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ANALYZING HEAVY ENDS OF CRUDE: BARTLETT OIL

By

G. P. Sturm, Jr.
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Date Published—May 1977

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

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ANALYZING HEAVY ENDS OF CRUDE: BARTLETT OIL

by

G. P. Sturm, Jr.,¹ P. W. Woodward,¹ J. W. Vogh,¹
S. A. Holmes,¹ and J. E. Dooley²

ABSTRACT

A heavy crude oil produced from the Bartlett field in southeastern Kansas by the Solfrac process developed by ERDA was characterized by procedures developed, in large part, by the ERDA Energy Research Centers in Bartlesville, Okla., and Laramie, Wyo., through the American Petroleum Institute Research Project 60. After removal of the solvent used in the Solfrac process, two distillate fractions accounting for about 50 percent of the solvent-free crude were prepared and analyzed by a combination of techniques including acid and base extractions, adsorption chromatography, gel permeation chromatography (GPC), mass spectrometry (MS), nuclear magnetic resonance (NMR) spectrometry, and gas chromatography. Concentrations of major hydrocarbon and sulfur compound types were well within the ranges observed for five previously studied crude oils, but acid and base fractions were smaller for the Bartlett crude. High-resolution mass spectral data for the Bartlett crude showed the presence of some oxygenate material which were not determined in the previous studies of petroleum crudes. These data plus physical and chemical properties determined by the ERDA/BERC routine crude oil analyses provided an extensive characterization of the portion of Bartlett crude boiling below 540°C. These data are valuable for determining appropriate refining processes for efficiently upgrading this crude to more useful products.

INTRODUCTION

Events of recent years have accentuated our Nation's need for an adequate, dependable energy supply. The Energy Research and Development Administration (ERDA) program includes efforts to conserve energy, to encourage development of alternate energy sources, and to increase domestic supplies of conventional energy sources.

Some of the ways to increase domestic petroleum supplies include enhanced recovery of oil from existing wells and development of methods for recovery of heavy oils. Heavy oils in

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¹ Research chemist.

² Project leader.

proved reserves amount to about 5.2 billion bbl (22)³. Heavy-oil resources are estimated to be an additional 107 billion bbl, not including numerous known heavy-oil deposits which have not been examined sufficiently for reliable estimates of their total oil content (1). ERDA engineers at the Bartlesville Energy Research Center (BERC) have been investigating new production methods at a test site near Bartlett in southeastern Kansas, in one of the major areas of heavy-oil deposits (3). The oil characterized in this study was produced from a well in the Bartlett field by the Solfrac process developed by BERC engineers (9,15-17).

In addition to improved production methods, increasing the efficiency of refining crude oils and upgrading the heavier ends of crudes to more useful products can contribute significantly to increasing conventional energy supplies. BERC has been developing methods for characterizing the heavy ends of petroleum crude oils (2,4-5,7-8,10-11,19-21) and synthetic crude oils (6,13,18,23) for several years to provide compositional information important in terms of refining, manufacturers end-use products, and, for synthetic crude oils, evaluating conversion processes.

The purpose of this study was to determine the composition of two distillate fractions of a heavy crude oil sample from the Bartlett field and to compare the results with those of earlier studies of typical full-boiling range crude oils (5). In large part, methods developed in the American Petroleum Institute (API) Research Project 60 were used in the characterization of the oil.

BARTLETT CRUDE OIL

The crude oil characterized in this study was produced from the Bartlesville sand Formation (Pennsylvanian), Bartlett field, Labette County, Kansas, at a well depth of 295 to 360 feet by the Solfrac process (9,15-17) developed by ERDA engineers. This production process involves fracturing the formation with explosives to establish communication between test wells and injecting solvent to increase oil mobility. As initially produced, the oil contains a considerable amount of the solvent, Carter Chemicals Espesol 1300.⁴ Most of the solvent was removed by distillation by use of a Podbielniak column at about 195°C pot temperature and 180°C overhead temperature. The residue, amounting to about 22 percent of the original material, was distilled further by use of a 4-inch-diameter Rota-Film still at about 220°C and atmospheric pressure. Another pass through the Rota-Film still at 140°C and 10 Torr pressure produced a 97-percent solvent-free Bartlett crude as determined by gas chromatography. Final yield of crude was about 18 percent of the original crude-solvent mixture.

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

⁴ Reference to specific trade names or manufacturers does not imply endorsement by the Energy Research and Development Administration.

The 97-percent solvent-free sample, hereafter referred to as Bartlett crude oil, was subjected to the ERDA/BERC routine method for crude oil analysis; the results are presented in table 1. In summary, the Bartlett crude is quite heavy (15.4° API) with a specific gravity of 0.963. Its color is brownish black; sulfur content, 0.89 percent; nitrogen content, 0.321 percent; and pour point, 40°F. The residuum accounts for over half of the crude as only 43.2 percent was taken overhead at 572°F (300°C) at 40 Torr corresponding to 420°C at 760 Torr. The higher sulfur and nitrogen values for the residuum (1.14 and 0.55 percent, respectively) indicate some concentration of sulfur and nitrogen compounds in the higher boiling fractions as is typical for most crude oils. The summary data at the bottom of table 1 further attest to the heavy nature of this crude. Comparison of the data in table 1 with corresponding data for a sample of Bartlett crude produced before the use of any solvents (9) shows a small amount of solvent in the current sample. However, the data also indicate very little or no loss of light ends from the Bartlett crude in the solvent stripping process.

