Chemical Characterization of Heavy Oils Using HPLC/FI-MS —Analysis of a Petroleum Vacuum Residue—

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An analytical system, in which a combination of two-stage HPLC and field ionization-mass spectrometry (FI-MS) are used and the results being processed with a computer, was applied to obtaining information on main chemical components contained in vacuum residue derived from crude oil. In the present study, a high degree of analytical accuracy, more so than in case of coal tar or coal derived liquids, should be strived for, because vacuum residue contains more complex chemical components. The sample oil, vacuum residue derived from Arabian crude oil, was pre-separated into 4 fractions by HPLC on silica gel columns, followed by further separation into totally 22 subfractions on cyano columns or ion-exchange resins. The data obtained from FI-MS analysis of all subfractions were presented in a tabular form with 14 columns by the computer so that members of any homologous series appear in the same column. The components in sample oils were classified into identifiable 75 compound classes. Based on these analytical data, the ratio of elements, number average molecular weight and aromaticity of the vacuum residue were calculated, which values being compared with measured values in order to evaluate the validity of the present analytical system.

1. Introduction

In the development of a technology for converting heavy oils, such as vacuum residues, into more valuable fuels by pyrolysis and hydrocracking, information on the chemical components of the heavy oils is essential. A vacuum residue consists of complex hydrocarbons having a wide range of molecular weight distribution, and its chemical components should differ greatly depending on its origin, resulting in significantly different mode of reaction when subjected to pyrolysis and hydrocracking. Several methods, such as component analysis and the analysis of average structures using NMR, are known for characterizing vacuum residue. On the other hand, in order to understand the structural transformation that occurs during processing, or to explain product properties, information on composition of reactants in greater detail becomes necessary. Incidentally there has been only a few studies conducted on analysis of petroleum heavy oils because of its extreme complexity. The most detailed analysis with HPLC/FI-MS conducted to date may be the study by Boduszynski¹⁾, in which vacuum gas oil

(650—1,000 °F) was distilled to yield narrow boiling range fractions, which were further separated by HPLC, and followed by the measurements taken by FI-MS for assignment of compound classes. The analyses of saturates²⁾, pentane-soluble fraction¹⁾ of the vacuum residue (>1,000 °F), had been tried. In spite of these efforts, the detailed analysis of all fractions in a vacuum residue have not yet been observed.

In the present study, we tried to analyze all fractions of the vacuum residue derived from Arabian crude oil, using the combination HPLC/FI-MS developed for routine analysis of chemical components of coal derived liquids as stated in a previous study³⁾, with partially modified HPLC separation scheme to meet the requirements of the separation of vacuum residue. The sample oil was pre-separated, in polarity, into 4 fractions by HPLC on silica gel columns, followed by separation of saturate fraction and aromatic fractions on cyano columns, and separation of polar fraction on ion-exchange resin columns, arriving at a total of 22 subfractions. The analysis of the subfractions was carried out with FI-MS. Assuming $MW=14n+U$ (MW , the molecular weight; n , U , integral numbers, $-11 \leq U \leq 2$), the FI-MS data were presented in a tabular form with 14 columns

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so that members of any homologous series appear in the same column and the components in the sample oil were divided into 75 compound classes assignable. In order to assure the usefulness of the present method, the ratios of the elements in sample oil (wt%), aromatic carbon (%C_{ar}), aromatic hydrogen (%H_{ar}) and number average molecular weights were calculated from the molecular weight distributions of the compound classes listed in the pattern table. The results were compared with the values measured by ultimate analysis, ¹³C-NMR etc. Both, the ratios of the elements (except sulfur) and number average molecular weight, reasonably agreed well with each value observed. The %C_{ar} was somewhat lower than the value observed, probably because the non-volatile polynuclear aromatic clusters in sample oil could not be detected by FI-MS.

2. Experimental

2.1 Sample, Solubility and Elemental Analysis

This study was focused on the vacuum residue derived from Arabian crude oil. The test method for solubility of the sample oil was essentially the same as that described previously⁹. The sample showed 91.2% solubility in a mixture of methylene chloride and hexane (50:50). Thus, we subjected the whole of the sample to preliminary separation by HPLC on silica gel. Elemental analysis of the sample oil is given in **Table 1**.

2.2 HPLC Separation

Two-stage HPLC separation scheme is shown in **Fig. 1**.

