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**CHARACTERIZATION OF A COLSTRIP COAL LIQUID DERIVED
FROM THE ZINC CHLORIDE HYDROCRACKING PROCESS**

By

G. P. Sturm, Jr., P. W. Woodward, J. W. Vogh,
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Date Published—May 1978

Bartlesville Energy Research Center
Department of Energy
Bartlesville, Oklahoma

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ABSTRACT

In a continuing series of characterization studies, the Bartlesville Energy Research Center characterized two distillates and a residue fraction derived from a Colstrip coal liquid produced by the Conoco Coal Development Co. molten zinc chloride catalytic liquefaction process. Procedures, established in earlier work on the heavy ends of petroleum, were slightly modified and applied to these materials. The techniques include several applications of chromatography and instrumental analyses. Although only 40 percent of the original coal liquid was submitted for analyses, the results were unique in that the portion of the coal liquid analyzed contained a significantly higher amount of monoaromatics as compared to other liquids characterized by use of these procedures.

INTRODUCTION

In recent years, our Nation has moved from the position of exporting petroleum and its products to that of importing about half of the petroleum we consume. The obvious national security problems and balance of trade problems and the relatively limited national and worldwide reserves of petroleum resources are among the reasons for the creation of the new Department of Energy (DOE). Part of the mission of DOE is the promotion of conservation of energy, development of alternate energy sources, and development and use of methods to increase domestic supplies of conventional energy sources.

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Coal, being our Nation's most abundant fossil energy resource, is prominent in most plans to meet our short-term and especially middle-term energy needs. In order to replace petroleum effectively for some of its major uses, especially for transportation, coal must first be converted to liquid or gaseous fuels. Technology for such coal-conversion processes has been known and used for several decades, especially in South Africa and Germany (9,16).³ However, except for these two countries, any major development of coal-conversion technology had been discouraged by economics and abundant petroleum supplies until the recent sharp rise in petroleum prices. Several coal-conversion processes are currently under intensive study and have been the subject of recent reviews (2,8-9,16,18,23).

Development of methods and procedures for the characterization of coal liquefaction products also recently has received increased interest and activity (1,6,14,19-22,24,26,30). Detailed knowledge of the composition of coal liquefaction products and other alternate fuels such as shale oils and tar sands liquids is important in evaluating conversion processes and different process conditions, in determining refining process needs, and in determining the best and most efficient end use. The Bartlesville Energy Research Center (BERC) has been involved in fossil fuel characterization studies for many years with such projects as the American Petroleum Institute (API) Research Project 60 for the characterization of heavy ends of petroleum. Recent studies have involved adaptation of the API RP 60 methods to the characterization of synthetic crude oils made from coal (6,14,24,30) and shale oil (29) as well as continued work on the heavy ends of petroleum (25). The four coal syncrudes characterized in our recent studies were produced by three different processes. This report describes the characterization of two distillates and a residuum fraction from the distillation of overhead products from the liquefaction of Colstrip subbituminous coal by a process under development by the Conoco Coal Development Co. (31).

COLSTRIP COAL LIQUID

The coal liquid characterized in this study was provided by Conoco Coal Development Co. It consisted of two distillate cuts and the pot bottoms from the distillation of overhead products from the conversion of Colstrip subbituminous coal in a bench-scale, continuous hydrocracker by use of molten zinc chloride as the catalyst. Typical reaction conditions were 775° F temperature, 3,000 psig hydrogen pressure, 1.5-to-1 weight ratio of ZnCl₂-to-coal, and 85 minutes residence time (31). The C₅ to 200° C fraction, comprising about 60.5 percent of the overhead products, was not received for analysis by BERC. The heavier overhead conversion products consisting of a nominal 200° to 325° C distillate (22.7 percent), a nominal 325° to 475° C distillate (10.3 percent), and a 475° C + pot bottoms (6.5 percent) from the distillation were analyzed as received by BERC characterization procedures based on those developed in the API RP 60 studies (10). Similar samples of this coal liquid, including the C₅ to 200° C fraction also, were characterized by Shell Oil Co., and the results were reported by Zielke of Conoco Coal Development Co. (31).

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

Some physical and chemical properties of the three distillation fractions are summarized in table 1. It is especially noteworthy that the sulfur and nitrogen content of each of the fractions is extremely low. Other physical and chemical property data normally acquired on such products were not determined for this coal liquid owing to insufficient sample.

TABLE 1. - Physical and chemical property data for
two distillates and a residuum fraction
from a Colstrip coal liquid

Property	200° to 325° C Distillate	325° to 475° C Distillate	475° C + Residuum
Weight fraction of total overhead product.....	0.227	0.103	0.065
Specific gravity, 60°/60° F.....	0.9542	1.0421	ND
Sulfur, D-1552, wt-pct.....	<0.03	<0.03	<0.04
Nitrogen, Kjeldahl, wt-pct.....	<0.02	<0.02	<0.04

ND — Not determined.

