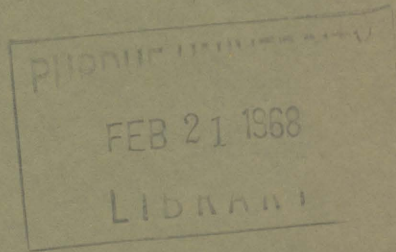


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QUALITATIVE AND QUANTITATIVE ASPECTS OF CRUDE OIL COMPOSITION

By Harold M. Smith



UNITED STATES DEPARTMENT OF THE INTERIOR

1968

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QUALITATIVE AND QUANTITATIVE ASPECTS OF CRUDE OIL COMPOSITION

by

Harold M. Smith¹

Abstract

This publication summarizes the literature on the composition of petroleum, with special emphasis on naphtha and gas oil, and provides a source book for the known qualitative and quantitative facts on crude oil composition. The discussion points out the known facts from supposition, and suggests new researches needed in various areas.

Introduction

In 1965 the author published a paper generally concerned with the qualitative aspects of crude oil. This publication was subtitled "The Petroleum World" (167)² and was a fanciful portrayal of factual qualitative data covering our knowledge of the composition of petroleum as of April 1965. It was prepared primarily for non-scientists and scientists in fields of work that would not normally require intimate knowledge of crude oil composition.

This paper is an attempt to provide quantitative interpretations of the qualitative facts on the composition of crude oil, with particular emphasis on naphtha and gas oil portions. (Naphtha and gas oil are explicitly defined in the section on representative crude oils from the entire spectrum.) The underlying theme of this paper comes from the geochemical concept that petroleum originates from organic precursors which under the influence of environmental parameters, especially time, temperature, and catalysis, gradually form light hydrocarbons. If this is true then qualitative and quantitative data on the naphthas and gas oils should be important in several ways, and much of this paper is an attempt to evaluate and interpret these aspects of composition. One can go further and state that, because the organic precursors, time, temperature, catalysts, chemical agents, and other parameters will vary with each geographical location and geological environment, one should expect to find a wide variety of crude oils in terms of composition—a variety that would not be amenable to classification.

The first consideration arising from the data is the matter of the classification of crude oils. This is discussed and a spectrum-type approach is suggested that seems much more realistic to the author. To give substance to this view detailed data on 14 low-sulfur crude oils and seven high-sulfur crude oils are presented and analyzed. The basis for the discussion is the Bureau of Mines routine crude oil analysis. The relationships of the general characteristics are considered not only for the specific oils selected, but also on a statistical basis for several thousand analyses. Of particular interest and importance are the data depicting the effects of time and depth of burial on the content of naphtha and gas oil in crude oils. This is a direct link with the basic geochemical concept.

This general treatment is followed by graphical and discussion presentations

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² Italic numbers in parentheses refer to items in the list of references at the end of this report.

of the aromatic, naphthene, and paraffin content of the naphtha and the aromatic and paraffin-naphthene content of the gas oil, with a further breakdown of the latter fraction to naphthene ring and paraffin plus paraffin side chains. Various comparisons between oil types, based on gas-liquid chromatography (GLC) data when available and on Bureau analyses, serve to emphasize differences and similarities, and the inherent difficulties with a classification system. Geological factors are mentioned when known.

These data lead directly to a consideration of the detailed hydrocarbon composition of naphthas as given in the literature. The data are from several sources—the older being based on distillation and physical properties, the more recent data for hydrocarbons up to about C_8 include a number of GLC analyses. Comparison in detail of naphtha types leads to several conclusions regarding the relative contents among different hydrocarbons, as 2- and 3-methylalkanes, for example. The data tables are based on a complete list of hydrocarbons through C_{11} found in petroleum as of July 1966. Data for a number of Soviet crude oils are included.

Next quantitative relationships between pairs of individual hydrocarbons up to C_8 are shown graphically and these findings are considered both as to degree of occurrence and possible relationship to geologic origin of the oil.

