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**CHARACTERIZATION OF COAL LIQUIDS DERIVED
FROM THE H-COAL PROCESS**

By

S. A. Holmes
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J. E. Dooley

Date Published November 1976

Bartlesville Energy Research Center
Energy Research and Development Administration
Bartlesville, Oklahoma

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CHARACTERIZATION OF COAL LIQUIDS DERIVED FROM THE H-COAL PROCESS

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S. A. Holmes,¹ P. W. Woodward,¹ G. P. Sturm, Jr.,¹
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ABSTRACT

Compositional data of coal liquid products derived from the H-Coal process were obtained. Two overhead products (one from the fuel oil mode of operation and the other from the syncrude mode of operation) were prepared by Hydrocarbon Research, Inc. from Illinois No. 6 coal. The compositional data of these products are tabulated, and characteristics of the materials are discussed. Separation and characterization methods, with slight modification, as developed by the Bureau of Mines-API Research Project 60 for characterizing heavy ends of petroleum were successfully used in analyzing coal liquid distillates within the boiling range 200° to 540° C. Distillates boiling below 200° C were separated and analyzed using chromatographic and spectral techniques.

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² Project leader.

INTRODUCTION

Developmental work in coal liquefaction technology has become important to this country with the awareness of dwindling petroleum resources. Liquefaction research stresses not only producing a substitute refinery feedstock but also producing the maximum amount of low-cost, clean fuel suitable for direct use in boilers. A number of liquefaction processes with this defined purpose are currently under development (8,14)³; among them is the H-Coal process used by Hydrocarbon Research, Inc.

Only by thorough study of the chemical composition and character of these coal products can optimal conditions be established for various coal liquefaction processes. While no single analytical technique can give a completely detailed compositional analysis of a coal product, a combination of methods will characterize the sample adequately when done in a systematic manner. Previously reported methods used in coal liquid characterization include: gas chromatography (GC) (2); gel-permeation chromatography (GPC) (3-7,9,10,18,20-22); adsorption chromatography (3-7,10,18,20-22); high- and low-resolution mass spectrometry (1,3-7,10-11,15-16,18-19,20-22); ultraviolet spectroscopy (13,18), infrared spectroscopy (2); nuclear magnetic resonance spectroscopy (NMR) (37, 18-22); and various other methods (13). It is the objective of this work to characterize two liquid H-Coal products by means of compositional analyses. Various chemical separations and instrumental techniques used in these analyses are similar to those successfully used in previous studies of liquids derived by the COED process from Utah (6) and western Kentucky coal (18), and by the SYNTHOIL process from West Virginia coal (22). The analysis methods are adapted from those of the American Petroleum Institute (API) Research Project 60 for characterization of heavy ends of petroleum (3-5,7,9-10,20-21).

This report summarizes compositional data on two liquid H-Coal overhead products. One product is from the fuel oil mode of operation; the other is from the syncrude mode of operation (8,12,14). Illinois No. 6 coal was used as the feed coal for both modes of operation. Further work is in progress to study the higher boiling vacuum bottom products associated with both the fuel oil and syncrude modes of operation.

HISTORY OF TOTAL OVERHEAD PRODUCTS

One overhead product was processed by a fuel oil mode of operation and one overhead product was processed by a syncrude mode of operation (12). Each mode of operation also produced a vacuum bottom product. Both the overhead and the vacuum bottoms of each mode of operation were derived from the H-Coal process of Hydrocarbon Research, Inc. using Illinois No. 6 coal. Conditions for both modes of operation were 2,245 psig at reactor outlet and 850° F reactor temperature. Figure 1 presents the

³ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

FUEL OIL
Mode of Operation

SYNCRUDE
Mode of Operation

FIGURE 1. – Conditions of operation for producing coal products
using the H-Coal process

conditions of each mode of operation producing the coal products using the H-Coal process. In the fuel oil mode of operation, a coal feed rate of 62.4 lbs/hr/ft³ reactor with a hot separator reactor slurry recycle of 1.045 lbs/lb coal and a distillate recycle of 1.40 lbs/lb coal yielded a feed slurry containing 29.03 weight-percent coal. The blend of material produced by the reactor operation consisted of 27.9 weight-percent overhead product (distillate) and 72.1 weight-percent vacuum bottoms product. In the syncrude mode of operation, a coal feed rate of 31.2 lbs/hr/ft³ reactor with a hot separator reactor slurry recycle of 3.98 lbs/lb coal and a distillate recycle of 0.40 lbs/lb coal yielded a feed slurry containing 20.08 weight-percent coal. The blend of material produced by the reactor in the syncrude mode of operation consisted of 48.2 weight-percent overhead product and 51.8 weight-percent vacuum bottoms product. The amount of reacted hydrogen in the fuel oil and the syncrude mode of operation were determined to be 12.2 and 15.2 Mscf/ton coal, respectively. The catalyst used in both processes was American Cyanamid HDS-2A.

EXPERIMENTAL

The fuel oil and syncrude liquid products (total overheads) and their distillates discussed below underwent physical property testing utilizing the ERDA routine method for crude oil analysis. Asphaltene content was determined by extracting each overhead product with fifty volumes of n-heptane to one volume of sample. After the hot solution had been stirred 1 hour and left standing overnight, the solution was filtered. The precipitated asphaltenes were carefully evaporated over nitrogen, dried, and weighed. Each overhead product was processed into one low-boiling distillate and one high-boiling distillate using a 4-inch-diameter Roto-film molecular still. Simulated distillation by gas chromatography was done using a Dexsil 300 GC column to determine end-point temperatures for the low-boiling distillates. The end-point temperatures of the high-boiling distillates were determined by ASTM D-86 distillation.

The fuel oil and the syncrude low-boiling distillates were separated by using previously described extraction methods (6,18) into acidic, basic, and hydrocarbon components. Each hydrocarbon portion was then separated on silica by liquid chromatography, using refractive index and UV detectors, into fractions representing aliphatic saturates, aliphatic olefins, monoaromatics, and diaromatics. All acidic and basic components and the separated hydrocarbon fractions were analyzed by programmed temperature gas chromatography using a Carbowax 20-M glass column (2mm i.d. x 6 ft) and a flame ionization detector. In addition to the flame ionization detector, the bases were analyzed with a TRACOR® 310 Hall Electrolytic Conductivity Detector. Area measurements representing percent concentrations were determined from electronic integration. By use of appropriate internal standards of known concentrations, each fraction was calculated on a weight-percent basis. High-voltage, low-resolution mass spectral analyses using the ASTM D2789 procedure for determining hydrocarbon types in low olefinic gasoline were also obtained for the complete hydrocarbon portion of both these distillates. Carbon number 8 and 9 inverse matrices

for aromatics and carbon number 9 and 10 inverse matrices for paraffins were used in the analyses.

