

JOINT SYMPOSIUM ON OIL SHALE, TAR SANDS, AND RELATED MATERIAL
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.
AND THE DIVISION OF WATER, AIR, AND WASTE CHEMISTRY
AMERICAN CHEMICAL SOCIETY
SAN FRANCISCO MEETING, April 2-5, 1968

CHARACTERIZATION OF THE SATURATES AND OLEFINS IN SHALE-OIL GAS OIL

By

H. B. Jensen, J. R. Morandi, and G. L. Cook
Laramie Research Center, Bureau of Mines, U. S. Dept. of Interior, Laramie, Wyoming

INTRODUCTION

One of the most important phases of shale-oil research is the characterization of shale-oil distillate fractions. The naphtha fraction has been described in detail (1), but it comprises only 5 to 10 per cent of shale-oil crudes and extrapolation of the naphtha characterization to heavier distillates is not of much value. Although the middle-distillate fraction comprises about 20 per cent of shale-oil crudes, very little has been reported on the characterization of this material. The gas-oil fraction is the largest distillate fraction of shale oil, amounting to about 30 per cent of the shale oil, and it is characterization of the saturates and of the olefins in this gas oil that this paper will report.

Separation of a Green River shale-oil gas oil (boiling range 300 to 600°C) into compound-type concentrates has been previously described (2). Figure 1 is a flow diagram showing the methods used to separate the gas oil into a nitrogen-compound concentrate (43%), an aromatic concentrate (22%), an olefin concentrate (19%), and a saturate concentrate (16%). Characterization of the nitrogen-compound concentrate in terms of model compounds has been reported (3) and work is presently in progress to characterize the aromatic concentrate.

This paper describes the paraffins and olefins in shale-oil gas oil in terms of hydrocarbon-compound types within rather broad limits. The saturates are described with respect to the normal paraffin chain length, to the degree of branching in the branched paraffin, and to the number of condensed-ring structures. The olefins are described in the same terms as the saturates with the addition of describing the location of the double bond. Some possible precursors of the saturates and olefins in the original kerogen are also discussed.

CHARACTERIZATION OF SATURATE CONCENTRATE

The saturate concentrate, prepared as described earlier (2), was characterized utilizing one further separation step, that of thermal diffusion. The fractions from the thermal-diffusion separation were examined by mass spectroscopy (MS) and nuclear magnetic resonance spectroscopy (NMR).

Thermal-Diffusion Separation

A sample of the saturate concentrate was charged to a liquid-thermal-diffusion column operated under the following temperature conditions: Water outlet, 95°C; water inlet, 45°C; top of column, 110°C; middle of column, 100°C; and the bottom of the column, 70°C. The sample was in the column under these conditions for 100 hours. Table 1 lists the refractive indices of the fractions from this separation. The refractive indices show little difference in the composition of the first eight fractions from the thermal-diffusion column. This consistency of composition of the top eight fractions will also be shown in the characterization by mass and NMR spectroscopy.

Mass Spectral Characterization

High-voltage mass spectra of each of the thermal-diffusion fractions were obtained. These MS data were treated by Lumpkin's method (4) to determine the amounts of paraffins, noncondensed naphthenes, and condensed naphthenes with up to six rings per molecule. Lumpkin's method did not give a breakdown between normal paraffins and branched paraffins, and a method of estimating this breakdown was developed.

The method of estimating the normal paraffin-branched paraffin split, using 70-volt MS, is based upon three premises: (1. Branched paraffins have small parent ions, (2. a standard

TABLE I. - Refractive indices of thermal-diffusion fractions from the saturate concentrate

Fraction	Refractive index, $n_D^{60^\circ C}$
1	1.4346
2	1.4347
3	1.4348
4	1.4350
5	1.4351
6	1.4353
7	1.4357
8	1.4360
9	1.4395
10	1.4503

1/ Run at 60 °C because samples were solid at 20 °C.