Quantitative data on gas oil composition are very sparse. The general compositions of the gas oils of the 21 crude oils previously treated are given by considering volume-percent of aromatics and paraffins plus naphthenes; weight-percent naphthene rings, paraffins and paraffin side chains; carbon atoms in aromatic and naphthene rings and in paraffins plus paraffin side chains; and the number of aromatic, naphthene, and total rings per molecule for selected fractions. The relationships of model systems with experimental data are given. A list of all hydrocarbons found in gas oil completes the gas oil picture.

Following the hydrocarbon discussion the sulfur, nitrogen, and oxygen compounds that have been found in crude oils are listed and such quantitative data as are available are presented.

All of these deliberations lead back to the basic theme, the origin of petroleum, and the section on possible petroleum precursors considers sources for alkanes, cyclo-alkanes, and aromatics, as well as for sulfur, nitrogen, and oxygen compounds. The thermodynamic and geologic possibilities of some reactions are discussed.

The final section is based on the gaps in our knowledge of the composition of crude oil, and suggests a few researches that should aid materially in our understanding of petroleum—what it is and from whence it came.

From the foregoing it is obvious that this paper is designed for an audience familiar with crude oil and its distillation products; yet the information will be useful to scientists in other fields and the scientifically oriented layman.

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CRUDE OIL CLASSIFICATION

CLASSIFICATION SYSTEMS

When the correlation index was proposed in 1940 (166) as a means of interpreting crude oil analyses in lieu of a rigid classification system, an appendix to the report contained a review of crude oil classification attempts. Inasmuch as the present situation with regard to classification is essentially unchanged, a direct quote from this material including its table 9 seems appropriate at this point.

Bureau of Mines Systems

CLASSIFICATION OF CRUDE OILS

The varied and complex composition of crude oils has been recognized by petroleum chemists for many years, yet, regardless of this complexity, numerous attempts have been made to classify petroleum. Engler and Höfer¹ record several methods of classification dating back to 1900. Early American nomenclature in this regard is well stated by Bacon and Hamor,² who say:

From the viewpoint of the petroleum refiner, crude oil is of two general classes or types, namely: Those petroleum which carry practically no asphalt and which yield solid hydrocarbons of the paraffin series (C_nH_{2n+2}), and termed "paraffin-base"; and those which yield practically no solid paraffins, but are rich in asphalt, the "asphalt-base" petroleum. Strictly speaking, however, there is still another class, the "paraffin-asphalt", "semiasphalt", or mixed-base petroleum, * * * which contain both paraffin and asphalt, and are hence a combination of the two other classes.

Probably the first descriptive term used in this country was "paraffin base," due, according to Smith³ and Smith and Lane,⁴ to the fact that "the word 'base' is used much as it is in pharmaceutical work. For example, the 'base' or 'basis' of an ointment or salve is the fatty material (lard, petrolatum, or lanolin) used as a vehicle or carrier for the active medicinal principles. Apparently many of the pioneers in the petroleum industry conceived of crude oil as being similar in nature to * * * medicinal products, in that it consisted of a semisolid nonvolatile 'base' and a volatile portion that could be distilled off to make gasoline, kerosene, and other products." Many crude oils, among them those first discovered in this country, deposit a waxy material (paraffin) when chilled. This fact may have led to the designation paraffin-base.⁴

New types of crude oils accompanied the discovery of new oil fields. Some of these oils had asphaltic residues but no wax, some contained

both wax and asphalt, while still others were virtually without either wax or asphalt. Gradually the terms "asphalt-base," "intermediate-base," "naphthene-base," and others were coined to describe these crude oils. As the number and variety of analyses increased, chemists attempted to set definite limits for these various classes, at the same time realizing that while such limitations could never be entirely satisfactory, they did provide a means for the approximate classification of crude oils. The Bureau of Mines devised what is probably the best-known and most-used system of "base" classification because it had early adopted a standard procedure for analysis and had accumulated a large number of analyses. The first description of the system was published in 1927,⁵ and these classifications were amplified considerably in 1935.⁶ These two steps of its development are given in table 9.