SEPARATIONS AND ANALYSES OF THE DISTILLATION FRACTIONS

The two distillate fractions and the pot bottoms fraction from the Colstrip coal liquid were further separated before analysis. Asphaltenes were precipitated from the 475° C + pot bottoms fraction in benzene solution by addition of 50 volumes of normal pentane (17). The precipitate was washed with n-pentane until the filtrate was clear, dried, and weighed. The separated asphaltenes accounted for 15.8 percent of the 475° C + fraction. The 200° to 325° C distillate, the 325° to 475° C distillate, and the asphaltene-free 475° C + fraction were separated and analyzed by the procedure shown in figure 1 which follows closely the methods developed in API RP 60 (10) except for acid and base extractions. Chromatography of each distillation fraction on dual silica-alumina gel adsorption columns produced four concentrates corresponding to saturates, monoaromatics, diaromatics, and polyaromatic-polars. The adsorption chromatogram for the 200° to 325° C distillate fraction is shown in figure 2. The chromatogram shows more structure in the monoaromatic and diaromatic regions than typical chromatograms for petroleum distillate fractions (12). This may be due to abnormally high concentrations of specific compounds produced from the coal or from the slurry solvent used in the conversion process (8 percent polystyrene in benzene) (31). Nevertheless, the adsorption separation was sufficient to produce concentrates which were predominantly of one major compound type -- for example, saturates or monoaromatics.

FIGURE 1. - Analysis scheme for the 200° to 325° C and 325° to 475° C distillates and the 475° C + asphaltene-free residuum.

FIGURE 2. - Adsorption chromatogram of the 200° to 325° C Colstrip coal liquid distillate.

After the adsorption chromatography separations, acids and bases were extracted from the 325° to 475° C and 475° C + polyaromatic-polar concentrates by methods reported in earlier syncrude characterization studies (6,24) except that weak acids and strong acids were left together. Acids and bases were not extracted from the 200° to 325° C polyaromatic-polar concentrate owing to insufficient sample size. The results of the various separations are summarized in table 2. The saturate fractions were analyzed by mass spectral means by the method of Hood and O'Neal (15) without further separation. The acids, bases, and asphaltene fractions were characterized roughly by direct analysis with mass spectrometry. Each of the aromatic concentrates was further separated into about 40 subfractions by gel permeation chromatography (GPC). The resulting chromatograms are shown in figure 3. These curves exhibit some structure which was not usually encountered in previous studies of petroleum crudes (3-7, 25,27-28) and other synthetic crudes (6,14, 24,29-30). Again, this may be due to abnormally high concentrations of specific compounds produced from the coal or from the slurry solvent. Selected GPC subfractions were analyzed by high- and low-resolution mass spectrometry (MS) and infrared spectroscopy (IR). Semiquantitative results and compound type identifications were obtained from previously established GPC-MS correlations (11,13) with the aid of high-resolution MS and IR results.

Saturates

Saturate concentrates from adsorption chromatography accounted for 4.58 percent of the 200° to 325° C distillate, 9.75 percent of the 325° to 475° C distillate, and 4.71 percent of the 475° C + pot bottoms. Mass spectral data for the three saturate concentrates, summarized in table 3, were obtained by use of n-alkane C₁₆, C₂₂, and C₃₁ matrices, respectively (15). Zero-ring compounds predominated, accounting for about 29, 59, and 36 percent, respectively, of the three saturate concentrates. One-ring naphthenes also accounted for appreciable percentages of the two higher boiling concentrates (19.4 and 28.8 percent, respectively). The 200° to 325° C and 475° C + saturate concentrate results indicated high amounts of monoaromatics (6.56 and 5.27 percent, respectively). These values may be overestimated since the matrices used in these calculations were developed for petroleum saturate fractions and may not apply exactly to syncrude saturates. Also, the monoaromatic contents indicated are quite low on a distillate basis since the saturate fractions comprise only about 6 percent of the 200° C + portion of this coal liquid. Comparative saturate contents for other synthetic crude oils range from 7 to 28 percent (6,14,24,30). Comparative petroleum 370° to 535° C distillate total saturates range from 37 to 74 percent (5). Zielke reported somewhat similar amounts of saturates in the Colstrip 200° to 475° C distillate (about 10 percent compared to our value of about 6 percent) (31).

Monoaromatics

Selected subfractions from the GPC separations of the three distillate monoaromatic concentrates were analyzed by low-voltage mass spectrometry and previously established GPC-mass spectral correlations (11,13). The results of the analysis, summarized in table 4,

TABLE 2. - Fractional yields and elemental (S&N) analysis of fractions from separations of a Colstrip coal liquid

Separation Fraction	200° to 325° C Distillate				325° to 475° C Distillate				475° C + Residue			
	Yield, wt-pct		wt-pct sulfur	wt-pct nitrogen	Yield, wt-pct		wt-pct sulfur	wt-pct nitrogen	Yield, wt-pct		wt-pct sulfur	wt-pct nitrogen
	Distillate basis	Crude basis			Distillate basis	Crude basis			Distillate basis	Crude basis		
Saturates	4.58	1.04	0.04	0.008	9.75	1.00	0.02	0.013	4.71	0.31	0.00	0.010
Monocaromatics	66.05	14.99	.04	.008	12.08	1.24	.03	.026	5.16	.34	.00	.072
Diaramatics	18.64	4.23	.00	.012	37.45	3.86	.00	.012	7.01	.46	.00	.011
Polyaromatic-Polar	8.89	2.02	.25	.088	41.03	4.23	ND	ND	65.36	4.25	ND	ND
Hydrocarbons-neutrals .	NS	NS	NAP	NAP	37.03	3.81	.12	.034	63.14	4.10	.00	.02
Acids	NS	NS	NAP	NAP	3.60	.37	ND	.02	.78	.05	ND	.12
Bases	NS	NS	NAP	NAP	.40	.04	ND	.29	Tr	Tr	ND	ND
Asphaltenes	NAP	NAP	NAP	NAP	NAP	NAP	NAP	NAP	15.8	1.03	.08	.09
Total sample handling loss (gain)	1.84	.42	NAP	NAP	(.31)	(.03)	NAP	NAP	¹ 3.40	.22	NAP	NAP

ND — Not determined.

