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HEAVY RECYCLE SOLVENT STUDIES IN TWO-STAGE COAL
LIQUEFACTION

Final Technical Report for September 1, 1982—December 30, 1983

By
James R. Longanbach

January 10, 1984

Work Performed Under Contract No. FG22-82PC50783

Battelle Columbus Laboratories
Columbus, Ohio

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FINAL TECHNICAL REPORT

on

HEAVY RECYCLE SOLVENT STUDIES
in
TWO-STAGE COAL LIQUEFACTION

to

U.S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER

Contract No. DE-FG22-82PC50783
Battelle No. G-8389

Period Covered:
September 1, 1982 - December 30, 1983
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SUMMARY

Illinois #6 coal and SCT recycle solvent and SCT heavy oil product made from Illinois #6 coal at the ITSL Process pilot plant were obtained from the C-E Lummus Co. for this study. Each liquid sample was vacuum distilled to 454 C to obtain light and heavy recycle solvent samples. The vacuum distillation samples were separated by liquid chromatography into fractions containing aliphatic hydrocarbons, aromatic hydrocarbons, N-containing aromatics and O-containing aromatics. The N-containing aromatics were further separated into concentrated fractions of primary, secondary and tertiary N-containing aromatics. A separate heptane soluble (asphaltene) fraction was also obtained from the +454 C recycle solvent.

Elemental analyses (C, H, N, S), H^1 -NMR to obtain hydrogen distribution, and molecular weight measurements (by Vapor Phase Osmometry in THF solvent) were done on each solvent fraction. In addition, the following measurements were made on those fractions which contained nitrogen and oxygen: basic nitrogen (by titration with perchloric acid in acetic acid), acidic hydrogen (by reaction with metallic sodium followed by water addition and back titration with HCl) and exchangeable hydrogen (by integration of H^1 -NMR spectra taken in D_8 -THF after addition of excess D_2O to form HDO by hydrogen exchange). The solvent fractions were also analyzed by GC-MS to identify the major volatile components.

Analysis of the -454 C and +454 C SCT heavy oil product and SCT recycle solvent fractions showed that the SCT heavy oil product hydrogen concentration is not significantly decreased. Thus, it was not extensively studied. The +454 C SCT heavy oil product fractions have higher heteroatom contents and lower H/C ratios.

The aliphatic hydrocarbons are complex mixtures of paraffins, olefins and naphthenes. The aromatic hydrocarbons contain significant quantities of hydroaromatics and alkyl substituted aromatics. The weight percentage of nitrogen decreases with increasing molecular weight. Variations in the sulfur and oxygen concentrations and types in the fractions separated by nitrogen type suggest that the occurrence of heteroarom types is related. The O-containing aromatics which elute during the column chromatography separation procedure are not highly polar; they contain about 62 percent of

their nitrogen in nonbasic forms and 93 percent of their high oxygen content (2-4 atoms/molecule) in non-acidic form.

The average structure of the heptane precipitate (asphaltene) material in the +454 C recycle solvent is made up of an N-containing piece bonded to an O-containing piece both covalently and by a hydrogen bond between a basic nitrogen and a phenolic oxygen. The oxygen in this fraction is >99 percent phenolic. Only the neutral O-containing molecules are eluted in the column chromatographic procedure.

All of the coal liquefaction experiments were done in a micro-autoclave liquefaction apparatus. The product gases were analyzed by GC and the liquids were fractionated by their solubilities in THF, toluene and heptane into IOM plus ash, preasphaltenes, asphaltenes and oils. Yields were calculated and a complete mass balance was done for each experiment.

The effect of time and temperature on the liquefaction of Illinois #6 coal was studied to determine where the yields from the standard conditions used in this program (5 minutes at 427 C) were in the overall liquefaction reaction sequence. Good but not optimum yields were desired. The liquefaction of the heaviest solvent components (heptane insolubles) versus time was also studied. They convert very slowly under the reaction conditions. SCT recycle solvent was found to be a better solvent than the THF soluble portion of the SCT heavy oil product as expected. Liquefaction under hydrogen results in a small net usage of hydrogen while liquefaction under helium usually results in a small net production of hydrogen. Liquefaction under hydrogen also produces a higher conversion to THF solubles and more preasphaltenes and asphaltenes, less oils and more H_2S , CH_4 and C_2H_6 and less CO and CO_2 .

Additional -454 C SCT recycle solvent increases the conversion of coal to THF solubles while the net effect of adding +454 C SCT recycle solvent is to decrease coal conversion to THF solubles. The +454 C aliphatics were a better solvent than the corresponding -454 C fraction but the opposite was true for the aromatic hydrocarbon fraction. All of the hydrocarbon fractions increases the conversion to THF solubles. Neither N-containing or O-containing aromatic fraction increased conversion of coal to THF solubles. The order of conversion of coal to THF solubles for the three separate N-aromatic fractions was secondary > primary >> tertiary.

Recycle solvents undergo many reactions during the liquefaction of coal and many properties are important in determining overall solvent quality. The comparison of coal conversions to THF solubles under hydrogen and helium for a given solvent is a simple method of estimating solvent quality. Measurement of potentially donatable hydrogen by assigning certain regions of the H^1 -NMR spectrum to hydroaromatic hydrogen does not correlate with solvent quality in coal liquefaction. Net hydrogen lost during liquefaction has been used to estimate the extent of hydrogen shuttling by a solvent fraction. A correlation between net hydrogen lost and coal conversion to THF solubles was obtained. Relationships were seen between the types of heteroatoms in the coal derived recycle solvents. Additional study of these relationships may lead to a better understanding of the structures present in these materials.

Among the conflicting properties of higher molecules weight solvent components which can affect their efficiency as liquefaction solvent components are the improved facility for hydrogenation reactions, the lower amount of donatable hydrogen present, the lower vapor pressure at elevated temperature and the possibility that their size has a negative steric effect on their ability to transfer hydrogen. Comparisons of solvent fractions of differing molecular weights gave mixed results. The heavy solvent components which were expected to react primarily by H-transfer (N-aromatics and aromatic hydrocarbons) were less effective, possibly because of steric effects, but the heavy components expected to act only as physical solvents (aliphatic hydrocarbons and O-containing aromatics) were more effective than the corresponding low molecular weight fractions.

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

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INTRODUCTION

During the past few years, it has become widely recognized that there is exceptional solvent value for the direct liquefaction of coal in the high molecular weight material produced in the process.

Solvent molecules can undergo at least three reactions during coal dissolution. Each of these reactions can be done particularly well by the larger molecules present in the heavier part of the solvent. First, the solvent cycles between a hydroaromatic state and an aromatic state. During the hydroaromatic to aromatic conversion, solvent loses hydrogen, transferring it to the coal to stabilize reactive coal fragments. Large aromatic systems require less energy to add a molecule of hydrogen to produce a hydroaromatic system and the large, partially hydrogenated aromatic systems which are formed are able to dehydrogenate readily.

Second, the solvent acts as a physical solvent. Following the rule, "like dissolves like", the largest solvent molecules are most "like" the coal "molecules" and are best able to stabilize them in solution.

Finally, the solvent molecules contain heteroatoms which can form hydrogen bonds with the coal molecules and thus disrupt the hydrogen bonding system of the coal, helping the coal to dissolve. The largest solvent molecules contain more heteroatoms, particularly nitrogen, and the larger aromatic ring systems make the heteroatom electrons more available for hydrogen bond formation.

Recycling the solvent around a loop consisting of coal dissolution, separation and hydrogenation results in an equilibrium composition of recycle solvent. The molecules in equilibrium are those which have precursors in the particular coal being processed, those which are stable enough to survive repeated heating and hydrogenation, and those which have boiling points in the range which is separated into the recycle solvent fraction. Experience by others with the ITSL Process has shown that the equilibrium recycle solvent composition is relatively simple, consisting of a number of major components and groups of related compounds⁽¹⁾. It is this simplicity, and the fact that all of the +343 C soluble material in the process is recycled to the solvent which suggests that this solvent should be ideal for a study of the chemistry of heavy recycle solvent components.

OBJECTIVE

The objective of this program has been to study the chemistry of the components with high boiling points in a direct coal liquefaction recycle solvent and to identify those components which lead to higher overall yields and improved product stability in the initial coal dissolution step of direct coal liquefaction processes.

EXPERIMENTAL APPROACH

The experimental program was divided into four tasks as follows:

Task 1: Separation of Heavy Recycle Solvent Components

Use vacuum distillation and solvent chromatography to separate fractions which contain a predominant component or a mixture of related compounds from ITSL process recycle solvent.

Task 2: Identification of Principal Components

Use elemental analyses, molecular weights and H^1 -NMR spectra of separated, chemically similar fractions to obtain averaged structural information, GC-MS to identify the major components of each fraction and capillary GC to follow the identified components.

Task 3: Coal Liquefaction Studies

Add significant amounts of each major heavy (+454 C) recycle solvent component and the corresponding -454 C fraction separately to -454 C recycle solvent. Do coal liquefaction studies in microautoclaves attached to a wrist action shaker and heated with a fluidized sand bath. Analyze the whole liquefaction product mixture to obtain conversions to preasphaltenes, asphaltenes and oils.

Task 4: Data Correlation and Analysis

Determine the effect of each major chemical type in the +454 C recycle solvent on the conversions to various classes of products. Compare the results obtained with the same -454 C fraction of each chemical type to examine the effects of higher molecular weight.

TASK 1. SEPARATION OF HEAVY RECYCLE SOLVENT COMPONENTS

Coal and Solvents

The coal used in this work was obtained from the Lummus ITSL process pilot plant in New Brunswick, New Jersey. At the time this work was initiated, October of 1982, Illinois No. 6 coal was being processed and both the coal and the solvent were obtained at that time. As shown in Table 1, the coal has been dried to 4 percent moisture and has been ground to approximately 80 percent -200 mesh.

F. K. Schweighardt, in studying data from the Wilsonville coal liquefaction pilot plant, has reported that anomalous gas yields and liquefaction conversions occur when the solvent used to liquefy the coal is not made from the same coal⁽²⁾. The fact that the coal and solvent used in this study are "matched" should minimize gas yields and result in "normal" conversions to THF soluble products.

Two liquid samples were received, SCT recycle solvent (2SCT 16-1122) and SCT heavy oil product (2SCT 16-1122). These liquid samples represent equivalent solvent fractions from before and after the SCT step of the ITSL process.

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

<u>Proximate Analyses, Wt. %</u>	As-Received	Dry
Moisture	3.99	-
Ash	9.72	10.56
<u>Elemental Analyses, Wt. %</u>		
Carbon	69.73	75.78
Hydrogen	4.93	4.88
Nitrogen	1.18	1.28
Sulfur	2.88	3.13
Oxygen (By difference)	7.57	4.37
H/C		0.77
<u>Particle Size Distribution, Wt. %</u>		
+70 mesh	0.07	
-70 +120	3.64	
-120 +200	18.90	
-200 +325	14.84	
-325	62.55	

Vacuum Distillation of Liquid Samples

The SCT heavy oil product was broken up and ground to -6 mesh and then distilled to 427 C. The initial boiling point was approximately 315 C. A second distillation to a slightly higher cut point was also done. The two distillates were combined and the two +427 C fractions were combined.

The SCT recycle solvent was also distilled under vacuum (0.15 - 1.2 mm Hg) to 427 C to obtain equivalent fractions. The results of the vacuum distillations are summarized in Table 2 below.

TABLE 2. SUMMARY OF VACUUM DISTILLATIONS OF LUMMUS ITSL SAMPLES

Sample Description	Wt % -427 C Distillate	Wt % +427 C Residue	Residue % THF Solubility
SCT Recycle Solvent	35.6 ⁽¹⁾	64.4	92.9
SCT Heavy Oil Product	38.2 ^(1,2)	61.8 ⁽²⁾	88.8

(1) Residue in apparatus included with distillate.

(2) Average of results from two distillations.

The 427 C cutpoint was chosen because this appeared to be the highest temperature which could be reached without cracking the solvent significantly. A 454 C cutpoint was preferable for the purpose of comparing the results with the results obtained from the ITSL pilot plant since 454 C was used as the cutpoint in their vacuum flashing process step.

The THF solubilities of the +427 C fractions from both distillations were measured. The results are also listed in Table 2. Since the SCT heavy oil product contained the IOM and ash from liquified Illinois No. 6 coal, the +427 C fraction was dissolved in THF, filtered, and the filter cake was extracted with THF in a Soxhlet extractor to remove THF insolubles. It was assumed that all of the -427 C material was soluble in THF.

Two additional vacuum distillations were done to obtain light and heavy SCT recycle solvent fractions for separation studies. These distillations were cut at 454 C by increasing the vacuum obtainable in the distillation apparatus. The results from these distillations are compared with the previous distillation to 427 C in Table 3 below.

TABLE 3. COMPARISON OF VACUUM DISTILLATIONS OF LUMMUS ITSL RECYCLE SOLVENT (2SCT16-1122)

Maximum Distillation Temp., ° C	Wt % Distillate	Wt % Residue
427	35.6	64.4
454	39.3, 40.8	60.7, 59.2

Approximately 4.5 percent of the total material in the recycle solvent boils between 427 and 454 C. This is a small but significant amount and may increase the applicability of the results of this program research to the Lummus ITSL pilot plant program.

A plot of structure (on a molecular weight scale) versus boiling point for some aromatic hydrocarbons is shown in Figure 1. The 454 C cutpoint is in the four aromatic ring region with all of the three ring aromatic hydrocarbons in the distillate and all of the five ring aromatic hydrocarbons in the residue. Other series, including N-aliphatics, N-containing aromatics and O-containing aromatics are included for comparison. Aliphatics of the same boiling point have much higher molecular weights while typical polar compound types in the same boiling point range have lower average molecular weights. One exception is the furan/benzofuran series which has a similar boiling point/molecular weight ratio to the aromatic hydrocarbons. The SCT recycle solvent distilled to 454 C was used for the separation studies described below.

FIGURE 1. STRUCTURE (MOLECULAR WEIGHT) VERSUS BOILING POINT

Separation of Chemical Types by Liquid Chromatography

The second step in the process of evaluating the effects of heavy recycle solvent components on direct coal liquefaction was separation of the components in the +454 C fraction into chemical classes by liquid chromatography.

The method of Later, et al.⁽³⁾ was used as the starting point for the separations. The method is shown in Figure 2. The first step was scaled up to separate 10 grams of sample/column as follows: A 6 cm diameter by 40 cm long glass chromatography column was built with a fritted glass disk to hold the alumina packing. The column assembly also includes a 4 mm Teflon stopcock to control the liquid flow, an 8 mm solvent reflux line from the top of the column to the joint below the stopcock, a 6 mm liquid level line from about 20 cm above the fritted disk to the joint below the stopcock, and two 24/40 joints, one at the bottom of the column to connect to a receiver and one at the top to attach to a reflux condenser.

