

CHARACTERIZATION OF "HEAVY" CRUDE COMPONENTS

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The current trend toward processing petroleum residua or whole "heavy" crudes requires adequate compositional information to understand the chemistry of reactions that are involved. Monitoring compositional changes by a mere comparison of operationally defined fractions or by a determination of "average structures" for feedstock and product components provides inadequate and frequently misleading information. (1) Much more detailed compositional data are needed to unravel the structural transformations which occur during processing or to explain product properties.

This paper discusses recent results of characterization work on "heavy" crudes and petroleum residua. The emphasis of this paper is on distribution of homologous series of compounds, their molar mass and structure, all as a function of boiling point. The detailed discussion of the experimental procedures used in this study is beyond the scope of this paper. It is important to note, however, that the unique combination of short-path distillation, high performance liquid chromatography (HPLC), and field ionization mass spectrometry (FIMS) was essential for obtaining the detailed compositional information which was not available before. The nitrogen-rich, 13.6°API gravity, Kern River crude oil (a blend of crudes from San Joaquin Valley, California) is used as an example.

EXPERIMENTAL

Kern River crude oil was first distilled using a Penn State column to produce two distillates, Cut 1 and Cut 2, and atmospheric residuum (~650°F+). The residuum was then fractionated into eight distillates, Cut 3 through Cut 10, and the nondistillable residuum (~1300°F+) using the short-path distillation. The detailed description of the short-path distillation apparatus, DISTACT, can be found elsewhere. (2, 3) The true boiling point (TBP) distributions of the distillation cuts were determined using a vacuum thermal gravimetric analysis (VTGA) method developed at Chevron Research. (4) The molar mass distributions of all cuts were determined using FIMS and field desorption mass spectrometry (FDMS). (5) The FIMS data were obtained at SRI International,

Encl. - Table I
Figures 1-8

Menlo Park, California. Average molecular weights were determined by vapor pressure osmometry (VPO) using toluene as a solvent. Carbon (C), hydrogen (H), sulfur (S), total nitrogen (N_t), basic nitrogen (N_b), and oxygen (O) were determined using standard procedures. Nickel (Ni), vanadium (V), and iron (Fe) were determined by inductively coupled plasma (ICP) emission spectroscopy method.

Chromatographic separations of all distillation cuts involved a two-step procedure. First, a fraction of polar components (mainly N-, O-, and metal-containing compounds) was isolated from each distillation cut before further HPLC separation to prevent possible damage of high efficiency columns. "Polars" were separated using liquid chromatography on basic alumina. In the second step, the "polars-free" fraction was further separated into saturates, monoaromatics, diaromatics, triaromatics, tetraaromatics, pentaaromatics, and a fraction designated "hexaaromatics and/or azarenes."

The HPLC system consisted of two preparative columns, ZORBAX-NH₂ and ZORBAX-SIL, connected through a switching valve. The system was calibrated using model compounds. The actual cut points between the aromatic ring-type fractions were determined using ultraviolet (UV) spectra collected from 200-400 nm by the UV photodiode array detector at 20-sec. intervals. Weight percent yields of the fractions were determined gravimetrically. The HPLC fractions were analyzed by FIMS. The principles of the HPLC/FIMS approach and its application to characterization of coal-derived liquids were reported previously. (6-8) However, a different HPLC system was used in this study. Elemental analysis, infrared spectrometry, ¹H and ¹³C nuclear magnetic resonance (NMR) spectrometry, and EIMS were used occasionally to aid interpretation of the HPLC/FIMS data.

RESULTS AND DISCUSSION

How Heavy is the "Heavy" Crude Oil?

The adjectives "heavy," "high boiling," and "high molecular weight" are commonly but inappropriately used as equivalent terms to describe crude oils or their fractions. The term "heavy" refers to crude oil density. Heavy crudes, of which Boscan (10.1°API gravity in Figure 1) is a classic example, have high densities (low °API gravities) because they are rich in high density naphthene-aromatics and heteroatom-containing compounds and poor in low density alkanes. They are commonly either immature or degraded. (9) Light crudes, which have low densities (high °API

gravities) are rich in alkanes. Altamont crude oil (42.2°API gravity in Figure 1), an extreme example, has an exceptionally high alkane content as a result of its predominant source being lacustrine algae, which also happens to have been the source of the nearby Green River shale. (9)

For each of the crudes considered in Figure 1, the °API gravity decreases with increasing depth of distillation. Hence the term "heavy ends" tends to correlate with "high boiling" within a given crude. However, the correlation between "heavy" and "high boiling" does not necessarily hold if different crudes are being compared. For example, the nondistillable residuum (~1300°F+) from Altamont crude has a lower density (higher °API gravity) than whole Boscan, Kern River, or Maya crude.

