SEPARATION AND ANALYSES OF PETROLEUM RESIDUES

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INTRODUCTION

Petroleum residues are a valuable raw material for the production of fossil fuels. The efficient utilization of this resource requires knowledge of the chemical composition of the residue. The composition work described here is an extension of previous work involving the separation and analyses of high-boiling petroleum distillates (1) and residues (2). The purpose of this paper is 1) to describe the separation of residues, using modifications of techniques previously developed for the separation of high-boiling distillates, 2) to obtain compositional data on the residues, and 3) to compare the composition of the residues and high-boiling distillates.

Much of the characterization work on petroleum residues and asphalts has been performed on unseparated samples (3-6). The separation of these high-molecular-weight mixtures became possible as chromatographic techniques were developed. Kleinschmidt (7) developed a method to separate asphalts into fractions of asphaltenes, water white oils, dark oils, and asphaltic resins. The separation of asphalts using the method of Corbett (8) produces fractions of saturates, naphthene-aromatics, polar aromatics and asphaltenes. The "SARA" method developed by Jewell and co-workers (9) separates petroleum residuals into fractions of saturates, aromatics, resins, and asphaltenes. Bunger (2) modified the separation techniques developed by API Project 60 (1) to separate both tar sand bitumens and petroleum residues.

This paper describes the separation of petroleum vacuum residues that do not distill at a boiling point of 675 °C (corrected). The residue was separated into acids, bases, neutral nitrogen compounds, saturate hydrocarbons, and aromatic hydrocarbons, using ion exchange, complexation, and adsorption chromatography. Acids and bases are removed from the residue with ion exchange resins. Neutral nitrogen compounds are isolated by complexation with ferric chloride adsorbed on Attapulgus clay. Saturate and aromatic hydrocarbons are separated using silica gel. These separations have been applied to residues from four crude oils. Elemental analyses of the major fractions obtained from these separations are discussed. The composition of residues from four oils are compared, and the composition of a residue is compared with the composition of high-boiling distillates from the same crude oil.

EXPERIMENTAL

Reagents

Amberlite IRA 904 and Amberlyst 15, the anion- and cation-exchange resins, were obtained from Rohm & Haas. The Attapulgus clay (LVM, 50/80 mesh) was obtained from Engelhard Minerals and Chemicals Corp., and the silica gel (grade 62, 60/200 mesh) came from Davidson Chemical Co. Reagent-grade ferric chloride hexahydrate and potassium hydroxide were obtained from Baker and Adamson Co. Cyclohexane and n-pentane (99%, Phillips Petroleum) were purified by flash distillation and by percolation through activated silica gel; benzene, methanol, and 1,2-dichloroethane (reagent grade, Baker and Adamson) were flash distilled; isopropyl amine (reagent grade, Eastman) was used as received.

Apparatus

The separations were made on a liquid chromatographic column 1.4-cm i.d. by 119-cm long. The column was water jacketed and contained a recycling arrangement that permits the continuous elution of the sample without the need for large quantities of solvent. Solvent was removed from the fractions using a rotary evaporator followed by a nitrogen gas sweep at steam-bath temperature until a constant sample weight was obtained.

Preparation of Petroleum Residues

Petroleum residues representing portions of crude oils that did not distill at a boiling point of 675 °C (corrected) were prepared at the Bartlesville (Okla.) Energy Research Center (10). The residues were prepared by vacuum distillation of crude oils in a wiped-wall still at 5×10^{-3} torr and 296 °C. Thermal exposure of the oil to heated surfaces was minimized by short residence time, and no decomposition was detected during these distillations. Vacuum residues from four crude oils--Wilmington (Calif.), Gach Saran (Iran), South Swan Hills (Alta.), and Recluse (Wyo.)--were prepared.

Preparation of Resins and Adsorbents

Anion-Exchange Resin. - Amberlite IRA 904 resin (1000 g) was placed in a glass column and activated by the following procedure. The initial washes were made with 1 N hydrochloric acid (7.8 liters) and distilled water (2.0 liters), using a flow rate of 8 bed volumes per hour. The resin was activated using 1 N sodium hydroxide (7.8 liters). This washing sequence was repeated, starting with hydrochloric acid. The resin was then washed with distilled water (2.0 liters). Final preparation of the resin was made by washing with the following solvent sequence: 75% water-25% methanol (1.0 liter); 50% water-50% methanol (1.0 liter); 25% water-75% methanol (1.0 liter); methanol (2.0 liter); benzene (3.0 liter); cyclohexane (3.0 liter). The resin was stored under cyclohexane. (Important: Do not allow resin to dry or to be exposed to heat.)