2.2.1 Preparative-scale HPLC on Silica Gel

Separations were performed using a Waters model Prep500 series HPLC. The silica gel column was equilibrated initially with *n*-hexane. The sample (2.0 g) was dissolved in 1–2 ml methylene chloride and loaded onto the column. Hexane was pumped at 40 ml/min and the effluent monitored with a differential refractive index detector. Both “saturates” and “mono- and di-aromatics” were elutriated with hexane, and the peak attributed to “saturates”, was almost down to the baseline before the “mono- and di-aromatics”

SG, silica gel column; CN, cyano column; I.E.C., ion-exchange chromatography.

Fig. 1 HPLC Separation Scheme

Fig. 2 Refractive Index Detector Response of the Preparative-scale HPLC of Total Vacuum Residue on Silica Gel

began to elutriate (**Fig. 2**). Furthermore, color of the effluent also turned from colorless to pale yellow at that time. The first fraction (Fraction 1) was largely saturates, and the second (Fraction 2) was mono- and di-aromatics.

After the second fraction had elutriated, the solvent was switched to a mixture of hexane (80%) and methylene chloride (20%) to collect Fraction 3. The color of the effluent turned to dark yellow or red and consisted mainly of polyaromatics. Again, when the signal approached the baseline, after *ca.* 400 ml, the solvent was switched to a mixture of methylene chloride (90%) and methanol (10%) to collect Fraction 4, “polars”. Approximately 300 ml were collected, by which time the detector showed a flat response. Solvent was removed from the different fractions by evaporation, first in a rotary evaporator, and then at 100 °C/1 torr/overnight.

Table 1 Elemental Analyses of the Whole Oil and the Silica Gel Fractions

Sample	Elemental analysis [wt%]				
	C	H	O ¹⁾	N	S
Whole oil	84.32	9.92	0.21	0.40	5.15
Fraction 1	85.66	13.16	0.07	0.16	0.95
Fraction 2	84.42	11.34	0.09	0.05	4.10
Fraction 3	83.57	9.45	0.66	0.29	6.03
Fraction 4	82.03	8.81	1.71	1.03	6.42

1) By difference.

2.2.2 Semi-preparative Scale HPLC on Cyano Column

Fractions 1, 2 and 3 from the preparative scale HPLC of the whole sample oil were further fractionated on a Waters 5000 chromatograph using a 10 mm by 250 mm Altech column packed with CN-bonded silica-gel beads. Solvents used were *n*-hexane (45 min) for the chromatography and a mixture of methylene chloride and methanol (90:10) being used to flush out any "polars". A mixture containing *n*-butylbenzene, *iso*-tetralin, 2-methylnaphthalene, phenanthrene, and pyrene was analyzed to optimize the flow rate. Best separations were obtained at 1.5 ml/min. We also determined the retention times for some other compounds containing heteroatoms, such as indole, carbazole, dibenzofuran, and dibenzthiophene, under the same conditions.

The samples were first chromatographed on an analytical scale so as not to overload the UV detector, 254 nm, and obtain an elutriation profile. Appropriate cut-points were determined by examining the chromatograms of the standard mixtures and the samples.

2.2.3 Ion-exchange Chromatography

The polar fraction from silica gel, fraction 4, was further separated into neutral, acidic, and basic subfractions using nonaqueous ion-exchange chromatography, as described by Green and co-workers⁴. We used Biorad AG MP-1 (anion exchange) and AG MP-50 (cation exchange) resins, particle size of both being 200 to 400 mesh. The resins were activated before use by sequence of washing with solvents: 1 to 2 N HCl, water; 1 to 2 N NaOH, water; 1:1 water, 2-propanol; 2-propanol, ether, *n*-pentane, and cyclohexane. The resins were packed into glass columns, 9 mm by 115 mm. The two glass columns were connected in series with the anion exchange column at the head. About 40 mg of the sample was dissolved in 1 ml cyclohexane and loaded on the anion exchange column. Cyclohexane was passed through the system at 1 ml/min.

As the materials passed through the columns, darkening of the resins was noted. About 80% of the length of the anion exchange resin was darkened; the last 20% remained light, indicating that a sufficient amount of anion exchange resin was present. Likewise, only about first one-third of the cation exchange resin darkened. Neutral materials are not retained by either of the columns and are elutriated with cyclohexane. The acidic and basic subfractions were removed from the anion and cation exchange resins, respectively, by subjecting to sonolysis of the resins with benzene/formic acid and benzene/propylamine

mixtures, respectively.

2.3 Examination by Other Techniques

The whole sample and various chromatographic fractions were examined by other analytical techniques such as UV, NMR and FT-IR to obtain additional information helpful in making structural assignment.