The terms "heavy" and "high boiling" are frequently but incorrectly used as if they were synonymous with "high molecular weight." The boiling point of a compound at a given pressure is a rough measure of the attractive forces between the molecules. These forces vary with the structure of molecules, leading to the great differences in boiling point for compounds of a given molar mass but a different chemical structure. This is illustrated in Figure 2. Compounds having similar molar masses cover a broad boiling point range and, conversely, a narrow boiling point cut contains a wide molar mass range. The molar mass range increases rapidly with increasing boiling point, as illustrated by the extended curves "A" and "C" at the right side of Figure 2. For a given class of compounds, the boiling point increases with molar mass. This is due to the increase of the weak, van der Waals attractive intermolecular forces as molecules of a given type become larger. However, compounds having fused aromatic rings and functional groups capable of hydrogen bonding or other types of polar interactions have additional attractive intermolecular forces and may have a relatively low molar mass but a high boiling point and thus are expected to concentrate in the "heavy ends."

Figure 3 shows boiling point, molar mass, and heteroatom distributions in Kern River petroleum. The apparent molar mass distributions of all distillation cuts, including the nondistillable residuum, were measured by FIMS and FDMS. The results obtained by both techniques were in very good agreement. The molar mass distributions are illustrated in Figure 3 by using the molar mass scale as a radius of each "slice." The radius of the inner circle corresponds to the lowest molar mass of that cut while the radius of the outer circle extends to the highest molar mass value. A significant trend can be observed. The molar mass range of the successive distillation cuts widens with increasing boiling

point in a fashion that is consistent with the trend indicated by the curves in Figure 2. The low molar mass end of each cut (radius of the "hole" in each slice) shows only a moderate increase with increasing boiling point while the high molar mass end soars. The resulting significant molar mass overlapping between the cuts is mainly due to the increasing concentration of polynuclear aromatic and heteroatom-containing compounds which have high boiling points but relatively low molar masses.

Interestingly, most of these heavy crude components do not exceed a molar mass of about 1500 and only a few have molar masses extending up to about 1900. The molar mass data for Kern River crude oil are in agreement with the previously reported results for other crudes (10-12) and provide further support for the early speculations by Dean and Whitehead (13) who suggested a molecular weight maximum of 2000 for all compounds in petroleum.

Data in Table I give distributions of elements (C, H, N, S, O, Ni, and V) on a molecular basis. The decreasing Z value in the general formula $C_nH_{2n+Z}X$ for each successive cut indirectly indicates the increasing "aromaticity." The C number range and the concentration of heteroatom-containing molecules also increase with increasing boiling point. For example, the low boiling Cut 1 (385-499°F) consists of molecules having about 10-14 C atoms, with only two molecules in 100 containing S and one in 1000 containing a N atom. The high boiling Cut 5 (795-943°F) involves molecules having about 18-48 C atoms and on the average every other molecule may contain a heteroatom. The nondistillable residuum has the highest concentration of heteroatoms and shows the greatest H deficiency (lowest Z value) among all distillation cuts. One must bear in mind, however, that the above are only average estimates which cannot reveal the actual distribution of heteroatoms in the diverse molecules present in each cut.

What are the Components of a "Heavy" Crude Oil?

The complexity of petroleum increases rapidly with increasing boiling point as the result of the increasing number of atoms in a molecule and the immense number of their possible structural arrangements. It has long been recognized that compositional analysis of high boiling petroleum fractions by the isolation of individual compounds is a practical impossibility. (14) Instead, many attempts have been made to separate those complex mixtures into groups or classes of compounds. Numerous separation methods and schemes have been developed over the years. (15) One of the most recent systematic studies on composition of petroleum high

boiling distillates and residua was the American Petroleum Institute Research Project 60 and the later work based on the characterization scheme developed under this project. (10-12, 16-22)

Petroleum components can be viewed as two major groups of compounds, namely, hydrocarbons and nonhydrocarbons. Hydrocarbons include acyclic alkanes (paraffins) and cycloalkanes (naphthenes), both commonly referred to as saturates, and the third group known as aromatics. Most of the aromatics bear normal or branched chains and naphthenic cycles. A molecule containing one aromatic ring is regarded as monoaromatic, a molecule with two aromatic rings--diaromatic, etc., even if several naphthenic rings and side chains are attached to the aromatic ring. In the same manner, naphthenes containing both saturated rings and chains are defined by the number of rings, i.e., monocyclic, dicyclic, etc. Nonhydrocarbons include compounds which in addition to C and H atoms also involve one or several heteroatoms such as S, N, O, Ni, V, and Fe.