The high-boiling distillates of the fuel oil and of the syncrude were separated and characterized following the methods, except for slight modifications, developed by the Bureau of Mines-API Research Project 60 for characterizing heavy ends of petroleum. Each of these high-boiling distillates was separated using gradient elution through adsorption columns (10) into saturate, monoaromatic, diaromatic, and polyaromatic-polar concentrates. Sulfur and nitrogen content were determined for all concentrates. The saturate concentrates were analyzed by high-voltage (70 eV), low-resolution mass spectrometry and were characterized by means of mass spectral matrices developed by Hood and O'Neal (11). A C_{16} n-alkane inverted matrix, which has provisions for four naphthene rings and an estimate of any monoaromatic concentration present were used. The monoaromatic and diaromatic concentrates were separated by GPC into equal incremental elution volumes of 25 ml each and then were semiquantitatively analyzed by low-voltage (11 eV), low-resolution mass spectrometry. In addition, 60-MHz proton NMR results and high-resolution mass spectral results using electron impact and field ionization sources were obtained for selected GPC fractions that cover the entire GPC elution volume range. The more complex nature of the polyaromatic-polar material required removal of the strong and weak acids and the bases from each of these concentrates prior to further characterization study. The neutral hydrocarbons remaining after the acid and base extractions were separated by GPC into fractions in the same way as the diaromatic and monoaromatic concentrates. The strong acids, weak acids, bases, and selected hydrocarbon GPC fractions covering the entire GPC elution volume range were analyzed by low-voltage, low-resolution mass spectrometry. Selected GPC fractions of the neutral hydrocarbons were also studied by high-resolution mass spectrometry using both electron impact and field ionization sources, proton NMR, and fluorescence spectrophotometry. It was necessary to separate components within a GPC fraction using high-pressure liquid chromatography (HPLC) in conjunction with a flow-through cell in the spectrophotometer for the fluorescence study (17). Corrected excitation and corrected emission spectra were obtained for several of these separated components.

The results from these experimental procedures are shown in the following figures and tables. These results characterize each of the two overhead products studied.

RESULTS

Physical Property Testing of Total Overhead Products

Physical property data for the fuel oil and syncrude total overhead products are listed in tables 1 and 2. Both brownish-black products

Synthetic Fuel Oil
H-Coal Process
Burning Star Mine Illinois No. 6 coal

Illinois

GENERAL CHARACTERISTICS

Gravity, specific, 0.935 Gravity, ° API, 19.8 Pour point, ° F., below 5
Sulfur, percent, 0.21 Color, brownish black
Viscosity, Saybolt Universal at 77° F, 38 sec; 100° F, 35 sec Nitrogen, percent, 0.440

DISTILLATION, ERDA'S ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 754 mm. Hg
First drop, 144 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API. 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud 1/ test, ° F.
1	122									
2	167									
3	212	4.6	4.6	0.760	54.7	-	1.41756	145.5		
4	257	5.5	10.1	.783	49.2	42	1.43517	151.1		
5	302	6.8	16.9	.818	41.5	51	1.45236	163.4		
6	347	10.1	27.0	.874	30.4	71	1.47633	168.2		
7	392	13.9	40.9	.919	22.5	86	1.47155	217.7		
8	437	14.3	55.2	.939	19.2	90				
9	482	10.9	66.1	.947	17.9	88				
10	527	9.3	75.4	.964	15.3	92				

STAGE 2—Distillation continued at 40 mm. Hg

11	392	7.5	82.9	1.001	9.9	105			48	
12	437	7.3	90.2	1.030	5.9	115			68	
13	482	5.8	96.0	1.071	.6	131			171	
14	527									
15	572									
Residuum.		3.8	99.8	1.140	-					

Carbon residue, Conradson: Residuum, 17.5 percent; crude, 0.8 percent.

Residuum:
Sulfur, percent, 0.25
Nitrogen, percent, 1.762

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	4.6	0.760	54.7	
Total gasoline and naphtha	40.9	0.855	34.0	
Kerosine distillate	-	-	-	
Gas oil	39.4	.954	16.8	
Nonviscous lubricating distillate	13.4	1.009-1.074	8.7-0.3	50-100
Medium lubricating distillate	2.3	1.074-1.088	0.3	100-200
Viscous lubricating distillate	-	-	-	Above 200
Residuum	3.8	1.140	-	
Distillation loss	.2			

1/ Fractions too dark for determination.

2/ Distillation discontinued at 482° F.

TABLE 1. - Preliminary data of coal liquid
from fuel oil mode of operation

Syncrude
H-Coal Process
Monterey Mine Illinois No. 6 coal

Illinois

GENERAL CHARACTERISTICS

Gravity, specific, 0.953 Gravity, ° API, 17.0 Pour point, ° F., below 5
Sulfur, percent, 0.27 Color, brownish black
Viscosity, Saybolt Universal at 77° F, 59 sec; 100° F, 46 sec Nitrogen, percent, 0.633

DISTILLATION, ERDA'S ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 746 mm. Hg
First drop, 138 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud 1/test, ° F.
1	122									
2	167									
3	212	6.0	6.0	0.744	58.7	-	1.41259	134.2		
4	257	9.3	15.3	.775	51.1	38	1.42667	138.5		
5	302	5.3	20.6	.811	43.0	48	1.44643	154.8		
6	347	10.7	31.3	.865	32.1	67	1.47238	174.0		
7	392	10.7	42.0	.911	23.8	82	1.49868	194.2		
8	437	10.5	52.5	.936	19.7	88	1.51897	216.4		
9	482	7.1	59.6	.955	16.7	92				
10	527	5.4	65.0	.973	13.9	96				

STAGE 2—Distillation continued at 40 mm. Hg

11	392	3.8	68.8	1.001	9.9	105			43	
12	437	5.2	74.0	1.045	3.9	122			55	
13	482	5.3	79.3	1.063	1.6	127			111	
14	527	4.9	84.2	1.087	-	136			over 400	
15	572	5.2	89.4	1.112	-	144			do	
Residuum		10.5	99.9	1.158	-					

Carbon residue, Conradson: Residuum, 18.0 percent; crude, 2.3 percent.

Residuum:
Sulfur, percent, 0.42
Nitrogen, percent, 1.457

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	6.0	0.744	58.7	
Total gasoline and naphtha	20.6	0.775	51.1	
Kerosine distillate	-	-	-	
Gas oil	49.0	.928	21.0	
Nonviscous lubricating distillate	10.7	1.027-1.078	6.3	50-100
Medium lubricating distillate	9.1	1.078-1.100	-	100-200
Viscous lubricating distillate	-	-	-	Above 200
Residuum	10.5	1.158	-	
Distillation loss	.1			

1/ Fractions too dark for determination.

TABLE 2. - Preliminary data of coal liquid from syncrude mode of operation

from the fuel oil and syncrude operations have nearly the same specific gravity values (0.935 and 0.953) and low sulfur content (0.2 and 0.3 percent). Nitrogen values of 0.44 percent and 0.63 percent of total overhead for the fuel oil and the syncrude were also determined. A greater concentration of lighter boiling material in the total overhead of the fuel oil as compared to the syncrude is observed from the ERDA routine distillation. About 90 percent of the fuel oil and 74 percent of the syncrude distilled at 225° C (437° F) at 40 torr. The amount of overhead residuum in the syncrude is almost three times that amount in the fuel oil. Gravity measurements indicate the fuel oil product to be lighter than the syncrude.