PREPARATION OF DISTILLATES

Two distillates and a residuum fraction were prepared from the Bartlett crude using the Rota-Film molecular still (2). Yields and distillation conditions are shown in figure 1. The lower boiling-range distillate (225°-360°C) and higher boiling distillate (360°-540°C) accounted for 17.6 and 28.9 percent of the crude, respectively. The residue accounted for 52.1 percent, and distillation losses amounted to 1.3 percent. Boiling ranges of the two distillates were determined from simulated distillation data obtained by gas chromatography (6). Physical-property data for the two distillates and the residuum are summarized in table 2. The nitrogen and sulfur content is concentrated to a degree in the higher boiling fractions as is typical for petroleum crudes. The residuum, not being amenable to our current characterization procedures, was not analyzed further and will be included in later characterization studies.

SEPARATIONS AND ANALYSIS OF THE DISTILLATES

The two distillate fractions were further separated before analysis. The procedure (figure 2) followed closely the methods developed in API Research Project 60 (8) except for acid and base extractions. Acids and bases were extracted from each of the distillates by use of alcoholic NaOH and aqueous-alcoholic HCl, as reported earlier in syncrude characterization studies (6, 18), rather than the time-consuming anion and cation exchange separations employed in the API Project 60 studies. Each acid- and base-free distillate was chromatographed on dual silica-alumina gel adsorption columns producing four fractions each, corresponding to saturates, monoaromatics, diaromatics, and polyaromatics. The saturate fractions were analyzed by mass spectral means without further separation by the method of Hood and O'Neal (14). Each of the aromatic fractions was further separated into about 40 subfractions by gel permeation chromatography (GPC). The resulting chromatograms are shown in figure 3. Selected subfractions were then analyzed

TABLE 1. - CRUDE PETROLEUM ANALYSIS

BARTLESVILLE ENERGY RESEARCH CENTER
BARTLESVILLE, OKLAHOMA 74003

Sample 76015

IDENTIFICATION

Bartlett, North field
Bartlesville, Pennsylvanian
295 - 360 feet

Kansas
Labette County

GENERAL CHARACTERISTICS

Gravity, specific, 0.963 Gravity, ° API, 15.4 Pour point, ° F., 40
Sulfur, percent, 0.89 Color, brownish black
Viscosity, Saybolt Universal at 100° F., >6,000 sec; 130° F., 2,201 sec Nitrogen, percent, 0.321

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 737 mm. Hg
First drop, 388° 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 test, ° F.
1	122									
2	167									
3	212									
4	257									
5	302									
6	347									
7	392									
8	437	6.3	6.3	0.865	32.1	-	1.47684	151.5		
9	482	2.8	9.1	.875	30.2	54	1.47829	152.9		
10	527	4.0	13.1	.880	29.3	52	1.48187	155.0		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	3.2	16.3	0.885	28.4	50	1.48550	157.7	45	Below 5
12	437	6.3	22.6	.892	27.1	50	1.49061	160.0	53	do.
13	482	7.3	29.9	.900	25.7	50	1.49926	165.2	77	22
14	527	6.7	36.6	.911	23.8	52	1.50748	171.9	171	40
15	572	6.6	43.2	.926	21.3	56	1.51209	200.4	375	50
Residuum		55.5	98.7	1.015	7.9					

Carbon residue, Conradson: Residuum, 15.3 percent; crude, 9.0 percent.

Residuum:
Sulfur, percent, 1.14
Nitrogen, percent, 0.550

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline				
Total gasoline and naphtha				
Kerosine distillate				
Gas oil	17.7	0.875	30.1	
Nonviscous lubricating distillate	10.3	.889-.903	27.6-25.3	50-100
Medium lubricating distillate	6.2	.903-.913	25.3-23.5	100-200
Viscous lubricating distillate	9.0	.913-.933	23.5-20.1	Above 200
Residuum	55.5	1.015	7.9	
Distillation loss	1.3			

FIGURE 1. - Distillation of Bartlett crude (percent of total crude).

Figure 2. - Analysis scheme for the 225° to 360° C and 360° to 540° C distillates of Bartlett crude.

Figure 3. - GPC chromatograms for three aromatic compound type concentrates of the 225° to 360° C and 360° to 540° C distillates of Bartlett crude.

by NMR spectroscopy and high- and low-resolution mass spectrometry. Semiquantitative results and compound type identifications were obtained from previously established GPC-MS correlations (10,12) with the aid of high-resolution mass spectral and NMR results. Yields from the acid and base extractions, the adsorption chromatography separations, and sulfur and nitrogen analyses for each separation fraction are summarized in table 3.

TABLE 2. - Physical property data for Bartlett crude oil distillates and residuum

Property	225° to 360°C distillate	360° to 540° C distillate	>540°C residuum
Specific gravity, 60°/60° F	0.894	0.934	ND
Gravity, °API	26.8	20.0	ND
Pour point, ASTM D-97, °F	36	<5	ND
Cloud point	<5	NA	NA
Kinematic viscosity, 100°F, ... ASTM D-445, Cs	8.2	143.7	ND
Color, ASTM D-1500	1.5	5.5	NA
Sulfur, D-1552, wt-pct	.50	.80	1.25
Nitrogen, Kjeldahl, wt-pct	.022	.119	.635
Carbon residue (Conradson), ... ASTM D-189, wt-pct	ND	ND	26.1

ND--Not determined.

NA--Not applicable.