The column was packed with Brockman Activity I Neutral Alumina (100 g, 80-200 mesh, Fisher Scientific) in hexane, forming a layer about 3 cm deep. An additional 200 g of the same alumina was mixed with a solution of the recycle solvent (10 grams) in enough THF to dissolve it (100-200 ml) and the THF was then removed using a rotary evaporator. This ratio of sample to alumina ensured that all of the sample would contact the alumina surface as it passed through the column. The coated alumina was dried for at least 24 hours in a vacuum oven at ~100 C to insure that all of the THF was removed. The dried alumina was then passed through a 20 mesh screen to remove any lumps and packed onto the column in hexane. The column was eluted with refluxing hexane to recover aliphatic hydrocarbons until a yellow band was about to elute. This was followed with successive elution with benzene, chloroform and THF/10% ethanol to remove successively: (1) aromatic hydrocarbons and sulfur containing aromatics, (2) nitrogen containing aromatics; and (3) oxygen containing aromatics.

FIGURE 2. SCHEME FOR SEPARATION OF FRACTIONS INTO CHEMICAL CLASSES BY COLUMN CHROMATOGRAPHY

The capacity of the liquid chromatography separation system was increased by using four chromatography columns. In addition, since the THF/ethanol fraction was of limited interest and constitutes approximately 60 percent of the total weight of the +454 C fraction, most of it was removed by first precipitating a solution of the +454 C fraction, dissolved in THF, in boiling heptane. The aliphatic hydrocarbons, aromatic hydrocarbons, and N-containing aromatic hydrocarbons were found to be totally soluble in heptane. This effectively allowed up to 100 g of +454 C recycle solvent sample to be separated per operation of the four liquid chromatography columns. A comparison of the recoveries from early separations of the total +427 C SCT recycle solvent and THF soluble SCT heavy oil product are shown in Table 4 below.

TABLE 4. SEPARATION OF +427 C FRACTIONS BY LIQUID CHROMATOGRAPHY

Solvent/Chemical Class	SCT Recycle Solvent (weight percent)	SCT Heavy Oil Product (weight percent)
Hexane/Aliphatic Hydrocarbons	5.6	1.7
Benzene/Aromatic Hydrocarbons	22.6	27.3
Chloroform/N-Aromatics	7.1	12.0
THF-EtOH/O-Aromatics	<u>26.8</u>	<u>59.0</u>
Total Recovery	62.1	100.0

The majority of the samples are eluted in the THF-EtOH soluble fraction. The larger amounts in the chloroform and THF-EtOH fractions from the SCT heavy oil product reflect the higher concentrations of heteroatoms in this material. Approximately one-quarter of the samples consist of aromatic hydrocarbons. There is a small amount of aliphatic hydrocarbons and 7-12 percent of N-containing aromatics. The most polar components do not elute with these solvents.

In later separations the +454 C recycle solvent fraction was first precipitated in heptane. About 62 percent of the +454 C recycle solvent was insoluble in heptane. The majority of this material was from the noneluted and O-containing aromatic fractions. The heptane solubles were completely eluted from the column as shown in Table 5.

When NMR spectra were taken on the eluted aliphatic hydrocarbon fractions it became clear that significant amounts of aromatics were eluting in hexane with the aliphatic fraction even though the elution was stopped before the first noticeable yellow band was eluted from the column. These materials are hydroaromatics and some alkyl substituted aromatics. Hexane elution fractions were taken at short intervals from both the -454 C and +454 C separations and examined by NMR to determine an optimum time to make the aliphatic/aromatic split. These were determined to be 10 minutes hexane elution time for the -454 C and 30 minutes hexane elution time for the +454 C SCT recycle solvent fractions. The solvent was then changed to benzene to elute the aromatic hydrocarbons. When the optimum hexane elution time (30 minutes) was used with the +454 C fraction only about 1 percent of the total solvent was found to be aliphatic hydrocarbons. The resulting +454 C hexane eluate is pure aliphatic hydrocarbons as shown by NMR. About 27 percent of the +454 C fraction is aromatic hydrocarbons with small amounts of nitrogen-containing aromatics, and the majority of the sample, almost 70 percent, is asphaltenes. The same separation procedure was used on the -454 C fraction. Only about 4 percent of the -454 C recycle solvent was retained on the column. The aliphatic hydrocarbon fraction was also shown to be contaminated with hydroaromatic and alkyl substituted aromatic material by NMR if elution with hexane was carried to completion. When the 10 minute hexane extraction time was used approximately 10 percent of the -454 C recycle solvent was obtained in the aliphatic hydrocarbons. These were contaminated with some hydroaromatics however. The remainder of the sample consisted of about 73 percent aromatic hydrocarbons and small amounts of N-containing aromatics and O-containing aromatics.

TABLE 5. LIQUID CHROMATOGRAPHIC SEPARATION OF SCT
RECYCLE SOLVENT ON NEUTRAL ALUMINA

Component/(Solvent)	-454 C Recycle Solvent		+454 C Heptane Soluble Recycle Solvent		
	Complete Hexane Extraction, Wt %	10 min. Hexane Extraction	Total +454 C Recycle Solvent	Complete Hexane Extraction	30 min. Hexane Extraction
Aliphatic hydrocarbons/ (Hexane)	60.2	9.6	4.9	5.6	1.3
Aromatic hydrocarbons/ (Benzene)	22.0	72.9	27.9	22.9	27.0
N-Containing aromatics/ (Chloroform)	5.6		4.8	4.4	
O-Containing aromatics/ (THF/10% EtOH)	8.4		33.3	7.7	
Heptane insolubles	-		-	61.7	
TOTAL RECOVERY	96.2		70.9	102.3	

Separation of the N-Containing Aromatic Fraction into Fractions by Nitrogen Type

The second step in the separation procedure consists of separation of the N-aromatic fraction on silicic acid (-100 mesh $\text{SiO}_2 \times \text{H}_2\text{O}$, Mallinkrodt Analytical AR^{TM} Reagent) which is partially deactivated by the addition of 3 weight percent deionized water to the silicic acid before it is coated with the N-aromatic fraction. The N-aromatic fraction eluted from the previous column with chloroform was isolated by removing the chloroform on a rotary evaporator and drying in a vacuum oven. This fraction was dissolved in THF and coated onto the deactivated silicic acid (7.2 g N-aromatic/215 g silicic acid· H_2O) and a rotary evaporator was used to remove most of the THF. Final removal of THF was done by drying the coated material in a vacuum oven at 65 C overnight.

The method of Later et al.⁽⁴⁾ describes the elution of secondary nitrogen compounds (pyrroles and carbazoles, etc.) with 1:1 hexane-benzene, the elution of an enriched fraction of primary nitrogen compounds (primary amines, etc.) with benzene, and finally the elution of tertiary nitrogen compounds (pyridines, etc.) with 1:1 diethylether-benzene. However, this procedure was used on a very small scale employing only 0.5 g of coated silicic acid. For the large scale separation of these fractions it was desirable to use single component solvents for each fraction so that the solvents could be recycled by refluxing and the extraction could be run continuously.

A comparison of solvent properties, shown in Table 6, suggested that carbon tetrachloride and chloroform might be substituted for 1:1 hexane-benzene and 1:1 diethyl ether, respectively, in the separation procedure.

TABLE 6. COMPARISON OF THE SOLVENT PROPERTIES OF SINGLE AND TWO-COMPONENT SOLVENTS FOR SEPARATION OF THE N-AROMATIC FRACTION

Solvent	Polarity	Elutrophic Value	Dipole Moment	Dielectric Constant
1:1 Benzene-hexane ⁽¹⁾	1.4	0.16	0.04	2.08
Carbon tetrachloride	1.6	0.18	0.00	2.24
Benzene	2.7	0.32	0.00	2.27
1:1 Benzene-ether ⁽¹⁾	2.75	0.35	0.57	3.30
Chloroform	4.1	0.40	1.15	4.81

(1) Averaged values for each single-component solvent were used to calculate the solvent properties of the two-component solvents.

Carbon tetrachloride seemed to work well, although no extensive determination of purity of the resulting nitrogen compound types in each fraction has been attempted. However, since chloroform and benzene-ether did not remove all of the material from the column, increasingly polar solvents were used for the final elution, going from benzene-ether in the first run, to chloroform followed by THF in the second, and then to acetone followed by 1:1 THF-methanol, which required only one column volume to elute everything remaining on the column in the third run. The fractions obtained by the double elutions with separate strong solvents were combined from the second and third runs before analysis, as were the secondary-N fractions from the three runs and the three primary-N fractions. Recoveries of material from each of the three runs are shown in Table 7 below.

TABLE 7. RECOVERIES OF N-AROMATIC FRACTIONS, WT %

N-Aromatic Type	Secondary	Primary	Tertiary	Total
Run No.				
1	28.0	13.2	42.4	83.6
2	22.1	25.3	{ 8.4 (CHCl ₃) 21.3 (THF)	77.1
3	19.2	NM	~21.9 { (Acetone) 1:1 (THF/MeOH)	-

This qualitative data indicate that 20-30 percent of the N-aromatic fraction is secondary nitrogen (acidic) and that 20-40 percent is tertiary nitrogen (basic). The remaining material (30-60 percent) is in the primary nitrogen fraction. However, Later, et al.⁽⁵⁾ have shown that this fraction contains significant quantities of tertiary nitrogen compounds, primarily those in which the nitrogen is sterically "protected" In an SRC II fraction, they reported that derivatization with trifluoroacetyl anhydride showed that only about 15 percent of the material in this fraction was actually primary amines. The amount of primary amines in the fraction obtained in this work is unknown.

The recoveries are typical of such experiments. Later, et al.⁽⁶⁾ reported that recoveries of a series of amino PAH standard compounds ranged from 39-74 percent from the silicic acid chromatography step. The recoveries may be enhanced by partial deactivation of the silicic acid⁽⁷⁾.

In addition to the three rough cuts of N-containing aromatic types, it would also be highly desirable to obtain the hydroaromatic fraction using another method described by Wozniak, et al.⁽³⁾, however, this was not possible within the limits of time and funds available for this project. This and other fractions which exclude the polar materials which predominate in the recycle solvent heavy ends, such as the heptane insolubles, would make interesting heavy solvent fractions to test with the -454 C solvent in future liquefaction experiments.

TASK 2. IDENTIFICATION OF PRINCIPAL SOLVENT COMPONENTS

The purpose of this task was to characterize the various solvent fractions so that their liquefaction behavior could be correlated with their chemical structures.

First, the solvents and the separated fractions were characterized by measuring molecular weight (by Vapor Phase Osmometry using THF as the solvent), elemental analyses and H^1 -NMR. These data were used to obtain average structural parameters by application of the Brown-Ladner equations^(9,10).

Second, GC-MS analyses were done on each fraction to identify the major components. A heated vaporizer was used rather than on-column injection to avoid fouling the capillary column, since the components were not expected to be completely volatile. Non-volatile losses were significant and were measured by comparing total GC detected counts to the weight of sample injected for each fraction, using the -454 C aromatic hydrocarbons as a standard. The results are listed in Table 8 below. More complete results could be obtained for the polar fractions by using supercritical liquid chromatography-mass spectrometry as reported by Smith and coworkers at the Washington National ACS Meeting⁽¹⁰⁾.

TABLE 8. PERCENTAGES OF VOLATILE MATERIAL IN EACH RECYCLE SOLVENT FRACTION

Fraction	-454 C	+454 C
Aliphatic hydrocarbons	110	88
Aromatic hydrocarbons	(100)	79
N-Containing aromatics	67	16
O-Containing aromatics	63	1

The FID detector is more sensitive to aliphatic than aromatic hydrocarbons accounting for the > 100 percent value for the -454 C aliphatic hydrocarbon fraction. Part of the losses noted for the +454 C fractions occurred because they were not eluted completely with the time-temperature program used on the GC-MS. This is apparent in some of the figures which follow.

Finally, various methods were used to measure acidic and basic functional groups in the separated solvent fractions. These included basic N titration using perchloric acid in acetic acid⁽¹¹⁾, acidic hydrogen titration using the method of Sternberg⁽¹²⁾, and estimation of exchangeable hydrogen by NMR.

The latter two techniques required some development to make them applicable to the heavy coal-derived liquids used in this work.

Titration of Acidic Hydrogen

As described by Sternberg, this method consists of dissolving carefully weighed sample in toluene, refluxing in the presence of an excess of metallic sodium, removal of the sodium by filtration, the addition of water to react with the sodium to form NaOH and titration with standardized 0.1N aqueous HCl. However, the heavy N-containing and O-containing aromatic samples are not completely soluble in toluene. They were, therefore, dissolved in THF. A blank THF sample was found to not react significantly with metallic sodium followed by water addition and titration with HCl. The blank did show two small breaks in the titration curve which may have been due to impurities such as H₂O in the THF.

Toluene (Bp 111C) has a much higher boiling than THF (Bp 64 C). When the reaction was done in THF with phenol or m-cresol used a standard, it was found that sodium reacted very slowly. Refluxing times of 8 hours were required to insure that complete reaction was obtained at the lower reflux temperature. For example, with phenol only 68% of the theoretical amount of acidic hydrogen was obtained by refluxing for 90 minutes in THF.

As many as three breaks occur when a complex mixture such as the recycle solvent was analyzed using this technique. An attempt to identify these breaks using a series of oxygen-containing and nitrogen-containing model compounds showed that the first and third breaks also occur with a THF blank. The first blank has been subtracted from the results reported below. These model compound titrations also showed that only secondary nitrogen and phenolic oxygen reacted completely under these conditions. It does not appear possible to assign one break in the titration curve to acidic oxygen and the other to acidic nitrogen.

The results of the model compound titrations are listed in Table 9 below.

TABLE 9. TITRATION OF MODEL COMPOUNDS FOR ACIDIC HYDROGEN

Compound	Acidic Hydrogen, % of Theoretical(1)
Piperidine	109
M-Cresol	103
1-Naphthol	102
1-Cyano-naphthalene	44
Quinoline	9
Indole	8
Aniline	2
THF	0.005

(1) Uncorrected for THF blank

The model compounds were unpurified samples. Each was dissolved in THF (~ 0.2 g/100 ml THF) and refluxed for 8 hours in an apparatus protected from moisture. After filtration to remove excess sodium, water (1 ml) was added and the sample was titrated automatically using 0.1 N HCl while pH vs. ml acid added was continuously recorded on a strip chart.

Partial hydrolysis of cyano-naphthalene may have occurred during storage or during the reaction. Primary and tertiary nitrogen and ether oxygen are not acidic as expected. The data, which will be discussed later, are probably only accurate enough to indicate trends.