Although the residuum comprised only 3.8 percent of the fuel oil overhead, about 4.5 percent of the total overhead sulfur content and 15 percent of the total overhead nitrogen content were found in the residuum. The syncrude's residuum comprising 10.5 percent of the total overhead contained about 16 percent of the total overhead sulfur content and 24 percent of the total overhead nitrogen content. The tendency for sulfur and nitrogen compounds to concentrate in the heavy ends of these two coal products corresponds to previously characterized coal liquid from the SYNTHOIL liquefaction process and in petroleum crudes. Asphaltene content comprised about 1 percent total fuel oil overhead and 3.4 percent total syncrude overhead.

Preparation of Distillates

Each overhead product was processed into a high- and low-boiling distillate. Distillate cut points at atmospheric pressure and the concentration of each distillate for the fuel oil and syncrude products are shown in figure 2. Low-boiling distillate end-point temperatures were determined at 203° C for fuel oil and at 197° C for the syncrude. From ASTM D-86 distillation, the high-boiling distillate end-point temperatures were determined at 413° C for the fuel oil and at 493° C for the syncrude. About 65 percent of each overhead product was found in the high-boiling distillates. Since both samples were overhead products of the H-Coal process, it was to be expected that any heavy end material would be of minimal concentration as shown by the ASTM D-86 distillation results. Only a 0.7 percent and a 0.2 percent loss of total overhead material occurred in the fuel oil and syncrude distillations.

Physical property data for each distillate is summarized in table 3. Low sulfur levels are indicated in the low-boiling distillates but increasing in the high-boiling distillates. The amount of nitrogen registers a strong increase going from the low-boiling distillate to the high-boiling distillate of the syncrude while the amount of nitrogen does not show such a strong increase in the high-boiling distillate of the fuel oil. The carbon residue in the syncrude high-boiling distillate is twice that value in the high-boiling distillate of the fuel oil.

FIGURE 2. – Distillation of H-Coal total overhead products

TABLE 3. - Physical property data for distillates
from Illinois No. 6 coal liquids

Property	Fuel oil		Syncrude	
	<203° C distillate	>203° C distillate	<197° C distillate	>197° C distillate
Specific gravity, 60°/60° F	0.864	0.979	0.838	1.025
Gravity, ° API	32.3	13.0	37.4	6.6
Pour point, ASTM D-97, °F	<5	<5	<5	<5
Color, ASTM D-1500 or (BuMines description).	NPA6	Brownish black	NPA4-1/2	Brownish black
Kinematic viscosity @ 100° F, ASTM D-445, C _s	1.08	3.87	0.96	14.90
Saybolt viscosity, SUS, 100° F	-	39	-	77
Sulfur (Bomb) ASTM D-129, wt-pct ...	0.13	0.29	0.06	0.35
Nitrogen, Kjeldahl, wt-pct	0.420	0.446	0.212	0.871
Carbon residue (Conradson) ASTM-524, wt-pct	0	2.33	0	5.44

Separation and Characterization of the <203° C and <197° C Distillates

Acids, bases, and neutral hydrocarbons were isolated from the fuel oil <203° C distillate and syncrude <197° C distillate. The weight-percent amounts of these acids, bases, and hydrocarbons are listed on a distillate and total overhead basis in table 4. Almost 8 percent more acids were found in the fuel oil distillate (22.3 percent) as compared to the syncrude (14.5 percent) distillate. GC analyses of the acidic portions showed each consisting entirely of phenols ranging from C₆ to C₉ in carbon number. The bases represented a small amount of material in each distillate accounting for about 1.1 percent of the total distillate in the fuel oil and 0.85 percent of the total distillate of the syncrude. GC analyses showed two main classes of nitrogens present--pyridines and anilines. Non N-substituted anilines comprised most of the basic components. No neutral nitrogen compounds were detected.

The greatest amount of material in these two low-boiling distillates was present in the hydrocarbon portion. The fuel oil distillate contained about 74 percent hydrocarbon compared to 78 percent hydrocarbon in the syncrude distillate. The hydrocarbon portion of each distillate was separated into fractions representing saturates, aliphatic olefins, monoaromatic, and diaromatic hydrocarbons. The percent concentrations of these fractions determined from GC analyses are listed in table 4. The fuel oil and syncrude distillates varied the most in saturate concentration being 33.9 percent and 42.6 percent respectively. The olefin concentrations amounted to 5.9 percent and 3.6 percent and the monoaromatic concentrations amounted to 34.2 and 31.4 percent of the fuel oil and syncrude respectively. Only trace amounts of diaromatic hydrocarbons were found in both these distillates.

In addition to the GC analyses of the hydrocarbon material, mass spectral results presented a slightly different perspective as to the makeup of this hydrocarbon portion. From mass spectral analyses of the total hydrocarbon portion it was possible to semiquantitatively estimate the amounts of paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes, indans and/or tetralins, and naphthalenes. The results on a weight-percent basis are shown in table 5. The percent of monocycloparaffins calculated from the matrix inverse have had the olefin concentration subtracted assuming all olefins are monoolefins. The syncrude distillate on a weight-percent of total overhead basis shows a greater amount of paraffins and monocycloparaffins, but smaller amounts of dicycloparaffins and indanes and tetralins than the fuel oil distillate. Both distillates indicated about equal amounts of alkylbenzenes and naphthalenes. These particular mass spectral results are not completely reliable since the ASTM D2789 procedure is applicable to low olefinic <3.0 percent gasoline. As a consequence mass spectral results in comparison to previous GC results may overestimate the concentrations of saturate material and underestimate the concentration of aromatic material.

TABLE 4. - Compositional analyses of low-boiling distillates

Chemical class type	Fuel oil		Syncrude	
	<203° C distillate, weight-percent	Total overhead, weight-percent	<197° C distillate, weight-percent	Total overhead, weight-percent
Acids	22.3	7.94	14.5	5.01
Bases:				
Pyridines	.19	.07	.1	.04
Anilines	.88	.31	.7	.25
Total bases..	1.07	.38	.85	.29
Hydrocarbons:				
Saturates	33.9	12.08	42.6	14.73
Olefin	5.9	2.10	3.6	1.24
Monoaromatics...	34.2	12.18	31.4	10.86
Diaromatics	Trace	Trace	.2	.07
Total hydrocarbons	74.0	26.36	77.8	26.90
Loss	2.6	.93	6.85	2.37

TABLE 5. – Ring distribution in hydrocarbon portion of
low-boiling distillates

Hydrocarbon type	Fuel oil		Syncrude	
	<203° C distillate weight-percent	Total overhead, weight-percent	<197° C distillate, weight-percent	Total overhead, weight-percent
Paraffins	9.5	3.38	10.7	3.70
Monocycloparaffins.....	15.6	5.56	21.7	7.51
Dicycloparaffins	13.8	4.92	13.2	4.57
Alkylbenzenes.....	14.4	5.13	14.3	4.94
Monocyclic benzenes (indanes and tetralins) ...	11.8	4.20	11.0	3.80
Naphthalenes.....	<u>3.0</u>	<u>1.07</u>	<u>3.3</u>	<u>1.14</u>
Hydrocarbon sum, excluding olefins ...	68.1	24.26	74.2	25.66

Summation of acids, bases, and neutral hydrocarbons in the fuel oil and the syncrude distillates amounted to about 97.4 and 93.2 percent respectively. The 3- and 7-percent sample losses were attributed to additive handling losses occurring within the separation steps.