NS — Not separated.

NAP — Not applicable.

¹ This includes 1.44 percent of emulsion material encountered in extraction of bases.

FIGURE 3. - GPC chromatograms for three aromatic compound type concentrates of the 200° to 325° C, 325° to 475° C, and 475° C + distillation fractions from a Colstrip coal liquid.

TABLE 3. - Ring distributions of the saturate concentrates

Ring Number	200° to 325° C Distillate			325° to 475° C Distillate			475° C + Residue		
	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude
0	29.35	1.344	0.305	58.74	5.727	0.590	35.70	1.681	0.109
1	15.90	.728	.165	19.41	1.892	.195	28.79	1.356	.088
2	15.13	.693	.157	6.56	.640	.066	8.81	.415	.027
3	25.56	1.171	.266	5.45	.531	.055	15.19	.715	.046
4	7.50	.344	.078	5.10	.497	.051	4.67	.220	.014
5	-	-	-	3.35	.327	.034	.56	.026	.002
6	-	-	-	-	-	-	1.02	.048	.003
Monoaromatics	6.56	.300	.068	1.40	.137	.014	5.27	.248	.016

TABLE 4. - Semiquantitative analysis of the monoaromatic concentrates

Mass Z Series	200° to 325° C Distillate			325° to 475° C Distillate			475° C+ Residue			Probable Compound Types
	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	
-6	¹ 11.75	7.76	1.762	3.63	0.439	0.045	24.98	1.289	0.084	Alkylbenzenes.
-8	^{1,2} 58.18	38.43	8.724	10.28	1.242	.128	20.71	1.069	.069	Alkylindans/Tetralins.
-10	^{1,2} 19.30	12.75	2.894	² 26.89	3.248	.335	10.59	.546	.035	Alkyldinaphthenobenzenes.
-12	2.09	1.38	.313	40.17	4.853	.500	6.86	.354	.023	Alkyltrinaphthenobenzenes.
-14	-	-	-	13.17	1.591	.164	3.72	.192	.012	Alkyltetranaphthenobenzenes.
-16	-	-	-	3.29	.397	.041	2.43	.125	.008	Alkylpentanaphthenobenzenes.
-18	-	-	-	.36	.043	.004	1.20	.062	.004	Alkylhexanaphthenobenzenes.
-12	-	-	-	.53	.064	.007	-	-	-	Alkyl naphthalenes.
-14	-	-	-	.23	.028	.003	-	-	-	Alkyl naphthenonaphthalenes and/or Alkyldiphenylalkanes.
-16	-	-	-	.01	.0012	.0001	-	-	-	Alkyldinaphthenonaphthalenes and/or Alkyl naphthenodiphenylalkanes.
-18	-	-	-	Tr	Tr	Tr	-	-	-	Alkyltrinaphthenonaphthalenes and/or Alkyldinaphthenodiphenylalkanes.
-6,-20	-	-	-	-	-	-	.32	.017	.001	Unknown.
-8,-22	-	-	-	.05	.006	.001	.08	.004	.0003	Unknown.
-10,-24	6.68	4.41	1.001	-	-	-	-	-	-	Unknown.
-12,-26	1.15	.76	.173	.63	.076	.008	-	-	-	Unknown.
-14,-28	.15	.10	.023	-	-	-	-	-	-	Unknown.
--	.70	.46	.104	.76	.092	.009	³ 29.12	1.503	.098	Not Analyzed.

¹ These results are based in part on MS analysis of the whole concentrate. Owing to considerable low boiling material in this concentrate, losses amounting to about 26 percent were incurred in evaporating the benzene solvent from the GPC fractions.

² Includes small amounts of -10(O) or -12(O) oxygenates, probably benzofurans.

³ Consists mainly of material which could not be volatilized sufficiently to produce mass spectra of adequate intensity.

show most of the 200° to 325° C monoaromatic concentrate to consist of alkylindans/tetralins and alkylindaphthenobenzenes (about 58 and 19 percent, respectively). These values are based in part on mass spectral analysis of a sample of the whole concentrate since about 26 percent sample losses occurred in evaporating benzene solvent from the GPC fractions. These sample losses were unusually high for this sample due to the presence of considerable material boiling below 200° C. Redistillation of the 200° to 325° C cut in a metal mesh spinning band still (Perkin-Elmer)⁴ showed about 9 percent of the material boiling below 200° C. The other study on this coal liquid indicated even more material boiling below 200° C (about 35 percent) (31). High-resolution MS results indicate small amounts of -10(O) and -12(O) oxygenates (probably benzofurans and naphthenobenzo-furans) present along with the hydrocarbons. No sulfur or nitrogen compound types were identified which is consistent with the very low S and N values indicated in table 2.

Results for the 325° to 475° C distillate monoaromatic concentrate, also shown in table 4, show a predominance of -10 and -12 mass Z series compound types, corresponding to alkylindaphtheno- and alkyltrinaphthenobenzenes, respectively, as they account for 67 percent of this concentrate. Some small amounts of diaromatics, oxygenates, and unknown compound types were noted. Again no sulfur or nitrogen compound types were detected which is in good agreement with the very low S and N contents shown in table 2 and with the results reported from another study of this sample (31).