TABLE II. - Composition of thermal-diffusion fractions from the saturate concentrate, volume-percent

Alkane type	Fraction							Total concentrate
	1	2	5	7	8	9	10	
n-Paraffins	58	61	60	52	49	31	13	50
Branched paraffins	42	39	39	45	45	46	28	40
1-Ring naphthenes	--	--	1	3	6	19	30	7
2-Ring condensed naphthenes	--	--	--	--	--	3	14	2
3-Ring condensed naphthenes	--	--	--	--	--	1	8	1
4-Ring condensed naphthenes	--	--	--	--	--	--	4	} <1
5-Ring condensed naphthenes	--	--	--	--	--	--	2	
6-Ring condensed naphthenes	--	--	--	--	--	--	1	

TABLE III. - Normal-paraffin distribution in saturate concentrate

Carbon number of n-paraffin	Volume-percent of total n-paraffins
22	1
23	1
24	4
25	15
26	23
27	27
28	18
29	10
30	1

TABLE IV. - Types of olefins in the thermal-diffusion fractions from the olefin concentrate by IR spectroscopy

Thermal-diffusion fraction	Mole-percent identified					Total
	Trans			Cis		
	RCH=CHR'	RCH=CH ₂	RR'C=CH ₂	RR'C=CHR''	RCH=CHR'	
1	31	21	-	7	8	67
2	31	20	-	5	6	62
3	32	19	-	8	4	63
4	33	18	1	8	5	65
5	31	15	1	7	6	60
6	26	12	1	10	4	53
7	17	8	1	10	3	39
8	13	5	2	9	2	31
9	12	3	2	11	3	31
10	12	3	2	10	2	29
Average	24	12	1	9	4	50

TABLE V. - NMR determination of hydrogen types in thermal-diffusion fractions of olefin concentrate

Thermal-diffusion fraction	Atom-percent total hydrogen		
	Methyl ^{1/} hydrogen	Methylene and methine hydrogens ^{2/}	Vinyl ^{3/} hydrogen
1	7.2	88.7	4.1
2	7.5	88.6	3.9
3	8.5	88.0	3.5
4	11.5	85.1	3.6
5	11.7	85.0	3.3
6	16.9	80.2	2.9
7	27.4	70.3	2.3
8	31.7	66.6	1.7
9	36.3	62.2	1.5
10	34.0	64.9	1.1

^{1/} 0.70 to 1.17 ppm.

^{2/} 1.17 to 3.00 ppm.

^{3/} 5.00 to 6.30 ppm.

total ionization for equal volumes of hydrocarbons (either mixtures or pure samples) can be calculated by Hood's method (5), and (3. the average carbon number for the branched and cyclic saturates is the same as for the normal paraffin in each fraction.

The following steps are necessary to use this method:

1. Determine the sensitivity of the monoisotopic molecular ion for a standard total ionization for each normal paraffin. This is done using available pure normal paraffins.
2. Calculate monoisotopic peak height for the molecular ions for the normal paraffins in the unknown sample.
3. Divide these monoisotopic peak heights by the sensitivity for each carbon number. This gives the relative volume (V_R) of each normal paraffin in the sample.
4. Determine the average carbon number of the sample by dividing the sum of the products of the carbon number times the V_R of each carbon number by the sum of the relative volumes.
5. Calculate the standard total ionization (I_S) for the sample according to Hood's method (5).
6. Add all peak heights in the spectrum from m/e 39 to the end of the spectrum of the unknown sample to get the observed total ionization (I_t) for the sample.
7. The following calculation then gives the volume-per cent normal paraffins in the sample:

$$\frac{I_S \times \sum V_R \times 100}{I_t} = \text{volume-per cent normal paraffins}$$

Table II lists the alkane-type composition of selected thermal-diffusion fractions and the total saturate concentrate as obtained by a combination of Lumpkin's calculations and the above calculation for the amount of normal paraffin in a sample.

The method of estimating the normal paraffins was also used to determine the carbon-number distribution of the normal paraffins in the thermal-diffusion fractions. This distribution is calculated as follows:

$$\frac{V_R \times 100}{\sum V_R} = \text{per cent of total normal paraffin in each carbon number}$$

Table III is the summation of the normal-paraffin distribution from the thermal-diffusion fractions from the saturate concentrate. Thus, 93 per cent of the total normal paraffins in the saturate concentrate had chain lengths from 25 to 29 carbon atoms.