Proton and carbon-13 NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer. The procedure used for the ¹H-NMR was the same as used earlier³. ¹³C-NMR of the whole sample was obtained by suspending 1 g of the sample in 3 ml CDCl₃. The mixture was filtered, and was used to dissolve a 20 mg portion of chromium acetyl acetonate, Cr(acac)₃. Further, the paramagnetic chromium complex was used to shorten the time required for relaxation of ¹³C spins. The solution was taken in a 10 mm NMR tube. A pulse width corresponding to a flip angle of 60 °C and a pulse delay of 8 s were used to acquire free induction decay of 6,000 pulses. Proton decoupling was applied only during the data acquisition to minimize any nuclear overhauser enhancements.

All FT-IR spectra were recorded with a Digilab FTS-20E spectrometer and FTS-IMX 091-0080F data system. A smear of the sample was prepared by dropping a solution of the sample in methylene chloride on sodium chloride plates and allowing the solvent to evaporate. We usually acquired 250 scans at a resolution of 2 cm⁻¹.

2.4 FI-MS Analysis

The FI-MS measurements for the subfractions were obtained at SRI International, Menlo Park, CA, by using procedures described previously³. In this work, the spectrometer was scanned over the mass range of 50 to 2,000 amu.

3. Results

3.1 HPLC Fraction

3.1.1 Preparative Scale HPLC on Silica Gel and Spectroscopic Examination of Fractions

Separation of the whole sample on silica gel resulted in four fractions as described in 2.2.1. The various silica gel fractions were examined by ¹H-NMR, FT-IR, and UV spectroscopies. ¹H-NMR spectra showed that Fraction 1 had hardly any aromatic protons (<1%) and the aromatic proton content increased in the subsequent fractions. The absence of aromatic protons in Fraction 1 and their progressively increased amounts in the subsequent fractions was also borne out by the FT-IR spectra. The UV spectrum of Fraction 1, however, showed absorption in the 200 to 300 nm region, indicating the presence of some benzenes, naphthalenes and possibly higher aromatics as

well. A quantitative assessment of the absorption reveals that the aromatic content is less than 5 wt%. The aromatic structures that elutriate in Fraction 1 are most likely to be heavily substituted with alkyl groups or have the aromatic ring surrounded by naphthenic rings. In both cases, the aromatic proton content will be small. UV spectra of Fractions 2 and 3 showed that shift of the absorbance maximum to longer wavelengths for successive fractions was in keeping with the fact that larger aromatic clusters absorb at longer wavelengths.

Elemental analysis was obtained for the whole sample and four silica gel fractions. The data are given in **Table 1**. Nitrogen and oxygen are concentrated in Fraction 4, the "polar" fraction. Sulfur, on the other hand, is distributed fairly evenly in all but the first fraction. The lower sulfur content in Fraction 1, which contains nonpolar aliphatic structures, suggests that alkyl sulfides are relatively unimportant.

3.1.2 Semi-preparative Scale HPLC on Cyano Column

Performance of cyano column was tested with a variety of standard mixtures using *n*-hexane as the solvent. Retention times of different hydrocarbons were found to follow the number of "double bonds". Sulfur and oxygen heterocycles elutriated slightly later than the corresponding hydrocarbons, while even the neutral nitrogen compounds, indoles and carbazoles, were retained strongly. These compounds elutriated only during column flush with a mixture of methylene chloride and methanol (90–10).

Silica gel Fractions 1, 2 and 3 were first analyzed on the cyano column on an analytical scale to determine appropriate cut points for the semi-preparative scale experiments. Fraction 1 was

divided into five subfractions and Fractions 2 and 3 into seven subfractions, each. The retention time and yields of the various subfractions to the whole sample are shown in **Fig. 3**. Material recovery was 94%, 90% and 98% for the three silica gel fractions, respectively. The top line of **Fig. 3** gives the retention times of the various standard compounds. Based on the elutriation times of standard compounds, some judgment can be made as to the nature of materials presented in the different subfractions, as discussed later.

3.1.3 Ion-exchange Chromatography

The polar fraction, Fraction 4, was separated into neutral, acidic and basic subfractions using nonaqueous ion-exchange chromatography. Most of the sample, 67.2%, elutriated in the acidic subfraction. Neutrals constituted 9.8% of the sample, and the basic materials 23%. Material balance was 100%.