A complete separation of hydrocarbons from nonhydrocarbons in high boiling petroleum fractions is not possible. S-containing compounds which during chromatographic separations behave similarly to hydrocarbons of the equivalent molar structure (i.e., dibenzothiophene and fluorene) are commonly found in hydrocarbon fractions. Some N heterocycles (azarenes), particularly those with the N atom sterically hindered or N-substituted, also frequently interfere with hydrocarbons. Nonhydrocarbons having "polar" functional groups such as -COOH, -OH, -NH, C=O or those containing several heteroatoms in a molecule (i.e., metalloporphyrins) are less difficult to separate from hydrocarbons.

The separation method used in this study produced up to eight "compound-class" fractions from each distillation cut depending on the cut composition. The fraction of "polars" which is regarded as a concentrate of mainly N-, O-, and metal-containing species was separated from each cut prior to further separations of the remaining "polars-free" portion into saturates, monoaromatics, diaromatics, triaromatics, tetraaromatics, pentaaromatics, and a fraction designated "hexaaromatics and/or azarenes." The last fraction reflects the difficulty in separating polycyclic aromatic hydrocarbons having six or more rings from azarenes.

It is important to note, however, that even the most sophisticated HPLC system cannot provide a complete separation and the adjacent fractions therefore show some overlapping. This, however, is detected by the following FIMS analysis of the fractions. The FIMS provides further "separation" into various homologous series according to the Z value in the general formula C_nH_{2n+Z} and reveals the molar mass (C number) distribution of the components.

The structural assignments are based on the HPLC retention data, UV spectra (for aromatics), and if necessary are aided by such analytical techniques as ^1H and ^{13}C NMR, and EIMS.

Figures 4, 5, and 6 show examples of the HPLC/FIMS analyses for distillate Cuts 2, 6, and 10, respectively. Only a few most prominent homologous series are presented. Most likely structures are shown although various isomers are possible. The extensive compositional information provided by this analytical approach is evident. Of particular importance are series of polycyclic molecules many of which are related to steroid and terpenoid structures ranging from the saturated form to various stages of aromatization.

The earlier discussed effect of chemical structure on molar mass distribution for components of a given distillation cut is illustrated in Figure 5. The molar mass profile of acyclic alkanes shows the maximum at C_{39} while that of the pentaaromatic $\text{C}_n\text{H}_{2n-30}$ series has the maximum at C_{30} . Molar mass profiles of "polars" (not shown) were "shifted" even further toward lower molar mass values than those of the corresponding hydrocarbons but showed similar patterns in terms of wide C number distributions. The interpretation of the FIMS data for "polars" is much more difficult than in the case of hydrocarbons, particularly if more than one heteroatom per molecule is involved. Infrared and NMR data, together with elemental analysis results, provided important additional information. Compounds having pyrrolic NH groups (i.e., carbazoles) and amide types were found to be particularly abundant. Although various homologous series were identified, the results indicate the need for further separation of "polars" to facilitate the interpretation of data.

Figure 7 shows distributions of various "compound-class" fractions in the heavy Kern River crude oil. The concentration of "polars" increases steadily with increasing boiling point from zero in Cut 1 to about 82 wt % in the nondistillable residuum. Notably, "polars" in the distillable portion (Cut 1 through Cut 10) account for over 42% of total "polars" present in this heavy crude oil. The mono- through pentaaromatics and the fraction designated "hexaaromatics and/or azarenes," together show a peculiar distribution pattern with two minima, one at the top and the other at the bottom of the barrel. The concentrations of individual fractions vary in each successive distillation cut. The mono- and diaromatics predominate in the low boiling cuts. It is worthwhile noting, however, that the composition of the individual fractions within these classes changes considerably with increasing boiling point. For example, the monoaromatics in Cut 2 are rich in di- and

tricyclomonaromatics (homologous series C_nH_{2n-8} and C_nH_{2n-10}) while the monoaromatics in Cut 4 involve mainly tri-, tetra-, and pentacyclomonaromatics (homologous series C_nH_{2n-10} , C_nH_{2n-12} , and C_nH_{2n-14}).

The data in Figure 7 show a dramatic decrease in saturates with increasing boiling point from about 88 wt % in Cut 1 to only about 1 wt % in the nondistillable residuum. Similarly, as with other compound-class fractions, the composition of saturates changes with increasing boiling point. This is illustrated in Figure 8 which shows distributions of the alkane homologous series in the entire Kern River crude oil. Acyclic alkanes (paraffins) are almost completely absent in this degraded heavy crude oil. The concentrations of tetra-, penta-, and hexacyclics increase with increasing boiling point at the expense of mono-, di-, and tri-cyclic alkanes. Steranes and hopanes were found to be particularly abundant in Cuts 3 through 6.