A further comparison of our results with those of the previous study (31) is possible by combining our 200° to 325° C and 325° to 475° C data for several compound types. Thus, our results indicate alkylbenzenes, alkylindans/tetralins, and alkylindaphthenobenzenes account for 5.5, 27, and 9.2 percent of the 200° to 475° C distillate cut. The corresponding values from the other study are 24, 26, and 6.9 percent, respectively. Agreement is good except for the alkylbenzene values. The alkylbenzene discrepancy may be due in part to sample lost in our separation procedures, which were not designed for material boiling below 200° C. Also, based on the redistillation results mentioned previously, there appears to be significantly less lower boiling material in the 200° to 325° C distillate in our study. Comparison of the results for the 200° to 325° C, 325° to 475° C, and 475° C+ cuts individually is not possible due to lack of corresponding data from the other study.

The most prominent compound types determined in the 475° C+ monoaromatic concentrate were -6 and -8 mass Z series types corresponding to alkylbenzenes and alkylindans/tetralins which account for 25 and 21 percent of the concentrate, respectively. This reversed a trend in the first two monoaromatics which peaked in the -8 and -12 mass Z series, respectively. However, a large amount (29 percent) of the 475° C+ concentrate was not analyzed since several of the GPC subfractions contained material of sufficiently low volatility to prevent the acquisition of adequate mass spectral data with our 340° C inlet

⁴ Reference to specific brand names is made for identification only and does not imply endorsement by the Department of Energy.

system and sensitivity limitations. High-resolution mass spectral data on a sample of the 475° C + monoaromatic concentrate indicated the presence of only -6 through -18 mass Z series hydrocarbons which is in agreement with the GPC-MS correlation results. The absence of sulfur and nitrogen types is consistent with the very low values indicated by S (0.00 percent) and N (0.072 percent) elemental analysis of the concentrate listed in table 2.

The trend in the total monoaromatic content of the three distillate fractions in table 2 is noteworthy. The monoaromatic fraction accounts for about 66 percent of the 200° to 325° C distillate. The corresponding values for the 325° to 475° C distillate and the 475° C + resid fractions drop to 12 and 5 percent, respectively. The direction of this trend is not unusual since more diaromatic and polyaromatic compounds are possible in the higher boiling distillate fractions due to boiling point considerations alone. However, the magnitude of the decrease is significant, and the 66 percent total monoaromatic content of the 200° to 325° C distillate is high compared to previously studied syncrudes which ranged from 16 to 42 percent for 200° to 370° C distillate fractions (6, 14, 24, 30). When the data for the distillates from 200° to 530° C are combined for each coal liquid, the Colstrip liquid still has the highest monoaromatic content as shown in table 5.

TABLE 5. - Monoaromatic content of the 200° to 530° C distillates of six coal liquids

Coal Description	Colstrip	Western Kentucky	Illinois No. 6	Illinois No. 6	West VA. Pittsburgh Seam	Utah A-Seam
Liquefaction Process	Conoco ZnCl ₂	FMC COED	H-Coal Fuel-Oil	H-Coal Syncrude	Synthoil	FMC COED
Monoaromatics ^{1/} , wt-pct	^{2/} 41.9	^{2/} 37.0	^{3/} 32.2	^{4/} 16.6	25.8	^{2/} 24.0

^{1/} Based on silica-alumina gel adsorption chromatography separations.

^{2/} Boiling endpoints only approximately 530° C.

^{3/} Boiling endpoint about 410° C.

^{4/} Boiling endpoint about 490° C.

Diaromatics

Data from the analysis of the diaromatic concentrates are summarized in table 6. Alkyl-naphthenonaphthalenes and/or alkyl-diphenylalkanes/biphenyls account for about 64 percent of the 200° to 325° C diaromatic concentrate. Small amounts of -8 Z and -10Z monoaromatics and -16 Z acenaphthalenes and/or fluorenes were also detected. No oxygenates, sulfur compounds, or nitrogen compounds were observed which is consistent