Nuclear Magnetic Resonance Characterization

The NMR spectra of the 10 thermal-diffusion fractions were used to estimate the relative amounts of the different kinds of hydrogen in each of the thermal-diffusion fractions. Using carbon tetrachloride as the solvent and tetramethylsilane as an internal standard, the 0.70- to 1.05-ppm band was used to determine the methyl hydrogens, and the 1.05- to 2.00-ppm band was used to determine the combined methylene and methine hydrogens. Integration of the NMR spectra of the thermal-diffusion fractions shows that fractions 1 through 8 are similar and contain 88 per cent methylene-plus-methine hydrogens and 12 per cent methyl hydrogens. These data indicate that there is an average of three methyl groups per branched paraffin molecule, or only an average of one branch per molecule.

The bottom two thermal-diffusion fractions show substantial increases in methyl hydrogens. The percentage of methyl hydrogen in thermal-diffusion fraction 9 was 16 per cent, and in thermal-diffusion fraction 10 it was 18 per cent. From these data and those in Table II it can be calculated that the number of methyl groups per average cyclic molecule is 4 for fraction 9 and is 3.5 for fraction 10.

Discussion of the Saturate Concentrate

The overall picture of the saturate concentrate from the shale-oil heavy gas oil is that it contains 50 per cent straight-chain paraffins, 93 per cent of which have chain lengths from 25 to 29 carbon atoms. The branched paraffins comprise 40 per cent of the saturates and have only one branch per molecule. The 10 per cent of the saturates that is cyclic material is predominantly 1-ring cyclic but shows evidence of compounds with up to six condensed rings. This cyclic material is either multisubstituted or the substitutions are branched because the NMR spectra indicate that the average cyclic molecule has four methyl groups per molecule.

CHARACTERIZATION OF OLEFIN CONCENTRATE

One portion of the olefin concentrate, prepared as described earlier (2), was separated into 10 thermal-diffusion fractions and each fraction was examined by IR, NMR, and UV spectroscopy.

TABLE VI. - Number of vinyl hydrogens per average olefin molecule in the thermal-diffusion fractions of the olefin concentrate

Fraction	Number of vinyl hydrogens per average olefin molecule
1	2.2
2	2.1
3	2.0
4	1.9
5	1.8
6	1.6
7	1.3
8	1.0
9	0.7
10	0.5

TABLE VII. - Composition of the thermal-diffusion fractions from the HOC, volume-percent

Alkane type	Fraction										Total HOC
	1	2	3	4	5	6	7	8	9	10	
n-Paraffins	85	82	75	73	71	28	5	--	--	--	42
Branched paraffins	15	18	25	27	18	25	26	9	--	--	16
1-Ring naphthenes	--	--	--	--	10	34	31	20	7	2	10
2-Ring condensed naphthenes	--	--	--	--	1	9	21	21	15	10	9
3-Ring condensed naphthenes	--	--	--	--	--	3	11	23	28	28	9
4-Ring condensed naphthenes	--	--	--	--	--	1	5	15	23	22	7
5-Ring condensed naphthenes	--	--	--	--	--	--	1	8	16	20	4
6-Ring condensed naphthenes	--	--	--	--	--	--	--	2	8	11	2
7-Ring condensed naphthenes ^{1/}	--	--	--	--	--	--	--	2	3	5	1
8-Ring condensed naphthenes ^{1/}	--	--	--	--	--	--	--	--	--	2	<1

^{1/} By extension of Lumpkin's mass spectrometry method.

TABLE VIII. - Carbon-number distribution^{1/} of normal alkanes in the thermal-diffusion fractions of the HOC, volume-percent

Carbon No.	Fraction							Average ^{2/}
	1	2	3	4	5	6	7	
21	1	1	1	1	1	1	-	1
22	2	2	2	1	1	2	2	2
23	3	3	2	2	3	2	4	3
24	5	5	5	5	6	5	11	6
25	20	20	20	20	16	22	20	20
26	24	24	25	23	23	23	24	24
27	22	23	23	23	23	22	25	23
28	15	15	16	17	18	16	12	15
29	6	5	5	6	7	7	2	5
30	2	2	1	2	2	-	-	1
Average carbon number for each fraction ^{3/}	26.3	26.2	26.3	26.3	26.4	26.3	25.9	26.3

^{1/} Values are in volume-percent of the total n-alkane in each fraction.