ACIDS AND BASES

The acid and base extractions with the 225° to 360°C distillate produced three fractions: 1) Acids accounting for 0.82 percent; 2) Bases accounting for 0.21 percent; and 3) Neutrals accounting for 95.52 percent. Losses incurred in sample handling amounted to 3.46 percent. A low-voltage mass spectrum of the acid fraction showed material in all seven even nominal mass Z series and two odd mass Z series (-5, -19, and -7, -21) with a molecular-weight range from 150 to 350 amu. No one mass Z series predominated although about 30 percent of the material fell in the -6, -20 and -8, -22 nominal series suggesting alkylnaphtho-phenols and alkylnaphthalene diols as possible compound types. Possible compound types in the nominal -5, -19 and -7, -21 mass Z series include alkylbenzamides and alkyl-naphthenobenzamides. The low-voltage mass spectrum of the base fraction showed fairly

6

SEPARATION FRACTION	225° to 360° C DISTILLATE				360° to 540 ° C DISTILLATE			
	Yield	Wt. Percent	Wt. Percent Sulfur	Wt. Percent Nitrogen	Yield	Wt. Percent	Wt. Percent Sulfur	Wt. Percent Nitrogen
	Distillate Basis	Crude Basis			Distillate Basis	Crude Basis		
ACIDS	0.82	0.14	0.39	0.045	0.13	0.04	ND ^{1/}	ND
BASES	.21	.04	1.21	1.89	.23	.07	0.82	2.54
HYDROCARBONS-NEUTRALS	95.52	16.81	ND	ND	99.81	28.80	ND	ND
SATURATES	62.9	11.07	.00	.002	53.7	15.52	.08	.002
MONCAROMATICS	18.2	3.20	.11	.001	18.2	5.26	.21	.007
DIAROMATICS	6.5	1.14	1.65	.000	9.2	2.66	1.59	.000
POLYAROMATIC-POLARS	5.7	1.00	4.79	.144	16.7	4.83	3.16	.57
TOTAL SAMPLE HANDLING LOSS	5.56	.98	NA ^{2/}	NA	1.8	0.52	NA	NA

^{1/} NOT DETERMINED
^{2/} NOT APPLICABLE

even distribution of material in all 14 nominal mass Z series with a molecular-weight range of 180 to 350 amu. Possible compound types include amines, pyridines, anilines, and their naphthenologs for the odd mass Z series and hydrocarbons, sulfur compounds, and di-nitrogen compounds for the even mass Z series.

Separations for the 360° to 540° C distillate produced an acid fraction (0.13 percent), a base fraction (0.23 percent) and hydrocarbons-neutral (99.81 percent). A net gain of 0.16 percent in the extractions probably resulted from incomplete solvent removal from the hydrocarbon-neutral fraction. A low-voltage spectrum of the acid fraction showed material in all seven even mass Z series and five odd mass Z series with a molecular-weight range of 160 to 390 amu. Material in the 0, -14 and -2, -16 nominal mass Z series accounted for about 30 percent of the total ionization. Hydroxyfluorenes and hydroxyphenanthrene/anthracenes are possible compound types for these mass Z series. The -1, -15 and -3, -17 mass Z series accounted for most of the ionization in the odd mass Z series present suggesting carbazoles and naphthenocarbazoles. The low-voltage mass spectrum for the base fraction showed fairly even distribution of material in all 14 nominal mass Z series with a molecular-weight range of 200 to 380 amu. Possible compound types include amines, pyridines, anilines, and their naphthenologs for the odd mass Z series and hydrocarbons, sulfur compounds, and di-nitrogen compounds for the even mass Z series.

SATURATES

Analysis of the saturate concentrates from the adsorption chromatography, which accounted for 65.8 percent of the 225° to 360° C hydrocarbons-neutrals (62.9 percent of the distillate) and 53.9 percent of the 360° to 540° C hydrocarbons-neutrals (53.7 percent of the distillate), proceeded directly by the high-voltage mass spectrometric method of Hood and O'Neal (14). The data, summarized in table 4, were obtained using a C₁₇ matrix for the 225° to 360° C saturates and a C₂₂ matrix for the 360° to 540° C saturates. One- and two-ring compounds predominated slightly and accounted for about 53 percent of the 225° to 360° C saturates and 44 percent of the 360° to 540° C saturates. One notable feature is the lower amount of zero-ring saturates in this crude as compared to that of five other petroleum crudes reported previously (5). The total saturates in the 360° to 540° C distillate (54 percent) falls well within the range of the five crudes from the earlier study (37 to 74 percent) (5). Also, the higher quantity of four-ring compounds in the 360° to 540° C saturates relative to three- and five-ring compounds is consistent with a trend noted in the earlier study. Finally, the absence of monoaromatics in the saturates indicates good separations were achieved on the silica-alumina gel adsorption columns.

MONOAROMATICS

Selected subfractions from the GPC separations of the two distillate monoaromatic concentrates were analyzed by low-voltage mass spectrometry and the GPC-mass spectral

TABLE 4. - Ring distributions of the saturate concentrates

Ring Number	225° to 360° C Distillate			360° to 540° C Distillate		
	Wt. Pct. Concentrate	Wt. Pct. Distillate	Wt. Pct. Crude	Wt. Pct. Concentrate	Wt. Pct. Distillate	Wt. Pct. Crude
0	13.7	8.6	1.52	10.93	5.87	1.69
1	25.4	16.0	2.82	23.43	12.58	3.63
2	27.1	17.0	2.99	20.97	11.26	3.25
3	20.4	12.8	2.25	16.18	8.69	2.51
4	13.4	8.4	1.48	17.37	9.33	2.69
5	-	-	-	11.12	5.97	1.72
Monoaromatics	.0	.0	.0	.0	.0	.0

correlations previously established (10,12). High-resolution mass spectra and NMR spectra of selected subfractions were also used to confirm compound type assignments. The results of the analysis are summarized in table 5. About 60 percent of the 225° to 360° C monoaromatic concentrate consists of alkyldindans/tetralins and alkyldinaphthenobenzenes in the -8 and -10 mass Z series respectively. Some diaromatics were detected, but the relatively small amount (about 4 percent) indicates a good separation on the silica-alumina gel adsorption columns. A small amount of benzothiophenes (0.32 percent) and a smaller amount of an unknown (0.053 percent) were found also. Material lost in sample handling and material under the tail regions of the GPC curve (where sample size was insufficient for MS analysis) amounted to 2.95 percent of the concentrate and is identified as "not analyzed" in table 5. No nitrogen-containing compound types were detected which is in good agreement with the extremely small amount of nitrogen indicated for the concentrate in table 3. Assuming an average molecular weight of 260, only 0.02 percent of compound types containing one nitrogen atom per molecule would be expected. Corresponding calculations based on the sulfur content from table 3 indicates 0.9 percent sulfur compound types which agrees reasonably well with the 0.32 percent found, as shown in table 5.