3.2 FI-MS Analysis and Compound Class Assignment

The FI-MS spectra of the 22 subfractions were recorded, corrected for the natural abundance of ^{13}C , and normalized to 100,000. The spectra were also weighed in accord with the relative yield of the subfraction and an additional adjustment was also made of the fraction of the sample that was not volatilized (and hence not analyzed) during FI-MS analysis, although most subfractions were volatilized more than 90%. Compound class assignment was made on the basis of chromatographic behavior and the apparent degree of unsaturation, *U*, as was done in the preceding work⁹. We have tried to limit the total number of compound types and included only those that data compelled. In all, we included 75 compound classes. The subfractions, in which the individual compound classes were considered to be present, are also given in **Table 2**. In many instances, a given compound class was present in more than one subfraction.

As an example, the spectrum and pattern table with 14 columns of subfraction 2.1 are shown in **Fig. 4** and **Table 3**, respectively. The intensities of peaks below 300 amu are very low, an indication of the lack of substantial fragmentation. The intensities of the even mass peaks are considerably greater than those for odd mass peaks. The odd mass peaks result from molecular ions of species containing one (or any odd number of) nitrogen atom(s), fragment ions, or ^{13}C -abundance. This subfraction is not expected to contain much nitrogen and hence the very low odd mass intensity. We expected "3 double bond" aromatics like benzenes, tetralins, octahydrophenanthrenes and dodecahydrochrysens, based on the chromato-

Fig. 3 Summary of HPLC Separations on Cyano Column

Table 2 Distribution of Compound Types in Arabian Oil Derived Vacuum Residue

Compound type	<i>U</i>	Subfractions present (No.)	Relative molar amount (parts per 100,000)
Acyclic alkanes	2	1.2, 1.3, 2.1	664
Olefins ¹⁾	0		0
Monocyclic alkanes	0	1.2, 1.3, 2.1, 2.2	2122
Bicyclic alkanes	-2	1.2, 1.3, 2.1, 2.2	1910
Tricyclic alkanes	-4	1.2, 1.3, 1.4, 2.1, 2.2, 3.1	1743
Tetracyclic alkanes	-6	1.2, 1.3, 2.1	1538
Pentacyclic alkanes	-8	1.2, 1.3, 2.1	1476
Hexacyclic alkanes	-10	1.2, 1.3, 2.1	1292
Benzenes	-6	1.2, 1.4, 2.1, 2.2, 3.1	1302
Tetralins	-8	1.3, 1.4, 2.1, 2.2, 2.3, 3.1	1339
Octahydrophenanthrenes	-10	1.3, 2.1, 2.2, 2.3, 3.1	1120