^{2/} Shows the carbon-number distribution for the n-alkanes in the HOC.

^{3/} Values shown here are for the n-alkanes in each fraction.

TABLE IX. - Comparison of the C/H weight ratios of the thermal-diffusion fractions of the HOC

Fraction	C/H weight ratios	
	Combustion	MS
1	5.72	5.78
2	5.70	5.78
3	5.78	5.78
4	5.75	5.78
5	5.75	5.80
6	6.08	5.92
7	6.13	6.07
8	6.21	6.44
9	6.36	6.73
10	6.84	6.80
Average ^{1/}	6.03	6.09

^{1/} Value on original HOC = 6.00.

Another portion of olefin concentrate was hydrogenated with Raney nickel at one atmosphere of hydrogen and 85°C. This hydrogenated olefin concentrate was separated into 10 thermal-diffusion fractions which were examined by MS and NMR spectroscopy. Carbon-type composition of each of the thermal-diffusion fractions was determined by a density-refractivity intercept method (6), and carbon-hydrogen ratios were determined on each fraction.

Unhydrogenated Olefin Concentrate

A portion of the olefin concentrate was charged to the thermal-diffusion column with the operating conditions being the same as shown for the thermal-diffusion separation of the saturate concentrate. Each of the 10 thermal-diffusion fractions was examined by IR and NMR spectroscopy.

IR Examination

The IR method of Saier (7) was used to estimate the types of olefinic linkages in each of the thermal-diffusion fractions. The method was developed by Saier for use in the naphtha boiling range so that the present extrapolation to the gas-oil range contains the assumption that the molar absorptivities of the several types of double bonds are constant. This method does not yield information on the concentrations of tetrasubstituted or cyclic olefins; hence, the information presented in Table IV characterizes only the chain portion of the concentrate. About half of this chain unsaturation occurs as trans internal olefin; a fourth as terminal, or alpha olefin without beta substitution; a sixth as the trisubstituted internal olefin; a tenth occurs as the cis internal olefin; and a very small amount occurs as the terminal olefin with beta substitution. These data show that only 50 per cent of the molecules in the olefin concentrate have unsaturation in the chain portion of the molecule.

NMR Examination

The NMR spectra of the 10 thermal-diffusion fractions were used to determine amounts of the different kinds of hydrogen. Using carbon tetrachloride as solvent and tetramethylsilane as an internal standard, the following bands were used to estimate the types of hydrogen: Methyl hydrogen from 0.70 to 1.17 ppm; methylene and methine hydrogen from 1.17 to 3.00 ppm; and vinyl hydrogen from 5.00 to 6.30 ppm. Table V gives the results of these integrations. The percentages of vinyl hydrogen were used with the data on average carbon and hydrogen numbers to calculate the average number of vinyl hydrogens per molecule. (The data on the average carbon and hydrogen numbers will be developed in the section on HOC.) Table VI lists the average number of vinyl hydrogens per molecule in each thermal-diffusion fraction. The data in Tables IV and VI show that doubly bonded carbons in the bottom thermal-diffusion fractions are more highly substituted than they are in the top fractions.

UV Examination

The UV spectra of the 10 thermal-diffusion fractions from the olefin concentrate showed that there was not present a significant quantity of aromatics. An attempt was made to calculate the concentration of conjugated diolefins and cyclic diolefins by a matrix method using molar extinction coefficients for available compounds. These reference compounds had molecular weights much lower than the compounds in the heavy-gas-oil olefin concentrate; thus, the results are only approximate. The calculations showed a constant level of about 1 volume-per cent conjugated diolefins in each of the top seven thermal-diffusion fractions. They showed no conjugated cyclic diolefins in the top four fractions, 2 per cent in fraction 5, 4 per cent in fraction 6, and 6 per cent in fraction 7. Fractions 8 to 10 had UV spectra too complicated to interpret with the matrix used.