Measurement of Exchangeable Hydrogen by NMR

This technique consists of taking the H^1 -NMR spectrum of a solvent fraction dissolved in D_8 -THF and then adding a drop of D_2O . The D_2O , in great excess, exchanges with the exchangeable hydrogen in the dissolved solvent fraction and the resulting HDO peak is seen in the H^1 -NMR spectrum at 3.4-3.6 ppm.

The spectrum is integrated to measure the amount of exchangeable hydrogen. In addition, comparison of the H^1 -NMR spectra before and after D_2O addition clearly shows where the exchangeable hydrogen was located in the solvent molecule.

This method has only been tried on a few samples and no controls have been run but it appears that there is much more exchangeable hydrogen than can be accounted for by phenolic or acidic nitrogen species and that the majority of the exchange is taking place on hydrogens attached to carbon in the range of 2.0 - 3.4 ppm in the NMR. These are hydrogens α to an aromatic ring and are expected to be readily lost when hydrogen is transferred to the dissolving coal during liquifaction. However, it is surprising that they are exchangeable at room temperature with D_2O .

The two results which have been obtained are listed in Table 10 below. A comparison of the H^1 -NMR spectra of the +454 C primary N-containing aromatic fraction before and after the addition of D_2O is shown in Figure 3.

TABLE 10. CHANGES IN THE H^1 -NMR SPECTRA DUE TO EXCHANGE OF LABILE HYDROGEN WITH D_2O

Sample	Before D_2O Addition			After D_2O Addition		
	Aliphatic	Aromatic	OH(1,2)	Aliphatic	Aromatic	Exchangeable(3)
+454 C Recycle Solvent	64.7	33.3	2.0	51.1	24.5	24.5
+454 Primary N- containing Aromatic	60.9	36.6	2.5	65.1	26.5	8.4

(1) Assuming all oxygen is phenolic and that OH appears in the aromatic H region (> 5 ppm).

(2) Integrated by the "cut and weigh" technique.

(3) Integrated by machine

This technique is interesting but requires further development before its value can be accurately assessed.

FIGURE 3. ^1H -NMR SPECTRA OF +454 C PRIMARY N-CONTAINING AROMATIC FRACTION IN D_8 -THF BEFORE AND AFTER ADDITION OF D_2O

Analyses of Distillates and Residues

Analyses of the as-received Lummus samples and the -427 C and +427 C fractions are listed in Table 11. They include elemental analyses, molecular weight measurements by Vapor Phase Osmometry in THF solution and H^1 -NMR analyses. From these data molecular formulas and aromaticities have been calculated. These fractions have boiling point ranges which are too large to obtain useful results from application of the Brown-Ladner equations

The low molecular weight of the +427 C fraction of the SCT Recycle Solvent may be due to cracking during distillation. The H/C ratio is about 0.84 for each +427 C fraction and about 0.94 for each -427 C fraction. The aromaticities and H/C ratios suggest that the heavy oil product is not depleted in hydrogen compared to the recycle solvent. Since the primary purpose of obtaining the SCT heavy oil product was intended to be measurement of the effect of hydrogen depletion in the solvent on the SCT liquifaction step, the SCT heavy oil product was not extensively used in subsequent liquifaction experiments.

Analyses of the SCT recycle solvent shows that this material, which is hydrotreated +343 C material obtained from the process, contains about 1.3 percent ash as received. The +427 C material comprises 65 weight percent of the total, but contains 80 percent of the nitrogen, 84 percent of the sulfur, and 76 percent of the oxygen.

The analytical results for the separated SCT recycle solvent fractions are summarized in Table 12 except for the GC-MS results which are listed separately for each fraction. The SCT heavy oil product was not characterized further.

GC-MS Analysis Procedure

Samples analyzed by GC-MS were diluted using benzene or, for the high-polarity fractions eluted with THF/ethanol, ~ 9:1 benzene:pyridine. The benzene soluble samples were diluted to concentrations of 4 mg/ml (residue basis). The THF soluble fractions required dilution to 2-3 mg/ml due to their lower solubilities. The +454 C benzene fractions required additional dilution to 0.8 mg/ml to avoid mass spectrometer signal saturation. Solvent

TABLE 11. SUMMARY OF ANALYTICAL RESULTS ON LUMMUS ITS-L
LIQUID SAMPLES AND DISTILLATION FRACTIONS

Sample	SCT Recycle Solvent					SCT Heavy Oil Product				
	Total	MAF	-427 C	+427 C	MAF	Total	MAF	-427 C	+427 C	MAF
Elemental Analyses, Wt %										
Ash	1.30	-	< 0.01	2.00	-	3.61	-	< 0.01	0.88	-
Carbon	86.77	87.91	90.96	87.88	89.67	85.87	89.09	90.64	87.46	88.24
Hydrogen	6.88	6.97	7.12	6.18	6.31	5.74	5.95	7.01	6.14	6.19
Nitrogen	0.94	0.95	0.57	1.30	1.33	1.02	1.06	0.56	1.46	1.47
Basic N			0.21	0.60						
Non-basic N (diff)			0.36	0.70						
Sulfur	0.53	0.54	0.23	0.69	0.70	0.99	1.03	0.23	0.89	0.90
Oxygen (difference)	3.58	3.63	1.12	1.95	1.99	2.77	2.87	1.56	3.17	3.20
Molecular Weight, grams/mole	477		257	456		424		257	472	
Hydrogen distribution, % of total hydrogen										
Aliphatic			33.1		16.5			27.0		15.2
Aliphatic α to aromatic			43.0		48.2			39.9		53.1
Aromatic ⁽¹⁾			22.9		33.3			31.7		28.5
Phenolic ⁽²⁾			1.0		2.0			1.4		3.2
Exchangeable H ⁽³⁾			0.62	3.5						
fa, aromaticity			0.64		0.73			0.69		0.71
Molecular Formula, (MAF)										
C		35.4	19.5		34.8		32.7	19.4		35.0
H		33.7	18.3		29.4		26.2	13.0		29.5
N		0.3	0.1		0.4		0.3	0.1		0.5
S		0.08	0.02		0.1		0.1	0.02		0.1
O		1.1	0.2		0.6		0.8	0.3		1.0
H/C		0.95	0.94		0.84		0.80	0.93		0.84

(1) Corrected for phenolic

(2) Assumes all oxygen is phenolic

(3) Measured by D₂O addition and integration of
H¹-NMR spectrum taken in D₈-THF

TABLE 12. ANALYSES OF -454 C AND +454 C RECYCLE SOLVENT FRACTIONS SEPARATED BY COLUMN CHROMATOGRAPHY

Fraction Temp Solvent	Aliphatic Hydrocarbons		Aromatic Hydrocarbons		N-Aromatics		+454 C N-Aromatic Fractions			OH-Aromatics		Heptane	Precipitate
	-454 C Hexane	+454 C	-454 C Benzene	+454 C	-454 C Chloroform	+454 C	Secondary-N Carbon Tetrachloride	Primary-N Benzene	Tertiary-N Chloroform	-454 C THF/Ethanol	+454 C		
Elemental Analyses, wt % MAF													MAF
Carbon	89.03	87.26	92.40	93.18	36.30	87.14	38.83	88.12	36.89	76.50	73.02	84.00	86.74
Hydrogen	10.97	12.70	7.59	6.58	6.32	6.51	7.05	6.33	7.05	7.20	7.21	5.54	5.72
Nitrogen	0.00	0.00	0.00	0.00	4.41	2.47	1.64	2.53	2.03	1.86	1.37	1.86	1.92
Sulfur	0.00	0.00	0.00	0.00	0.56	0.57	0.29	0.44	1.07	1.02	0.58	1.02	1.05
Oxygen (diff.)	0.00	0.00	0.00	0.00	1.85	3.31	2.19	2.58	2.96	13.42	17.82	4.43	4.57
H/C	1.48	1.75	0.99	0.84	0.95	0.90	0.95	0.86	0.97	1.13	1.18	0.79	
Molecular Weight, g/mole	289	352	247	300	230	347	398		381	396	217	325	836
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	20.8
Aliphatic α to aromatic	22.0	0.0	41.0	35.4	42.5	30.8	28.2		29.8	35.0	45.5	54.4	44.0
Aromatic (1)	3.8	0.0	28.0	38.7	35.3	42.8	35.1		36.6	35.6	16.0	5.6	32.9
Phenolic (2)	0.0	0.0	0.0	0.0	1.7	3.2	1.9		2.5	2.6	11.7	15.9	2.2
Exchangeable H(3)									8.4				
Structural Parameters (4)													
f_a - aromaticity	0.29 ⁵⁾	-	0.65	0.74	0.70	0.76	0.70		0.77	0.70	0.58	0.54	0.74
R_A - number of aromatic rings	-	-	2.6	4.1	2.4	4.0	4.4		5.1	3.6	1.	1.	9.5
H_{aro}/C_{aro} - substitutable aromatic	-	-	0.74	0.65	0.76	0.69	0.67		0.60	0.74	1.	1.	0.62
edge atoms/total aromatic atoms	-	-	-	-	-	-	-		-	-	-	-	-
σ - fraction aromatic edge atoms substituted	-	-	0.42	0.31	0.41	0.32	0.33		0.34	0.28	0.57	0.67	0.46
C_A - total no. aromatic C atoms	-	-	12.3	17.2	11.6	19.0	20.6		20.7	20.1	8.0	10.5	44.7
R_S - substituted aromatic ring carbons	-	-	3.9	3.5	3.6	4.2	4.6		4.2	4.2	4.6	7.0	12.7
n - carbon atoms/saturated substituent	-	-	1.8	1.7	1.5	1.8	2.2		2.0	1.8	1.6	1.5	1.5
Molecular Formula													
C	21	26	19	23	17	25	29		28	29	14	20	60
H	32	45	19	20	16	23	28		24	28	16	23	48
N					0.7	0.6	0.5		0.7	0.6	0.3	0.3	1.1
S					0.04	0.06	0.04		0.05	0.13	0.07	0.06	0.3
O					0.3	0.7	0.2		0.6	0.7	1.8	3.6	2.4
Nitrogen types, wt % MAF													
Basic nitrogen					2.08	0.84	0.09		0.52	1.58	0.69	0.54	1.06
Non-basic nitrogen (diff.)					2.33	1.63	1.55		2.01	0.45	1.17	0.83	0.86
Acidic hydrogen, % of total hydrogen					0.0	1.3	0.21		0.76	2.9	1.8	1.5	0.20

(1) Corrected for phenolic hydrogen

(2) Assumes all oxygen is phenolic

(3) Measured by addition of D₂O and reintegration of H¹-NMR spectrum in D₈-THF

(4) From application of Brown-Ladner parameters to NMR data

(5) Aliphatics contaminated with some aromatics

blank samples were analyzed by GC-MS along with the oil fractions to assure that the dilution procedure introduced no artifacts to the analyzed sample aliquots.

A Finnigan 3200 quadrupole MS interfaced to a Carlo Erba 4160 GC via the direct introduction of the GC column outlet into the MS ion source was used for this work. The GC column was a Brotde made, wide bore (0.31 mm ID) 30-meter pyrex glass column equipped with 5-m retention gaps at both the inlet and outlet. The stationary phase was immobilized SE-54 (film thickness $\sim 0.15\mu$). The GC carrier gas was helium with a flow velocity of ~ 40 cm/sec. Sample aliquots (0.1 or 2.0 ml) were injected via the Carlo Erba cold on-column injector. The GC program was: 70 C for 2-min; 70 C to 290 C at 4 C/min; hold at 290 C for 10 to 30 min. The mass range (40 to 350 amu) was scanned with a cycling time of 1.0 sec and a Finnigan INCOS MS data system was used for data processing. Sample components were identified on the basis of their mass spectra and GC retention times. In addition, the data was examined for the presence of heterocyclic species and their related alkylated homologues using computer software provided by the INCOS data system. All GC-MS data were archived on 9-track magnetic tape.

Characterization of Aliphatic Hydrocarbons

The Brown-Ladner equations do not give very useful results with aliphatic hydrocarbon fractions. The -454 C fraction has an average molecular structure of $C_{24}H_{32}$ and the +454 C fraction has an average molecular formula of $C_{26}H_{45}$. The -454 C aliphatic fraction is contaminated with approximately 36 percent hydroaromatic material and has an H/C ratio of only 1.48.

The percentage of aromatics was calculated by assuming that the H/C ratios are 1.0 and 1.75 for the aromatic and aliphatic components, respectively. Tetralin has an H/C ratio of 1.2. The +454 C fraction contains no aromatics (confirmed by NMR) and has an H/C ratio of 1.75.

GC-MS analysis shows that both aliphatic hydrocarbon fractions are very complex mixtures of paraffins, olefins and naphthenes (Figures 4 and 5). In Figure 5, the incomplete elution of the +454 C fraction is clearly shown. No specific structural assignments were made by GC-MS for these fractions.

FIGURE 4. GC-MS CHROMATOGRAPH OF -454 C RECYCLE SOLVENT FRACTION ELUTED FROM NEUTRAL ALUMINA BY HEXANE (ALIPHATICS)

FIGURE 5. GC-MS CHROMATOGRAM OF +454 °C RECYCLE SOLVENT FRACTION ELUTED FROM NEUTRAL ALUMINA WITH HEXANE (ALIPHATICS)

Characterization of Aromatic Hydrocarbons

Average structures of the -454 C and +454 C aromatic hydrocarbon fractions are shown in Figure 6. The molecular formula of the -454 C fraction is $C_{19}H_{19}$ and is $C_{23}H_{20}$ for the +454 C fraction. The aromaticities (f_a) are low for both fractions because they are hydrogenated materials and there are significant amounts of hydroaromatic materials present. The average number of aromatic rings is about 2.6 for the -454 C fraction and 4.1 for the +454 C fraction. The number of carbons per saturated substituent on each aromatic ring averages in the range of 1.5 - 2.6 carbons for every solvent fraction. These are probably present as 5 and 6 carbon saturated rings since NMR shows no obvious CH_3 groups α or β to aromatic rings. In the Brown-Ladner nomenclature a five membered ring would contain 1.5 carbons/saturated substituent and a six membered ring would contain 2.0 carbons/saturated substituent. GC-MS shows that the -454 C fraction contains large concentrations of pyrene, fluoranthene, chrysene, and benzanthracene, as well as methyl and hydrogenated derivatives (Figure 7, Table 13). The +454 C fraction contains significant quantities of benzpyrene, dimethylchrysene, perylene, and benzfluoranthene (Figure 8, Table 14).