The NMR data for the 225° to 360° C monoaromatic concentrate show the same trends as those observed in the API Project 60 studies (5). Data for the early eluting GPC fractions show a predominance of fairly long alkyl side chains ($n > 5$). Data for later eluting GPC fractions indicate shorter side chains. Some diaromatic content was noted which is consistent with the GPC-MS results. A small, broad peak near 3.6 ppm below tetramethylsilane (TMS) appeared in spectra of several fractions. Possible assignments include the CH_3 group in methyl phenyl ethers and CH_2 groups in dihydrobenzofuran, indene, diphenylmethane, fluorene, and related compounds.

High-resolution mass spectral data indicated small amounts of oxygenates in the -8(0), -10(0), -12(0), and -14(0) mass Z series were present in several GPC subfractions. These oxygenates could not be separated from the hydrocarbons on the basis of the GPC-low-resolution MS analysis. Some typical examples of the oxygenate-hydrocarbon doublets observed in the high-resolution spectra are listed in table 6. In general, the high-resolution data were in good agreement with those of the GPC-MS correlation, and no additional components of any significance were detected.

The 360° to 540° C monoaromatic concentrate data in table 5 show about the same trends as those of the corresponding data from the earlier API study (5). The -10 mass Z series hydrocarbons (alkyldinaphthenobenzenes) were present in the highest concentration (20.81 percent). The slight shift from the 225° to 360° C monoaromatic results (from -8 Z to -10 Z) is consistent with the higher boiling range and higher molecular weight range for the 360° to 540° C distillate concentrates. Again, only a small amount of diaromatic material (1.46 percent) was observed. No nitrogen compounds were detected, and about 0.2 percent sulfur compounds were found. These values are in fair agreement with the values (0.2 percent and 2.5 percent, respectively) calculated from the elemental analyses (table 3), assuming one heteroatom per molecule and an average molecular

TABLE 5. - Semiquantitative analysis of the monoaromatic concentrates

MASS Z SERIES	225° to 360° C DISTILLATE			360° to 540° C DISTILLATE			PROBABLE COMPOUND TYPES
	Wt. Pct. Concentrate	Wt. Pct. Distillate	Wt. Pct. Crude	Wt. Pct. Concentrate	Wt. Pct. Distillate	Wt. Pct. Crude	
-6	1/ 16.53	3.01	0.529	7.27	1.32	0.385	ALKYLBENZENES.
-8	2/ 30.97	5.64	.991	16.83	3.06	.892	ALKYLINDANS/TETRALINS.
-10	3/ 28.50	5.19	.912	20.81	3.79	1.103	ALKYLDINAPHTHENOENZENES.
-12	4/ 14.47	2.63	.463	18.25	3.32	.967	ALKYLTRINAPHTHENOENZENES.
-14	1.67	.30	.053	12.52	2.28	.664	ALKYLTETRANAPHTHENOENZENES.
-16	.55	.10	.018	7.31	1.33	.387	ALKYLPENTANAPHTHENOENZENES.
-18	-	-	-	3.85	.70	.204	ALKYLHEXANAPHTHENOENZENES.
-20	-	-	-	1.84	.33	.098	ALKYLHEPTANAPHTHENOENZENES.
-22	-	-	-	.57	.10	.030	ALKYLOCTANAPHTHENOENZENES.
-14	3.23	.59	.103	.56	.10	.030	ALKYLDIPHENYLALKANES/BIPHENYLS AND/OR ALKYLNAPHTHENOENAPHTHALENES.
-16	.75	.14	.024	.65	.12	.034	ALKYLNAPHTHENODIPHENYLALKANES/BIPHENYLS AND/OR ALKYLDINAPHTHENOENAPHTHALENES AND/OR ALKYPENTANAPHTHENOENZENES.
-18	-	-	-	.20	.036	.011	ALKYLDINAPHTHENODIPHENYLALKANES/BIPHENYLS AND/OR ALKYLTRINAPHTHENOENAPHTHALENES AND/OR ALKYLHEXANAPHTHENOENZENES.
-20	-	-	-	.05	.009	.003	ALKYLTRINAPHTHENODIPHENYLALKANES/BIPHENYLS AND/OR ALKYLTRINAPHTHENOENAPHTHALENES.
-10S	.20	.036	.006	-	-	-	ALKYLBENZOTHIOPHENES.
-12S	.12	.022	.004	.14	.025	.007	ALKYLNAPHTHENOENBENZOTHIOPHENES.
-14S	-	-	-	.05	.009	.003	ALKYLDINAPHTHENOENBENZOTHIOPHENES.
-4, -18	.053	.010	.002	-	-	-	UNKNOWN.
-	2.95	.54	.094	9.10	1.66	.482	NOT ANALYZED.

1/ CONTAINS ALSO A SMALL AMOUNT OF OXYGENATE [-8 (0)] MATERIAL.

2/ CONTAINS SMALL AMOUNTS OF -10(0) OXYGENATES (PROBABLY BENZOFURANS) AND -12S SULFUR COMPOUNDS (PROBABLY NAPHTHENOENBENZOTHIOPHENES).

3/ CONTAINS A SMALL AMOUNT OF -12(0) OXYGENATES (PROBABLY NAPHTHENOENBENZOFURANS).

4/ CONTAINS A SMALL AMOUNT OF -14(0) OXYGENATES (PROBABLY DINAPHTHENOENBENZOFURANS).