The increase in the number of classifications from four to nine is indicative of the desire of the chemist to bring all oils into some classification and also of the difficulties of accomplishing this. However, even in a system as flexible as that used by the Bureau of Mines there remain several defects after classes for all crude oils have been established and named.

One of the biggest disadvantages of any "class" system is that as soon as an object is placed in a definite class it immediately becomes identified with the attributes of that class. Thus, similarities are emphasized, but usually no provision is made for indicating differences that may be equally as important as or more important than the similarities.

Another defect in classification systems resides in the fact that crude oils vary in kind from asphaltic seepages to the light crude oils from distillate wells. Between these two extremes is a virtually continuous range in characteristics. Consequently, arbitrary divisions, however carefully placed, must coincide with or approach closely the key data for some crude oils, thus making their classification doubtful to an extent dependent upon the magnitude of the experimental error in the data. Further if the division limits are wide, crude oils at the two extremes of the same classification will be dissimilar, and the purpose of classification is nullified.

A further disadvantage lies in the complex composition of even relatively "simple" crude oil. The advancement in our knowledge of petroleum hydrocarbons in the last decade has shown very clearly the misconceptions that attend the use of "base" classification names. For example, even in the gasoline from a Pennsylvania paraffin-base petroleum considerable amounts of naphthenes are found and probably the only paraffins in the heavy oils are the waxes. Naphthene-base oils, in addition to naphthenes, may contain asphaltic material that is not naphthenic, aromatic hydrocarbons, and even paraffin wax. Thus, the very names used to designate the classes are misnomers. It is true that the term "paraffin base" does, within limits, indicate a certain type of crude oil, but as much cannot be said for certain of the other classification terms. For

¹ Engler, C., and Höfer, H. von, *Das Erdöl*: Vol. 1, Leipzig, 1913, pp. 225-230.

² Bacon, R. F., and Hamor, W. A., *The American Petroleum Industry*: Vol. 2, New York, 1916, p. 447.

³ Smith, N. A. C., *The Interpretation of Crude-Oil Analyses*: Bureau of Mines Rept. of Investigations 2806, 1927, 20 pp.

⁴ Smith, N. A. C., and Lane, E. C., *Tabulated Analyses of Representative Crude Petroleum of the United States*: Bureau of Mines Bull. 291, 1928, 69 pp.

⁵ Smith, N. A. C., Work cited in footnote 13.

⁶ Lane, E. C., and Garton, E. L., "Base" of a Crude Oil: Bureau of Mines Rept. of Investigations 3279, 1935, 12 pp.

TABLE 9.—*Classification of crude oils according to base (Bureau of Mines system)*FIRST SYSTEM (1927)¹

Gravity of key fraction 1		Pour point of key fraction 2, °F.	Base of crude
°A.P.I., 60° F.	Specific gravity, 60/60° F.		
40.0 or lighter.....	0.8251 or lighter.....	Above 5.....	Paraffin.
33.1 to 39.9.....	0.8597 to 0.8256.....do.....	Intermediate.
33.0 or heavier.....	0.8602 or heavier.....do.....	Hybrid.
Do.....do.....	Below 5.....	Naphthene.

SECOND SYSTEM (1935)²

Gravity of key fraction 1		Gravity of key fraction 2		Base of crude	
°A.P.I., 60° F.	Specific gravity, 60/60° F.	°A.P.I., 60° F.	Specific gravity, 60/60° F.	Light fraction	Heavy fraction
40.0 or lighter.....	0.8251 or lighter.....	30.0 or lighter.....	0.8762 or lighter.....	Paraffin ³	Paraffin.
Do.....do.....	20.1 to 29.9.....	0.9334 to 0.8767.....do.....	Intermediate.
Do.....do.....	20.0 or heavier.....	0.9340 or heavier.....do.....	Naphthene.
33.1 to 39.9.....	0.8597 to 0.8256.....	30.0 or lighter.....	0.8762 or lighter.....	Intermediate.....	Paraffin.
Do.....do.....	20.1 to 29.9.....	0.9334 to 0.8767.....do.....	Intermediate.
Do.....do.....	20.0 or heavier.....	0.9340 or heavier.....do.....	Naphthene.
33.0 or heavier.....	0.8602 or heavier.....do.....do.....	Naphthene ³	Do.
Do.....do.....	20.1 to 29.9.....	0.9334 to 0.8767.....do.....	Intermediate.
Do.....do.....	30.0 or lighter.....	0.8762 or lighter.....do.....	Paraffin.