TABLE 6. - Semiquantitative analysis of the diaromatic concentrates

Mass Z Series	200° to 325° C Distillate			325° to 475° C Distillate			475° C + Residue			Probable Compound Types
	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	
-12	20.34	3.79	0.860	1.83	0.68	0.070	2.43	0.170	0.011	Alkyl naphthalenes.
-14	63.59	11.85	2.690	¹ 19.87	7.44	.766	5.60	.393	.026	Alkyl naphthenonaphthalenes and/or Alkyldiphenylalkanes/Biphenyls.
-16	5.46	1.02	.231	¹ 35.10	13.14	1.354	7.42	.520	.034	Alkyldinaphthenonaphthalenes and/or Alkylnaphthenodiphenylalkanes/Biphenyls.
-18	-	-	-	¹ 12.17	4.56	.469	12.03	.843	.055	Alkyltrinaphthenonaphthalenes and/or Alkyldinaphthenodiphenylalkanes/Biphenyls.
-20	-	-	-	5.19	1.94	.200	15.31	1.073	.070	Alkyltetranaphthenonaphthalenes and/or Alkyltrinaphthenodiphenylalkanes/Biphenyls.
-22	-	-	-	2.19	.82	.084	15.70	1.101	.072	Alkylpentanaphthenonaphthalenes and/or Alkyltetranaphthenodiphenylalkanes/Biphenyls.
-24	-	-	-	.30	.11	.012	10.25	.719	.047	Alkylhexanaphthenonaphthalenes and/or Alkylpentanaphthenodiphenylalkanes/Biphenyls.
-26	-	-	-	-	-	-	4.15	.291	.019	Alkylheptanaphthenonaphthalenes and/or Alkylhexanaphthenodiphenylalkanes/Biphenyls.
-28	-	-	-	-	-	-	.76	.053	.003	Alkylactanaphthenonaphthalenes and/or Alkylheptanaphthenodiphenylalkanes/Biphenyls.
-30	-	-	-	-	-	-	.14	.010	.001	Alkylnonanaphthenonaphthalenes and/or Alkylactanaphthenodiphenylalkanes/Biphenyls.
-8	.13	.024	.005	-	-	-	-	-	-	Alkylindans/Tetralins.
-10	.48	.089	.020	-	-	-	-	-	-	Alkyldinaphthenobenzenes.
-16	.43	.080	.018	-	-	-	-	-	-	Alkylacenaphthalenes/Fluorenes.
-18	-	-	-	4.23	1.58	.163	-	-	-	Alkyl naphthenoacenaphthalenes/Fluorenes and/or Alkylphenanthrenes/Anthracenes.
-20	-	-	-	6.71	2.51	.259	-	-	-	Alkyldinaphthenoacenaphthalenes/Fluorenes and/or Alkyl naphthenophenanthrenes/Anthracenes.
-22	-	-	-	5.09	1.91	.196	-	-	-	Alkyldinaphthenophenanthrenes/Anthracenes and/or Alkylpyrenes/Fluoranthenes.
-24	-	-	-	.10	.04	.004	-	-	-	Alkyltrinaphthenophenanthrenes/Anthracenes and/or Alkyl naphthenopyrenes/Fluoranthenes and/or Alkylchrysenes.
-21N	-	-	-	-	-	-	.26	.018	.001	Unknown.
--	^a 9.58	1.79	.406	7.23	2.71	.279	25.95	1.819	.118	Not analyzed.

¹ Includes small amounts of -16(O), -18(O), or -20(C) oxygenates, probably dibenzofurans and their naphthenologs.

^a Primarily losses resulting from removal of solvent from GPC fractions. Analysis of the whole concentrate indicated the material was mostly alkyl naphthalenes.

with the low S and N contents as listed in table 2 and with the high-resolution mass spectral results for the concentrate. On the basis of the MS results of the whole concentrate, the 9.6 percent of the concentrate not analyzed consisted primarily of low-molecular-weight alkylnaphthalenes which were lost in evaporating the benzene solvent from the GPC subfractions.

The data for the 325° to 475° C diaromatic concentrate in table 6 show a maximum in the concentrations at the -16 mass Z series which accounts for about 35 percent of the concentrate. About 16 percent of the concentrate appeared to be polyaromatic hydrocarbons indicating the adsorption chromatographic separation was less efficient than normal. High-resolution mass spectral results indicated that small amounts of -16(O), -18(O), and -20(O) oxygenates (probably dibenzofurans and naphthenologs) were present. About 7 percent of the concentrate, listed as not analyzed, was lost in the GPC separation. No sulfur or nitrogen compounds were detected which was consistent with the low S and N content indicated in table 2.

Data for the 475° C + diaromatic concentrate, also summarized in table 6, show a maximum in the concentrations in the -20 and -22 mass Z series corresponding to tetra- and pentanaphthenonaphthalenes and/or tri- and tetranaphthenodiphenylalkanes/biphenyls. No monoaromatics or polyaromatics were readily apparent in the mass spectral patterns of GPC fractions indicating a good silica-alumina gel separation for this residue fraction. About 0.3 percent of the material was designated unknown, and 26 percent was not analyzed. As no sample handling losses occurred in the GPC separation, the 26 percent of the concentrate not analyzed resulted from early GPC fractions with heavy material of insufficient volatility to produce mass spectral data of adequate intensity for evaluation. High-resolution mass spectral results on the concentrate indicated no detectable amounts of oxygenates or nitrogen compounds present. Also, the GPC-MS correlations showed no nitrogen or sulfur compound types present which is in good agreement with the low S and N contents shown in table 2 for this concentrate.

Asphaltenes, Acids, and Bases

The asphaltene fraction, comprising 15.8 percent of the 475° C + residuum, was examined by high-resolution mass spectrometry. Only about 25 percent of the sample was volatilized at 340° C, and the molecular-weight region, from about 275 to 420 m/e units, was somewhat lower than that expected for most asphaltenes. The high-resolution MS results showed hydrocarbons and/or sulfur compounds in the -24 to -46 mass Z series and small amounts of -28(O), -39N, and -43N heteroatomic types. The predominant peaks corresponded to -32 Z through -42 Z hydrocarbons. These results suggest that most of the volatile components in this sample resulted from hydrocarbons adsorbed on the asphaltenes.

The acid and base extractions with the 325° to 475° C polyaromatic-polar concentrate yielded an acid fraction (3.60 percent on a distillate basis), a base fraction (0.40 percent), and a hydrocarbon-neutral fraction (37.03 percent). High-resolution MS results for the acid fraction indicated a molecular weight-range of about 160 to 280 amu.