Separation and Characterization of >203° C and >197° C Distillates

Further characterization of the >203° C fuel oil and >197° C syncrude distillates required separation of each distillate into four concentrates: saturate, monoaromatic, diaromatic, and polyaromatic-polar components. Table 6 gives the weight-percent of each concentrate on a distillate and on a total overhead basis. The fuel oil monoaromatic concentrate accounted for nearly one-third of the distillate and it was twice that of the syncrude; whereas, the syncrude polyaromatic-polar concentrate accounted for one-half the total distillate. Only traces of nitrogen and sulfur were found in the saturate, monoaromatic, and diaromatic concentrates while the polyaromatic-polar concentrates showed the greatest nitrogen and sulfur concentration. On a distillate basis about 0.52 percent sulfur and 1.23 percent nitrogen were determined in the fuel oil polyaromatic-polar concentrate while 0.45 percent sulfur and 1.74 percent nitrogen were determined in the syncrude polyaromatic-polar concentrate.

GPC chromatograms showing the weight-percent distribution of these aromatic concentrates versus elution volume are presented for each distillate in figure 3. Although the concentrates from both distillates gave similar very broad distributions, it is of interest to find earlier eluting material from the syncrude in comparison to the fuel oil. This is especially obvious in the polyaromatic-polar concentrate. The earlier eluting material suggests compounds of larger molecular volume are present in the syncrude. Results of GPC-MS correlations presented later substantiate this observation.

Saturates

The >203° C fuel oil and the >197° C syncrude saturate concentrates were analyzed by high-voltage, low-resolution mass spectrometry. The data of table 7 give the ring distribution in the high-boiling distillates calculated on a weight-percent of distillate and of total overhead bases. The saturate concentrate on a weight-percent distillate basis amounted to 12 percent of the fuel oil and to 7.4 percent of syncrude. The zero-, one- and two-ring saturate systems account for about 75 percent of the saturate concentrate in both distillates. The fuel oil is weighted heaviest in the one and two-naphthene ring systems while the syncrude is weighted heaviest in the zero-ring system with less amounts of one- and two-naphthene ring systems. Both saturate concentrates contained little monoaromatic material (about 2 percent of the high-boiling distillate) indicating good separation on the adsorption columns. The concentration of this monoaromatic material overlapping into the saturate concentrates is presented in the monoaromatic analyses.

TABLE 6. - Concentrate distribution from adsorption chromatographic separation of the high-boiling distillates

Adsorption chromatographic concentrate	Fuel Oil		Syncrude	
	>203° C distillate, weight-percent	Total overhead, weight-percent	>197° C distillate, weight-percent	Total overhead, weight-percent
Saturates	12.0	7.65	7.4	4.83
Monoaromatics	31.8	20.26	16.3	10.64
Diaromatics	16.7	10.64	13.9	9.07
Polyaromatic-polars	29.5	18.79	50.7	33.09
Unanalyzed (separation loss)	10.0	6.37	11.7	7.64

FIGURE 3. - GPC chromatograms for three aromatic compound-type concentrates of the fuel oil and of the syncrude high-boiling distillates.

TABLE 7. - Ring distribution of saturate compound types
in the >203° C and >197° C distillates

Ring number	Fuel oil		Syncrude	
	>203° C distillate, weight-percent	Total overhead, weight-percent	>197° C distillate, weight-percent	Total overhead, weight-percent
0	2.699	1.720	2.179	1.422
1	3.248	2.069	1.758	1.147
2	2.988	1.904	1.619	1.057
3	1.836	1.170	.967	.631
4	.977	.622	.696	.454

Monoaromatics

Monoaromatic concentrates amounting to 31.8 percent of the fuel oil and 20.3 percent of the syncrude distillates were separated by GPC into equal eluting volumes and were semiquantitatively analyzed by low-resolution mass spectrometry. In table 8 semiquantitative data for monoaromatic compound types are listed. About 72 percent of each concentrate consisted of alkylbenzenes and the naphthenologs thereof with up to seven and eight naphthene rings on a benzene nucleus. "Average" carbon number for the monoaromatics of both distillates was C_{13} with an approximate molecular carbon number range of C_{10} to C_{28} for the fuel oil and C_{10} to C_{30} for the syncrude. Total monoaromatic concentration in these high boiling distillates amounted to 23.21 percent of the fuel oil and to 11.80 percent of the syncrude. About 21 percent of each monoaromatic concentrate contained an alkylnaphthalene nucleus as a result of overlapping compound types from the adsorption separations and is reported in the appropriate diaromatic compound type in table 9. A greater percentage of higher numbered ring structures was found in the syncrude than in the fuel oil as indicated by the data. High resolution mass spectral analyses indicated several oxygenate and dioxygenate series: -8(O), -10(O_2); -10(O), -12(O_2); -12(O), -14(O_2). No quantitation of these oxygenates is presently available. A small amount of sulfur-containing material was identified in both concentrates and is listed with the polyaromatic-polars. Physical property data corroborates the relatively small amount of sulfur in each of these concentrates.

TABLE 8. - Semiquantitative analysis of monoaromatic compound types
in the >203° C and >197° C distillates

Mass Z Series	Weight-percent in >203° C fuel oil	Weight-percent total overhead fuel oil	Weight-percent in >197° C syncrude	Weight-percent total overhead syncrude	Suggested compound types
- 6 and - 8(O),-10(O ₂)	1.545	0.984	1.288	0.841	Alkylbenzenes and alkylacetophenones/ phthalaldehydes.
- 8 and -10(O),-12(O ₂)	12.295	7.833	6.264	4.089	Alkyl naphthenobenzenes and alkylbenzofurans/ benzopyrones.
-10 and -12(O),-14(O ₂)	7.884	5.023	3.253	2.123	Alkyldinaphthenobenzenes and alkylphenylfu- furans/naphthaquinones.
-12	.953	.607	.529	.345	Alkyltrinaphthenobenzenes.
-14	.183	.115	.162	.106	Alkyltetranaphthenobenzenes.
-16	.083	.053	.057	.037	Alkylpentanaphthenobenzenes.
-18	.007	.004	.030	.020	Alkylhexanaphthenobenzenes.
-20	.010	.006	.026	.017	Alkylheptanaphthenobenzenes.
-22	-	-	.007	.005	Alkyloctanaphthenobenzenes.
ND ¹	.252	.161	.181	.118	Monoaromatics--not classified as to specific types.