Dodecahydrochrysenes	2	2.2, 2.3, 3.1	1085
Naphthalenes	2	1.3, 1.4, 2.3, 3.3	1327
Tetrahydrophenanthrenes	0	1.4, 2.3, 3.2, 3.3	2043
Octahydrochrysenes	-2	1.4, 2.3, 3.2, 3.3	1913
Dihydrophenanthrenes	-2	2.4, 3.4	233
Biphenyls	0	1.3, 1.4, 2.4, 3.4	282
Phenanthrenes	-4	1.3, 1.4, 2.4, 2.5, 3.2, 3.3, 3.4	2078
Dihydropyrenes/Dihydrofluoranthenes	-6	2.4, 3.4	258
Pyrenes/Fluoranthenes	-8	1.4, 2.4, 2.5, 3.4, 3.5	838
Chrysenes	-10	1.4, 2.4, 2.5, 3.4, 3.5	834
Benzpyrenes/Perylenes	0	1.5, 2.5, 2.6	49
Benzchrysenes	-2	1.5, 2.5, 2.6, 3.5, 3.6	737
Benzo[ghi]perylene	-6	2.6, 3.6	192
Naphthylbenzenes	-6	1.5, 2.5, 3.5	567
Binaphthyls	2	2.5, 2.6, 3.5, 3.6	752
Naphthylphenanthrenes	-4	1.5, 2.6, 3.6	213
Naphthylpyrenes	-8	1.5, 2.6, 3.6	209
Dibenzofurans	0	2.4, 3.4	74
Benzothiophenes	-6	1.4, 2.3, 3.2, 3.3	2022
Tetrahydrodibenzothiophenes	-8	3.2, 3.3	1806
Dibenzothiophenes	2	1.5, 2.4, 3.4	270
Tetrahydrotribenzothiophenes	0	3.2, 3.3	1860
Tribenzothiophenes	-4	1.5, 2.5, 3.5	605
Tetrabenzothiophenes	-10	2.6, 3.6	202
<i>N</i> -Alkylindoles	-9	2.7, 3.7, 4.1	1096
<i>N</i> -Alkyltetrahydrocarbazoles	-11	2.7, 3.7, 4.1	1074
<i>N</i> -Alkylcarbazoles	-1	2.7, 3.7, 4.1	1097
<i>N</i> -Alkyltetrahydrobenzocarbazoles	-3	2.7, 3.7, 4.1	1081
<i>N</i> -Alkylbenzocarbazoles	-7	2.7, 3.7, 4.1	1085
<i>N</i> -Alkyloctahydrodibenzocarbazoles	-5	2.7, 3.7, 4.1	1035
<i>N</i> -Alkyldibenzocarbazoles	1	2.7, 3.7, 4.1	1089
Alcohols	-10	2.7, 3.7, 4.1	1724
Monocyclic alcohols	2	2.7, 3.7, 4.1	1732
Bicyclic alcohols	0	2.7, 3.7, 4.1	1736
Tricyclic alcohols	-2	2.7, 3.7, 4.1	1681
Tetracyclic alcohols	-4	2.7, 3.7, 4.1	1722
Pentacyclic alcohols	-6	2.7, 3.7, 4.1	1749
Hexacyclic alcohols	-8	2.7, 3.7, 4.2	1658
Phenols	-4	4.2	593
Tetralols/Indanols	-6	4.2	649
Octahydrophenanthrols	-8	4.2	292
Naphthols	-10	4.2	367
Tetrahydrophenanthrols	2	4.2	566
Dihydrophenanthrols	0	4.2	614
Phenanthrols	-2	4.2	624
Hydroxychrysenes	-8	4.2	278
Acyclic carboxylic acids	-10	4.2	154
Benzoic acids	-4	4.2	141
Naphthic acids	-10	4.2	118
Indoles	-9	4.2	587
Tetrahydrocarbazoles	-11	4.2	388
Carbazoles	-1	4.2	405
Tetrahydrobenzocarbazoles	-3	4.2	468
Benzocarbazoles	-7	4.2	390
Octahydrodibenzocarbazoles	-5	4.2	368
Dibenzocarbazoles	1	4.2	408
Pyridines	-5	4.3	161
Quinolines	-11	4.3	117
Phenylquinolines	-5	4.3	40
Azapyrenes	-7	4.3	198
Acridines	-3	4.3	210
Azachrysenes	-9	4.3	190
Dihydroacridines	-1	4.3	199
Tetrahydroacridines	1	4.3	203
Azabenzopyrenes	-11	4.3	38