Characterization of N-Containing Aromatics

The average structures for the nitrogen-containing aromatic fractions are shown in Figure 9. These materials have higher aromaticities and the +454 C fraction has a significantly higher molecular weight than the corresponding aromatic hydrocarbons. This cannot be due to the concentration of nitrogen in the heavier ends (discussed below). The more polar nitrogen containing materials would normally be expected to have lower molecular weights than the corresponding aromatic hydrocarbons within the same boiling point fraction (Figure 1). The -454 C material was shown by GC-MS to contain significant amounts of benzcarbazole and azapyrene, as well as hydrogenated derivatives (Figure 10, Table 15). The +454 C material contains significant amounts of azabenzpyrene, azaperylene, and methylbenzacridene as well as the usual methyl and hydrogenated derivatives (Figure 11, Table 16). When the nitrogen-containing aromatic fractions were analyzed by gas chromatography and the effluent was split into FID and nitrogen-specific detectors almost every molecule was shown

-454 C
FA=.65
MW=247

+454 C
FA=.74
MW=300

FIGURE 6. AVERAGE STRUCTURES OF AROMATIC HYDROCARBON FRACTIONS

FIGURE 7. GC-MS CHROMATOGRAM OF -454 C RECYCLE SOLVENT ELUTED FROM NEUTRAL ALUMINA WITH BENZENE (AROMATIC HYDROCARBONS)

FIGURE 8. GC-MS CHROMATOGRAM OF +454 C RECYCLE SOLVENT ELUTED FROM NEUTRAL ALUMINA WITH BENZENE (AROMATIC HYDROCARBONS)

-454 C
 FA = .70
 MW = 230

+454 C
 FA = .76
 MW = 347

32

FIGURE 9. AVERAGE STRUCTURES FOR N-CONTAINING AROMATIC FRACTIONS

TABLE 13. GC-MS IDENTIFICATION OF COMPOUNDS IN
-454 C AROMATIC HYDROCARBON FRACTION

Compound Number	Compound Name
1	Fluoranthene
2	Pyrene
3-5	Methylpyrene/fluoranthene
6	Dimethylpyrene/fluoranthene
7-8	Tetrahydrochrysene
9-11	Chrysene/benzanthracenes
12	Butylpyrene (?)
13	Methylchrysene/benzanthracene

TABLE 14. GC-MS IDENTIFICATION OF COMPOUNDS IN THE
+454 C AROMATIC HYDROCARBON FRACTION

Compound Number	Compound Name
1	Methylchrysene/benzanthracene
2-3	Dimethylchrysene (?)
4	Benzpyrene/fluoranthene
5	Dimethylchrysene (?)
6-8	Benzpyrene/perylene/benzfluoranthene
9	Methylbenzpyrene
10	Unknown
11	Indinopyrene/benzperylene

FIGURE 10. GC-MS CHROMATOGRAM OF -454 C RECYCLE SOLVENT ELUTED FROM NEUTRAL ALUMINA WITH CHLOROFORM (N-CONTAINING AROMATICS)

FIGURE 11. GC-MS CHROMATOGRAM OF +454 C RECYCLE SOLVENT ELUTED FROM NEUTRAL ALUMINA WITH CHLOROFORM (N-CONTAINING AROMATICS)

TABLE 15. GC-MS IDENTIFICATION OF COMPOUNDS IN
+454 C N-AROMATICS FRACTION

Compound Number	Compound Name
1	Acridine
2	Phenanthridine
3	Carbazole
4a-d	Methylcarbazoles
5	5-Azafluoranthene
6	7-Azafluoranthene
7	Azapyrene
8	Benzo(def)carbazole
9-10	C ₄ -Carbazoles
11-12a,b	Tetrahydrobenzcarbazoles
13	Benz(a)carbazole
14	Benz(c)carbazole
15	Benz(b)carbazole
16	Diethylphthalate (artifact)
17a-c	Methylbenzcarbazoles
18	Azabenzpyrene

TABLE 16. GC-MS IDENTIFICATION OF COMPOUNDS IN
+454 C N-AROMATIC FRACTION

Compound Number	Compound Name (Relative Amounts)
1	Tetrahydrobenzcarbazole (1) Tetrahydroazachrysene or (2) Tetrahydrobenzacridine
2	Azachrysene (4) Tetrahydrobenzcarbazole (1)
3	Benz(a)carbazole
4	Benz(c)carbazole
5	Benz(b)carbazole
6a-c	Methylbenzcarbazoles
7	Methylbenzacridine
8	Benzpyrene
9	Tetrahydrobenzpyrene/perylene
10	Perylene + methylbenzacridine
11-12	Azabenzpyrene/perylene
13	Dimethylbenzacridine (1) Benzobenz(def)carbazole (2)
14	Dimethylbenzacridine
15	Methylbenzobenz(def)carbazole
16	Dibenzcarbazole
17	Dibenzacridine (2) Dibenzcarbazole (1)
18	Benzperylene Indinopyrene
19	Dibenzcarbazole
20	Dibenzcarbazole (1) Unknown (1)

to contain a nitrogen atom. In addition, the molecular formula indicates that the +454 C material also contains an average of one oxygen atom per molecule.

The nitrogen in the -454 C fraction consists of 47 percent basic (tertiary) nitrogen and 53 nonbasic nitrogen. The heavier, +454 C fraction contains less total nitrogen, only 56 percent of the nitrogen concentration in the lighter fraction. This suggests that the nitrogen concentration does not increase as fast as the carbon number so that the N/C ratio drops with increasing molecular weight. The heavier asphaltene fraction contains even less nitrogen, only 44 percent of the concentration in the -454 C fraction. The nitrogen in the +454 C fraction consists of 34 percent basic nitrogen and 66 percent nonbasic nitrogen. The nitrogen in the asphaltene fraction is 55 percent basic nitrogen and 45 percent nonbasic. It appears that nitrogen types also shift with increasing molecular weight. Previous studies have indicated that the basic nitrogen titration technique gives accurate and reproducible data⁽¹³⁾. These are probably the best of the functional group analyses reported.

The acidic hydrogen titration results indicate that more of the nonbasic nitrogen and oxygen is acidic in the heavier +454 C N-aromatic fraction.

Characterization of N-Aromatic Fractions

The separation of the +454 C nitrogen containing aromatics into fractions by nitrogen type has resulted in some interesting observations even though the purity by nitrogen type is not optimized. One indication of N-purity can be seen in the basic/nonbasic N ratios measured for the three fractions. The 2°-N fraction is 95 percent acidic as expected, but the 1°-N fraction is only 79 percent nonbasic and the 3°-N fraction is only 78 percent basic. Thus, these two fractions are not one nitrogen type. All three fractions have nearly the same number average molecular weight, suggesting that there is little variation of nitrogen type with increasing molecular weight in the +454 C fraction. All of the fractions also have similar aromaticities, although the 1°-N fraction has the highest aromaticity (0.77) and lowest H/C ratio (0.86). The nitrogen content varies from a low of 1.64 percent in the 2°-N fraction to 2.53 in the 1°-N fraction. The 2°-N fraction contains less than 0.5 oxygen per molecule and barely 0.5 nitrogen per molecule. This suggests that it may be contaminated with some hydrocarbon material resulting from incomplete extraction with benzene in the previous step of the separation procedure. The 1°-N and 3°-N fractions both contain more than 0.5 atoms of oxygen per molecule but this oxygen is 95 percent acidic (phenolic) in the 3°-N fraction and the 1°-N fraction contains no acidic oxygen (the oxygen is probably in an ether linkage). The sulfur percentages range from 0.29 weight percent in the 2°-N fraction to 1.07 weight percent in the 3°-N fraction, a factor of 3.7. Apparently, the sulfur and oxygen concentrations and perhaps types in each nitrogen containing fraction are related to nitrogen type.

The NMR data gave very similar results for each fraction. Average structures for each fraction are shown in Figure 12. The 1°-N fraction requires the largest number of condensed rings, while the 2°-N fraction is more "open". The biggest differences, however, are in the types of nitrogen and oxygen shown in each structure.

This work was done late in the program so no GC-MS analyses were done on the separated fractions.

FIGURE 12. AVERAGE STRUCTURES FOR +454 C RECYCLE SOLVENT NITROGEN CONTAINING AROMATICS

Characterization of O-Containing Aromatics

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. Most of this oxygen was originally thought to be phenolic. However, if it is assumed that the ratio of 2°-N/1°-N in the non-basic N is about 4/1, then this information combined with the amount of acidic N plus O present, as measured by acidic H titration, presents a very different picture and suggests that very nearly 100 percent of the oxygen in both of the O-containing aromatic fractions is nonacidic. (It is probably in the form of substituted benzofurans.) This calculation also assumes that no hydrogen bonded to carbon is "acidic". Based on the preliminary data for hydrogen exchange with D₂O by NMR this may be a very poor assumption.

When the heteroatom characterization results are taken into account, the average structures for the two "light asphaltene" fractions (Figure 13) appear to be very different from the hydroxyl containing structures presented previously (Figure 14). The nitrogen in both the -454 C and +454 C fractions is about 62 percent nonbasic.

Most (63 percent) of the -454 C fraction eluted from the GC-MS (Figure 15), but, because the material contains many functional groups and is highly substituted, it was difficult to assign definite structures to any of the peaks. (The largest peak in Figure 15 is an artifact, not a solvent component.) Almost none (1 percent) of the +454 C fraction eluted from the GC-MS. It may be possible to improve the volatility and decrease the polarity of these materials by derivatizing the polar functionality before attempting to separate the material on the GC-MS. This technique would also allow the ether/hydroxyl oxygen ratio to be measured more accurately. As mentioned earlier, another technique for analyzing these materials would be LC-MS, as reported by Smith, et al. at Pacific Northwest Laboratory⁽¹¹⁾.

-454 C
Fa=.58
MW=217

+454 C
Fa=.54
MW=325

FIGURE 13. AVERAGE STRUCTURES (ETHERIC) FOR O-CONTAINING AROMATIC FRACTIONS.

-454 C
FA = .58
MW = 217

+454 C
FA = .54
MW = 325

FIGURE 14. AVERAGE STRUCTURE (PHENOLIC) FOR O-CONTAINING AROMATIC FRACTIONS

FIGURE 15. GC-MS CHROMATOGRAPH OF -454 C RECYCLE SOLVENT ELUTED FROM NEUTRAL ALUMINA WITH THF/10 PERCENT ETHANOL (O-CONTAINING AROMATICS)

Characterization of Heptane Precipitate (Asphaltenes)

An average structure for the asphaltene (heptane precipitate) fraction of the +454 C recycle solvent is shown in Figure 16, again based on molecular weight, elemental analyses and H^1 -NMR data. This structure is the combination of a relatively large N-containing molecule and a smaller, highly substituted O-containing molecule, such as those based on the average structures in the +454 C recycle solvent N-containing and O-containing fractions, combined by a covalent CH_2 linkage and a hydrogen bond between a phenolic hydrogen and a basic nitrogen.

The average structural parameters show that the aromaticity is similar to that for the N-containing fraction. The H/C ratio is lower because there are more condensed aromatic rings in this high molecular weight fraction. The substituent length is similar to all of the other fractions. The elemental analysis shows one nitrogen and two oxygen atoms per molecule. H^1 -NMR data clearly show that one oxygen is a hydrogen bonded phenol. This hydroxyl proton has a very low chemical shift (10.9 ppm). The H^1 -NMR spectra of the O-containing and N-containing fractions did not show this indication of hydrogen bonding. An analysis of the acidic and basic functional groups suggests that all of the oxygen in the asphaltene fraction is non-acidic in contrast with the NMR results. This will require further study to resolve. It is clear that in the separation procedure, only the nonpolar ether-containing fraction can be eluted under the separation conditions which were used. The Oh-containing material was retained on the column.

No GC-MS analyses were attempted.

FIGURE 16. AVERAGE STRUCTURE FOR THE +454 C RECYCLE SOLVENT
HEPTANE INSOLUBLE FRACTION (ASPHALTENES)

TASK 3 - COAL LIQUEFACTION STUDIES

Description of Microautoclave Liquefaction Apparatus

All of the coal liquefaction studies were done in microautoclaves. The microautoclave design as well as the heating and mixing facilities were based on information provided by Bruce Utz of the Pittsburgh Energy Technology Center. A diagram of the microautoclave is shown in Figure 17. It consists of a 3/4-inch union-tee microreactor which has a volume of 22.4 cc. The microautoclave assembly consists of 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. A 3/8-inch ball bearing is added to facilitate mixing. The microautoclave is heated in a sand bath and shaken horizontally. The heat input to the sand bath is regulated with a Leeds & Northrup Series 60 Controller which proportions the amount of current to all four heaters in the sand bath. The sand bath temperature is measured with a 1/8-inch diameter, steel sheath chromel-alumel thermocouple immersed 6" into the center of the bath and insulated from temperature fluctuations with a 1/4-" OD x 1" long piece of stainless steel at the couple. In most cases the sand bath was preheated to $\sim 430^{\circ}\text{C}$ before the microautoclave was introduced. Recovery to 421°C (10°F below the desired reaction temperature) was not exceptionally fast and usually required ~ 2.0 minutes.

Only one severe problem was encountered during six shakedown microautoclave runs. The top fitting, a 3/4" to 1/4" reducer, on the autoclave leaked after every run. This was apparently due to thermal shock which loosened the fitting when the reactor was quenched by suddenly immersing it in cold water. The fact that the 3/4" plugs on each end of the tee did not leak suggested that the problem was due to leakage between the ferrules and the fitting rather than between the ferrules and the nut, since the ferrules on the plugs were not separate pieces but were a wedge shape cut onto the fitting itself. When a substitute adapter was made by silver soldering a 3/4" plug, in which the ferrule was part of the fitting, to a 1/4" cap and then drilled to allow passage of the thermocouple into the autoclave, the problem disappeared.

FIGURE 17. MICROAUTOCLAVE REACTOR

The Techne sand bath apparently was defective as delivered and had to be returned for repairs. The temperature controlled provided with the sand bath was totally unsatisfactory.

Microautoclave Liquefaction Procedure

After filling the autoclave with the desired amounts of solvent and coal, usually 3g of coal and 6g of solvent plus any additives, and pressurizing the autoclave with either helium or hydrogen to ~ 1000 psig, the autoclave is checked for leaks and the pressure and temperature are carefully measured. The autoclave is manually submerged to a depth of ~ 6 inches in the sand bath and attached to the arm of the wrist action shaker before beginning agitation. This typically takes 15-20 sec. Agitation is then started and measurement of the reaction time begins when the temperature reaches 10F below the desired operating temperature. Heatup time averages 1.9 minutes.

After reaction at the desired temperature and time, the autoclave is manually removed from the sand bath and immersed in cold water to quench the reaction. The time needed to quench the reaction (to $< 315\text{C}$) averages 0.50 minutes. By anticipating the time required to make the manual autoclave switch, excellent control of the residence time-temperature is achieved. Typical actual residence times and maximum operating temperatures (desired levels in parentheses) obtained during the initial runs were 4 minutes 59 seconds (5:00) at 428.8C (426.7C). A typical plot of pressure and temperature versus time is shown in Figure 18.