¹Compound types not determinable as to specific mass Z series.

NMR analyses of these GPC fractions were consistent with monoaromatic character. A lesser amount of diaromatics as noncondensed (biphenyl) or naphthenonaphthalenes was found in all fractions analyzed. Two small peaks at 4.78 ppm δ and 3.59 ppm δ were tentatively identified as vinylic hydrogen structure and $=CH$ structure (such as in indene) respectively. The trend of decreasing length of substituents and/or decreasing substitution as the GPC elution volume increases was well demonstrated with the NMR data of monoaromatics. This was also found in the diaromatic and polyaromatic-polar concentrates.

Diaromatics

GPC-MS correlations of diaromatic concentrates (fuel oil, 17 percent of distillate; syncrude, 14 percent of distillate) proceeded along similar lines to the study of the monoaromatics. The data of table 9 summarizes the semiquantitative analyses for only the diaromatic compound types of both H-Coal products. These diaromatic compound types, together with the diaromatics overlapping in the monoaromatic concentrate summed to 21.36 percent of the fuel oil distillate and to 16.37 percent of the syncrude distillate. The fuel oil diaromatic concentrate had an average carbon number of C_{14} with a molecular carbon number range of C_{11} to C_{26} , and the syncrude had an average carbon number of C_{14} with a molecular carbon number range C_{11} to C_{34} . The appreciably heavier syncrude material extended from -10 to -28 mass Z series while the fuel oil went from -10 to -26 mass Z series with only minute amounts of -26 present. Comparatively, the syncrude concentrate had a greater amount of higher numbered ring systems than the fuel oil. A small amount of material was tentatively identified as alkyldibenzo-thiophenes (-16S) and is listed with the polyaromatic-polars. Physical property data corroborated the amount of sulfur present; however, these data did suggest that more sulfur was present in the syncrude diaromatic concentrate than was identified from mass spectral data.

NMR analyses of selected GPC fractions of the fuel oil and syncrude diaromatic concentrates substantiated MS interpretations. Both substituted naphthalenes and diphenylalkanes were indicated by the data. Also, a minimal amount of monoaromatic material was detected in each concentrate. Condensed polyaromatics were present in the later eluting GPC fractions. Phenanthrene was identified as comprising the majority of material in the last eluting GPC fraction of both overheads analyzed by NMR.

TABLE 9. - Semiquantitative analysis of diaromatic compound types
in the >203° C and >197° C distillates

Mass Z Series	Weight-percent in >203° C fuel oil	Weight-percent total overhead fuel oil	Weight-percent in >197° C syncrude	Weight-percent total overhead syncrude	Suggested compound types
-10	0.364	0.232	0.324	0.211	Alkylindenes.
-12	8.270	5.269	5.393	3.520	Alkyl naphthalenes.
-14 and -16(0)	5.336	3.400	4.329	2.826	Alkyl naphthenonaphthalenes and alkyl dibenzofurans.
-14	1.511	.963	.624	.407	Alkyl diphenylalkanes/biphenyls.
	1.040	.663	.583	.381	Alkyl naphthenonaphthalenes and/or alkyl diphenylalkanes.
-16 and -18(0)	2.067	1.317	2.431	1.587	Alkyl dinaphthenonaphthalenes and alkyl acenaphthalenes and alkyl fluorenones.
-16	1.677	1.068	.290	.189	Alkyl naphthenodiphenylalkanes/biphenyls.
	.240	.153	.226	.148	Alkyl dinaphthenonaphthalenes and/or alkyl naphthenodiphenyl- alkanes.
-18 and -20(0)	-	-	1.127	.736	Alkyl trinaphthenonaphthalenes and/or alkyl dinaphthenodi- phenylalkanes and/or alkyl naphthenoacenaphthalenes and alkyl diphenylfurans.
-18	.685	.436	.078	.051	Alkyl trinaphthenonaphthalenes and/or alkyl dinaphtheno- cipherylalkanes and/or alkyl naphthenoacenaphthalenes.
-20	.065	.041	.461	.301	Alkyl tetranaphthenonaphthalenes and/or trinaphthenodi- phenylalkanes.
-22	.020	.013	.287	.187	Alkyl pentanaphthenonaphthalenes and/or alkyl tetranaphtheno- diphenylalkanes.
-24	-	-	.060	.039	Alkyl hexanaphthenonaphthalenes.
	-	-	.080	.052	Alkyl pentanaphthenodiphenylalkanes and/or alkyl trinaphtheno- phenanthrenes/anthracenes.
	.018	.011	-	-	Alkyl hexanaphthenonaphthalenes and/or alkyl pentanaphtheno- diphenylalkanes and/or alkyl trinaphthenophenanthrenes/ anthracenes.
-26	.003	.002	.055	.036	Alkyl heptanaphthenonaphthalenes and/or alkyl hexanaphtheno- phenylalkanes and alkyl diaceanthracenes.
-28	-	-	.023	.015	Alkyl octanaphthenonaphthalenes and/or alkyl heptanaphtheno- diphenylalkanes and/or alkyl perylenes.
-10,-24	.060	.038	-	-	Unknown diaromatic types.

Polyaromatic-Polar

Results from chemical extractions of strong acids, weak acids, bases and hydrocarbon-neutrals are shown in table 10. Each of these classes of compounds separated from the polyaromatic-polar concentrates is discussed below.

The strong acid portions of the polyaromatic-polar concentrates accounted for 8.1 percent and 7.2 percent of the fuel oil and syncrude distillates, respectively. About 73 percent of each strong acid portion was identified as phenols and/or benzoic acids and phenyl phenols and their respective naphthenologs. A distinguishing difference between the two overhead strong acid portions was that about 11 percent of the strong acids in the fuel oil was phenol and/or benzoic acid compared with 34 percent of the same type in the syncrude. The fuel oil showed predominance of the naphthenophenols.

Bases accounted for the smallest amount of material in the polyaromatic-polar concentrate (1.4 percent of the fuel oil and 3.8 percent of the syncrude distillates); 64 percent of the bases in the fuel oil were found in decreasing concentration order in mass Z series: -5N, -11N, -13N and -17N. These mass Z series are represented by pyridines, quinolines, naphthenoquinolines and acridines, respectively. Sixty-four percent of the bases in the syncrude were found to be widely distributed among a number of mass Z series in order of decreasing concentration: -7N, -21N; -5N, -19N; -13N. The aceacridines and acridines were predominant types.