TABLE 6. - Some examples of oxygenate-hydrocarbon doublets from the high-resolution mass spectrum of GPC fraction 19 of the 225° to 360° C monoaromatic concentrate.

Molecular Formula	Z Series	Calculated m/e	Observed m/e	Δ m/e
C ₁₂ H ₁₀ O	-14(0)	170.0732	170.0745	0.0013
C ₁₃ H ₁₄	-12	170.1096	170.1105	.0009
C ₁₂ H ₁₂ O	-12(0)	172.0888	172.0931	.0043
C ₁₃ H ₁₆	-10	172.1252	172.1233	-.0019
C ₁₂ H ₁₄ O	-10(0)	174.1045	174.1066	.0021
C ₁₃ H ₁₈	- 8	174.1409	174.1431	.0022
C ₁₄ H ₁₄ O	-14(0)	198.1045	198.1025	-.0020
C ₁₅ H ₁₈	-12	198.1409	198.1389	-.0020
C ₁₄ H ₁₆ O	-12(0)	200.1201	200.1192	-.0009
C ₁₅ H ₂₀	-10	200.1565	200.1532	-.0033
C ₁₄ H ₁₈ O	-10(0)	202.1358	202.1383	.0025
C ₁₅ H ₂₂	- 8	202.1722	202.1711	-.0011

weight of 375 amu. Some sulfur compounds may be masked by hydrocarbons or may be included in the 9.1 percent of the concentrate not analyzed owing to sample-handling losses and insufficient material in GPC fractions in the tail region of the GPC chromatogram .

The NMR data for the 360° to 540° C monoaromatic concentrate GPC subfractions showed predominantly monoaromatic character and were similar to the corresponding data from earlier studies (5) of petroleum crudes. Some diaromatic content was observed which is consistent with the GPC-MS results. The peak at about 3.6 ppm was not as prominent or as prevalent as in the 225° to 360° C monoaromatic data. The high-resolution spectral data were in good agreement with the GPC-MS correlation data. The oxygenate-hydrocarbon doublets observed in the 225° to 360° C monoaromatic spectra were almost completely absent in the 360° to 540° C monoaromatic spectra, and no additional components of any significance were detected.

DIAROMATICS

Data from the analysis of the diaromatic concentrates are summarized in table 7. Alkyl naphthalenes and alkyl naphthenonaphthalenes and/or alkyl diphenylalkanes/biphenyls account for about 65 percent of the 225° to 360° C diaromatic concentrate. A considerable amount of alkyl benzothiophenes and their mono- and dinaphthenologs were observed. The NMR data were consistent with mostly diaromatic character with some monoaromatic character present which could be explained by noncondensed diaromatics (diphenylalkanes and/or biphenyls). The peak at about 3.6 ppm was noted in several fractions. Overall trends were typical of those observed for other petroleum diaromatic concentrates. There was no evidence of any condensed polyaromatics thereby indicating a good silica-alumina gel separation. High-resolution mass spectrometric data indicated the presence of small amounts of oxygenates, as noted in table 7. No nitrogen compounds were observed which is in agreement with the elemental analysis. Sulfur balance was quite good with the observance of 14.3 percent sulfur-containing compounds compared to 12.4 percent predicted from the elemental sulfur analysis assuming an average molecular weight of 240 and one sulfur atom per molecule. About 3.28 percent of the concentrate was classified as not analyzed resulting from sample-handling losses encountered in the GPC separation and insufficient sample size in the tail regions of the GPC chromatogram.

The data for the 360° to 540° C diaromatic concentrate in table 7 show a maximum in the concentrations at the -16 mass Z series which is consistent with corresponding data from earlier studies (5). About 16.6 percent of the concentrate was designated as sulfur compound types, primarily benzothiophenes, dibenzothiophenes, and their naphthenologs. Other sulfur compound types accounting for about 5 percent were diphenyldisulfides, arenocyclic sulfides, and their naphthenologs. All of these compound type assignments were consistent with results from earlier studies. The balance of this concentrate consisted of 0.037 percent designated unknown and 3.91 percent not analyzed. The NMR data