Oxygenates in mass Z series -10(O) through -26(O) and -16(O₂) were observed and were probably mostly phenolic types. Some hydrocarbons were also observed in the -14 through the -26 mass Z series. The most abundant compound types present were the -14(O), -16(O), and -18(O) oxygenates. Moderate amounts of -20(O) and -22(O) oxygenates and -20, -22, and -16 mass Z hydrocarbons were indicated. High-resolution MS results for the 325° to 475° C bases showed about the same 160 to 280 amu range of molecular weights. The base fraction appeared to be mostly hydrocarbons in the -14 through -28 mass Z series with the -18, -20, and -22 series predominant. Smaller amounts of oxygenates in mass Z series -14(O) through -28(O) were indicated and were probably furan types mostly. Only one nitrogen compound type (-13N) was observed. The nitrogen content of this fraction (0.29 percent) was quite low for a base fraction. Assuming one nitrogen atom per molecule and an average molecular weight of 220, only about 4.6 percent of the compounds in the base fraction would be nitrogen compound types.

The acid and base extractions with the 475° C + polyaromatic-polar concentrate gave an acid fraction (0.78 percent on a distillate basis), a base fraction (trace), an emulsion (1.44 percent), and a hydrocarbon-neutral fraction (63.14 percent). High-resolution MS results for the acid fraction showed a molecular-weight range of about 200 to 400 amu. Hydrocarbon compounds present were in the -22 through the -38 mass Z series, with the -26, -32, -34, and -36 mass Z series the most abundant. Oxygenate compounds present were in the -16(O) through the -38(O) and the -22(O₂) through the -32(O₂) mass Z series. The -22(O) through -28(O) mass Z oxygenates were the most abundant. The 475° C + bases extraction yielded a trace amount of bases and an emulsion amounting to 1.44 percent of the total residue fraction. Mass spectrometric results for the emulsion sample showed only hydrocarbon types present in the -20 through the -42 mass Z series. Compounds in the -24, -26, -28, -32, -34, and -36 mass Z series were most abundant. The molecular-weight region of about 210 to 420 was similar to that of the 475° C + acid fraction. No nitrogen compounds were observed.

Polyaromatic-polar Hydrocarbons-neutrals

The semiquantitative analysis data from the GPC-MS correlation characterization of the entire 200° to 325° C polyaromatic-polar (PAP) concentrate and the hydrocarbons-neutrals portions of the 325° to 475° C and 475° C + polyaromatic-polar concentrates are summarized in table 7. Compound types in the -16 and -16(O) mass Z series account for about 52 percent of the 200° to 325° C PAP concentrate. The -16 mass Z series compound types are probably alkylacenaphthalenes and/or alkylfluorenes. The -16(O) mass Z series compounds probably include hydroxyacenaphthalenes and/or hydroxyfluorenes, benzophenones, and dibenzofurans. About 11 percent of the material was not identified, and 20 percent was not analyzed owing to GPC sample handling losses (13.85 percent) and insufficient sample in fractions in the tail region of the GPC chromatogram (6.44 percent). Mass spectral analysis of the total concentrate sample indicated most of the material lost in sample handling was in the -14 and -16 mass Z series. The high oxygenate content of this concentrate (about 35 percent) was due, at least in part, to the fact that acids (and

TABLE 7. - Semiquantitative analysis of the polyaromatic-polar material

Mass Z Series	200° to 325° C Distillate			325° to 475° C Distillate			475° C + Residue			Probable Compound Types
	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	
-16	¹ 25.23	2.243	0.509	5.61	2.077	0.214	¹ 4.47	2.82	0.183	Alkylacenaphthalenes/Fluorenes.
-18	¹ 4.96	.441	.100	¹ 12.14	4.495	.464	¹ 2.85	1.80	.117	Alkylinaphthenoacenaphthalenes/Fluorenes and/or Alkylphenanthrenes/Anthracenes.
-20	.84	.075	.017	¹ 14.81	5.484	.564	¹ 3.52	2.22	.144	Alkylidinaphthenoacenaphthalenes/Fluorenes and/or Alkylinaphthenophenanthrenes/Anthracenes.
-22	.24	.021	.005	¹ 35.14	13.012	1.340	¹ 9.08	5.73	.372	Alkyltrinaphthenoacenaphthalenes/Fluorenes and/or Alkylidinaphthenophenanthrenes/Anthracenes and/or Alkylpyrenes/Fluoranthenes.
-24	-	-	-	¹ 12.94	4.792	.493	¹ 28.01	17.69	1.150	Alkyltetranaphthenoacenaphthalenes/Fluorenes and/or Alkyltrinaphthenophenanthrenes/Anthracenes and/or Alkylinaphthenopyrenes/Fluoranthenes and/or Alkylchrysenes/Naphthacenes/Triphenylenes.
-26	-	-	-	¹ 2.28	.844	.087	¹ 14.57	9.20	.598	Alkylpentanaphthenoacenaphthalenes/Fluorenes and/or Alkyltetranaphthenophenanthrenes/Anthracenes and/or Alkyltrinaphthenopyrenes/Fluoranthenes and/or Alkylidinaphthenochrysenes/Naphthacenes/Triphenylenes and/or Alkylidaceanthracenes/Benzofluoranthenes.
-28	-	-	-	.44	.163	.017	¹ 5.97	3.77	.245	Alkylhexanaphthenoacenaphthalenes/Fluorenes and/or Alkylpentanaphthenophenanthrenes/Anthracenes and/or Alkyltrinaphthenopyrenes/Fluoranthenes and/or Alkylidinaphthenochrysenes/Naphthacenes/Triphenylenes and/or Alkylinaphthenodiaceanthracenes/Benzofluoranthenes and/or Alkylbenzopyrenes/Perylenes.
-30	-	-	-	-	-	-	¹ 3.70	2.34	.152	Alkylheptanaphthenoacenaphthalenes/Fluorenes and/or Alkylhexanaphthenophenanthrenes/Anthracenes and/or Alkyltetranaphthenopyrenes/Fluoranthenes and/or Alkyltrinaphthenochrysenes/Naphthacenes/Triphenylenes and/or Alkylidinaphthenodiaceanthracenes/Benzofluoranthenes and/or Alkylinaphthenobenzopyrenes/Perylenes and/or Alkylpicenes.
-32	-	-	-	-	-	-	2.69	1.70	.111	Alkyloctanaphthenoacenaphthalenes/Fluorenes and/or Alkylheptanaphthenophenanthrenes/Anthracenes and/or Alkylpentanaphthenopyrenes/Fluoranthenes and/or Alkyltetranaphthenochrysenes/Naphthacenes/Triphenylenes and/or Alkyltrinaphthenodiaceanthracenes/Benzofluoranthenes and/or Alkylidinaphthenobenzopyrenes/Perylenes and/or Alkylinaphthenopicenes.
-34	-	-	-	-	-	-	.74	.47	.031	Alkylnonanaphthenoacenaphthalenes/Fluorenes and/or Alkyloctanaphthenophenanthrenes/Anthracenes and/or Alkylhexanaphthenopyrenes/Fluoranthenes and/or Alkylpentanaphthenochrysenes/Naphthacenes/Triphenylenes and/or Alkyltetranaphthenodiaceanthracenes/Benzofluoranthenes and/or Alkyltrinaphthenobenzopyrenes/Perylenes and/or Alkylidinaphthenopicenes.
-28	-	-	-	-	-	-	2.01	1.27	.083	Alkylbenzopyrenes/Perylenes.
-30	-	-	-	-	-	-	1.08	.68	.044	Alkylinaphthenobenzopyrenes/Perylenes and/or Alkylpicenes.
-32	-	-	-	-	-	-	8.29	5.23	.340	Alkylidinaphthenobenzopyrenes/Perylenes and/or Alkylinaphthenopicenes and/or Alkylanthranthrenes/Benzperylene/Phenyleneperylene.