CONCLUSIONS

Data derived from this study dispel many misconceptions about the composition of high boiling components in petroleum. The results presented show that the molecular structure more than molecular weight of petroleum components predominantly determines the boiling point distribution and density ($^{\circ}$ API gravity) of the crude oil. The majority of compounds found in the "heavy" Kern River crude oil have molar masses not exceeding about 1500 with only a few extending up to about 1900. They involve mainly polycyclic structures with varying degree of aromatization, and many of them contain N and O atoms with pyrrolic and amide types prevailing.

The results of this study also demonstrate the necessity of a high degree of sample fractionation in order to obtain meaningful compositional information.

ACKNOWLEDGMENTS

The author expresses his appreciation to Messrs. T. H. Attoe, R. M. Bly, R. J. Brown, M. Karigaca, C. E. Rechsteiner, F. Su, X. Urrutia, and D. M. Wilson of Chevron Research Company; R. Malhotra and G. St. John of SRI International; S. Hughes of UIC Inc.; and W. Fischer of Leybold-Heraceus GmbH for their contributions to this study.

Appreciation is also expressed to Messrs. K. H. Altgelt, T. R. Hughes, A. L. McClellan, and J. H. Shinn of Chevron Research Company for helpful suggestions and review of this manuscript.

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TABLE I
DISTRIBUTIONS OF C, H, N, S, O, Ni, AND V ATOMS
IN KERN RIVER PETROLEUM

Cut No. 1	Cumulative Wt % from Crude Oil	Approximate C Atom Range ²	Average Number of Atoms in Molecule ³							Total Hetero-atoms	z in $C_nH_{2n+z}X_4$
			C	H	N	S	O	Ni	V		
1	6.4	10-14	13.2	24.1	0.001	0.02	-	-	-	0.02	-2.3
2	18.0	12-24	17.8	29.9	0.015	0.06	0.05	-	-	0.12	-5.7
3	35.8	14-36	22.6	36.9	0.07	0.10	0.08	-	-	0.25	-8.3
4	45.0	16-42	27.3	43.5	0.12	0.12	0.11	-	-	0.35	-11.1
5	53.2	18-48	30.6	47.8	0.20	0.15	0.16	-	-	0.51	-13.4
6	60.3	20-53	35.7	55.3	0.28	0.18	0.19	2 x 10 ⁻⁵	-	0.65	-16.1
7	66.0	22-62	41.7	63.8	0.35	0.24	0.26	3 x 10 ⁻⁴	8 x 10 ⁻⁵	0.85	-19.6
8	70.9	25-71	47.0	71.1	0.47	0.29	0.39	1.3 x 10 ⁻³	5 x 10 ⁻⁴	1.15	-22.9
9	74.7	27-81	52.1	77.9	0.59	0.31	0.43	2 x 10 ⁻³	9 x 10 ⁻⁴	1.34	-26.3
10	79.1	29-93	58.5	87.4	0.70	0.33	0.48	1.4 x 10 ⁻³	7 x 10 ⁻⁴	1.51	-29.6
Nondistillable Residuum	100.0	32-134	84.8	116.4	1.49	0.54	0.82	5 x 10 ⁻³	3 x 10 ⁻³	2.86	-53.2

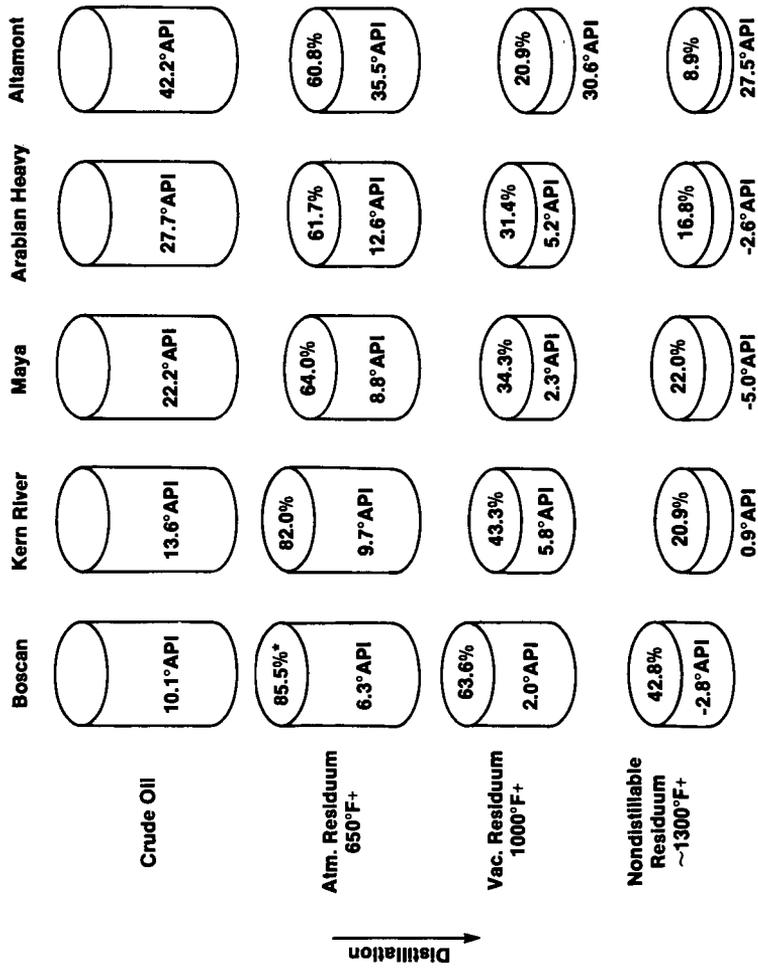
¹See Figure 3.