TABLE 7. - Semiquantitative analysis of the diaromatic concentrates

MASS Z SERIES	225° to 360° C DISTILLATE			360° to 540° C DISTILLATE			PROBABLE COMPOUND TYPES
	Wt. Pct. Concentrate	Wt. Pct. Distillate	Wt. Pct. Crude	Wt. Pct. Concentrate	Wt. Pct. Distillate	Wt. Pct. Crude	
-12	27.51	1.79	0.315	3.96	0.36	0.107	ALKYLNAPHTHALENES.
-14	^{1/} 37.79	2.46	.431	^{1/} 14.22	1.31	.384	ALKYLNAPHTHENONAPHTHALENES AND/OR ALKYLDIPHENYLALKANES/BIPHENYLS.
-16	^{1/} 13.50	0.88	.154	^{1/} 18.90	1.74	.510	ALKYLDINAPHTHENONAPHTHALENES AND/OR ALKYLNAPHTHENODIPHENYLALKANES/BIPHENYLS.
-18	3.43	.22	.039	^{2/} 15.87	1.46	.428	ALKYLTRINAPHTHENONAPHTHALENES AND/OR ALKYLDINAPHTHENODIPHENYLALKANES/BIPHENYLS.
-20	.333	.002	.0004	^{1,2/} 12.32	1.13	.333	ALKYLTETRAPHTHENONAPHTHALENES AND/OR ALKYLTRINAPHTHENODIPHENYLALKANES/BIPHENYLS.
-22	.317	.001	.0002	^{2/} 7.58	.70	.205	ALKYLPENTANAPHTHENONAPHTHALENES AND/OR ALKYLTETRAPHTHENODIPHENYLALKANES/BIPHENYLS.
-24	.308	.001	.0001	^{3/} 4.17	.38	.113	ALKYLHEXANAPHTHENONAPHTHALENES AND/OR ALKYPENTANAPHTHENODIPHENYLALKANES/BIPHENYLS.
-26	-	-	-	^{2/} 2.47	.23	.067	ALKYLHEPTANAPHTHENONAPHTHALENES AND/OR ALKYLHEXANAPHTHENODIPHENYLALKANES/BIPHENYLS.
-10S	9.52	.62	.109	^{1/} 1.84	.17	.050	ALKYLBENZOTHIOPHENES.
-12S	3.17	.21	.036	2.46	.23	.066	ALKYLNAPHTHENOBENZOTHIOPHENES.
-14S	1.56	.11	.019	1.88	.17	.051	ALKYLDINAPHTHENOBENZOTHIOPHENES.
-16S	-	-	-	2.38	.22	.064	ALKYLDIBENZOTHIOPHENES AND/OR ALKYLTRINAPHTHENOBENZOTHIOPHENES.
-18S	-	-	-	2.55	.23	.069	ALKYLNAPHTHENODIBENZOTHIOPHENES AND/OR ALKYLTETRAPHTHENOBENZOTHIOPHENES.
-20S	-	-	-	.37	.034	.010	ALKYLDINAPHTHENODIBENZOTHIOPHENES AND/OR ALKYPENTANAPHTHENOBENZOTHIOPHENES.
-14S ₂	-	-	-	1.40	.13	.038	ALKYLDIPHENYLDISULFIDES.
-16S ₂	-	-	-	1.32	.12	.036	ALKYLNAPHTHENODIPHENYLDISULFIDES.
-18S ₂	-	-	-	.89	.082	.024	ALKYLDINAPHTHENODIPHENYLDISULFIDES.
-6S ₂ , -16S	-	-	-	.31	.029	.008	ALKYLTHIENOCYCLIC SULFIDES AND/OR ALKYLBNZOPENTACYCLIC SULFIDES.
-8S ₂ , -18S	-	-	-	.37	.034	.010	ALKYLTHIENOCYCLIC SULFIDES AND/OR ALKYLBNZOHEXACYCLIC SULFIDES.
-10S ₂ , -20S	-	-	-	.47	.043	.013	ALKYLTHIENOTRICYCLIC SULFIDES AND/OR ALKYLBNZOHEPTACYCLIC SULFIDES.
-12S ₂ , -8S	-	-	-	.31	.029	.008	ALKYLTHIENOTETRACYCLIC SULFIDES AND/OR ALKYLBNZOXYCLIC SULFIDES.
-10, -24	-	-	-	.037	.003	.001	UNKNOWN.
-	3.28	.21	.037	3.91	.36	.106	NOT ANALYZED.

^{1/} INCLUDES SOME OXYGENATE MATERIAL [-16 (0) through -22 (0)], PROBABLY DIBENZOFURANS AND THEIR NAPHTHENOLOGS.
^{2/} PROBABLY INCLUDES SMALL AMOUNTS OF CONDENSED POLYAROMATICS ALSO.

were again consistent with primarily diaromatics allowing for some noncondensed diaromatics. The peak at about 3.6 was present again in the spectra of most of the GPC fractions. Spectra of the later fractions showed small amounts of polyaromatics present. Nevertheless, the silica-alumina gel separation appeared to be fairly efficient. High-resolution mass spectral data indicated small amounts of oxygenates in the -16 (0) through -22 (0) mass Z series were present in some of the GPC subfractions, as noted in table 7. These oxygenates were probably alkyl dibenzofurans and their naphthenologs. No nitrogen compounds were detected which agrees with the elemental nitrogen analysis for this concentrate. The sulfur balance was good with the observance of about 16.6 percent sulfur compounds compared to 18.6 percent calculated assuming one sulfur atom per molecule and an average molecular weight of 375. The observed value is actually somewhat higher as some of the assigned compound types contained two sulfur atoms per molecule. The total percent of sulfur compound types fell about midrange of the corresponding data for the five crudes in the earlier study which ranged from 5 to 41 percent (5).

POLYAROMATIC-POLAR MATERIAL

The semiquantitative analysis data from the GPC-MS correlation characterization of the polyaromatic-polar concentrates are summarized in table 8. About 38 percent of the 225° to 360° C concentrate is composed of alkylacenaphthalenes/fluorenes and their mononaphthenologs and alkylphenanthrenes/anthracenes in the -16 and -18 mass Z series. Alkyl dibenzothiophenes account for about 13.5 percent of the concentrate. A total of about 20 percent of the concentrate was identified as separate sulfur compound types. Several of the listings in table 8 under hydrocarbon types contained some sulfur compounds also, as explained in footnotes 2 and 3 of the table. Based on the sulfur analysis of the concentrate and assuming an average molecular weight of 230 and one sulfur atom per molecule, about 34 percent of the concentrate should be sulfur compound types which is in good agreement with the observed results. Corresponding calculations for nitrogen indicate 2.4 percent nitrogen compounds expected which is in good agreement with the 2.7 percent observed. Unknown compound types comprised 3.9 percent of the concentrate and material not analyzed amounted to 5.7 percent. The NMR data were consistent with polyaromatic content allowing for some contribution from the alkylacenaphthalenes/fluorenes and some noncondensed polyaromatics. The individual spectra and overall trends were similar to the corresponding data from earlier studies. High-resolution mass spectrometric data indicated the presence of small amounts of oxygenates coincident with hydrocarbon types, as noted in table 8.