Weak acids accounted for 2.5 percent of the fuel oil and 6.3 percent of the syncrude distillates. Forty-two percent of the weak acid portion from the fuel oil consisted of odd mass number compounds in the -5N, -7N, -9N, -11N, -15N, and -17N mass Z series, predominantly carbazoles, anilines or pyridines, and indoles. The other 58 percent material was a mixture of hydrocarbons and oxygenates. The hydrocarbon compound types were found in the -16, -18, -20, -22 (mostly pyrenes), and -26 mass Z series. The oxygenate compound types were found in the following mass Z series in order of decreasing concentration: -6(O), -20(O); -8(O), -10(O₂); -14(O₂); -14(O); -16(O). The syncrude's weak acids consisted of 48 percent odd mass peaks in the -7N, -21N; -9N, -23N; -11N, -13N, -15N, -17N mass Z series. Carbazoles, aceacridines and naphthenocarbazoles were the predominant weak acid types of these compounds. The other 52 percent of the syncrude's weak acids was a mixture of hydrocarbons and oxygenates. The oxygenate and neutral hydrocarbon compound types were similar to those found in the fuel oil, but of different predominant mass Z series. The syncrude indicated predominance of the higher mass Z series of the hydrocarbon and oxygenates.

The extracted polyaromatic-polar hydrocarbon-neutrals made up 17.3 percent of the total material in the fuel oil distillate and 33.0 percent in the syncrude distillate. Table 11 presents semiquantitative

TABLE 10. - Polyaromatic-polar concentrates chemically extracted into four classes

Classes in polyaromatic-polar concentrate	Fuel oil			Syncrude		
	Concentrate, weight- percent	Distillate, weight- percent	Overhead, weight- percent	Concentrate weight- percent	Distillate, weight- percent	Overhead, weight- percent
Hydrocarbon-neutrals	58.7	17.32	11.03	65.1	33.0	21.54
Strong acids	27.4	8.08	5.15	14.2	7.20	4.70
Weak acids	8.6	2.54	1.62	12.4	6.29	4.10
Bases	4.8	1.42	.90	7.4	3.75	2.45
Loss	.5	.15	.09	.9	.46	.30

TABLE 11. - Semiquantitative analysis of polyaromatic-polar hydrocarbon-neutral compound types in the >203° C and >197° C distillates

Mass Z Series	Weight-percent in >203° C fuel oil	Weight-percent total overhead fuel oil	Weight-percent in >197° C syncrude	Weight-percent total overhead syncrude	Suggested compound types
-14 and -16(0), -18(0 ₂)	1.847	1.177	1.339	0.874	Alkylacenaphthenes and alkylbenzofurans/xanthenes.
-16	1.528	.973	.833	.544	Alkylacenaphthalenes.
-18 and -20(0)	3.722	2.371	2.763	1.803	Alkylnaphthenoacenaphthalenes and/or alkylphenanthrenes/ anthracenes and alkylphenylfurans.
-18	2.012	1.282	.823	.537	Alkylphenanthrenes/anthracenes.
-20 and -22(0)	.553	.352	2.103	1.373	Alkylnaphthenophenanthrenes/anthracenes and/or alkyl- naphthenoacenaphthalenes and alkylbenzonaphthenofurans.
-20	.611	.389	.587	.383	Alkyldiacenaphthalenes.
	1.841	1.173	1.752	1.144	Alkyldiacenaphthalenes and/or alkylnaphthenophenanthrenes/ anthracenes and/or alkylidnaphthenoacenaphthalenes.
-22 and -10(0) and -125	2.984	1.901	1.684	1.099	Alkylpyrenes and/or alkylfluoranthrenes and alkylbenzofurans and alkylindanthiophenes.
-22	.042	.027	.019	.012	Alkylfluoranthrenes and/or alkylpyrenes.
	1.286	.819	4.394	2.868	Alkyldinaphthenophenanthrenes/anthracenes and/or alkyl- naphthenodiacenaphthalenes and/or alkyltrinaphtheno- acenaphthalenes.
-24 and -26(0)	.384	.245	-	-	Alkyltetranaphthenoacenaphthalenes and/or alkyltri- naphthenophenanthrenes/anthracenes and/or alkyl- naphthenodiacenaphthalenes and alkyl-naphthylethers.
	-	-	3.301	2.155	Alkyltetranaphthenoacenaphthalenes and/or alkyltrinaphtheno- phenanthrenes/anthracenes and/or alkyl-naphthenopyrenes and alkyl-naphthylethers.
-24	.111	.071	-	-	Alkyl-naphthenopyrenes and/or alkyl-naphthenofluoranthrenes.
	.112	.071	.553	.361	Alkylchrysenes and/or alkyl-naphthenopyrenes.
-25	.130	.083	1.248	.815	Alkylpentanaphthenoacenaphthalenes and/or alkyltetra- naphthenophenanthrenes/anthracenes and/or alkyltri- naphthenodiacenaphthalenes.
	.098	.062	1.431	.934	Alkyltrinaphthenodiacenaphthalenes and/or alkylidnaphtheno- pyrenes and/or alkylidnaphthenofluoranthrenes and/or alkyl- naphthenochrysenes and alkyl-diacanthracenes.
	.011	.007	.052	.034	Alkyl-naphthenochrysenes and/or alkyl-diacanthracenes.

TABLE 11. - Semiquantitative analysis of polyaromatic-polar hydrocarbon-neutral compound types in the >203° C and >197° C distillates--Continued

Mass Z Series	Weight-percent in >203° C fuel oil	Weight-percent total overhead fuel oil	Weight-percent in >197° C syncrude	Weight-percent total overhead syncrude	Suggested compound types
-28	.095	.051	2.119	1.383	Alkylpentanaphthenophenanthrenes/anthracenes and/or alkyltetranaphthenodiacenaphthalenes.
	.031	.020	.643	.420	Alkylbenzopyrenes and alkylperylene.
-30	.034	.022	1.004	.655	Alkylhexanaphthenophenanthrenes/anthracenes and/or alkylpentanaphthenodiacenaphthalenes.
	-	-	.603	.394	Alkylpicenes and/or alkyl-naphthenoperylenes and/or alkyl-naphthenobenzopyrenes.
-32	.008	.005	.595	.388	Alkylheptanaphthenophenanthrenes/anthracenes and/or hexanaphthenodiacenaphthalenes.
	.006	.004	.477	.311	Alkyldibenzopyrenes and/or alkylbenzoperylenes.
-34	-	-	.245	.160	Alkyloctanaphthenophenanthrenes/anthracenes and/or alkyl-heptanaphthenodiacenaphthalenes.
	-	-	.050	.033	Alkyltrinaphthenoperylenes.
-36	-	-	.045	.029	Alkyloctanaphthenodiacenaphthalenes.
-18,-32	-	-	.009	.006	Unknown polyaromatic-polar types.
-26	-	-	.006	.004	Unknown polyaromatic-polar types.
-6(0) and -85	.166	.106	.346	.226	Alkylmethoxybenzenes and/or alkylphenols and alkylpenta-cyclicsulfides.
-8(0) and -10S	.052	.033	.162	.106	Alkylacetophenones and/or alkyl-naphthenophenols and alkyl-benzothiophenes.
-12(0)	.015	.010	-	-	Alkyl-naphthylpropylethers and/or alkylphenylfurans.
-14(0)	.211	.134	.410	.268	Alkylacetoxymethylnaphthalenes and/or alkylphenylphenols.
-16(0)	.222	.141	.098	.064	Alkylbenzophenones and/or alkyl-xanthenes.
-18(0)	.442	.282	.771	.503	Alkyl-naphthenodibenzofurans and/or alkylfluorenones.
-24(0)	Trace	-	.129	.084	Alkylacetylpyrenes.
-10S	.100	.064	-	-	Alkylbenzothiophenes.
-14S	-	-	Trace	-	Alkylthiabenzoindans and/or alkylacenaphthenothiols.
-16S	.060	.038	.178	.116	Alkyldibenzothiophenes.