Cation-Exchange Resin. - Amberlyst 15 resin was prepared in the manner described for the anion resin with the exception that the acid-base washing sequences were reversed.

Ferric Chloride on Attapulgus Clay. - Ferric chloride hexahydrate (10 weight percent in methanol) was contacted with Attapulgus clay for 1 hour. The ferric chloride-Attapulgus clay was filtered, washed several times with cyclohexane, extracted with cyclohexane for 24 hours in a Soxhlet extractor to remove nonadsorbed metallic salt, and dried at room temperature. The material contained 0.7 to 2.0 percent by weight of iron.

Silica-Gel Adsorbent. - The Davidson Chemical Co. grade 62 silica gel was used as received.

Separation Procedure

The separation procedure is shown in Figure 1. The residues are separated into five fractions: acids, bases, neutral nitrogen compounds, saturate hydrocarbons, and aromatic hydrocarbons. Acids are isolated using anion-exchange resin, bases with cation-exchange resin, and neutral nitrogen compounds by complexation with ferric chloride adsorbed on Attapulgus clay. The remaining hydrocarbon fraction is separated on silica gel to produce saturate and aromatic hydrocarbon fractions.

Anion-Exchange Chromatography. - A sample of residue (20 g) was dissolved in cyclohexane (250 ml) and charged to the resin (60 g) that had been wet-packed in the column. Unreactive material was washed from the resin with cyclohexane (200 ml) for approximately 12 hours, using the recycling arrangement of the column. After removal of the unreactive materials, the reactive compounds (acids) were recovered by successive 12- to 24-hour elutions with benzene, followed by 60% benzene-40% methanol (azeotrope). The resin was then removed from the column and placed in a Soxhlet extractor. A final elution was then made with 80% benzene-20% methanol saturated with carbon dioxide. These three solvents remove compounds of increasing acid strength, and the fractions can be analyzed separately or combined to give a total acid fraction. The data reported in this paper were obtained on the total acid fraction.

Cation-Exchange Chromatography. - The procedure for the removal of the bases was similar to that used for the removal of acids. The sample of acid-free residue was dissolved in cyclohexane and charged to the A-15 resin that had been wet-packed in the column. Unreactive material was washed from the resin with cyclohexane (200 ml) for approximately 12 hours. The reactive material (bases) was removed from the resin by successive 12- to 24-hour elutions with benzene, followed by 60% benzene-40% methanol. A final elution was made in a Soxhlet extractor using 54% benzene-38% methanol-8% isopropyl amine. The three base fractions were combined to give a total base fraction.

Ferric Chloride Coordination Chromatography. - Ferric chloride-Attapulgus clay (280 g) suspended in cyclohexane was wet-packed in a column. A sample of acid- and base-free residue (10 g), dissolved in cyclohexane, was slowly percolated through the column. The entrained oil was removed by 24-hour elution with cyclohexane. The first fraction was desorbed from the clay by 60- to 72-hour elution with 1,2-dichloroethane. The nitrogen compound-ferric chloride complexes in this fraction were broken by passing the 1,2-dichloroethane solution over anion-exchange resin contained in a second column. The ferric chloride salt was retained on the resin, and the nitrogen compounds were recovered in the eluate. A second fraction was removed from the clay by 60- to 72-hour elution with 45% benzene-5% water-50% ethanol (1000 ml). The solvent was removed, and the organic compounds were redissolved in benzene and then filtered; the solvent was again removed to eliminate traces of water and ethanol. The organics were redissolved in benzene and passed over anion-exchange resin to remove ferric chloride. The nitrogen compounds were recovered in the eluate. The two subfractions were combined to give a total neutral nitrogen fraction.

Silica Gel Chromatography. - A portion of the acid-, base-, and neutral nitrogen-free residue (300 mg) was dissolved in n-pentane (10 ml) and was placed on a silica gel column (90 g) that had been wet-packed with n-pentane. The column was eluted with n-pentane (600 ml) to remove the saturate hydrocarbons. Aromatic hydrocarbons were eluted from the column, using 85% n-pentane-15% benzene (400 ml), and 60% benzene-40% methanol (300 ml). The two aromatic subfractions were combined to form a total aromatic hydrocarbon fraction. Ultraviolet analyses of the saturate fraction indicated that trace amounts of aromatic hydrocarbons were present. The amount of saturates in the aromatic fraction, if any, is unknown.

RESULTS AND DISCUSSION

The four crude oils used in this work were obtained through a sampling program conducted by API Research Project 60 and were selected for study because they represent crude oils having different geological classifications (11). The separation and analyses of the residues from these particular oils allows us to 1) demonstrate the applicability of the separation scheme to the separation of 675 °C residues predicted to have large differences in composition and 2) compare the composition of the 675 °C residues with the composition of high-boiling distillates from the same oils.