The hydrocarbon data for the 360° to 540° C distillate, also in table 8, show a maximum in the concentration distribution at the -22 mass Z series which is consistent with corresponding data from the earlier petroleum crude studies. Material listed in table 8 as separated sulfur compound types amounted to about 24 percent of the concentrate. An additional 22.5 percent of the concentrate was designated as a mixture of hydrocarbon types and cyclic sulfides. Therefore, most of the expected amount of sulfur compound

TABLE 8. - Semiquantitative analysis of the polyaromatic-polar concentrates

Mass Z Series	225° to 360° C Distillate			360° to 540° C Distillate			Probable Compound Types
	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	
-16	1/ 17.20	0.980	0.172	1/ 2.38	0.397	0.114	(A) Alkylacenaphthalenes/fluorenes.
-18	1/ 20.62	1.175	.206	1/ 5.85	.977	.281	(B) Alkylphenanthroacenaphthalenes/fluorenes and/or alkylphenanthrenes/anthracenes.
-20	1/ 6.10	.348	.061	1/ 7.58	1.266	.364	(C) Alkylindaphthenoacenaphthalenes/fluorenes and/or alkylindaphthenophenanthrenes/anthracenes.
-22	1/ 4.99	.284	.050	1/ 9.15	1.528	.439	(D) Alkyltrinaphthenoacenaphthalenes/fluorenes and/or alkyltrinaphthenophenanthrenes/anthracenes and/or alkylpyrenes/fluoranthrenes.
-24	1,2/ 3.08	.176	.031	1/ 6.88	1.149	.330	(E) Alkyltetranaphthenoacenaphthalenes/fluorenes and/or alkyltrinaphthenophenanthrenes/anthracenes and/or alkylphenanthrenes/fluoranthrenes and/or alkylchrysenes.
-26	1,2/ 3.45	.197	.035	1/ 3.91	.653	.188	(F) Alkylpentanaphthenoacenaphthalenes/fluorenes and/or alkyltetranaphthenophenanthrenes/anthracenes and/or alkyltrinaphthenophenanthrenes/fluoranthrenes and/or alkylindaphthenochrysenes.
-28	1/ 0.14	.008	.0014	2.12	.354	.102	(G) Alkylhexanaphthenoacenaphthalenes/fluorenes and/or alkylpentanaphthenophenanthrenes/anthracenes and/or alkyltrinaphthenophenanthrenes/fluoranthrenes and/or alkylindaphthenochrysenes and/or alkylbenzopyrenes.
-30	-	-	-	0.56	.094	.027	(H) Alkylheptanaphthenoacenaphthalenes/fluorenes and/or alkylhexanaphthenophenanthrenes/anthracenes and/or alkyltetranaphthenophenanthrenes/fluoranthrenes and/or alkyltrinaphthenochrysenes and/or alkylindaphthenobenzopyrenes.
-32	-	-	-	.49	.082	.024	(I) Alkylacetanaphthenoacenaphthalenes/fluorenes and/or alkylheptanaphthenophenanthrenes/anthracenes and/or alkylpentanaphthenophenanthrenes/fluoranthrenes and/or alkyltetranaphthenochrysenes and/or alkylindaphthenobenzopyrenes.
-28	.11	.006	.0011	-	-	-	Alkylbenzopyrenes.
-16,-65	-	-	-	3.13	.523	.150	Alkyltetraacyclic sulfides and hydrocarbons (A) above.
-18,-85	-	-	-	3.48	.581	.167	Alkylpentacyclic sulfides and hydrocarbons (B) above.
-20,-105	-	-	-	3.73	.623	.179	Alkylhexacyclic sulfides and hydrocarbons (C) above.
-22,-125	-	-	-	3.38	.564	.162	Alkylheptacyclic sulfides and hydrocarbons (D) above.
-24,05	-	-	-	2.68	.448	.129	Alkylcyclic sulfides and hydrocarbons (E) above.
-26,-25	-	-	-	2.98	.498	.143	Alkylbicyclic sulfides and hydrocarbons (F) above.
-28,-45	-	-	-	3.17	.529	.152	Alkyltricyclic sulfides and hydrocarbons (G) above.
-14,-16(0)	1.43	.082	.014	.073	.012	.004	Alkylphenanthroacenaphthalenes and alkylindobenzofurans.
-145	1.11	.063	.011	.29	.048	.014	Alkylthienindenes.
-165	13.46	.767	.135	4.86	.817	.233	Alkylindobenzothiophenes.
-185	2.25	.128	.023	5.01	.837	.240	Alkylphenanthrobenzothiophenes.
-205	1.23	.070	.012	3.98	.665	.191	Alkylindaphthenodibenzothiophenes.
-225	.60	.034	.006	5.28	.882	.253	Alkyltrinaphthenodibenzothiophenes and/or alkylbenzophenothiophenes.
-245	-	-	-	2.93	.489	.141	Alkyltetranaphthenodibenzothiophenes and/or alkylindaphthenobenzothiophenes.
-265	-	-	-	.60	.100	.029	Alkylpentanaphthenodibenzothiophenes and/or alkylindaphthenobenzothiophenes.
-285	-	-	-	.47	.078	.023	Alkyltrinaphthenobenzophenothiophenes and/or alkylindaphthenothiophenes.
-305	-	-	-	.19	.032	.009	Alkyltetranaphthenobenzophenothiophenes and/or alkylindaphthenodibenzothiophenes.
-325	-	-	-	.095	.016	.005	Alkylpentanaphthenobenzophenothiophenes and/or alkylindaphthenodibenzothiophenes.
-365	-	-	-	.041	.007	.002	Alkylthienindaphthenobenzopyrenes.