TABLE 1. - Semiquantitative analysis of polyaromatic-polar hydrocarbon-neutral compound types in the >203° C and >197° C distillates--Continued

Mass Z Series	Weight-percent in >203° C fuel oil	Weight-percent total overhead fuel oil	Weight-percent in >197° C syncrude	Weight-percent total overhead syncrude	Suggested compound types
-18S	.016	.010	.057	.037	Alkyl naphthenodibenzothiophenes.
-18S,-8S ₂	.004	.003	.009	.006	Alkyl arenocyclic sulfides.
-20S	-	-	.033	.022	Alkyl dinaphthenodibenzothiophenes.
-22S	-	-	.147	.096	Alkyl phenanthrenothiophenes.
-24S	-	-	.242	.158	Alkyl acephenanthrenothiophenes.
-13N	.013	.008	-	-	Alkyl dibenzylamines.
-15N	.531	.338	.778	.508	Alkyl carbazole.
-17N	.072	.046	.458	.299	Alkyl naphthenocarbazole.
-19N	.007	.004	.096	.063	Alkyl dinaphthenocarbazole.
-21N	.029	.018	.388	.253	Alkyl benzocarbazole.
	.003	.002	-	-	Alkyl triphenylamines.
	.002	.001	.017	.011	Alkyl trinaphthenocarbazoles.
-23N	.006	.004	.122	.080	Alkyl naphthenobenzocarbazoles.
-25N	.003	.002	.143	.093	Alkyl dinaphthenobenzocarbazoles.
	.010	.006	-	-	Alkyl diethylaminonaphthalenes.
-27N	-	-	.065	.042	Alkyl trinaphthenobenzocarbazoles.
-15N	-	-	.017	.011	Unknown.
-17N	.003	.002	.015	.010	Unknown.
-19N	.006	.004	.004	.003	Unknown.
-	1.060	.675	.487	.318	Unanalyzed GPC material ¹ in monoaromatic concentrate.
-	.268	.171	.120	.078	Unanalyzed GPC material ¹ in diaromatic concentrate.
-	.791	.534	1.182	.771	Unanalyzed GPC material ¹ in polyaromatic-polar concentrate.

¹Material represented by the tail regions of the GPC chromatograms not analyzed because of subfraction quantity limitations.

data from GPC-MS correlations characterizing these hydrocarbon and heteroatomic types together with equivalent chemical types found in the overlap of both the monoaromatic and diaromatic concentrates. Both products showed major compound types in the -22, -20, -18 and -16 mass Z series representing pyrene and/or fluoranthene, phenanthrene/anthracene, acenaphthalenes respectively and their naphthenologs. Considerable material also was found in the -14 nominal mass Z series suggesting alkylacenaphthenes and alkyl dibenzofurans. The average carbon number for the fuel oil distillate polyaromatic-polar hydrocarbons is C_{16} in the -18 mass series with a range from C_{12} in the -15N mass Z series to C_{29} in the -30 mass Z series. Likewise, the average carbon number for the syncrude distillate is C_{20} in the -22 mass Z series with a range from C_{12} in the -15N mass Z series to C_{34} in the -34 mass Z series. These hydrocarbon-neutral portions contained nitrogen compounds amounting to 0.69 percent of the fuel oil and 2.11 percent of the syncrude distillates. Both distillates had nitrogen compound types in the -15N, -17N, -19N, -21N, -23N, and -25N mass Z series. The syncrude showed more nitrogen in all mass Z series than did the fuel oil. Separately identifiable oxygenates were also found in these polyaromatic-polar hydrocarbon fractions belonging mostly to -6(0), -14(0), -16(0) and -18(0) mass Z series. They amounted to about 1.11 percent and to 1.92 percent of the fuel oil and syncrude distillates. Oxygenates identified from high resolution mass spectroscopy were found in the -16(0), -18(0₂), -20(0), -22(0), -10(0), and -26(0) mass Z series. It is not possible at this time to quantify the amounts of these oxygenates. In the syncrude a low concentration of sulfur compounds was identified (less than 0.7 percent of distillate), and in the fuel oil a small amount of sulfur compounds was also identified (less than 0.2 percent of distillate). Most sulfur compound types identified in the syncrude were in the -16S, -18S, -20S, -22S, and -24S mass Z series consisting of dibenzothiophenes and phenanthrenothiophenes and their naphthenologs. Overall, more heteroatomic types and higher mass Z series hydrocarbons were found in the polyaromatic-polar concentrate of the syncrude than in the fuel oil.

NMR data of the polyaromatic-polar hydrocarbons substantiated many of the observations from GPC-MS correlations. Total aromatic-type hydrogens were more in the fuel oil as compared to the syncrude; however, a higher concentration of hydrogen types existing as α -CH₂-, α -CH₃, and possibly ethers were present in the syncrude.

In this laboratory, work is in progress to apply fluorescence spectrophotometry on selected GPC fractions from coal liquids. An exhaustive study was not made on these samples, but correlation with certain mass spectral data was obtained. Fluorescence did identify in the later eluting GPC fractions of both coal liquids benzo[a]pyrene-(B(a)P), benzo[e]pyrene, 1,12-benzoperylene and, tentatively in the syncrude, 1,2-benzocarbazole. Fluorescence reference spectra of pure compounds corroborated in these assignments. Less B(a)P was identified in the fuel oil in agreement with semiquantitative mass spectral results. The highly resolvable and well separated component peaks within several chromatograms of the syncrude GPC fractions studied were in contrast to those

chromatograms of the fuel oil. This supports the observation from mass spectral data that numerous concentrated components are present within this molecular weight range of the syncrude.

Fluorescence spectroscopy often provides an insight into compound identification, and together with GPC-MS correlations indicates the presence or absence of a particular component type. The last eluting GPC fraction of the syncrude analyzed by mass spectroscopy left some question as to whether a particular mass distribution continued to be identified as dibenzopyrene and/or benzoperylene. Fluorescence spectra had verified the presence of 1,12-benzoperylene in an earlier eluting GPC fraction; but in the later eluting fraction where the dibenzopyrene and/or benzoperylene presence was questioned, fluorescence spectra disproved this identification in this later fraction. Evidently dibenzopyrene and benzoperylene had by now entirely eluted from the GPC column and a new component type of the same mass Z series had begun to elute. Insufficient reference fluorescence spectra prevented identification of this compound. Work is continuing in the use of fluorescence spectrophotometry data in support of GPS-MS correlations.