After quenching the autoclave to room temperature, the pressure and temperature are carefully measured and compared to starting values to determine the amount of gas generated. The microautoclave is attached via a quick-connect to a 500cc pressure cylinder which is then evacuated up to the microautoclave value. The gas is then released into the evacuated pressure cylinder. Typical final pressures in the cylinder are slightly greater than 19 psig. The cylinder is then closed and attached to the inlet of a Carle Model 111H Analytical Gas Chromatograph. Sufficient gas is purged through the gas sample loop to remove any air and to obtain a representative gas sample before the gas sample is injected for analysis. The gases are analyzed for H_2 , CO_2 , C_2H_4 , C_2H_6 , H_2S , Kr,

FIGURE 18. TYPICAL MICROAUTOCLAVE PRESSURE, TEMPERATURE VERSUS TIME CURVE FOR SCT COAL LIQUEFACTION.

CH₄ and CO using a hydrogen separator to obtain the hydrogen in a stream of nitrogen carrier gas, to improve detector sensitivity. The remaining gases are separated by switching between Molecular Sieve and Poropak columns. High pressure gas cylinders containing small amounts of krypton in hydrogen and in helium are used to pressurize the microautoclave. The presence of krypton as an internal standard permits improved analysis of the small amounts of gases formed during coal dissolution. Helium is used as an inert gas instead of nitrogen to facilitate the analysis of krypton, which appears between nitrogen and methane on the chromatograph. Any nitrogen or oxygen present in the gas sample can then be assumed to be due to leaks at some stage in the recovery and analysis procedure. Gas yields are calculated on a weight percent of ac-fed coal basis.

Sample Workup Procedure

The workup procedure results in the measurement of conversion to THF solubles and to preasphaltenes, asphaltenes, and oils as well as a complete mass balance for each run. A diagram of the workup procedure is shown in Figure 19.

The microautoclave is washed out with THF and the solids suspended in THF are washed into a Soxhlet extraction thimble. The THF insolubles are extracted continuously with THF. The THF insolubles are used to calculate the conversion to THF solubles on an MAF coal basis.

The THF is stripped from the THF solubles on a rotary evaporator and a small amount of THF is added back. The concentrated THF solution is added dropwise to ~500 ml of boiling heptane to precipitate heptane insolubles. The THF boils off of the boiling heptane. After vacuum filtration, drying and weighing, the heptane insolubles are continuously extracted with toluene. The toluene insolubles are dried and weighed. Solvent is stripped from both the toluene solubles and hexane solubles and they are also dried in a vacuum oven and weighed. Corrections are made for weight losses which occur in the extraction thimbles.

Total recoveries are excellent with mass balances averaging 99.2 percent, excluding water (approximately 1.1 percent) and gases (0.2 percent). Net changes in the amounts of preasphaltenes (THF soluble-toluene insolubles), asphaltenes (toluene soluble-heptane insolubles) and

FIGURE 19. PRODUCT WORKUP PROCEDURE

oils (heptane solubles) as a fraction of MAF coal fed are calculated for each experiment. Since the coal and solvent are both partially soluble in THF and heptane it is necessary to run blank extractions on each solvent and the starting coal to determine net solubility changes resulting from liquefaction. The results of the blank extractions are summarized in Table 17. Only the +454C fraction eluted with THF/10% ethanol, the -454C, +454C and the total recycle solvent fractions contain non-heptane soluble materials. The results are not normalized. These data are used to calculate the solubilities of various coal/solvent/additive mixtures.

Coal liquefaction reproducibility tests

Several coal liquefaction experiments were done to examine the reproducibility of the whole liquefaction procedure under the following conditions:

- 3 g Illinois #6 coal (as received)
- 6 g -454C Lummus ITSL Recycle Solvent
- 1000 psi H₂ or He containing 1% Krypton
- 427C reaction temperature
- 5 minutes at temperature.

The early data were not sufficiently reproducible to confidently measure small changes in the THF conversions and solubility fractions. Conversations with other investigators using microautoclaves indicated that ± 2 percent on THF conversions could be obtained routinely and ± 1 percent was achievable in repeatability tests. Our early duplicate analyses for THF conversion differed by an average of 4.1 percent. Several steps were taken to improve reproducibility.

First, enough -454C recycle solvent was separated in one distillation to complete a series of experiments and, while still a homogenous liquid, was packaged in individual vials containing slightly more than 6 grams of solvent each and stored in a refrigerator to improve the reproducibility in the autoclave experiments and to retard thermal decomposition and oxidation.

Second, it was suspected that poor mixing might be the cause of the erratic results which were occasionally observed. A series of

TABLE 17. SUMMARY OF SOLVENT SOLUBILITIES OF RECYCLE
SOLVENT FRACTIONS AND ILLINOIS #6 COAL

Fraction wt% Insoluble in: Soluble in:	THF	Toluene THF	Heptane Toluene	Heptane
-454 C Recycle solvent	1.2	0.0	0.0	100.
Eluted by hexane	0.0	0.0	0.0	100.
Eluted by benzene	0.0	0.0	0.0	100.
Eluted by chloroform	0.0	0.0	0.0	100.
Eluted by THF/ethanol	0.0	0.0	0.0	100.
+454 C Recycle solvent	0.4	23.1	22.5	53.9
Eluted by hexane	0.0	0.0	0.0	100.
Eluted by benzene	0.0	0.0	0.0	100.
Eluted by chloroform	0.0	0.0	0.0	100.
Eluted by THF/ethanol	0.5	14.3	40.0	42.9
Total recycle solvent	7.4	12.3	14.0	66.3
Illinois #6 Coal	93.2	6.1	1.0	3.9

liquefaction experiments were done with and without the presence of a 3/8-inch ball bearing in the autoclave to facilitate mixing. The effect of adding a ball bearing in the autoclave to facilitate mixing is shown in Table 18. It appears to result in a 2-3 percent increase in the conversion to THF solubles. Thus a ball bearing is used in all of the liquefaction experiments.

The results in Table 18 also show that for most of the experiments reproducibility is good. For instance, the average results and range of the closest 5 of 8 repeat experiments show very good agreement. However, the other experiments are out of line. These "flyers" were discussed by several speakers during the symposium on coal liquefaction at the Washington National ACS Meeting and seem to be common in coal liquefaction studies done in microautoclaves. It is not known what causes them but it is clear that duplicate experiments must be done and if the results are not in satisfactory agreement a third experiment must be done to guard against producing spurious data points.

A set of experiments was done to check the reproducibility of the workup procedure. In these experiments liquefactions were done in two microautoclaves simultaneously so that the reaction conditions were identical. The results of two such experiments are listed in Table 19. Reproducibility between experiment pairs is excellent throughout the workup procedure, including the gas make (or loss) as indicated by the pressure measured before and after the experiment at the same internal temperature. Mass balances are identical in the same pair and may reflect small variations in the workup procedure such as drying and extraction times.

Workers at Oak Ridge National Laboratory have reported that the use of a nitrogen purge over Soxhlet extractions with pyridine can change yields by retarding oxidation and crosslinking in the coal liquefaction products⁽¹⁴⁾. Two experiments were done (Table 19) in which pairs of autoclaves were used to eliminate differences in reaction conditions and then an attempt was made to carefully keep one of the two liquefaction products under nitrogen during workup while the other was worked up using the normal unprotected routine. In the first experiment the nitrogen purge during THF extraction was too rapid causing the THF vapors to be carried out of the Soxhlet extractor. Only the conversions to THF solubles were obtained because these were based on the weights of THF insolubles. Coupled

TABLE 18. COAL LIQUEFACTION EXPERIMENTS TO DETERMINE THE REPRODUCABILITY
OF THE REACTION CONDITIONS AND THE EFFECT OF ADDING
A 3/8-INCH BALLBEARING TO FACILITATE MIXING
(3 g Illinois #6 coal, 6 g -454 C recycle solvent, 1.5 g +454 C
recycle solvent, 427 C, 5 min, 1000 psi H₂/Kr (room temp))

Experiment Number	Ball Bearing?	% MAF Conversion to THF Solubles	% Net Change of Total MAF Reactants Preasphaltenes	Asphaltenes	Oils	Mass Balance	Pressure Change, psi
44	Yes	79.3	5.2	9.4	3.8	99.1	-40
45	Yes	78.5	8.3	8.8	3.8	101.7	-31
46	Yes	84.8	8.2	6.1	3.7	97.4	-28
50	Yes	78.5	12.1	5.0	3.1	101.1	-33
50B	Yes	77.3	9.9	4.8	3.9	99.8	-45
50C	Yes	78.1	8.0	9.6	0.6	99.2	-10
53	Yes	78.5	8.6	5.2	8.2	102.8	-15
54	Yes	81.6	7.2	7.5	4.1	99.0	-15
Average	Yes	79.6 (84.8-77.3)	8.4 (12.1-5.2)	7.1 (9.6-4.8)	4.3 (8.2-0.6)	100.0 (102.8-97.3)	-27 (-10--45)
Average of best 5 experiments		78.6 (79.3-78.1)	8.1 (8.6-7.2)	6.5 (8.8-5.0)	3.7 (3.9-3.1)		
47	No	80.8	7.3	7.3	3.7	98.7	-18
48	No	68.3	5.3	5.5	4.2	98.6	+11
49	No	82.4	7.9	7.8	4.4	100.0	-45
Average ⁽¹⁾	No	81.6	7.6	7.6	4.1	99.4	-32

(1)

Excluding experiment no. 48

TABLE 19. COAL LIQUEFACTION EXPERIMENTS TO DETERMINE THE REPRODUCIBILITY
OF THE WORKUP PROCEDURE
(3 g Illinois #5 coal, 7.5 g -454 C recycle solvent, 427 C,
5 min, 1000 psi H₂/Kr (room temp))

Experiment Number	Nitrogen Purge	% MAF Conversion to THF Solubles	% Net Change of Total MAF Reactants			Mass Balance %	Pressure Change, psi
			Preasphaltenes	Asphaltenes	Oils		
<u>Reproducibility</u>							
1.	-	88.1	10.9	5.2	3.7	99.3	-8
	-	88.1	10.3	5.3	4.2	99.3	-7
2.	-	85.0	11.2	7.4	4.6	103.4	-101 ⁽¹⁾
	-	83.5	11.8	8.1	3.0	103.5	-26
<u>Effect of N₂ Purge During Workup</u>							
1.	No	88.9	(2)	-	-	-	-29
	Yes	89.6	-	-	-	-	-23
2.	No	85.0	8.5	10.2	-1.3	97.9	-32
	Yes	84.6	8.6	11.4	-1.7	98.9	-17

(1) Leak in autoclave

(2) THF soluble products were lost because N₂ purge was too rapid.

with the second experiment the results suggest that a nitrogen purge during workup does not have a significant effect when THF and toluene, rather than pyridine, are used as the extraction solvents.

However, agreement between experiments is not good. This indicates that control of the reaction conditions is the most important factor in obtaining good reproducibility. Since reactant concentrations and composition (the use of solvent aliquots was discussed earlier), initial gas pressure and composition, and agitation rate are all constant and controllable, the variation must be due to changes between runs in the time-temperature profile. Control of the sand bath temperatures was improved by using automatic proportional control of the current to the heating elements. In addition, each set of experimental conditions is done in duplicate to allow the range in yields caused by any variation in the experimental conditions to be seen and to eliminate "flyers".

Effect of Time and Temperature on Liquefaction of Illinois #6 Coal

For the experiments in this program, good but not optimum yields are desired under first stage coal liquefaction conditions so that differences between solvents can be detected. A five minute reaction time at 427 C was chosen as the standard conditions. MAF conversions versus reaction time at 427C are shown in Figure 20 for a 2.5:1 mixture of solvent to coal under 1000 psi (room temp) hydrogen. Good conversions to THF solubles, in the 80 to 90 percent range are obtained in 5 minutes, but optimum conversions are reached in 10 to 20 minutes. Preasphaltenes appear to decline with time while asphaltenes are steady or possibly increase slightly. Oil yields increase with increasing reaction time.

A similar curve for the reaction at 449C, near the maximum temperature used in the Lummus ITSL pilot plant, is shown in Figure 21. Optimum conversions of coal to THF solubles are obtained at about 10 minutes reaction time. Beyond this time, retrogressive reactions cause a decrease in THF conversion and oil yields. Preasphaltenes decline with increasing reaction time, while asphaltenes go through a maximum yield and then decline. These results are in agreement with the general mechanism in which coal is converted to preasphaltenes, then to asphaltenes, and then to oils in a sequential reaction mechanism. The results of these experiments are summarized in Table 20.

FIGURE 20. COAL LIQUEFACTION CONVERSION TO THF SOLUBLES AND YIELDS VERSUS TIME AT 427 C

FIGURE 21. COAL LIQUEFACTION CONVERSION TO THF SOLUBLES AND YIELDS VERSUS TIME AT 449 C

TABLE 20. EFFECTS OF TIME AND TEMPERATURE ON COAL LIQUEFACTION
(3 g Illinois #6 Coal, 7.5 g -454 C Recycle Solvent,
1000 psi [r.t.] hydrogen)

Temperature, °C	Time, min.	MAF Conversion to THF Solubles, %	Net Change of Total MAF Reactants			Gas Analyses Weight Percent of As Fed Coal						
			Preasphaltenes	Asphaltenes	Oils	H ₂	H ₂ S	CO ₂	CO	CH ₄	C ₂ H ₆	Total
427	0	75.7	8.3	8.2	-0.1	.13	NM ⁽¹⁾	.50	.073	.12	.073	.90
	2	81.9	9.3	8.5	1.7	.09	NM	.55	.094	.27	.17	1.18
	5	90.8	5.5	10.5	3.1	.14	NM	.9	.13	.54	.32	2.04
	10	94.7	6.6	7.1	5.3	.21	NM	1.21	.18	1.08	.64	3.32
	20	97.0	5.5	8.7	NM	.27	NM	1.05	.18	1.81	1.04	4.36
449	0	76.9	11.6	6.7	2.0	.12	.079	.38	.092	.23	.12	1.02
	2	82.7	7.6	8.3	3.4	.07	.16	.50	.16	.64	.33	1.86
	5	88.5	5.1	12.4	2.3	.04	.12	.70	.25	1.52	.69	3.32
	10	89.6	4.7	11.4	4.7	.14	.12	1.18	.27	2.61	1.14	5.46
	20	85.2	3.2	8.6	3.3	.27	.073	1.11	.22	4.23	1.42	7.32

(1) NM=Not measured

Liquefaction of Recycle Solvent Heptane Insolubles (Asphaltenes) at 427C

In addition to the coal added to the SCT step in two-stage coal liquefaction, the SCT step must also convert significant amounts of high molecular weight material recycled in the recycle solvent. This material was isolated as the heptane insoluble fraction from the +454C recycle solvent. It has been through the SCT step previously without being converted to -343C products but it has also passed through the 2nd stage LC-fining step where hydrogen has been added. It is known, from the Task 2 studies, to be heteroatom rich, hydrogen bonded, polar material, probably containing no aliphatic hydrocarbons and very few aromatic hydrocarbons and low molecular weight N- and O-containing aromatics.