TABLE 8. - Semiquantitative analysis of the polyaromatic-polar concentrates--CONTINUED

Mass Z Series	225° to 360° C Distillate			360° to 540° C Distillate			Probable Compound Types
	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	wt-pct Concentrate	wt-pct Distillate	wt-pct Crude	
05	0.32	0.018	0.003	-	-	-	Alkylcyclic sulfides.
-25	.55	.031	.006	-	-	-	Alkylbicyclic sulfides.
-145 ₂	.15	.009	.002	-	-	-	Alkyldiphenylsulfides.
-285 ₂	-	-	-	0.17	0.028	0.008	Alkyldithienonaphthenophenanthrenes/anthracenes.
-305 ₂	-	-	-	.054	.009	.003	Alkyldithienodiphenanthrenes/anthracenes.
-6(0)	1.67	.095	.017	-	-	-	Alkylphenylethers and/or alkylphenols and/or alkylnaphthenofurans.
-8(0)	1.68	.096	.017	-	-	-	Alkylnaphthenophenylethers and/or alkylnaphthenophenols and/or alkylindaphthenofurans.
-10(0)	.48	.027	.005	-	-	-	Alkylbenzofurans and/or alkylindaphthenophenylethers.
-12(0)	.29	.017	.003	-	-	-	Alkylindaphthenobenzofurans.
-16(0)	^{3/} 6.15	.351	.062	-	-	-	Alkyldibenzofurans and/or alkylindaphthenofurans.
-20(0)	.64	.036	.006	-	-	-	Alkyldiphenadibenzofurans and/or alkylindaphthenonaphthofurans.
-15N	1.42	.081	.014	3.26	.544	.156	Alkylcarbazoles.
-17N	.97	.055	.010	4.17	.696	.200	Alkylindaphthenocarbazoles.
-19N	.29	.017	.003	3.29	.549	.158	Alkyldiphenocarbazoles.
-21N	-	-	-	.92	.154	.044	Alkylbenzocarbazoles.
-23N	-	-	-	.067	.011	.003	Alkylindaphthenobenzocarbazoles.
-27N	-	-	-	.093	.016	.004	Alkyldibenzocarbazoles.
-12,-26	.092	.005	.001	.057	.010	.003	Unknown.
-14,-28	.25	.014	.003	-	-	-	Unknown.
-16,-30	.35	.020	.004	.080	.013	.004	Unknown.
-18,-32	.16	.009	.002	.068	.011	.003	Unknown.
-20,-34	1.68	.096	.017	-	-	-	Unknown.
-22,-36	.67	.038	.007	-	-	-	Unknown.
-24,-38	-	-	-	.056	.009	.003	Unknown.
-26,-165	.68	.039	.007	-	-	-	Unknown.
-3N,-17N	.054	.003	.0005	-	-	-	Unknown.
-	5.68	.324	.057	2.32	.387	.111	Not Analyzed.

1/ Contains small amounts of oxygenate material also (probably benzofurans, dibenzofurans, benzonaphthofurans, and their naphthenologs; -10(0) through -28(0)).

2/ Contains some sulfur compounds also (probably alkylthienindenes (-145) and alkylindibenzothiophenes (-165)).

3/ Contains small amount of -45 sulfur compounds (probably alkyltricyclic sulfides).

types (about 32 percent based on one sulfur atom per molecule and an average molecular weight of 320) was accounted for. The probable sulfur compound types designated were typical of those found for petroleum crudes in the earlier study. Alkyldibenzothiophenes, alkylbenzonaphthothiophenes, and their naphthenologs accounted for the bulk of sulfur compound types (23.5 percent). This was the case for corresponding data for two of the five crudes in the earlier study. The total sulfur compound type content for the Bartlett 360° to 540° C polyaromatic-polar concentrate fell at about the lower middle of the range of sulfur compound type content of the five crudes in the earlier study, which ranged from about 10 to 70 percent (5). Nitrogen compound types (primarily alkylcarbazoles and their naphthenologs) amounted to about 12 percent of the 360° to 540° C Bartlett polyaromatic-polar concentrate and compared very favorably with the 13 percent predicted from elemental nitrogen analysis. The balance of this concentrate consisted of 0.26 percent unknowns.

The NMR analysis data for the Bartlett 360° to 540° C polyaromatic-polar GPC subfractions showed typical polyaromatic character and were similar to those from the earlier studies of petroleum crudes. The main difference between these results and corresponding results for syncrudes made from coal is the evidence for fewer and longer alkyl side chains for the petroleum samples, especially in the earlier eluting fractions. High-resolution mass spectral results for selected GPC subfractions were consistent with compound type assignments in table 8. Small amounts of oxygenates were detected in conjunction with several of the hydrocarbon series in some of the GPC subfractions. These oxygenates were probably benzofurans, dibenzofurans, benzonaphthofurans, and their naphthenologs (-10(0) through -28 (0) mass Z series).

SUMMARY

A heavy crude oil produced from the Bartlett field in southeastern Kansas by the Solfrac process developed by BERC engineers was characterized by methods developed, for the most part, in API Research Project 60. After removal of the solvent used in the Solfrac process, two distillate fractions were prepared and analyzed by a combination of techniques including adsorption chromatography, gel permeation chromatography, mass spectroscopy, NMR spectroscopy and gas chromatography. The results indicated the hydrocarbon compound types and concentrations for the Bartlett crude were similar to the results for five crude oils in previous studies. Concentrations of each of the major hydrocarbon compound types and sulfur compound types were well within the ranges observed for the previously studied crude oils. Acid and base fractions were smaller for the Bartlett crude than for the previously studied crudes. High resolution mass spectral results for the Bartlett crude showed the presence of some oxygenate material which was not determined in the previous studies. Nitrogen content in the Bartlett crude fractions was extremely similar to that of the previous studies except for the polyaromatic-polar concentrate which contained about twice the amounts observed earlier. These results plus physical and chemical properties from the BERC routine crude oil analysis provide an extensive characterization of the portion of Bartlett crude boiling below 540° C,

thereby providing valuable data for determining appropriate refining processes for efficiently upgrading this crude to more useful products.

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