1) No peaks were assigned to olefins.

Table 3 Mass Spectral Data of Subfraction 2.1

<i>U</i>	-8	-7	-6	-5	-4	-3	-2	-1		0	1	2	-11	-10	-9
Mass									Mass>						
104>	0	0	0	0	0	0	0	69:	112>	72	0	0	0	0	0
118>	0	0	0	0	0	0	0	0:	126>	0	0	0	0	0	0
132>	0	0	0	0	0	0	0	0:	140>	0	0	0	0	0	0
146>	0	0	0	0	0	0	0	0:	154>	0	0	0	0	0	0
160>	0	0	0	0	0	0	0	0:	168>	0	0	0	0	0	0
174>	0	0	0	0	0	0	0	0:	182>	0	0	0	0	0	0
188>	0	0	0	0	0	0	0	0:	196>	0	0	0	0	0	0
202>	0	0	0	0	0	0	0	0:	210>	0	0	0	0	0	0
216>	0	0	0	0	0	0	0	0:	224>	0	0	0	0	0	0
230>	0	0	0	0	0	0	0	0:	238>	0	0	0	0	0	0
244>	0	0	0	0	0	0	0	0:	252>	0	0	0	0	0	0
258>	0	0	0	0	0	0	0	0:	266>	0	0	0	0	0	0
272>	0	0	0	0	0	0	0	0:	280>	0	0	0	0	0	0
286>	0	0	0	0	0	0	0	0:	294>	0	0	0	0	0	0
300>	0	0	0	0	0	0	0	0:	308>	0	0	0	0	0	0
314>	0	0	0	0	0	0	0	0:	322>	0	0	0	0	0	0
328>	0	0	0	0	0	0	0	0:	336>	26	0	0	0	0	0
342>	0	0	0	25	0	0	0	0:	350>	0	0	0	0	0	0
356>	0	0	0	0	0	0	25	0:	364>	0	24	0	0	0	0
370>	24	0	21	0	0	0	27	0:	378>	0	0	0	0	0	24
384>	0	0	22	0	0	0	0	22:	392>	17	17	17	15	22	15
398>	17	0	23	0	0	0	0	23:	406>	14	16	17	15	0	23
412>	19	15	15	0	22	13	19	22:	420>	14	16	22	13	20	17
426>	16	16	14	18	19	14	16	23:	434>	20	14	16	18	21	21
440>	18	22	19	16	20	19	18	24:	448>	22	13	23	16	22	20
454>	27	17	21	16	19	21	21	16:	462>	34	14	18	19	19	20
468>	31	20	34	0	27	20	19	22:	476>	34	12	24	19	30	19
482>	40	20	37	18	25	15	33	19:	490>	36	15	35	18	40	33
496>	37	23	53	11	33	21	30	18:	504>	37	23	34	24	45	15
510>	54	24	74	24	35	26	51	19:	518>	56	21	49	31	54	32
524>	65	29	89	20	45	17	55	18:	532>	61	22	61	24	79	23
538>	98	14	131	20	43	27	48	33:	546>	64	24	71	30	87	26
552>	124	23	162	21	72	18	72	35:	560>	85	16	94	17	101	29
566>	142	19	187	19	71	22	84	30:	574>	101	22	107	30	109	27
580>	163	30	216	19	85	20	99	28:	588>	127	17	129	17	128	33
594>	167	36	237	26	94	30	103	34:	602>	129	30	137	42	149	32
608>	187	35	280	10	122	28	126	31:	616>	141	21	150	32	169	33
622>	204	40	267	20	127	19	149	17:	630>	154	33	161	35	177	29
636>	242	19	311	19	139	28	152	29:	644>	184	26	168	38	176	39
650>	240	38	317	39	127	44	172	18:	658>	187	31	194	28	202	34
664>	248	35	342	31	141	44	166	35:	672>	192	32	200	33	203	40
678>	271	32	332	21	177	31	186	27:	686>	202	27	203	39	199	35
692>	268	39	329	15	181	35	187	28:	700>	210	32	216	15	243	25
706>	267	43	323	20	187	35	195	39:	714>	217	26	211	39	211	36
720>	266	44	320	25	198	35	191	43:	728>	192	33	223	35	215	28
734>	273	37	294	52	174	39	210	31:	742>	214	28	219	28	213	28
748>	279	29	308	22	212	10	221	32:	756>	206	42	208	32	209	62
762>	246	59	288	42	187	40	196	36:	770>	199	51	206	57	203	55

Note: Data of mass number 776—1,813 were not shown in this table.

Fig. 4 FI-Mass Spectrum of Subfraction 2.1 Showing the Dominance of Alkyl Benzenes and Tetralins

graphic behavior. The dominant homologous series are assignable to alkylbenzenes and alkyl-tetralins, according to the pattern table. The range of structures included within each broad class of compounds is discussed below.

1) Saturates

We have included acyclic and cyclic (up to six rings) alkanes in saturates. The HPLC/FI-MS procedure does not allow distinction between structural isomers.

2) Aromatics

Among the aromatics we have included the following structures: benzenes, naphthalenes, phenanthrenes, pyrenes, chrysenes, benzpyrenes, benzchrysenes, and benzo[ghi]perylene. Also included are biaryl structures like biphenyls, binaphthyls, naphthylbenzenes, naphthylphenanthrenes, and naphthylpyrenes. Hydroaromatic structures were limited to four-ring systems: tetralins, octahydrophenanthrenes, and dodecahydrochrysenes representing benzenes with one, two and three naphthenic rings; and tetrahydrophenanthrenes and octahydrochrysenes representing naphthalene series.

Although biphenyls and tetrahydrophenanthrenes have the same U value of 0, they differ in the number of formal double bonds and are expected to elutriate at different times from the cyano column. A larger portion of the $U=0$ is, therefore, assigned to biphenyls in the later subfractions.

3) Sulfur Compounds

The presence of oxygen and sulfur can not be ascertained from nominal mass alone. The portions of various U series assigned to sulfur- and oxygen-containing compounds were made on the basis of elemental abundance and anticipated chromatographic behavior. For this study, we considered sulfur only in thiophenic structures: benzothiophenes, dibenzothiophenes, tribenzothiophenes, tetrabenzothiophenes, and in a couple of hydroaromatic structures as well: tetrahydrodibenzothiophenes and tetrahydrotribenzothiophenes. These neutral structures behave much like their hydrocarbon analogs during HPLC.

4) Oxygen Compounds

Only dibenzofurans were included as represented nonpolar oxygen compounds. Alcohols and cycloalkane alcohols (up to six rings) were included among neutral polars. Phenols and carboxylic acids were included as the acidic compounds.