²From FIMS and wt & C data.

³Calculated using average molecular weight value by FIMS and elemental analysis results.

⁴X = heteroatom(s).

FIGURE 1
THE EFFECT OF DISTILLATION ON API GRAVITY FOR VARIOUS CRUDE OILS



*Wt % Yield from Crude Oil

FIGURE 2
THE EFFECT OF MOLECULAR STRUCTURE ON BOILING POINT

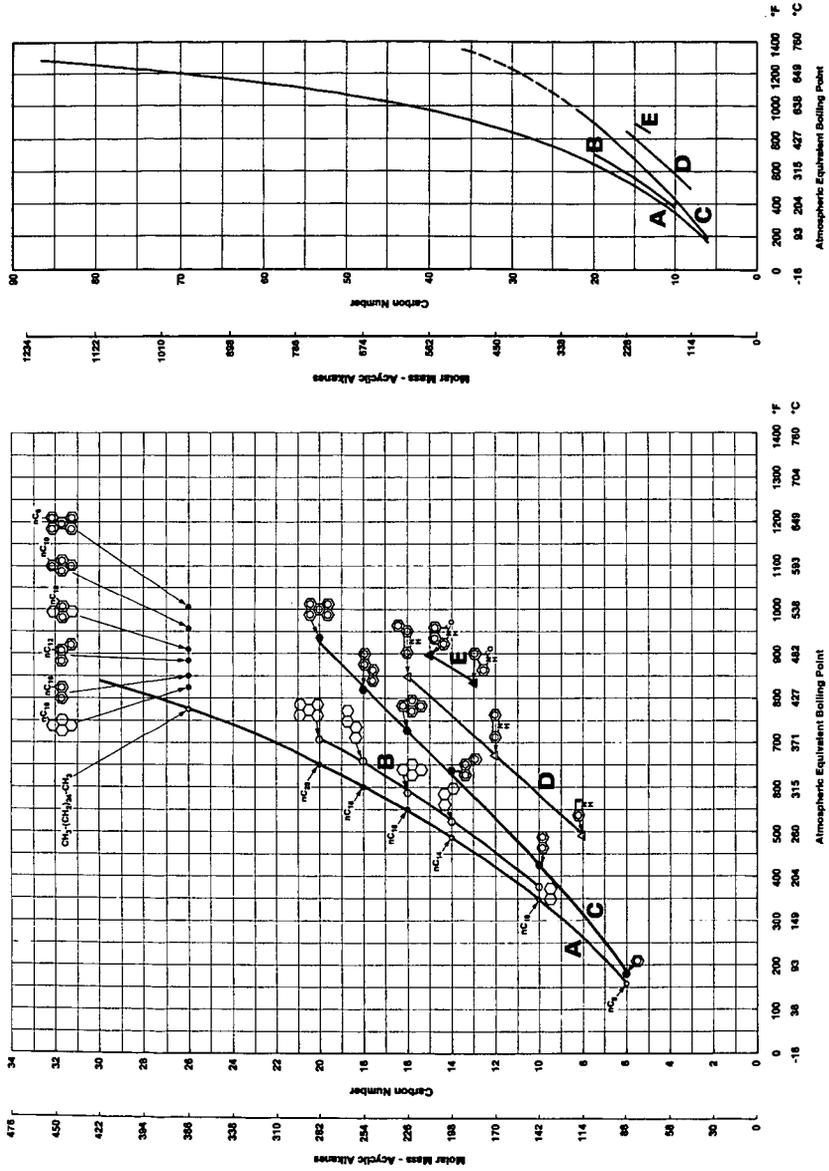


FIGURE 3
BOILING POINT, MOLAR MASS, AND
HETEROATOM DISTRIBUTIONS IN KERN RIVER PETROLEUM (13.6°API)