TABLE 7. - Semiquantitative analysis of the polyaromatic-polar material (Continued)

Mass Z Series	200° to 325° C Distillate			325° to 475° C Distillate			475° C+ Residue			Probable Compound Types
	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	
-34	-	-	-	-	-	-	1.77	1.12	.073	Alkyl naphthoanthranthrenes/Benzperylene/Phenyleneperylene.
-36	-	-	-	-	-	-	.62	.39	.025	Alkylaceanthranthrenes/Acebenzperylene/Acephenyleneperylene.
-38	-	-	-	-	-	-	.12	.08	.005	Alkyl naphthoaceanthranthrenes/Acebenzperylene/Acephenyleneperylene.
-12(0)	² .54	.048	.011	-	-	-	-	-	-	Alkyl naphthenobenzofurans.
-14(0)	² E.03	.714	.162	.80	.296	.030	-	-	-	Alkyl dinaphthenobenzofurans.
-16(0)	^{2,3} 26.89	2.391	.543	3.20	1.185	.122	.74	.47	.031	Alkyl dibenzofurans.
-18(0)	-	-	-	3.15	1.166	.120	-	-	-	Alkyl naphthenodibenzofurans.
-15N	-	-	-	.44	.163	.017	-	-	-	Alkyl carbazoles.
-17N	-	-	-	.85	.315	.032	-	-	-	Alkyl naphthenocarbazoles.
-19N	-	-	-	.15	.056	.006	-	-	-	Alkyl dinaphthenocarbazoles.
0, -14, -28	.21	.019	.004	.76	.281	.029	1.05	.66	.043	Unknown.
-2, -16, -30	.39	.035	.008	.54	.200	.021	.83	.52	.034	Unknown.
-4, -18, -32	2.82	.251	.057	.32	.118	.012	-	-	-	Unknown.
-6, -20, -34	2.87	.255	.058	.16	.059	.006	-	-	-	Unknown.
-8, -22, -36	¹ 1.97	.175	.040	.22	.081	.008	.31	.20	.013	Unknown.
-10, -24, -38	¹ 1.61	.143	.032	.13	.048	.005	.22	.14	.009	Unknown.
-12, -26, -40	3.11	.276	.063	.38	.104	.011	.09	.06	.004	Unknown.
-	⁴ 20.29	1.804	.410	5.64	2.088	.215	7.27	4.59	.298	Not analyzed.

¹Contains small amounts of oxygenate material, probably benzofurans, dibenzofurans, or benzonaphthofurans and their naphthenologs.

²Probably includes phenolic type oxygenates also.

³Includes some -14 mass Z hydrocarbon material also, probably diphenylalkanes and probably some alkylbenzophenones or other aromatic carbonyl compounds.

⁴About 6.44 percent: represents material under the tail region of the GPC where sample size was insufficient for MS analysis. About 13.85 percent was lost in solvent removal from GPC fractions. Analysis of the complete concentrate by MS indicated most of the material lost was in the 0, -14 and -2, -16 mass Z series.

bases) were not extracted because of insufficient sample. This fact may also explain the abnormally high amount of material which could not be identified. Nevertheless, the presence of only a small amount of diaromatics, primarily diphenylalkanes, indicated the adsorption separation to be good. Also, the absence of detectable amounts of sulfur and nitrogen compounds is in good agreement with the low S and N content indicated in table 2. High-resolution MS aided in the identifications, especially for the oxygenate compounds. Infrared spectra of two GPC subfractions near the peak of the GPC distribution showed strong absorption bands consistent with phenolic OH and aromatic carbonyl groups and also aided in compound type assignments.