As shown in Figure 22, the conversion of this material to THF solubles is slow at 427C, with only about 6 percent conversion in 20 minutes. Examination of the net changes in the different solvent solubility classes show that initial conversion produces a significant amount of oils. With increasing time the oils (solvent) react with preasphaltenes to form asphaltene type products.

A comparison of the gases (on a 100 g feed basis) formed from the reaction of coal and recycle solvent heptane precipitate at 427C versus time is shown in Figure 23. A comparison of the coal and heptane precipitate elemental analyses are given on an MAF basis, in Table 21 below:

TABLE 21. COMPARISON OF COAL AND RECYCLE SOLVENT ASPHALTENE COMPOSITIONS

	Illinois #6 Coal	Recycle Solvent Asphaltenes (+454C heptane precipitate)
Carbon	84.72	86.74
Hydrogen	5.46	5.72
Nitrogen	1.43	1.92
Sulfur	3.50	1.05
Oxygen	4.89	4.57
H/C	0.77	0.79

FIGURE 22. LIQUEFACTION OF HEPTANE INSOLUBLES FROM +454 C RECYCLE SOLVENT

FIGURE 23. COMPARISON OF GASES PRODUCED FROM LIQUEFACTION OF COAL AND ASPHALTENES IN THE RECYCLE SOLVENT

After removal of a hydrocarbon rich product as -343C material and hydrotreatment of the remaining material in the LC-finer the heavy ends of the recycle solvent contain much less sulfur, slightly less oxygen and slightly more nitrogen than the starting coal, as expected based on the relative ease of heteroatom removal during hydrotreatment. The heavy recycle solvent material also has a slightly higher H/C ratio again reflecting the hydrotreating step.

It might be expected that most of the easily removable alkyl groups are taken off in the first pass through the SCT step liquefaction step and this is shown to be the case in Figure 23. There is ~ 5 times more methane in the gases from coal liquefaction although the amounts of ethane are comparable. The amount of H₂S removed from the coal is expected to be high but it was not measured. More net hydrogen is also released from the coal. The largest difference, however, is in the large amounts of CO and CO₂ released by the coal compared to the very small amounts released by the asphaltenes in the recycle solvent. Apparently the easily removable oxygen is taken out in the first pass through the SCT step and the remaining oxygen, which is in nearly equal concentrations on a MAF coal basis, is very difficult to remove as CO or CO₂. The total amount of gas given off under identical conditions is much larger for coal than for the heavy recycle solvent. All of the results are summarized in Table 22.

Liquefaction Yields Using SCT Recycle Solvent and Heavy Oil Product as Solvents

Very early in this program several microautoclave liquefaction experiments were done to compare the use of SCT heavy oil product fractions and -427C and +427C SCT recycle solvent fractions as liquefaction solvents under both hydrogen and helium. In these experiments only THF insolubles (IOM and ash); heptane insoluble - THF solubles (asphaltenes plus preasphaltenes) and heptane solubles (oils) were separated in the workup procedure. A summary of the results is given in Table 23.

TABLE 22. LIQUEFACTION OF +454 C RECYCLE SOLVENT HEPTANE PRECIPITATE
(427 C, 1.71 g Heptane Precipitate, 4.29 g -454 C Recycle
Solvent, Solvent/Asphaltene=2.5, 1000 psi [r.t.] H₂)

Time, min.	MAF Conversion to THF Solubles, %	Net Change of Total MAF Reactants, %			Gases (Weight Percent of As Fed Coal)						
		Preasphaltenes	Asphaltenes	Oils	H ₂	H ₂ S	CO ₂	CO	CH ₄	CH ₆	Total
0	-1.0	-3.1	-1.2	10.1	.05	0.	.059	.0092	.012	.24	0.37
2	+2.0	-4.1	-1.6	8.9	.14	.24	.041	.013	.049	.35	0.83
5	-4.1	-6.3	-0.6	8.4	.02	.33	.0038	.019	.10	.44	0.91
10	+0.3	-7.3	1.1	4.0	.10	.37	.031	.024	.20	.51	1.24
20	+5.7	-9.9	2.0	0.7	.08	.37	.030	.031	.38	.75	1.64

TABLE 23. PRELIMINARY RESULTS FROM LIQUEFACTION EXPERIMENTS WITH ILLINOIS #6 COAL⁽¹⁾

Run No.	Solvent ⁽²⁾	Gas Atmosphere ⁽³⁾	Conversion to THF Solubles % of HAF Coal	Yield of Products		Distribution of Gases, (Volume %) ⁽⁴⁾				
				THF Sol./ Heptane Insol.	Heptane Sol.	H ₂	CO	CO ₂	CH ₄	C ₂ H ₄ /C ₂ H ₆
7	SCT Recycle Solvent	He	80.7	40.3	50.1	0.85	0.16	1.06	0.77	0.49
15	SCT Recycle Solvent	H ₂	77.7	39.1	52.5	-7.87	0.12	0.75	0.98	0.39
9	800°F SCT Recycle Solvent	He	81.5	22.0	70.8	1.09	0.13	1.15	0.75	0.35
17	800°F SCT Recycle Solvent	H ₂	86.5	23.2	72.0	(1.55)	0.14	0.58	0.90	0.34
13	SCT Heavy Oil Product (THF Solubles)	He	50.3	41.1	37.7	0.36	(0.87)	1.33	1.30	0.73
11	800°F SCT Heavy Oil Product	He	78.8	29.6	61.7	0.58	0.13	0.88	0.88	0.39
12	800°F SCT Heavy Oil Product	H ₂	81.1	22.0	70.8	-4.31	0.13	0.65	0.86	0.34

(1) 3 g of coal, 5 min, 800 F used for all experiments.

(2) 6 g of solvent used in all experiments.

(3) Cold initial pressure = 1000 ± 20 psi.

(4) Corrected to standard krypton concentration.

These results suggest that the recycle solvent is a significantly better solvent in terms of conversion to THF solubles than the heavy oil product. This is true of both the -427C fractions and the +427C fractions. The large differences in product distributions between heptane solubles and insolubles is due to differences in the initial solubilities of the solvents. The +427C fractions have significantly more heptane insolubles and less heptane solubles than the -427C fractions which are almost entirely heptane soluble.

Comparison of Liquefaction under Hydrogen and Helium

Table 24 summarizes the results of liquefaction experiments under hydrogen and helium. Each result is the average of 12 experiments using the same +454C solvent fractions and the total +454C solvent as additives to -454C solvent, in the ratio 2.0 solvent:1.0 coal:0.5 additive. Under hydrogen, MAF coal conversions to THF solubles are higher, and preasphaltene and asphaltene yields are also increased since these are the products of coal dissolution. Oil yields under hydrogen are decreased, reflecting the increased amount of solvent which has adducted to the dissolved coal. Under hydrogen, a small net consumption of hydrogen usually occurs and yields of H_2S , CH_4 , and C_2H_6 are higher. Yields of CO and CO_2 are increased under helium.

Effects of Adding +454C and -454C Recycle Solvent Under First Stage Coal Liquefaction Conditions

Table 25 shows a comparison of the effects of using total +454C and -454C recycle solvents as additives in coal liquefaction. When no solvent is added beyond the 2:1 ratio of -454C recycle solvent to coal, the conversion of total THF insolubles (MAF) to THF solubles (MAF) is 80 percent. A significant increase in conversion occurs when 1.5 grams additional -454C solvent is added. More preasphaltenes and asphaltenes are formed and slightly more oil is probably adducted to the increased amount of dissolving coal. When +454C solvent is added to increase the total solvent to coal ratio to 2.5:1, a drop in MAF conversion to THF solubles is observed, and a further drop occurs when the amount of +454C

TABLE 24. COMPARISON OF RESULTS UNDER HYDROGEN AND HELIUM
(427 C, 5 min, 1000 psi Overpressure,
3 g Illinois #6 Coal, 7.5 g Total Solvent)

Atmosphere	MAF Conversion to THF Solubles, %	Net Change of Total MAF Reactants, %			Weight Percent of As Fed Coal					
		Preasphaltenes	Asphaltenes	Oils	H ₂	H ₂ S	CO ₂	CO	CH ₄	C ₂ H ₆
Hydrogen ⁽¹⁾	77.9	8.11	7.68	0.34	-.080	.17	.31	.054	.21	.092
Helium ⁽¹⁾	74.9	7.95	7.50	0.95	.019	.13	.36	.064	.17	.078

TABLE 25. COMPARISON OF EFFECTS OF +454 C AND -454 C RECYCLE SOLVENTS ON COAL LIQUEFACTION
(427 C, 5 min, 1000 psi (r.t.) hydrogen, 3 g Illinois #6 coal, 6 g -454 C recycle solvent)

Added Solvent/g	Total Solvent/Coal	Net Change (MAF basis), % of MAF Coal ⁽¹⁾				Gases, Weight % of As Fed Coal						
		THF Insolubles	Preasphaltenes ⁽²⁾	Asphaltenes ⁽³⁾	Oils ⁽⁴⁾	H ₂	H ₂ S	CO ₂	CO	CH ₄	C ₂ H ₆	Total
	2.0:1	-80.4	34.3	13.7	20.5	-.12	.057	.25	.042	.14	.066	.44
-454 C/1.5	2.5:1	-86.1	42.9	25.3	19.5	-.063	.081	.34	.045	.10	.068	.55
+454 C/1.5	2.5:1	-77.2	29.2	34.6	12.4	-.36	.27	.24	.034	.18	.12	.48
+454 C/3.0	3.5:1	-76.7	15.7	42.3	3.6	-.12	.038	.26	.035	.16	.051	.43

(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.

added solvent is increased to a total solvent to coal ratio of 3.5:1. Thus, the overall effect on coal conversion to THF solubles of adding the +454 C portion of the recycle solvent is negative. The fact that the overall effect of recycling the +454 C solvent is negative is not surprising since ~ 60 percent of this material is asphaltenes (heptane precipitate), which must be dissolved themselves and were previously shown to do so slowly under these liquefaction conditions. The increased amount of heavy solvent material appears to form asphaltenes primarily, at the expense of preasphaltenes and oils, as was seen in the study of heptane precipitate liquefaction versus time. (Figure 22).

Effects of the Addition of Individual Recycle Solvent Fractions to First Stage Coal Liquefaction

Comparison of the effects of -454C and +454C solvent fractions on coal liquefaction (Table 26) shows that the +454C aliphatic hydrocarbons are a more effective solvent additive than the -454C aliphatic fraction even though the latter contains a significant amount of hydroaromatics. Surprisingly, the -454C aromatic hydrocarbon fraction is a better solvent than the +454C aromatic hydrocarbon fraction in spite of the arguments usually put forward for heavy aromatic solvent fractions such as those discussed in the introduction to this report. However, both the +454C and -454C solvent fractions increase conversions to THF solubles. The +454C N-containing aromatics are also a less effective solvent fraction, while neither N-containing aromatic fraction improves conversion.

Another measure of the extent of coal liquefaction is the conversion to the desirable products, asphaltenes and oils. The ratio of asphaltenes + oils to preasphaltenes ($\frac{A+O}{P}$) is a measure of the ability of the solvent not just to dissolve the coal but to convert it to stable products which will react favorably during further processing. The $\frac{A+O}{P}$ ratios obtained with the addition of each solvent fraction are listed in Table 27, along with other reaction parameters of interest such as relative conversion (no added solvent = 1.0). Oil out/oil in is a measure of solvent balance. Hydrogen usage indicates the total hydrogen incorporated into all products. Gas make can be an indicator of coke formation and hydrogen wasted.

TABLE 26. 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				Weight Percent of As Fed Coal						Total
		THF Insolubles	Preasphaltenes	Asphaltenes	Oils	H ₂	H ₂ S	CO ₂	CO	CH ₄	C ₂ H ₆	
None	-	-80.4	34.3	13.7	20.5	-.12	.057	.25	.042	.14	.066	.44
Aliphatic	-454	-81.2	33.3	33.7	5.4	-.15	.058	.15	.041	.095	.067	.28
Hydrocarbons	+454	-84.1	27.9	35.0	-2.8	.43	.42	.32	.040	.22	.063	1.54
Aromatic	-454	-87.6	33.1	27.2	15.5	.090	.076	.29	.041	.095	.087	.46
Hydrocarbons	+454	-83.4	33.8	28.9	9.4	-.14	.10	.28	.048	.11	.085	.51
N-Containing	-454	-79.5	25.6	40.6	7.3	-.065	.080	.29	.057	.12	.010	.58
Aromatics	+454	-67.1	30.3	47.6	-6.4	-.060	.18	.76	.091	.37	.27	1.42
O-Containing	-454	(-58.3)	24.6	38.9	-18.1	-.030	.10	.84	.17	.20	.28	1.56
Aromatics	+454	-71.1	30.8	26.9	0.6	-.050	-	.62	.12	.23	.15	1.02

TABLE 27. REACTION PARAMETERS FOR 1ST STAGE COAL LIQUEFACTION
 USING ADDED SOLVENT FRACTIONS
 (3 g Illinois #6 coal, 6 g -454 C Recycle Solvent,
 1000 psi H₂ (room temp), 427 C, 5 minutes)

Solvent Fraction	Temp, °C	Relative Conversion	Net Change of MAF Asphaltenes + Oils/ Preasphaltenes	Oils out/ Oils in	Weight % of as fed coal	
					H ₂	Total gas -H ₂
No Added Solvent	-	(1.00)	1.00	1.08	-.12	0.56
Total -454 C Recycle Solvent	-454 C	1.07	1.04	1.05	-.06	0.61
Aliphatic Hydrocarbons (Contaminated w/ aromatics)	-454 C	1.01	1.17	1.02	-.15	0.43
Aromatic Hydrocarbons	-454 C	1.09	1.29	1.05	-.09	0.56
N-Containing Aromatics	-454 C	0.99	1.87	1.03	-.07	0.65
O-Containing Aromatics	-454 C	0.73	0.85	0.94	-.03	1.59
Total +454 C Recycle Solvent	+454 C	0.96	1.61	1.05	-.36	0.84
Aliphatic Hydrocarbons	+454 C	1.05	1.15	0.99	+.48	1.12
Aromatic Hydrocarbons	+454 C	1.04	1.13	1.03	-.14	0.65
N-Containing Aromatics	+454 C	0.83	1.36	0.99	-.06	1.48
O-Containing Aromatics	+454 C	0.88	0.89	0.89	-.05	1.07

The total -454C recycle solvent and the -454C aromatic hydrocarbon fraction which comprises about 72 percent of the -454C recycle solvent give the best conversions of MAF coal to THF solubles. Other additives which give better yields than no solvent additive include the -454C and +454C aliphatic hydrocarbons, and the +454C aromatic hydrocarbons. These fractions total only about 30 percent of the total +454C recycle solvent. Addition of the O-containing aromatics, which are "low polarity asphaltenes", results in much lower conversions of MAF coal to THF solubles. Asphaltenes are present in very small amounts in the -454 C recycle solvent but constitute nearly 70 percent of the total +454C recycle solvent.