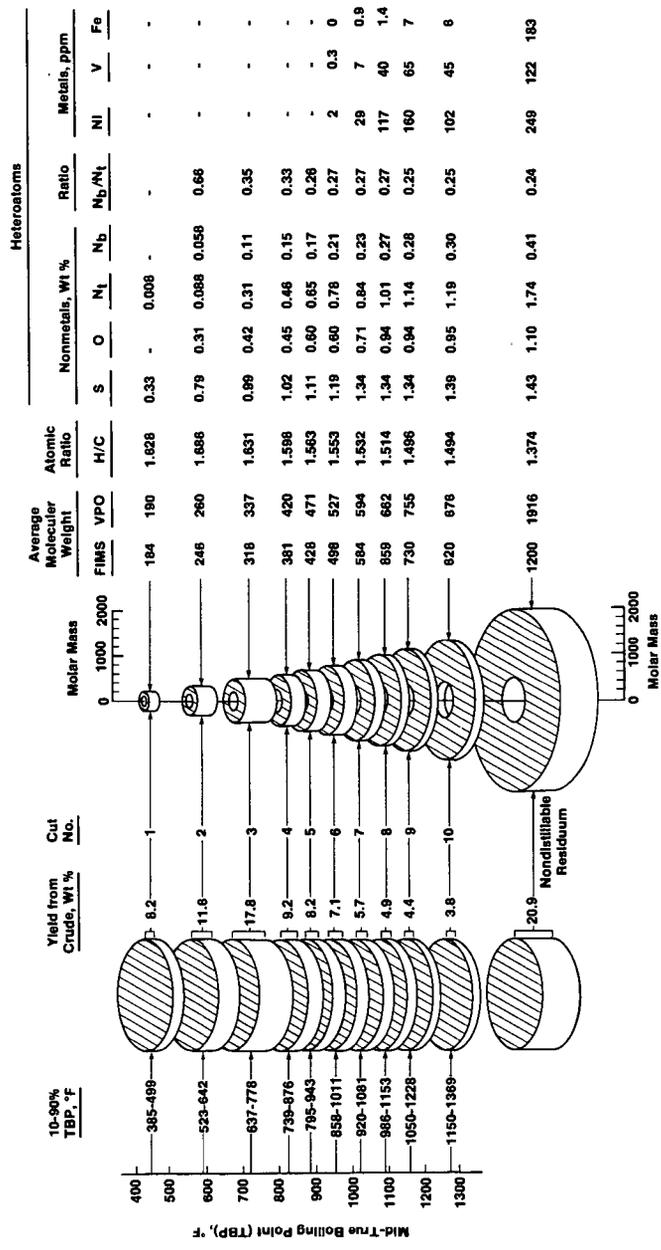


FIGURE 4
SCHEMATIC DIAGRAM OF HPLC-FIMS ANALYSIS OF
CUT 2 (523-642°F) FROM KERN RIVER PETROLEUM

Note: Only Selected Homologous Series Are Shown as Examples

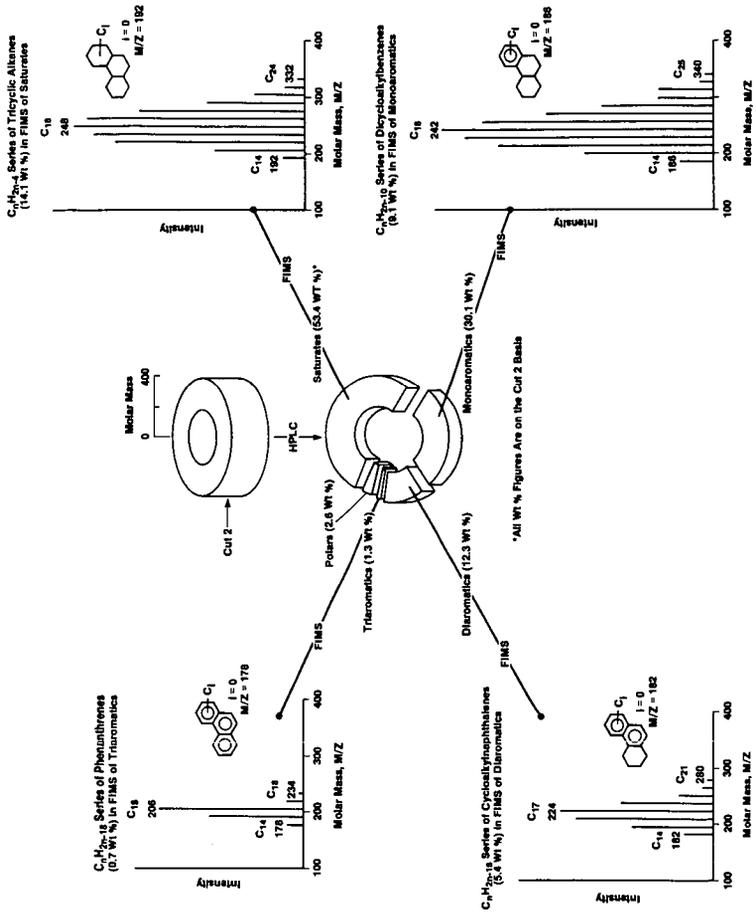


FIGURE 5
SCHEMATIC DIAGRAM OF HPLC-FIMS ANALYSIS OF
CUT 6 (858-1011°F) FROM KERN RIVER PETROLEUM
Note: Only Selected Homologous Series Are Shown as Examples

