solvation <sup>(1)</sup> (g/100 g)	Hydrogen Consumption <sup>(2)</sup> (g/100 g)	Yields <sup>(2)</sup> (g/100 g)		
				Oils	Asphaltenes	Preasphaltenes
Anthracene Oil	4.2	55.4	3.0	-7.0	29.9	19.9
+m-Cresol	4.3	58.3	2.4	9.6	30.2	27.0
+Phenol	4.4	58.5	2.1	-46.5	71.3	22.1
+OH-CONC	4.1	56.7	2.5	-9.9	33.5	23.6
Anthracene Oil	15.2	74.7	3.4	-35.5	82.9	6.7
+m-Cresol	19.1	80.2	4.3	-2.1	55.3	3.7
SRC-II Solvent	4.7	61.3	1.8	-5.3	41.8	14.0
OH-Reduced SRC-II	4.6	63.9	2.7	2.1	34.5	17.8
SRC-II Solvent	19.0	71.7	3.6	12.3	33.2	4.7
+m-Cresol	15.0	76.6	3.6	14.5	34.9	7.5

Notes: (1) Solvation is given as grams of tetrahydrofuran solubles/100 grams MAF coal.  
(2) Yields are given as grams/100 grams MAF coal.

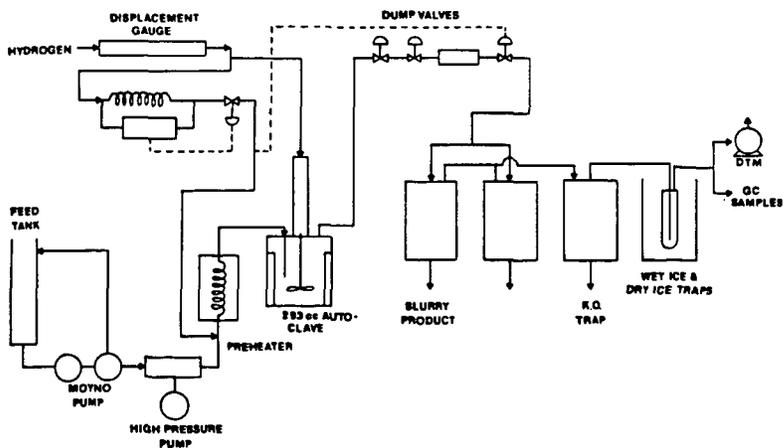


FIGURE 1 SCHEMATIC OF THE BENCH-SCALE CSTR UNIT

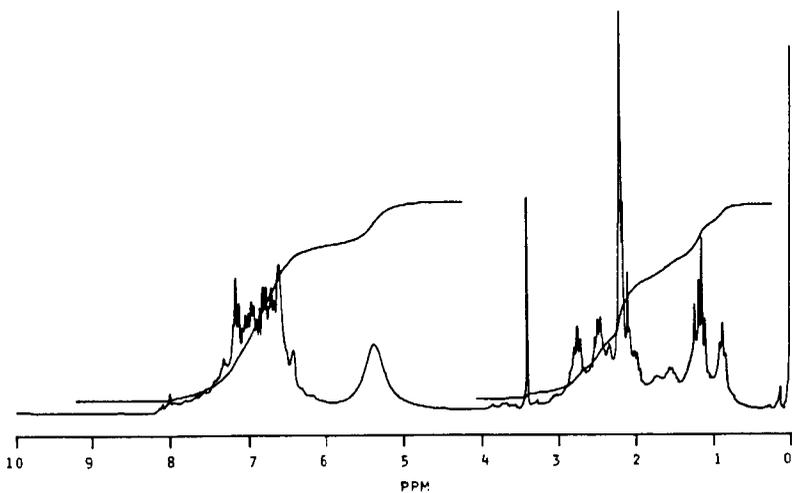


FIGURE 2  $^1\text{H}$ -NMR SPECTRUM OF SRC-II DERIVED HYDROXYL-CONCENTRATE

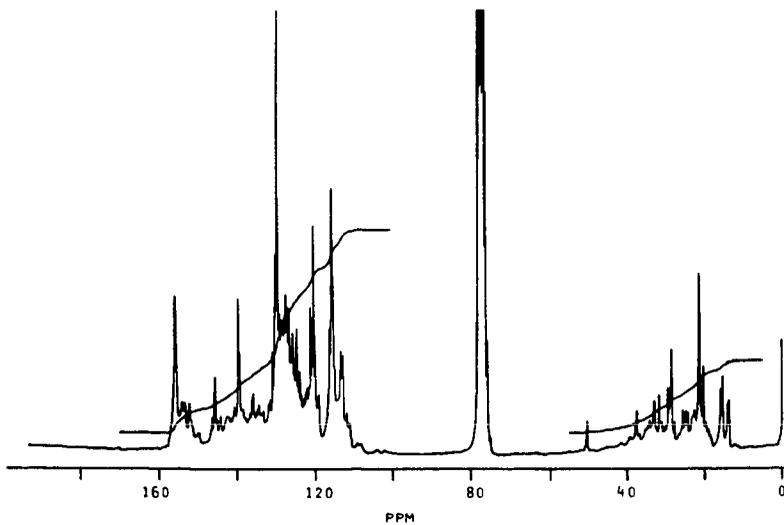


FIGURE 3  $^{13}\text{C}$ -NMR SPECTRUM OF SRC-II DERIVED HYDROXYL-CONCENTRATE