The $\frac{A+O}{P}$ ratio, which is a measure of the conversion of coal to usable products, not merely the dissolving of coal to THF solubles, indicates that the total -454C and +454C solvents and all of the fractions except the O-containing aromatics improve the yields. Solvent adduction to the dissolving coal is assumed to result in the formation of asphaltenes and not preasphaltenes and may account for part of the improved product distribution. Aromatic hydrocarbons seem to be average solvents by this measure while N-containing aromatics are very effective.

The aromatic hydrocarbons do not adduct as readily to the dissolving coal molecules as the solvent components which contain more heteroatoms as shown by the ratio of oils out/oils in. In general, less oil is recovered in the order aromatic hydrocarbons > N-containing aromatics > O-containing aromatics, probably reflecting increased adduction during coal liquefaction as the functionality of the solvent components increases.

Under 1000 psi H_2 , a small amount of H_2 is consumed (except for the +454C aliphatic hydrocarbon fraction). In the case of the other solvent fractions this may indicate the ability of the solvent to "shuttle" hydrogen gas to the dissolving coal. Hydrogen shuttling, as measured by this parameter, decreases in the order, for both -454C and +454C solvent components:

Aromatic hydrocarbons
N-containing aromatics
O-containing aromatics.

For both solvent fractions the total solvent seems to be better than the sum of the parts. No additional solvent also gave good oil yield and significant hydrogen shuttling.

Total gas produced under severe conditions can indicate the amount of coking which has occurred. In particular, the production of light hydrocarbons represents a waste of valuable hydrogen. However, at 427°C coking is probably minimized and the gases produced are those unavoidably formed in breaking linkages between larger molecules during coal dissolution.

Effects of Primary, Secondary, and Tertiary N-Aromatic Fractions on Liquefaction

The +454 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>	<u>Cyano</u>
<u>Symbol</u>	1°	2°	3°	
<u>Formula</u>				
	Aniline	Pyrrole	Pyridine	Benzonitrile

The fourth type of nitrogen (cyano) which may appear in coal liquids is probably contained in the 2° nitrogen fraction using this separation scheme. In addition, the nitrogen fraction is probably heavily contaminated with 3° nitrogen compounds and may contain less than half 1° nitrogen. The purity of the fractions by nitrogen type was not determined. Gas chromatograms for each fraction are shown in Figure 24. Very little of the 3°-N fraction, which consists of highly polar bases, elutes from the column. Each fraction is a complex mixture of many compounds.

All of the individual fractions are better solvents than the combined N-aromatics fraction as shown in Table 28. The tertiary nitrogen (pyridine bases) N-aromatics give the lowest conversions of the three fractions and the least preasphaltenes and most asphaltenes. They

FIGURE 24. GAS CHROMATOGRAMS OF N-AROMATIC FRACTIONS

TABLE 28. COMPARISON OF EFFECTS ON SCT LIQUEFACTION OF PRIMARY, SECONDARY AND TERTIARY N-AROMATIC FRACTIONS
(427 C, 5 min, 2.0:0.5:1 -454 C Recycle Solvent-Added N-Aromatic Fraction-Coal, 1000 psi H₂ (room temp)¹)

Added Solvent Fraction	Net Change (MAF Basis), % of MAF Coal				Weight % of As Fed Coal						Total
	THF Insolubles	Preasphaltenes	Asphaltenes	Oils	H ₂	H ₂ S	CO ₂	CO	CH ₄	C ₂ H ₆	
Primary Nitrogen Aromatic	-79.5	29.4	42.0	- 8.2	+0.05	0.36	0.66	0.11	0.18	0.36	1.72
Secondary Nitrogen Aromatic	-81.0	29.8	28.8	-15.2	-0.06	0.40	0.79	0.11	0.19	0.40	1.83
Tertiary Nitrogen Aromatic	-71.7	19.7	48.6	-14.0	0.00	0.14	0.59	0.12	0.22	0.14	1.21
Total N-Aromatic	-67.1	30.3	47.6	- 6.4	-0.06	0.18	0.76	0.09	0.37	0.18	1.52

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

produce the least gas and do not shuttle hydrogen. There is a large net oil loss.

The secondary (acidic pyrroles and cyano) 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 adducted to the dissolving coal. They show some indication of shuttling hydrogen. They also yield the largest amounts of gas.

Although the nitrogen compounds apparently can 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⁽¹⁵⁾, under the conditions used in these experiments they are relatively poor liquefaction solvents, particularly the 3⁰-N fraction.

TASK 4. DATA CORRELATION AND ANALYSIS

The Role of Solvent in Two-Stage Coal Liquefaction

In its simplest form the solvent in two-stage coal liquefaction serves two purposes. First, it is the physical vehicle which carries the coal particles and undissolved products from place to place in the process. To accomplish this it must remain substantially in the liquid state at high temperature with enough viscosity and density to support a slurry of the solids at a ratio of solvent to coal of as little as 1.5:1.0. It must not become so thick that it cannot be pumped at the lowest temperatures encountered in the process. Second, it acts as a catalyst, in effect, by promoting the liquefaction of coal in the overall process without being destroyed faster than it is formed. It must also be derived from the process feedstock, at least in the processes currently being developed, and it must be able to survive repeated heating and cooling cycles and dehydrogenation-hydrogenation reaction sequences.

Reactions of Coal Liquefaction Recycle Solvents

The reactions of coal liquefaction recycle solvents are many. The solvent, usually as hot as possible, is introduced to coal which has been partially dried and ground. Residual water is lost from the coal pores and ideally solvent replaces the water in the pores to improve solvent contact with the coal when it dissolves at a later stage. This diffusion into the pores is probably best done by lighter, smaller molecules which are somewhat polar, to better enable them to coexist with the water. Studies at Gulf and elsewhere have suggested that N-containing solvent molecules are particularly adept at this stage of the process⁽¹⁵⁾.

As the coal heats up, its structure, held together by hydrogen bonds, begins to break down. The coal swells, releasing smaller molecules trapped in the coal structure, and allowing additional

penetration by solvent molecules, probably by larger molecules than could penetrate the pores. Large aromatic systems might be particularly helpful at this stage because the pi electrons can form weak bonds with the aromatic molecules in the coal. Heteroatoms contained in the solvent molecules might also aid in this step by forming hydrogen bonds to replace the intramolecular hydrogen bonds in the coal. Strong acids and bases such as primary and tertiary N-compounds and phenols should be particularly effective.

Additional heating causes covalent bonds to break in the coal creating free radicals. This breakdown into smaller free radicals may be accelerated by the presence of certain types of functional groups in the solvent such as substituted phenols⁽¹⁶⁾⁽¹⁷⁾. Initiation of free radicals during liquefaction at lower temperatures can help avoid char formation which is favored at higher temperatures. The free radicals can (1) react with hydrogen atoms ($H^\bullet$) to "cap" the free radical sites, (2) rearrange to form more stable free radicals or even neutral molecules by breaking off another free radical, or (3) react with sites in the solvent capable of generating a more stable free radical or a neutral molecule. All of these reactions are capable of yielding useful liquid products. However, they can also react with free radicals in other large coal molecules to form very large, unreactive "polymeric" molecules which may lead finally to the formation of char, an undesirable product.

At this point the presence of reactive small molecules is critical. The presence of sufficient hydrogen atoms is ideal. These can come from solvent molecules, from the hydrogen molecules in the gas phase or from other hydrogen rich parts of the coal molecules themselves. Good liquefaction solvents are thought to be catalysts at this stage in the reaction, either by "shuttling" hydrogen from hydrogen rich to hydrogen poor regions of the coal, by transferring hydrogen from the gas phase to the solid phase or by donating hydrogen already present in the solvent molecule. All of these reactions involve hydrogenation-dehydrogenation chemistry and large aromatic systems are particularly effective because they are adept at adding and losing hydrogen. However, "catalytic" behavior implies contact between surfaces and it seems

likely that in addition to being able to readily undergo hydrogenation and dehydrogenation it may also be necessary to have small size and/or preferred steric conformations to react efficiently with the large dissolving coal fragments. This aspect of solvent chemistry has not been studied extensively so far.

The "dissolved" and stabilized coal fragments must finally be carried from the first stage in contact with a solvent either as a slurry of large particles, as a colloidal suspension or as molecules dissolved in the solvent, depending on the size of the final products of the coal dissolution reaction. This again requires that the solvent remain liquid, have good affinity for the dissolved coal and that the viscosity of the mixture be suitable for pumping and transport.

The dissolved coal-solvent mixture then goes on to separation, hydrotreating and hydrocracking operations resulting in the production of a slate of coal derived products and a solvent fraction to be recycled to the coal dissolution step.

Measurement of "Solvent Quality"

Although the term "solvent quality" represents the sum of a complex set of reactions, many groups have attempted to define solvent quality in terms of some readily measurable parameters. Probably the most publicized attempt is the work done at Exxon since it was developed to aid in the operation of the demonstration plant of the EDS process. The procedure used has been considered confidential but is supposed to consist of a GC or GC-MS based measurement of the concentrations of a series of key single components in the solvent and the use of these results in an empirical computation to relate the performance of the solvent on a linear scale. It seems likely that the overall procedure is cumbersome and that the scale may have to be redesigned for each coal and set of reaction conditions. Also well known and widely practiced are procedures of the type developed at Mobil and Conoco. At Mobil, a method for extensive fractionation of the solvent by sequential election with a series of nine solvents called Sequential Election with Specific Solvents Chromatography (SESC) was developed and the resulting

fractions were extensively characterized⁽¹⁸⁾. The method in its full form required nearly a week and gallons of very pure and expensive solvents.

At Conoco, a method based on two microautoclave reactions, an "equilibrium" test at 2/1 solvent/coal, 30 minutes, 750 F to measure the total hydrogen donor content of the solvent and a "kinetic" test at 8/1 solvent/coal, 10 minutes at 750 F to measure the kinetic activity of the hydrogen donors⁽¹⁹⁾. These tests are convenient but the use of a standard coal with a variety of solvents may produce unusual results, as discussed earlier, and the use of standard non-liquefaction conditions does not show what will happen under reaction conditions. This type of test may be useful for ranking solvents, if the effect of using "non-matched" coal-solvent pairs is not significant.

This study suggests another approach.

Use of Liquefaction Under Hydrogen and Helium to Estimate Solvent Quality

Observation of the results of a number of other workers studying recycle solvent chemistry⁽²⁰⁾ suggests that the difference in conversion to THF solubles which occurs when liquefactions are run under H_2 versus an inert atmosphere is a good method of measuring "solvent quality". Little or no difference results when a good solvent is used. Larger yields occur under H_2 when the "solvent quality" is not as high. A summary of the results of liquefactions done under H_2 and He with a number of solvent additives is given in Table 29. On the basis described above, the added +454 C solvents and solvent fractions can be ranked in order of decreasing solvent quality as follows:

+454 C aromatic (1.5 g)
 +454 C hexane
 +454 C THF/EtOH
 +454 C recycle solvent (3.0 g)
 no additive
 +454 C recycle solvent (1.5 g)
 +454 C benzene (1.5 g)
 +454 C $CHCl_3$ (1.5 g).

This order is roughly what would be expected, with two exceptions: (1) the relatively high rank of adding O-containing aromatics (+454 C THF/ethanol extract), and (2) the low ranking of adding 3 g of the aromatic hydrocarbon fraction (+454 C benzene extract). Since both of these are based on

TABLE 29. SUMMARY OF MICROAUTOCLAVE RESULTS (3 g Illinois #6 coal/6 g -454 C Lummus ITSL Recycle Solvent, 427 C, 5 mins., 1000 psig, cold gas pressure)

Gas Atmosphere	Additive	% MAF Conv. THF Insolubles to THF Solubles	% Net Change of Total MAF Reactants			Weight % of As Fed Coal					
			Preasphaltenes ⁽¹⁾	Asphaltenes ⁽²⁾	Oils ⁽³⁾	H ₂	CO ₂	C ₂ H ₆	H ₂ S	CH ₄	CO
H ₂	None	81.4	10.7	4.2	6.8	-0.17	0.17	0.045	0.040	0.13	0.020
	None	80.6	11.8	4.8	4.0	-0.06	0.32	0.088	0.073	0.15	0.064
He	None	76.0	12.5	8.3	1.0	0.014	0.30	0.037	0.015	0.10	0.13
	None	81.4	8.2	7.9	2.9	0.017	0.29	0.068	0.061	0.13	0.042
H ₂ -He		2.3	0.9	-3.6	3.5	-0.13	-0.05	0.014	0.019	0.03	-0.044
H ₂	1.5 g +454 C Recycle solvent	74.6	6.7	8.4	2.1	-0.36	0.26	0.17	0.49	0.24	0.038
	1.5 g +454 C Recycle solvent	82.4	8.3	9.7	1.9	-0.36	0.21	0.066	0.053	0.12	0.035
He	1.5 g +454 C Recycle solvent	74.6	7.6	5.7	4.0	0.022	0.46	0.064	0.037	0.14	-
	1.5 g +454 C Recycle solvent	74.6	7.5	8.5	3.3	0.020	0.30	0.071	0.054	0.16	0.040
H ₂ -He		3.9	-0.05	2.0	-1.7	-0.38	-0.15	0.051	0.23	0.04	-0.004
H ₂	3.0 g +454 C Recycle solvent	74.7	5.3	8.8	-2.1	-0.21	0.26	0.075	0.054	0.19	0.038
	3.0 g +454 C Recycle solvent	77.1	4.0	9.4	1.6	-0.02	0.26	0.027	0.021	0.13	0.032
He	3.0 g +454 C Recycle solvent	76.3	6.0	6.5	1.7	0.021	0.44	0.048	0.023	0.14	0.023
	3.0 g +454 C Recycle solvent	72.3	6.8	8.6	0.3	0.014	0.42	0.042	0.026	0.11	0.024
H ₂ -He		1.6	-1.8	1.6	-1.3	-0.13	-0.17	-0.006	0.013	0.04	0.012
H ₂	1.5 g +454 C aliphatics	84.1	7.1	7.4	-1.9	+0.48	0.32	0.063	0.42	0.22	0.040
	1.5 g +454 C aliphatics	83.4	9.0	5.5	-0.2	0.011	0.33	0.055	0.42	0.20	0.043
H ₂ -He		0.7	-1.9	1.9	-1.7	0.47	-0.01	0.008	0.00	0.02	-0.003
H ₂	1.5 g +454 C HC-aromatics	83.4	9.0	5.5	-0.2	+0.33	0.24	0.058	0.46	0.20	0.050
	1.5 g +454 C HC-aromatics	79.1	7.1	8.2	-2.0	0.0081	0.35	0.044	0.37	0.15	0.043
H ₂ -He		4.3	1.9	-2.7	1.8	0.32	-0.11	0.014	0.09	0.05	0.07
H ₂	3.0 g +454 C HC-aromatics	81.4	8.5	7.6	1.1	-0.01	0.20	0.019	0.014	0.10	0.030
	3.0 g +454 C HC-aromatics	81.0	8.2	6.2	3.0	0.0093	0.26	0.013	0.0095	0.090	0.022
H ₂ -He		0.4	0.3	1.4	-1.9	-0.019	-0.06	-0.006	0.004	0.01	0.008
H ₂	1.5 g +454 C N-aromatics	76.4	9.7	10.4	-1.8	-0.61	0.37	0.084	-	0.33	0.064
	1.5 g +454 C N-aromatics	67.3	8.3	9.1	-6.4	+0.08	0.54	0.26	0.053	0.47	0.12
He	1.5 g +454 C N-aromatics	73.2	6.5	10.2	0.5	0.0080	0.34	0.066	0.25	0.25	0.091
	1.5 g +454 C N-aromatics	57.7	7.8	9.6	-6.3	0.0072	0.41	0.15	-	0.28	0.078
H ₂ -He		6.4	1.9	-0.2	-1.2	-0.31	0.08	0.064	-0.099	0.14	0.009
H ₂	1.5 g +454 C O-aromatics	71.2	7.9	6.9	-1.0	-0.05	0.62	0.15	-	0.23	0.12
	1.5 g +454 C O-aromatics	69.7	8.2	4.8	3.2	0.01	0.78	0.28	0.18	0.29	0.17
H ₂ -He		1.5	-0.3	2.1	-4.2	-0.06	-0.16	-0.13	-	-0.6	-0.05