5) Nitrogen Compounds

Compounds containing one (or any odd number) of nitrogen atoms are relatively easy to identify with FI-MS because they have odd mass. The nitrogen content of the sample was low enough to render insignificant abundance of molecules with two or more nitrogens, in case the nitrogen is statistically distributed. Nitrogen-containing compounds included in this study were (a) neutrals, such as N -alkylated indoles and carbazoles; (b) acidic, such as indoles and carbazoles; and (c) basic, such as pyridines, quinolines, and other azaaromatic. A separated class for aminoaromatics was not included.

3.3 ^{13}C -NMR Spectroscopy

The whole sample was examined by ^{13}C -NMR spectroscopy. The spectrum is shown in **Fig. 5**. Literature assignments for the various peaks was used to calculate certain compositional parameters^{5),6)}. The paraffinic carbons resonate between 0 and 60 ppm and the aromatic carbons between 110 and 160 ppm. From the integrated areas in those regions, the aromatic carbon content (C_{ar}) was determined to be 38%.

In the paraffinic region there are a few sharp peaks and a broad unresolved hump. The sharp peaks are due to alkyl side chains, longer than four carbons, and the broad hump is due to naphthenic carbons and shorter side chains. The ratio of the

Fig. 5 ^{13}C -NMR Spectrum of the Total Sample

Fig. 6 Profiles of the Degree of Alkyl Substitution for Four Monoaromatics in the Total Sample

integrated areas of the sharp peaks and the broad hump is 1.3. This ratio has been taken as the ratio of acyclic to naphthenic carbons.

The peak at 30 ppm is assigned to internal methylene carbons of long chains and the peak at 14 ppm to the terminal methyl carbons. The ratio of the intensities of these two peaks was used to calculate the average chain length, and it turns out to be 8.5.

3.4 Molecular Weight Distribution of Each Compound Class

From the pattern table with 14 columns, we calculated the molecular weight distribution of each compound class assigned. For example, the intensity of FI-MS in the row of $U=-6$ in **Table 3**, assigned to benzene homologous series, began to appear from mass numbers 372 and continued over 1,300 with the interval of 14. Maximum intensity was observed between the range of mass number of 666—694, corresponding to 42—44 of carbons as alkyl substituents attached to the aromatic core. **Figure 6** gives the representative results of carbon numbers in alkyl substituents of benzenes, tetralins, octahydrophenanthrenes and dodecahydrochrysenes.

4. Discussion

The mass spectral data of the subfractions were compiled using a computer program and relative molar abundance (100,000 units) of 75 compound classes contained in sample oils, together with subfractions, are shown in **Table 2**. The fact that same compound type was observed in different subfractions might be results of, for example, the existence of larger ratio of aliphatic structures in aromatic components which would mask the aromatic character and give variation to the behavior in HPLC separation, as suggested in the previous study³⁾. This masking effect has been confirmed with the aid of UV measurement. It can be estimated from **Table 2** that various compound classes such as cyclic alkanes, aromatics, hydroaromatics etc. are contained, over a wide range, in Arabian oil derived vacuum residue. Further, **Fig 6** shows the wide distribution of alkyl carbons, ranging between 15–90, in monoaromatic components. These results suggest that chemical components of vacuum residue are significantly different from those of heat treated coal tar and the hydrocracked coal derived liquids.

In order to assure the usefulness of the present method, the contents of the elements in the whole sample (wt%), aromatic carbon (%C_{ar}), aromatic hydrogen (%H_{ar}), average molecular weight and average carbon numbers in alkyl groups were calculated based on the molecular weight distributions of the compound classes. The calculated results are listed in **Table 4**, together with the ultimate analysis and the observed values of %C_{ar} and %H_{ar} obtained from ¹³C-NMR measurements. The calculated and measured contents of the elements, except sulfur, and average molecular weight agreed reasonably well. From the calculated average value of total carbon number (44.5) in alkyl groups and the average length of side chains

(8.5), measured by ¹³C-NMR, five alkyl chains, on average (44.5/8.5), were estimated to attach to the aromatic or naphthenic core. On the other hand, the content of sulfur by calculation was comparatively lower, probably because only the existence of sulfur in benzothiophene type was considered in the present study. Sulfides and disulfides might have been present, but the sulfur content of Fraction 1, wherein these structures would have elutriated, was low and were ignored for the present. The sulfur content of the vacuum residue is such that, on average, every molecule contains more than one sulfur atom. Thus, there presumably existed many other sulfur-containing structures of the classes listed in **Table 2**. However, for simplicity, we limited the assignment of sulfur compounds to the structures mentioned above.