Hydrogenated Olefin Concentrate

A 100-gram sample of the olefin concentrate was dissolved in 400 ml of isooctane and 85 grams of activated, Raney-nickel catalyst were added to the mixture. The Raney-nickel catalyst was prepared according to the "C" method of Hurd (8). This mixture was heated to reflux temperature and hydrogen gas was bubbled through the refluxing solution for 8 hours. Ninety-nine grams of the hydrogenated olefin concentrate (HOC) were recovered from the hydrogenation reaction.

A sample of the HOC was charged to a thermal-diffusion column with the operating conditions the same as given for the thermal-diffusion separation of the saturate concentrate. MS and NMR spectroscopy were used to characterize the fractions from the thermal-diffusion column. This characterization was made with respect to the relative amounts of normal paraffins, branched paraffins, and naphthenic compounds in each fraction. These data were compared to the data obtained by the density-refractivity intercept method of Kurtz (6) and to carbon-hydrogen ratios obtained analytically.

TABLE X. - Thermal-diffusion separation of the HOC

Fraction	Density 20 °C D 4 °C	Refractive index, 20 °C n _D
1	0.8230	1.4551
2	0.8095	1.4494
3	0.7995	1.4507
4	0.7982	1.4496
5	0.8088	1.4539
6	0.8173	1.4567
7	0.8363	1.4648
8	0.8674	1.4767
9	0.9171	1.4976
10	0.9570	1.5124
Average ^{1/}	0.8439	1.4667

^{1/} The original HOC had a density of 0.8442 and a refractive index of 1.4677.

TABLE XI. - Comparison of carbon-type composition of thermal-diffusion fractions from the HOC as determined by Kurtz' method and by MS analysis

Fraction	Carbon-type composition			
	Kurtz' method ^{1/}		MS analysis ^{2/}	
	Paraffin atoms, percent	Naphthene atoms, percent	Paraffin atoms, percent	Naphthene atoms, percent
1	85	15	100	0
2	100	0	100	0
3	100	0	100	0
4	100	0	100	0
5	97	3	97	3
6	91	9	88	12
7	79	21	77	23
8	62	38	57	43
9	40	60	39	61
10	21	79	32	68

^{1/} See reference (6).

^{2/} Estimated from MS pattern.

TABLE XII. - NMR determination of hydrogen types in thermal-diffusion fractions of the HOC

Thermal-diffusion fraction	Atom percent total hydrogen		Average number methyl groups per nonlinear molecule ^{3/}
	Methyl hydrogens ^{1/}	Methylene and methine hydrogens ^{2/}	
1	11.9	88.1	3.0
2	12.9	87.1	3.9
3	14.4	85.6	4.5
4	14.5	85.5	4.4
5	16.0	84.0	5.1
6	22.2	77.8	4.7
7	30.8	69.2	5.4
8	38.4	61.6	6.5
9	45.5	54.5	7.4
10	48.0	52.0	7.6

^{1/} 0.75 to 1.05 ppm.

^{2/} 1.05 to 5.00 ppm.

^{3/} Calculated from: (1) Atom percent methyl hydrogen, (2) the composition data shown in table VII, and (3) the average carbon number shown in table VIII.

MS Characterization

The high-ionizing-voltage mass spectral data were treated by Lumpkin's method (4) to determine the amounts of paraffins, noncondensed naphthenes, and condensed naphthenes with up to six condensed naphthene rings per molecule. This method worked well for thermal-diffusion fractions 1 through 7; however, it was evident from MS patterns that the bottom three fractions contained compounds with more than six condensed naphthene rings. The method of Lumpkin was extrapolated by smooth lines to cover seven, eight, and nine condensed naphthene rings. The normal paraffin-branched paraffin split was made as described previously. Table VII shows the results of these calculations for the thermal-diffusion fractions and also shows the summary for the total HOC.