Table 1 shows the weight percent of the crude oils that does not distill at a corrected boiling point of 675 °C. The amount of residue is different for each crude oil, reflecting differences in composition of the crude oils. For example, the Wilmington crude oil contains 22 percent residue and the South Swan Hills crude oil contains 3 percent residue. The percentages of residual material in some of the crude oils are an indication of the large potential amounts of fossil fuel contained in the residue portion of the oils.

TABLE 1. - Weight percent of 675 °C residue in crude oils

Crude oil	Wt. percent
Wilmington, Calif.	22
South Swan Hills, Alta.	3
Gach Saran, Iran	16
Recluse, Wyo.	4

Table 2 shows the results of the separation of the four residues. The residues have large differences in composition. For example, the Wilmington and Gach Saran residues contain large amounts of polar materials--acids, bases, and neutral nitrogen compounds. In contrast, the South Swan Hills and Recluse residues contain smaller amounts of these compounds and larger amounts of hydrocarbons. The residues having a large polar compound content have more aromatic than saturate hydrocarbons; residues that are low in polar compound content have more saturate than aromatic hydrocarbons. The data in the table also show that the total amounts of acids and bases are variable from oil to oil and the amounts of acids are equal to or less than the amounts of bases. The duplicate separation of the Gach Saran residue indicates that the separation is reproducible. In general, the recovery of material after separation was 90 percent or better.

TABLE 2. - Composition of 675 °C petroleum residues

	Weight percent					
Crude oil	Acids	Bases	Neutral nitrogen compounds	Saturate hydro-carbons	Aromatic hydro-carbons	Recovery
Wilmington, Calif.	18	19	41	4	15	97
Gach Saran, Iran						
Run #1	17	25	14	8	30	94
Run #2	16	23	16	7	25	87
S. Swan Hills, Alta.	12	13	10	34	27	96
Recluse, Wyo.	9	10	8	44	26	97

The information in tables 1 and 2 shows that when a crude oil has a high 675 °C residue content most of the residue will be composed of acids, bases, and neutral nitrogen compounds. Conversely, when a crude oil has a low 675 °C residue content the composition of the residue will be mostly hydrocarbons.

Table 3 shows elemental analyses data for the total Wilmington residue and the separated fractions. Carbon and hydrogen ratios (C/H) are shown in the first column. The polar fractions show a C/H of from 0.72 to 0.74, and the saturate hydrocarbon fraction shows higher hydrogen content with a value of 0.56. The value of .66 for the aromatic hydrocarbons indicates the larger degree of unsaturation of this fraction relative to the saturate hydrocarbon fraction. The acids

are high in nitrogen and oxygen, and the bases are high in nitrogen. The neutral nitrogen compounds are lower in nitrogen than either the acid or the base fractions and may contain compounds other than nitrogen compounds. The separation scheme was effective in removing nitrogen compounds in the polar fractions--only 6 percent of the original nitrogen remained in the hydrocarbon fractions. The saturate hydrocarbons are essentially free of heterocompounds. The aromatic hydrocarbons contain small amounts of nitrogen and oxygen compounds and larger amounts of sulfur compounds. Sulfur is rather evenly distributed in polar and aromatic hydrocarbon fractions, indicating that sulfur compounds have not been concentrated in any of the fractions. The amount of nitrogen, oxygen, and sulfur in the total residue was compared with the sum of the nitrogen, oxygen, and sulfur in the fractions. The nitrogen and sulfur in the total residue equalled the sum of the amounts found in the separated fractions. The analyses for oxygen appear to be in error because 50 percent more oxygen was found in the fractions than was found in the total residue (oxygen analyses on small samples have not been reproducible).

TABLE 3. - Elemental analyses of Wilmington 675 °C residue and residue fractions

Sample	C/H	Percent carbon	Percent hydrogen	Percent nitrogen	Percent sulfur	Percent oxygen
Total residue	.72	84.50	9.73	1.62	2.57	1.46
Acids	.74	80.23	9.09	2.33	2.53	5.53
Bases	.72	83.17	9.64	1.96	2.31	2.67
Neutral nitrogen compounds	.74	83.02	9.36	1.78	2.71	1.30
Saturate hydrocarbons	.56	85.48	12.69	0.11	0.82	0.81
Aromatic hydrocarbons	.66	85.34	10.76	0.63	2.37	0.74

Table 4 shows a comparison of the composition of the residue with the composition of two high-boiling distillates from Wilmington crude oil. The data for the distillates were reported in an earlier publication (12). The weight percent of acids, bases, and neutral nitrogen compounds increases with the increase in boiling range. The weight percent of saturate and aromatic hydrocarbons decreases with increasing boiling range.