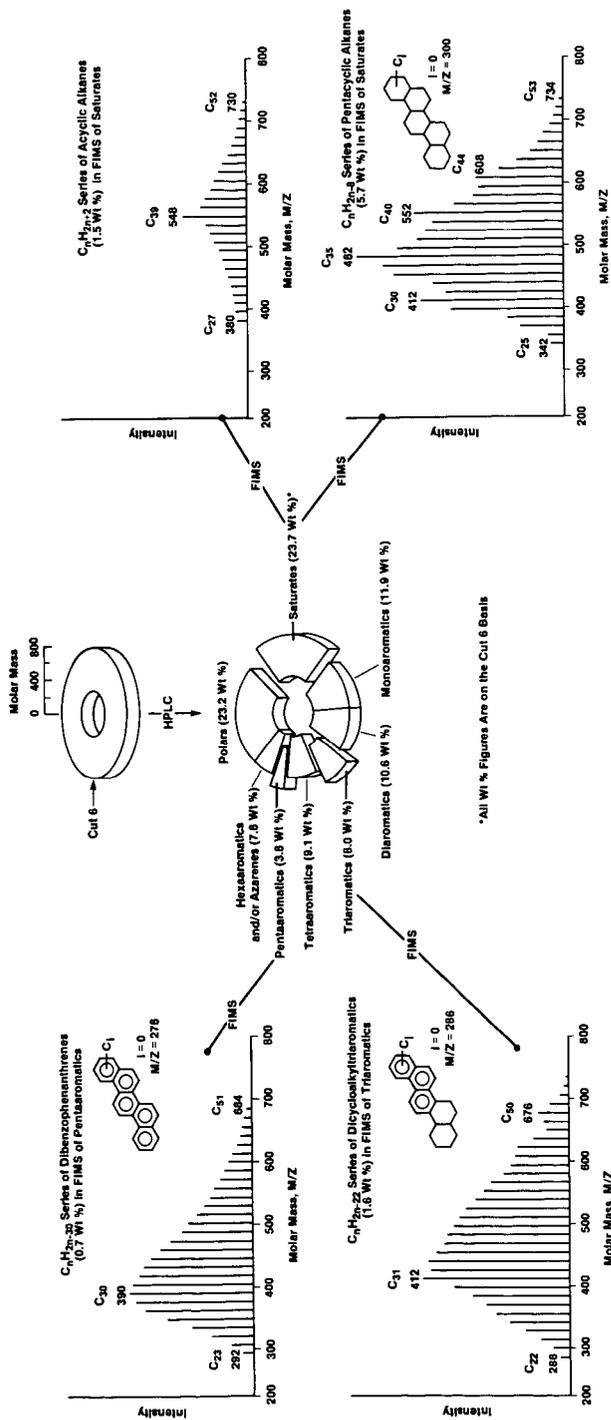
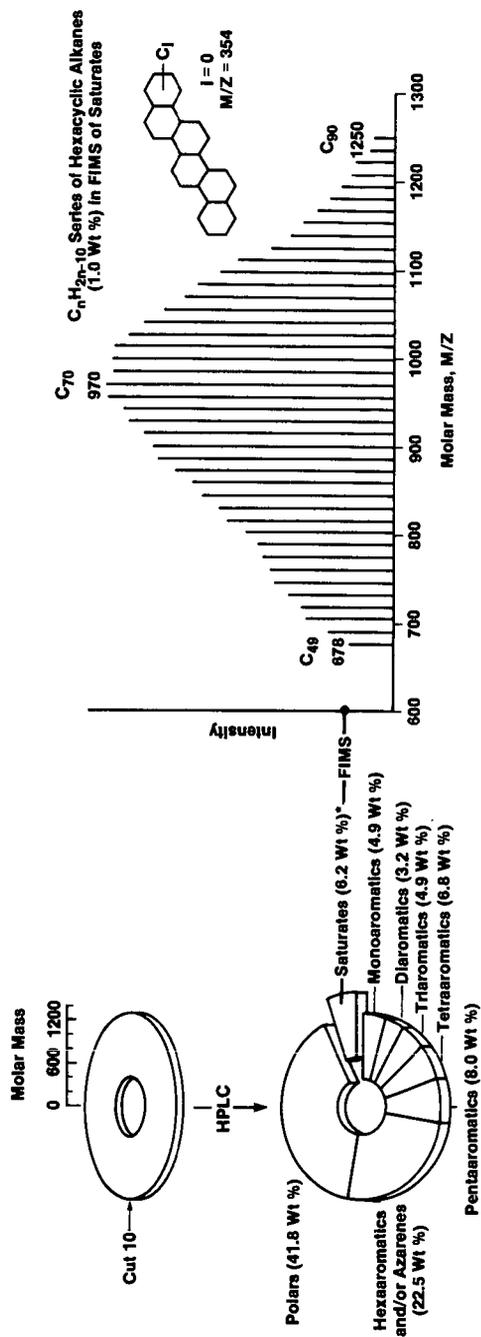
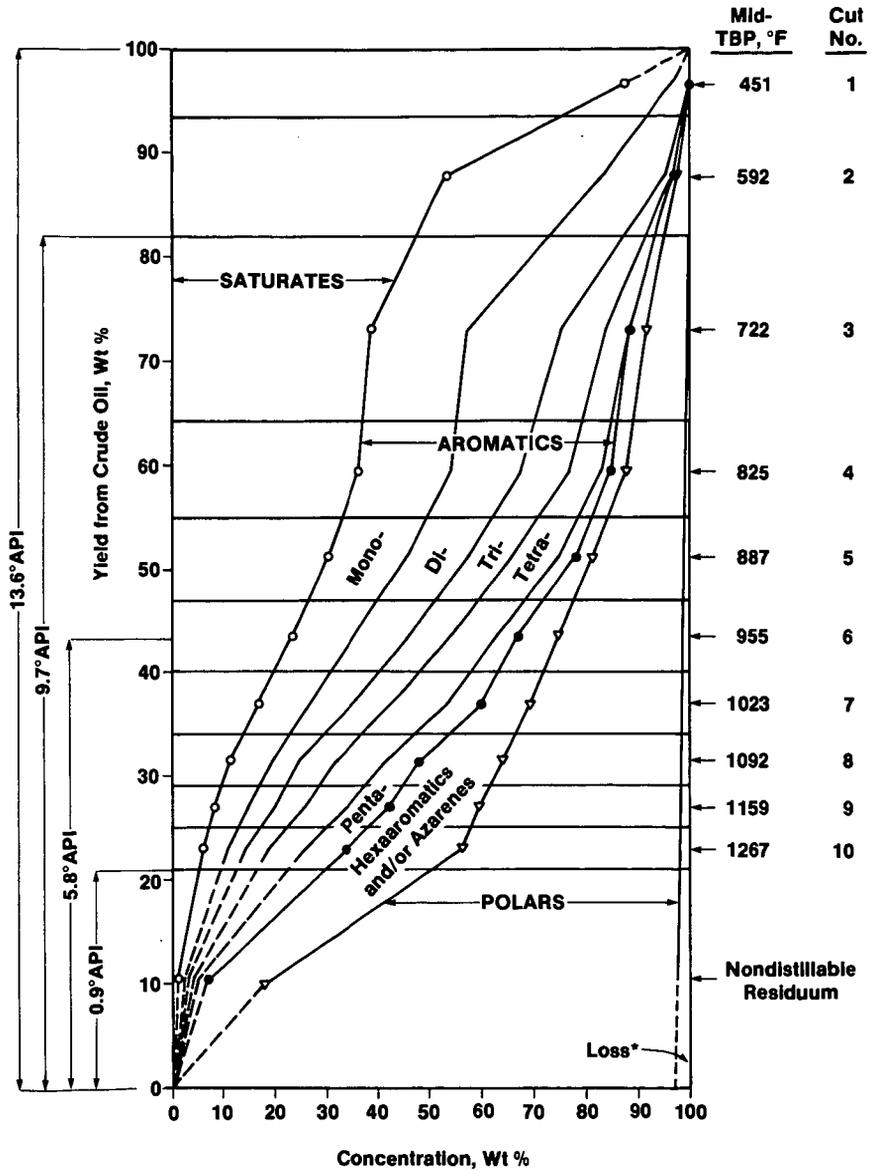


FIGURE 6
SCHEMATIC DIAGRAM OF HPLC-FIMS ANALYSIS OF
CUT 10 (1150-1369°F) FROM KERN RIVER PETROLEUM



*All Wt % Figures Are on the Cut 10 Basis

FIGURE 7
COMPOUND-CLASS DISTRIBUTIONS IN KERN RIVER PETROLEUM



*Unrecovered material during chromatographic separations.

FIGURE 8
DISTRIBUTIONS OF ALKANE HOMOLOGOUS SERIES IN
KERN RIVER PETROLEUM