As described in the saturate section, the MS data also provided an opportunity for estimating the carbon-number distribution for the normal paraffins in those fractions which have normal paraffins, and Table VIII shows these results.

The data in Tables VII and VIII were used to calculate carbon-hydrogen ratios for each of the thermal-diffusion fractions. The average ring-number content of each thermal-diffusion fraction was calculated using the data in Table VII. This average ring number was used to calculate the average Z number in the general hydrocarbon formula. The average carbon number listed in Table VIII and the average Z number are used to calculate the empirical formula and C/H value for each fraction. For thermal-diffusion fractions 8, 9, and 10 the average carbon number used was 26. The calculated C/H data are compared to combustion C/H data in Table IX. The agreement in the C/H values for each fraction is evidence that the data presented in Table VII with respect to the condensed structures are reasonable.

Physical Property Characterization of HOC

Kurtz (6) and coworkers have developed a method of correlating density and refractivity intercept with carbon-type composition. (Refractivity intercept is defined as the refractive index minus one-half of the density.) This correlation can be used for all types of viscous hydrocarbon oils and its application to the analysis of the thermal-diffusion fractions of the HOC provides a check on the MS method of hydrocarbon-type analysis. This check is in addition to the check provided by comparing C/H values as obtained by the MS method with C/H values determined by combustion.

Table X lists the density and refractive-index values for each of the 10 thermal-diffusion fractions. These values and the values for the average carbon number from Table VIII were used to obtain the carbon-type composition for each fraction shown under "Kurtz' Method" in Table XI. The composition values shown under MS analysis in Table XI were calculated from the data shown for each thermal-diffusion fraction in Table VII. In this calculation the condensed naphthene rings were assumed to be catacondensed and consist alternatively of five and six-membered rings. In general the MS results and the results using Kurtz' method agree. This supports the assumption that the condensed naphthenic structures in the HOC are of the catacondensed type.

NMR Characterization

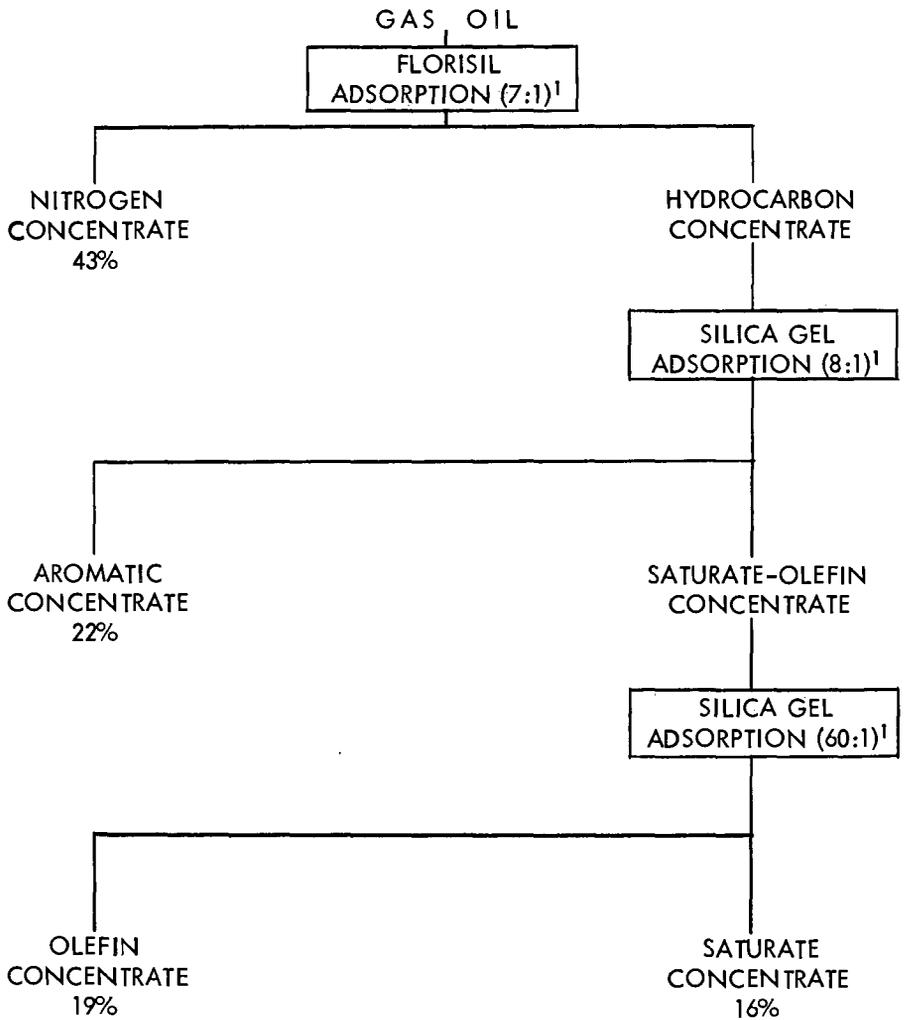
The NMR spectra of the 10 HOC thermal-diffusion fractions were used to show the relative amounts of the different kinds of hydrogens in each fraction. Using carbon tetrachloride as solvent and tetramethylsilane as an internal standard, the amount of methyl hydrogen in each fraction was obtained by integrating the 0.70- to 1.05-ppm band and the combined methylene and methine hydrogens by integrating the 1.05- to 2.00-ppm band. Table XII lists the percentage of hydrogen represented by the areas under each of these two bands and the average number of methyl groups per nonlinear molecule in each of the fractions. This average was calculated using:

1. The per cent methyl hydrogen,
2. the composition data shown in Table VI, and
3. the average carbon number as shown in Table VIII.

It may be only a fortuitous combination of data that shows the number of methyl groups to be three in the nonlinear part of thermal-diffusion fraction 1 (Table XII). Because there are no cyclic molecules in this fraction, these methyl groups are on branched paraffins and three is the minimum number of methyl groups possible per nonlinear, noncyclic molecule.

The data presented in Table XII show that fraction 1 has an average of one branch per nonlinear, noncyclic molecule; fraction 2 has an average of two branches; and fractions 3 and 4 both have 2.5. The data indicate neither the average length of the branch nor the point of branch attachment. In general, the lower the fraction in the column the greater is the average number of methyl groups per nonlinear molecule.

If we assume that the noncyclic branched-paraffin molecules in fraction 5 have the same

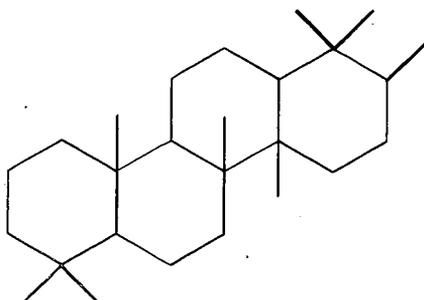


¹ Adsorbent-to-oil ratio.

FIGURE 1. - Separation of gas oil.

average number of methyl groups as were calculated for fraction 4 (4.5 groups per molecule), the calculated, average number of methyl groups per cyclic molecule is six. There is no way of determining the most likely configuration in which these six methyl groups are attached to the single, cycloparaffin ring; but if there are six methyls per average cyclic molecule, the average chain length for the alkyl substituent is three carbon atoms.

A similar calculation was made for thermal-diffusion fraction 10. This fraction had an average of eight methyl groups per molecule and an average of four condensed naphthene rings. If the ring system is catacondensed and the four rings are all six membered, there are no carbons left for chain construction. Although a single compound cannot be used to describe all of the molecules in this fraction, the following type structure is consistent with the NMR, the MS, the C/H-ratio, and the carbon-type data:



Whatever the case for ring structure, there must be several alkyl attachments in order to explain the large proportions of methyl hydrogens.

The particular type structure presented for the average condensed ring compounds in fraction 10 was chosen because it can be thought of as a possible thermal modification of a triterpane which has been identified in Green River kerogen (9). In general, these types of structures suggest that their precursors in the complex kerogen macrostructure may have been derived from materials related to steroids, triterpanes, or similarly condensed ring materials.