(1) Preasphaltenes = THF soluble-toluene insolubles

(2) Asphaltenes = Toluene soluble-heptane insolubles

(3) Oils = Heptane solubles

single determinations it is possible that each contains a bad data point. (These early data were subject to significant uncertainties as discussed earlier.)

Measurement of Donatable Hydrogen by H^1 -NMR to Estimate "Solvent Quality"

A second indirect measurement relating to solvent quality is the use of H^1 -NMR to measure hydrogen in hydroaromatic ring systems α or β to aromatic rings. This is hydrogen which might be expected to be readily donated to dissolving coal, with the formations of a larger aromatic ring system in the solvent molecule as the driving force. It only measures the amount of hydrogen potentially available and does not take into account the amount which is actually lost under actual liquefaction conditions (kinetically available). In this respect it is less appropriate than the comparison between yields under H_2 and He discussed previously which are measured under the reaction conditions. For this reason the previous method is also preferable to measurements of solvent quality carried out under standard "kinetic" or "equilibrium" conditions which are not the actual liquefaction reaction conditions.

Calculations were made to estimate the amount of potentially donatable hydrogen present in each solvent fraction. Several such calculations have been reported in the literature^(21,22). The method described below was used because it only required H^1 -NMR data. The H^1 -NMR spectra were obtained for each solvent fraction and divided into six regions corresponding to aromatics and OH protons (4.7-10.5 ppm), cyclic α (2.5-4.7 ppm), noncyclic α (2.0-2.5 ppm), cyclic β (2.4-2.0 ppm), noncyclic β (1.0-1.4 ppm) and γ to an aromatic ring (0.5-1.0 ppm). The data are listed in Table 30 in terms of weight percent hydrogen in each sample. The potentially donatable hydrogen is one half of the hydrogen in the region where a cyclic structure α or β to an aromatic ring would be seen. Of course, the NMR assignments are ranges which can also include noncyclic and other types of hydrogen, since the chemical shifts in large aromatic systems can be moved drastically by proximity to aromatic rings other than the one to which they are attached. This

TABLE 30. SUMMARY OF H^1 -NMR DETERMINATION OF DONATABLE HYDROGEN
IN RECYCLE SOLVENT FRACTIONS (Wt % of sample)

Solvent Fraction	Temp. °C	Aromatic & Phenolic	α -Cyclic	α -Non-Cyclic	β -Cyclic	β -Non-Cyclic	γ	Total Hydrogen	Donatable Hydrogen ⁽¹⁾
Benzene	-454	1.82	1.55	0.60	1.49	0.79	0.32	6.58	1.52
Chloroform	-454	2.48	1.80	0.55	1.05	0.49	0.13	6.51	1.43
THF/Ethanol	-454	2.02	1.64	0.96	1.41	0.91	0.28	7.21	1.53
Benzene	+454	2.92	1.65	0.58	1.18	0.86	0.40	7.59	1.42
Chloroform	+454	3.18	0.97	0.72	0.78	0.76	0.50	6.82	0.88
2°-N	+454	2.55	1.16	0.49	1.45	1.07	0.31	7.05	1.31
1°-N	+454	2.57	0.94	0.58	0.91	0.91	0.48	6.33	0.93
3°-N	+454	2.70	1.31	0.69	1.02	1.05	0.28	7.05	1.17
THF/Ethanol	+454	1.58	1.77	0.94	1.76	0.73	0.42	7.20	1.77
Heptane precipitate	+454	2.00	1.45	0.73	0.89	0.43	0.24	5.72	1.17

(1) Donatable hydrogen = $1/2 (\alpha\text{-cyclic} + \beta\text{-cyclic})$

method gives the following order of "donatable hydrogen" for the various +454 C and -454 C solvent fractions:

+454 C O-containing aromatics
 -454 C O-containing aromatics
 -454 C aromatics
 -454 C N-containing aromatics
 +454 C aromatics
 +454 C asphaltenes
 +454 C N-containing aromatics.

The amount of potentially donatable hydrogen alone does not correlate with the product yields and conversions obtained in this work. This is expected, as discussed earlier, because there are many factors associated with the quality of recycle solvents which might be equally or more important than the amount of potentially labile hydrogen.

The use of H^1 -NMR spectra in THF with D_2O added to exchange with hydrogen in the solvent molecule, which was previously discussed briefly, gives a measure of the hydrogen available as hydrogen ions (H^+) rather than hydrogen atoms ($H^\bullet$). This data may say something about the structure of the solvent molecules but is not likely to be directly related to hydrogen "donation".

Measurement of "Kinetic" Hydrogen Availability

A number of methods have been used to measure "kinetic" hydrogen donation, i.e. actual donation of hydrogen to hydrogenate model compounds thought to have structures similar to those present in coal. In one example, Bockrath and Bittner have generated benzyl radicals by the decomposition of dibenzyl mercury and allowed a hydrogen donor model compound to compete, by abstraction of hydrogen atoms, with radical recombination and the reaction of dibenzyl radicals with the solvent to obtain relative rates of hydrogen donation⁽²³⁾.

Benjamin, et.al. at Oak Ridge National Laboratories have studied hydrogen shuttling by looking at the exchange of deuterated diphenyl methane with a variety of coal and solvent model compounds⁽²⁴⁾.

Pannelker, S.V. et.al. have shown that nitrogen-containing aromatics react more rapidly than aromatic hydrocarbons in hydrogen

transfer systems with various solvent and coal model compounds⁽²⁵⁾.

Measurement of Hydrogen Shuttling by Net Hydrogen Loss

In this work hydrogen shuttling was measured indirectly by measuring the net amount of gaseous hydrogen lost from the system. These results (Table 27) gave the following relative rankings in decreasing order for hydrogen shuttling:

+454 C total recycle solvent
 -454 C aliphatics and hydroaromatics
 +454 C aromatics
 no added solvent
 -454 C aromatics
 -454 C N-aromatics
 -454 C total recycle solvent
 +454 C N-aromatics
 +454 C O-aromatics
 -454 C O-aromatics
 +454 C aliphatics (net hydrogen increase).

These data are the small differences between two large numbers and as a result are not very precise. They can also reflect the relative lack of hydrogen in the solvent fractions themselves, i.e. the H₂ gas lost may have been used to hydrogenate the solvent. However, there is a correlation between net hydrogen lost and conversion, shown in Figure 25, but not between potentially donatable hydrogen, as measured by H¹-NMR, and conversion.

Relationships Between Heteroatom Types in Recycle Solvents

The polarity of recycle solvents is an important factor in their behavior. The N-containing and O-containing solvents have been studied in some detail by others and have been found to interact⁽²⁶⁾. The hydrogen bonding interactions which occur can lead to solvent loss, at least temporarily, and the formation of "asphaltene" products as defined by their solubilities in the appropriate solvents. This was also clearly seen in this study; N-aromatics consistently produced the highest concentrations of asphaltenes (Table 26).

Others have shown that the position of the heteroatom on the ring in the solvent, using model compounds, can result in different reactivities⁽²⁷⁾. In this work there appeared to be a relationship

FIGURE 25. CORRELATION BETWEEN NET HYDROGEN LOST AND RELATIVE MAF CONVERSION TO THF SOLUBLES (No added solvent=1.0)

between the types of nitrogen heteroatoms in the solvent molecules and the presence of other heteroatoms. This relationship is summarized in Table 31 below:

TABLE 31. HETEROATOM CONCENTRATIONS ASSOCIATED WITH ACIDIC, BASIC AND NEUTRAL NITROGEN IN RECYCLE SOLVENT MOLECULES

Nitrogen Type	Primary	Secondary	Tertiary
Relative Acidity	Neutral	Acidic	Basic
Total Nitrogen, wt %	2.53	1.64	2.03
Nonbasic Nitrogen, %	79.	95.	22.
Basic Nitrogen, %	21.	5.	78.
Oxygen/Nitrogen ratio	0.89	1.17	1.28
Acidic oxygen, %	0.	0.	95.
Nonacidic oxygen, %	100.	100.	5.
Sulfur/Nitrogen ratio	0.076	0.077	0.23

The data suggest that oxygen content decreases in going from $3^{\circ}\text{-N} > 2^{\circ}\text{-N} > 1^{\circ}\text{-N}$ and that nonacidic oxygen is associated with neutral 1°-N and acidic 2°-N but acidic (phenolic) oxygen is associated with basic 3°-N . Sulfur is also associated more strongly with 3°-N . This type of data should be developed with more accuracy and detail to obtain information on the heteroatom containing structures which occur in coal derived materials.

Effect of Molecular Weight on Solvent Efficiency

As pointed out recently by Moroni, et.al. there are opposing factors affecting solvent efficiency as molecular weight increases⁽¹⁾. The higher molecular weight materials should be better H-donors but

there is less potential hydrogen to donate. There may be at least two other factors which must be taken into account. First, as also pointed out by Moroni, the lower molecular weight components ($\beta_p < 360$ C) may be in the vapor phase under process conditions and therefore can not exert a physical solvent effect. Second, the higher molecular weight materials which have larger structures may not be able to get close enough to the large dissolving coal fragments to exercise a "catalytic" hydrogen transfer reaction, i.e. steric considerations may also be important.

One piece of evidence which suggests that steric effects may be important is the fact that 9,10-dihydrophenanthrene is a better hydrogen donor than 9,10-dihydroanthracene even though the reaction with 9,10-dihydroanthracene is favored energetically⁽²⁷⁾. Steric effects should be studied more closely to see if they exert a significant effect.

In this study the effects of increasing molecular weight were studied by comparing the results of adding -454 C fractions and +454 C fractions of the same chemical type to the recycle solvent to study their effects on liquefaction. The results were mixed (Table 26). The heavier aliphatic hydrocarbons and O-containing aromatics gave higher conversions but the lower molecular weight aromatic hydrocarbons and N-containing aromatic fractions gave better conversions. It seems likely that the latter two fractions react significantly by hydrogen transfer, in which steric effects are important, while the aliphatics, which cannot transfer hydrogen, and the O-containing aromatics may be limited to largely physical solvency mechanisms which would be improved by increasing molecular weight.

Overall Effect of Recycling Heavy Ends in the ITSL Process

Although the overall effect of recycling the +343 C material in the solvent is negative on a single pass basis in the laboratory, there is a significant positive effect on the ITSL process because it allows the process to produce a single premium value liquid product. The overall yield of this product is higher than would be possible if the heavy ends were not recycled because the high molecular weight materials are at least partially converted to product liquids. The recycled heavy ends

also contain nearly all of the carcinogenic materials resulting from the process. A much more acceptable product is produced as a result of recycling the carcinogenic portion to extinction. Finally, some of the higher boiling point materials do have a positive effect on the first stage in the two-stage coal liquefaction process. These include all of the hydrocarbon fractions, aliphatic, hydroaromatic and aromatic, which together comprise about 25 percent of the +454 C portion of the recycle solvent.

Conclusions

The major conclusions resulting from this work may be summarized as follows:

- -454 C recycle solvent is primarily aromatic hydrocarbons (73%) and contains almost no asphaltenes
- +454 C recycle solvent is primarily asphaltenes (heptane insolubles ~ 60%) and aromatic hydrocarbons (23%)
- Recycle solvent also contains aliphatic hydrocarbons, N-containing aromatics and O-containing aromatics
- The heteroatoms in coal derived materials seem to be grouped by type, i.e. acidic O and basic N and sulfur occur together
- Under helium a small net amount of hydrogen and more CO and CO₂ are produced than under hydrogen
- Under hydrogen the amounts of H₂S and hydrocarbon gases are increased and a small amount of hydrogen gas is usually consumed
- Overall coal conversions to THF solubles are improved by adding more -454 C solvent but decreased by adding +454 C solvent
- For added fractions of -454 C solvent the percent conversion to THF solubles increases in the order aromatic hydrocarbons (+7.2) > aliphatic hydrocarbons (+0.8) > no added solvent (0.0) > N-containing aromatics (-0.9) > O-containing aromatics (-22.1)
- Percent conversion to THF solubles using -454 C solvent with +454 C solvent fractions added decrease in the order aliphatics (+3.7) > aromatic hydrocarbons (+3.0) > no added solvent (0.0) > O-containing aromatics (-9.3) > N-containing aromatics (-13.3)

- Of the +454 C solvent components, aromatic hydrocarbons and aliphatic hydrocarbons are beneficial but total only ~25% of the +454 C recycle solvent
- Steric effects may be important in determining the effectiveness of the heavier solvent components as liquefaction solvents

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