Further, the lower %C_{ar} measured may be attributed to the fact that the non-volatile polynuclear aromatic clusters contained in the sample oil could not be detected by FI-MS. Therefore, it is necessary to re-examine the handling of the sulfur-containing components and aromatic components with high molecular weight to accomplish the usefulness of the present method.

Generally, the multifunctional nature of a typical molecule (MW 1000) in the vacuum residue makes HPLC separation into chemically simple distinct compound classes inherently impossible. We have attempted to compromise that results in sufficient chemical details to provide a basis for describing the process changes without having to go so much in detail as to render the description computationally intractable. The procedure retains great detail in terms of size distribution, while consolidating together structures having similar chemical behavior. The success of this approach would also depend upon the ability to describe changes during processing, with relatively few reaction parameters that could be applied to a wide range of structures.

Table 4 Comparison of Computed¹⁾ and Directly Determined Composition Parameters for Arabian Oil Derived Vacuum Residue

Parameter	Computed	Measured
wt%C	85.82	84.32
H	12.89	9.92
N	0.33	0.65
O	0.53	0.21
S	0.43	5.15
%C _{ar}	12.5	38
%H _{ar}	4.5	8.8
Number average of MW	974	893

1) Computed from HPLC/FI-MS analysis.

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要 旨

HPLC/FI-MS 分析法による重質油のキャラクタリゼーション
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石油精製の過程で副生する減圧残さ等の重質油を熱分解や水素化分解により使いやすい燃料に変換する接術開発において、反応物の化学組成に関する情報は重要である。減圧残さは分子量の大きい複雑な炭化水素の集合体であり、原産地が違えばその化学組成が大幅に違い、熱分解や水素化分解に対する反応特性も異なったものとなる。減圧残さをキャラクタリゼーションする方法としては組成分析法や NMR による平均構造解析法があるが、プロセスの過程における化学組成の変動や得られる生成物の性状を理解するためには原料油の複雑なマトリックスの中から反応により大きく影響をうける化合物群を抽出し、その割合や同族体の炭素数分布といった化学組成について詳細で定量的な情報が必要である。石炭液化油については HPLC/FI-MS を組み合わせた方法を用いてこれまで相当詳しく調べられているが、石油系重質油については非常に複雑な化学組成をもつため研究例が少ない。HPLC/FI-MS による分析で最も詳細な研究は Boduszynski¹⁾ が vacuum gas oil (650~1,000°F) を蒸留によりせまい範囲の留分にカットし、その各留分を更に HPLC で分離した後、FI-MS の測定により化合物群を同定したものである。また減圧残さ (>1,000°F) については、飽和成分²⁾やペンタン可溶分¹⁾で試みた例があるが全成分についての詳細な分析例は見当たらない。

我々は既報³⁾で述べた HPLC/FI-MS によるコールタールの化学組成のルーチン分析システムをより複雑な化学組成をもつ

減圧残さに適用できるように HPLC の分離スキームの改良を行い、アラビア原油の減圧残さを対象に全成分の分析を行った。HPLC の分離では試料油をシリカゲルカラムにより予備的に 4 フラクションに極性分離した後、飽和成分と芳香族成分はさらにシアノカラムで、極性成分はイオン交換樹脂により 22 のサブフラクションに分離した。これらサブフラクションの FI-MS データは MW (分子量) = $14n + U$ (n , U : 整数, $-11 \leq U \leq 2$) として 14 カラムをもつパターンテーブルに整理した。同族化合物群がグルーピングされているパターンテーブルをもとに試料油の含有成分を帰属可能な 75 の化合物群に分類した。化合物群への帰属には FT-IR, NMR および UV を補助的に使用した。本方法の有用性を確認するため、パターンテーブルに示されている各化合物群の分子量分布データから試料油中の各元素の存在割合 (wt%), %C_{ar}, %H_{ar}, 数平均分子量を計算し、元素分析値や ¹³C-NMR より求めたそれらの実測値を比較した。硫黄を除く各元素の含有割合および数平均分子量の計算値と実測値が比較的良好に一致することがわかった。硫黄の量が少なかったのは試料油中に含まれている硫黄化合物をチオヘンタイプのみ注目したためであり、また %C_{ar} 値が計算値と比較して低いのは、試料中に FI-MS による分析が不可能な不揮発性の多環芳香族クラスターが含まれることによると推察される。

Keywords

Characterization, Heavy oil, Vacuum residue, Structural analysis, HPLC, FI-MS