TABLE 4. - Composition of Wilmington residue and distillates

	Weight percent		
Sample	370-535 °C distillate	535-675 °C distillate	675°C residue
Acids	5.6	9.3	18.0
Bases	6.8	12.7	19.0
Neutral nitrogen compounds	4.2	21.3	41.0
Saturate hydrocarbons	36.9	20.8	4.0
Aromatic hydrocarbons	46.5	36.0	15.0

CONCLUSIONS

The separation procedure described in this paper can be used to separate 675 °C residues having large differences in composition. The procedure provides useful information concerning the composition of the residues. For example, the South Swan Hills residue, which contains small amounts of acids and bases and large amounts of hydrocarbons relative to the Wilmington residue would be predicted to be more easily refinable than the Wilmington residue. The separation of the residue into chemically meaningful fractions lays the groundwork for further characterization according to compound type.

SUMMARY

Vacuum residues from four crude oils have been separated into fractions of acids, bases, neutral nitrogen compounds, saturate hydrocarbons, and aromatic hydrocarbons. The separation scheme was a modification of a separation scheme originally developed for separating high-boiling petroleum distillates. Elemental analyses were obtained for the residue fractions. The compositions of four residues were compared, and the composition of the Wilmington residue was compared with the composition of Wilmington high-boiling distillates.

REFERENCES

1. D. M. Jewell, J. H. Weber, J. W. Bunger, H. Plancher, and D. R. Latham, Anal. Chem. 44, 1391 (1972).

2. J. W. Bunger, Preprints, Div. of Fuel Chemistry, Amer. Chem. Soc., 19 (2), Los Angeles, Calif., April 1974, p. 231.

3. R. V. Helm and J. C. Petersen, Anal. Chem. 40, 1100 (1968).

4. J. W. Ramsey, F. R. McDonald, and J. Claine Petersen, Ind. Eng. Chem. Prod. Res. and Devel. 6, 231 (1967).

5. F. E. Dickson, B. E. David, and R. A. Wirkkala, Anal. Chem. 41, 1335 (1969).

6. D. Burton and E. Beitchman, J. of Res. Nat. Bur. Stand. 63A (2), 189 (1959).

7. L. R. Kleinschmidt, J. Res. Nat. Bur. Stand. 54, 163 (1965).

8. L. W. Corbett, Anal. Chem. 41, 576 (1969).

9. D. M. Jewell, E. W. Albaugh, B. E. Davis, and R. G. Ruberto, Ind. Eng. Chem. Fundam. 13 (3), 278 (1974).

10. H. J. Coleman, J. E. Dooley, D. E. Hirsch, and C. J. Thompson, Anal. Chem. 45, 1724 (1973).

11. J. F. McKay, T. E. Cogswell, J. H. Weber, and D. R. Latham, Fuel 54, 50 (1975).

12. Haines, W. E., and C. J. Thompson, ERDA Rept. of Inv., LERC/RI-75/5 and BERC/RI-75/2, July 1975, 30 pp.

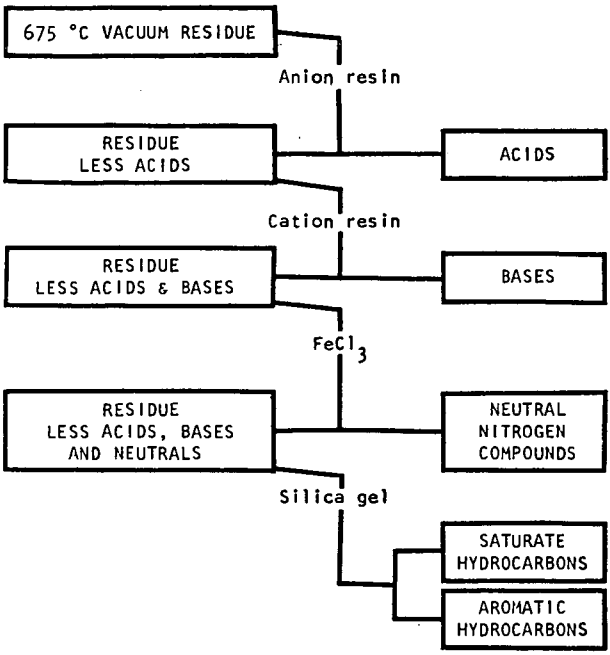

Figure 1. - SEPARATION SCHEME