DISCUSSION

Table 12 summarizes the compositional results of the fuel oil and syncrude overhead products. Similar compound types are totaled together with correction made for any adsorption separation overlap and extraction overlap. Whereas in the preceding section the results were briefly discussed on a weight-percent distillate basis, a more meaningful discussion involves results on a weight-percent of total overhead basis. The following discussion of fuel oil and syncrude products is based for the most part upon the accumulated results in table 12.

Effect of Operating Conditions in Determining Composition of H-Coal Product

Varying operating conditions within a coal liquefaction process produced two products from similar coal samples. One such varied condition between the fuel oil and syncrude modes of operation was the hydrogen rate used in producing the coal liquid. A greater amount of reacted hydrogen in the syncrude mode would ensure a greater yield of liquid product from the coal and of the hydrogenated components within its liquid product. The results given above for the lower boiling distillates indicate this increase of hydrogenation in the syncrude. A comparison of weight-percent total overhead for both products indicates only slight difference in concentration of the two hydrocarbon portions: fuel oil, 26.4 percent and syncrude 26.9 percent. The saturate fraction

TABLE 12. - Summary of compositional results from GPC-MS correlations and chemical extractions

Chemical classes	Low-boiling distillate, total overhead, weight-percent		High-boiling distillate, total overhead, weight-percent	
	fuel oil	syncrude	fuel oil	syncrude
Weak acids	-	-	1.62	4.10
Strong acids	7.94	5.01	5.15	4.70
Bases	.38	.29	.90	2.45
Olefins	2.10	1.24	-	-
Saturates ¹	12.08	14.73	7.48	4.71
Monoaromatics ¹	12.18	10.86	14.78	7.70
Diaromatics ¹	Trace	.07	13.61	10.71
Polyaromatic-polar ¹ hydrocarbons ...	-	-	11.11	18.73
Heteroatomic types ²	-	-	1.26	3.06
Extraction losses.	.93	2.37	6.46	7.94
MS unanalyzed ³ ...	-	-	1.35	1.17

¹Values for high-boiling distillate components from mass spectral analyses. Values for low-boiling distillate components from GC integration.

²Includes only those types separately resolvable with a quantitative estimate from low resolution mass spectroscopy.

³Material not analyzed from GPC separation.

at the expense in amount of olefins and monoaromatics is considerably greater in the syncrude than in the fuel oil. Also less acids are found in the syncrude overhead product.

An analysis of data from the higher boiling distillate is not as clear with respect to the degree of hydrogenation. The problem encountered is the greater concentration of heavier material including a large percentage of heteroatoms found in the syncrude as a result of a higher overhead distillate end-point temperature. The fact that more liquid material is found in the high-boiling distillate of the syncrude is an indication that more hydrogenation has occurred in the syncrude mode of operation. A greater amount of heavier material has been processed in the syncrude mode than in the fuel oil mode. Thus, more polyaromatic-polar material is present in the syncrude. The saturate, monoaromatic, and diaromatic concentrations are less in the syncrude product. An informative arrangement of mass spectral data showing the various ring distributions within each concentrate is presented for each distillate in table 13. Based upon mass spectral and NMR results of compound types, a greater degree of hydrogenation is observed even in this higher boiling distillate of the syncrude. Mass spectroscopy indicates a predominance of higher molecular weight naphthenologs versus aromatic types in the diaromatic concentrate and polyaromatic-polar hydrocarbon fraction of the syncrude. The fuel oil in contrast to the syncrude shows a greater abundance of condensed polyaromatics than corresponding naphthenologs.

The data suggest more hydrogenation has taken place in the syncrude mode of operation but without severe ring cracking which would presumably become evident under harsher operating conditions. The characterization of these liquid coal products correlated with operating parameters help determine the optimum refining processes.

SUMMARY

Two coal liquid overhead products, one from the fuel oil and one from the syncrude mode of operation by the H-Coal process, were characterized by a combination of analytical techniques. Each product was separated into various fractions rendering quick and reliable spectroscopic analyses of chemical composition. Separation techniques included distillation, adsorption chromatography, gel-permeation chromatography and high pressure liquid chromatography. Various routine crude oil analysis methods, gas chromatography, high- and low-resolution mass spectrometry, proton nuclear magnetic resonance spectrometry and fluorescence spectrophotometry were techniques used in compositional identification.

By changing operating conditions within the H-Coal liquefaction process, two modes of operation produced two distinct products from the same type coal. The fuel oil product requiring less hydrogen for its formation was characterized as having a greater concentration of more condensed polyaromatic material and less low-boiling saturated material

TABLE 13. - Ring number distributions of hydrocarbon concentrates

Concentrate and total number of rings determined (includes aromatic and aliphatic rings)	Fuel oil		Syncrude		Concentrate and total number of rings determined (includes aromatic and aliphatic rings)	Fuel oil		Syncrude	
	<203° C Distillate	203–413° C Distillate	<197° C Distillate	197–493° C Distillate		<203° C Distillate	203–413° C Distillate	<197° C Distillate	197–493° C Distillate
Weight-percent of total overhead									
Saturates:					Monoaromatics:				
Paraffins	–	1.72	–	1.42	1–ring	–	1.14	–	0.96
1–ring	–	2.07	–	1.15	2–ring	–	7.83	–	4.09
2–ring	–	1.90	–	1.06	3–ring	–	5.02	–	2.12
3–ring	–	1.17	–	.63	4–ring	–	.61	–	.34
4–ring	–	.62	–	.45	5–ring	–	.12	–	.11
Totals	12.08	7.48	14.73	4.71	6–ring	–	.05	–	.04
					7–ring	–	–	–	.02
					8–ring	–	.01	–	.02
					Totals	12.18	14.78	10.86	7.70
Di aromatics:					Polyaromatics:				
2–ring	–	6.36	–	4.14	3–ring	–	5.80	–	3.76
3–ring	–	5.11	–	3.40	4–ring	–	3.84	–	4.01
4–ring	–	1.47	–	1.74	5–ring	–	.98	–	3.65
5–ring	–	.44	–	.79	6–ring	–	.32	–	3.83
6–ring	–	.04	–	.30	7–ring	–	.08	–	.82
7–ring	–	.01	–	.24	8–ring	–	.06	–	1.42
8–ring	–	.01	–	.04	9–ring	–	.02	–	.66
9–ring	–	–	–	.04	10–ring	–	.01	–	.39
10–ring	–	–	–	.02	11–ring	–	–	–	.19
Totals	Trace	13.57	0.07	10.71	Totals	–	11.11	–	18.73

than the syncrude product. As more hydrogen was used in its formation, the syncrude indicated a greater conversion of total coal to its overhead liquid product. The syncrude product was characterized as being a more hydrogenated material as evidenced by a greater amount of saturated and naphthenic material even in its high-boiling distillate. This product also indicated a higher percentage content of total polyaromatic-polar and heteroatomic material resulting from a greater amount of heavier material than the fuel oil.

From such characterizational analyses of the coal liquid products presented here, various liquefaction processes can be developed in an environmentally acceptable manner to meet a growing demand for energy resources.

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