The data for the 325° to 475° C polyaromatic-polar hydrocarbons-neutrals, also in table 7, show a maximum in the concentration distribution at the -22 mass Z series corresponding to alkyltrinaphthenoacenaphthalenes/fluorenes and/or alkylidinaphthenophenanthrenes/anthracenes and/or alkylpyrenes/fluoranthenes. The -20, -22, and -24 mass Z series compounds together account for about 63 percent of this concentrate. Small amounts of nitrogen compounds (about 1.44 percent), probably carbazoles, were detected as were appreciable amounts of oxygenates (>7 percent), probably dibenzofurans and related types. About 2.4 percent of the concentrate was not identified, and 5.6 percent was not analyzed owing to insufficient sample in GPC subfractions in the tail regions of the GPC chromatogram. High-resolution MS data were consistent with the compound type assignments from the GPC-MS correlations. Some typical high-resolution MS results are summarized in table 8. The absence of detectable amounts of sulfur compounds and the small amount of nitrogen compounds observed are consistent with the low S and N contents indicated in table 2.

TABLE 8. - Some examples of hydrocarbon-oxygenate doublets from the high-resolution mass spectrum of the 325° to 475° C polyaromatic-polar hydrocarbon-neutral concentrate.

Molecular Formula	Z Series	Calculated M/E	Observed M/E	$\Delta M/E$	Percent Intensity
C ₁₅ H ₁₄	-16	194.1095	194.1081	-.0014	11.09
C ₁₄ H ₁₀ O	-18(O)	194.0732	194.0730	-.0002	2.89
C ₁₆ H ₁₆	-16	208.1252	208.1243	-.0009	10.03
C ₁₅ H ₁₂ O	-18(O)	208.0888	208.0884	-.0004	4.44
C ₁₇ H ₁₈	-16	222.1408	222.1396	-.0012	4.53
C ₁₆ H ₁₄ O	-18(O)	222.1045	222.1037	-.0008	4.34

The data for the 475° C + PAP hydrocarbons-neutrals, also in table 7, show that compound types in the -24 and -26 mass Z series account for about 42.6 percent of this concentrate. Molecular-weight considerations and the presence of more than one maxima in the distribution of concentrations of a given mass Z series across the GPC fractions enabled some hydrocarbon types to be separated from others of the same mass Z series as shown in table 6. These separations are approximate as there is usually considerable overlap between adjacent modes in the Z series concentration distribution. A particularly high amount of -32 mass Z series material (about 11 percent) is present in this concentrate, especially relative to the amounts of -30 and -34 mass Z series material (5.7 and 2.5 percent, respectively). About 2.5 percent of the concentrate was not identified, and 7.3 percent was not analyzed owing to insufficient sample size in the tail region and insufficient volatility of early GPC fractions. Small amounts of oxygenates were detected in the -16 (O) through -32(O) mass Z series by high resolution MS. No sulfur or nitrogen compounds were detected which is reasonable owing to the low S and N content listed in table 2.

In addition to the unusual occurrences of structure noted earlier in the silica-alumina gel adsorption chromatogram and in the GPC chromatograms, an anomaly was noted in the low-voltage MS spectra of several fractions in the GPC separations of the 325° to 475° C and 475° C + PAP hydrocarbons-neutrals and to a lesser extent in the 200° to 325° C PAP GPC chromatogram fractions. Abnormally high intensity peaks were observed at m/e values of 196, 300, 404 and 508 in the same GPC fraction in one case. For example, the 475° C + PAP hydrocarbons-neutrals GPC fraction 14, with a molecular-weight range of about 370 to 480 mass units had large peaks at each of the above m/e values. The peaks at 196 and 300 would not be expected in this GPC fraction unless they could be explained as fragment ion peaks or parent ions from thermal decomposition products from the sample in the 340° C inlet system. These ions most likely result from hydrogenation products of the polystyrene used in the slurry solvent system (8 percent polystyrene in benzene) in the conversion process (31).

SUMMARY

Two distillate fractions and the pot bottoms from the distillation of overhead products from the liquefaction of Colstrip subbituminous coal were characterized by methods adapted from those developed in API RP 60. The coal liquid fractions, which were supplied by the Conoco Coal Development Co., were produced in a bench-scale, continuous hydrocracker by use of molten zinc chloride catalyst and 3,000 psig hydrogen. The three fractions were analyzed by a combination of techniques including sulfur and nitrogen elemental analysis, adsorption chromatography, acid and base extractions, asphaltene precipitation, gel permeation chromatography, mass spectrometry, and infrared spectroscopy. The results showed higher monoaromatic and lower saturate content than that of other coal liquids analyzed in previous studies. Sulfur and nitrogen contents were each very low also. Adsorption chromatograms and gel permeation chromatograms showed more than the usual amount of structure probably due to abnormally high concentrations of some specific compounds produced from the slurry solvent system. The highly aromatic character of the

Colstrip liquid is typical of coal liquids and contrasting to most petroleum crude oils. Overall, the data present an extensive characterization of the 200° C+ portion of the overhead products from the conversion of Colstrip subbituminous coal providing useful information for further upgrading of this coal liquid to more useful products and for evaluation of the coal conversion process.

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