Discussion of the Olefin Concentrate

The data for the olefin concentrate from shale-oil heavy gas oil show that two-fifths of the olefin is straight chain; one-sixth branched olefin; one-tenth each of one-ring, two-ring condensed, and three-ring condensed olefins; and one-sixth of combined four-ring to eight-ring condensed olefins. Ninety per cent of the straight-chain olefins have chain lengths from 24 to 29 carbon atoms, and it is estimated from infrared spectra that about one-third of these normal olefins are alpha olefins, about one-half are trans internal olefins, and one-sixth are cis internal olefins.

The branched noncyclic olefins are not highly branched. For instance, those branched olefins in the top thermal-diffusion fraction (HOC fraction 1) have an average of only one branch per molecule, and the branched olefins in fractions 3 and 4 average 2.5 branches per molecule. The data for the branched olefins are not sufficiently detailed to allow positioning of the olefin bond with respect to the branching.

The cyclic compounds in the olefin concentrate appear to be highly substituted or highly branched. For example, the one-ring compounds that are in HOC thermal-diffusion fraction 5 have six methyl groups per average molecule. The average configuration of the molecule that fits the data for fraction 10 of the HOC indicates that the condensed cyclic olefins are catacondensed with an average of eight methyl groups per molecule.

The vinyl-hydrogen content of the thermal-diffusion fractions of the original concentrate is additional evidence for either cyclization or multisubstitution in the bottom-fraction material. The presence of terminal olefins in the top fraction provides a reasonable explanation of the 2.3 vinyl hydrogens per molecule because each internal normal olefin has two or less vinyl hydrogens and each terminal olefin has three. There is an average of only one-half of a vinyl hydrogen per molecule in fraction 10 which indicates multisubstitution on the olefinic carbons.

The data on neither the original olefin nor the hydrogenated olefin are sufficient to allow positioning of the double bond in the majority of the olefin-concentrate molecules, especially those molecules which are cyclic.

CONCLUSIONS

Spectral and chemical examinations of a saturate concentrate and an olefinic concentrate from a shale-oil heavy gas oil have shown 50 per cent of the saturates and 40 per cent of the olefins are straight chain. The branched paraffins are considerably less branched than are the branched olefins. The branched paraffins are 40 per cent of the saturates and the branched olefins are 15 per cent of the olefins.

The cyclic paraffins and cyclic olefins both show considerable range of ring condensation with up to six condensed saturate rings and evidence of nine condensed rings in the olefins. The cyclic naphthenes are 10 per cent of saturates and the cyclic olefins are 45 per cent of the olefins. The degree of substitution on the cyclics in both concentrates is large.

ACKNOWLEDGMENT

The work upon which this report is based was done under a cooperative agreement between the Bureau of Mines, U. S. Department of the Interior, and the University of Wyoming.

LITERATURE CITED

- (1) Dinneen, G. U., Van Meter, R. A., Smith, J. R., Bailey, C. W., Cook, G. L., Albright, C. S., and Ball, J. S., BuMines Bull. 593, 1961, 74 pp.
- (2) Dinneen, G. U., Smith, J. R., Van Meter, R. A., Albright, C. S., and Anthony, W. R., Anal. Chem. 27, 185 (February, 1955).
- (3) Dinneen, G. U., Cook, G. L., and Jensen, H. B., Anal. Chem. 30, 2026, (December, 1958).
- (4) Lumpkin, H. E., Anal. Chem. 28, 1946 (1956).
- (5) Hood, Archie, Anal. Chem. 30, 1218 (1958).
- (6) Kurtz, S. S., King, R. W., Jr., Stout, W. J., Peterkin, N. E., Anal. Chem. 30, 1224 (1958).
- (7) Saier, Eleanor, L., Pozefsky, Abbot, and Coggeshall, Norman, D., Anal. Chem. 26, 1258 (1954).
- (8) Hurd, Charles, D., and Rudner, Bernard, J.A.C.S. 73, 5157 (1951).
- (9) Hills, I. R., Whitehead, E. V., Anders, D. E., Cummins, J. J., and Robinson, W. E., Chem. Commun. (London), No. 20, 752 (October 19, 1966).