¹ Smith, N.A.C., The Interpretation of Crude-Oil Analyses: Bureau of Mines Report of Investigations 2806, 1927, 20 pp.² Lane, E. C., and Garton, E. L., "Base" of a Crude Oil: Bureau of Mines Report of Investigations 3279, 1935, 12 pp.³ When both light and heavy fractions have same classification the name is not repeated; thus paraffin base, not paraffin-paraffin base.

example, there is considerable confusion concerning the designations "asphalt-base" and "naphthene-base." Some assume that they are synonymous terms while others consider that they apply to two different types of crude oils.

System Proposed by Sachanen

In 1950 Sachanen (158) proposed a crude oil classification system having nine classes based on composition. This system represented a considerable advance over other classification systems, but was based on crude oil data that were not ordinarily available. He outlined the system in table XXI of reference 158, which is reproduced as follows:

TABLE XXI.—*Classification of crude oils*

Class	Composition	Crude oils
Paraffinic.....	Percentage of paraffinic side chains 75% or more.	Pennsylvania, Rodessa.
Naphthenic.....	Percentage of naphthenic hydrocarbons 70% or more.	Emba-Dossor.
Aromatic.....	Percentage of aromatic hydrocarbons 50% or more.	None.
Asphaltic.....	Percentage of resins and asphaltenes 60% or more.	(Bitumina of natural asphalt.)
Paraffinic-naphthenic.	Percentage of paraffinic side chains from 60 to 70% percentage of naphthenic rings at least 20%.	Many Mid-Continent crude oils.
Paraffinic-naphthenic-aromatic.	Percentage of paraffins, naphthenes, and aromatics approximately equal.	Malkop.
Naphthenic-aromatic.	Percentage of naphthenes or aromatics 35% or more.	Light Coastal and California crude oils.
Naphthenic-aromatic-asphaltic.	Percentage of naphthenes, aromatics, or asphaltic compounds 25% or more.	Heavy Coastal and California crude oils.
Aromatic-asphaltic.	Percentage of aromatics or asphaltic compounds 35% or more.	Ural, probably some heavy Mexican crude oils.

System Used by Creanga

Using the same basic composition data, Creanga (50) added several other parameters and suggested a more complex system approaching a spectrum-type characterization. The following Chemical Abstracts³ summary of his report best indicates the complexity of this system:

Chemical classification of crude oils: Carpatia classification. C. Creanga. *Acad. Rep. Populare Romine, Studii Cercetari Chim.* 9, 93-108 (1961).—The first criterion of the new crude oil classification method defines the oils by means of the structural indexes, % C'_P , % C'_N , % C'_A , which represent, resp., the percentage of paraffinic, naphthenic, and aromatic C. They are calcd. from % $C'_{P.N.A} = \Sigma \% C'_{P.N.A} R'/100$, where % C'_P , % C'_N , and % C'_A are the group values of the crude oil fractions, and R' is the yield of these fractions. The second criterion completes the characterization of the crude oils by taking into account chem. properties which are of practical importance: c , the wax content; r , the content of asphaltic and resinous compds.; s , the S content; d , the amt. distd. up to 200°. The first 3 of these properties define the class subdivision, and the last one expresses the oil volatility only, and does not enter into the category definition. Crude oils are divided into 7 categories: paraffinic, % $C'_P \geq 72$; paraffinic-naphthenic, % $C'_P \geq 50$, % $C'_P + \% C'_N \geq 90$; paraffinic-aromatic, % $C'_P \geq 50$, % $C'_P + \% C'_N \geq 90$; paraffinic-naphthenic-aromatic, % $C'_P \geq 50$, % $C'_N > \% C'_A$, % $C'_A > 10$; paraffinic-aromatic-naphthenic, % $C'_P \geq 50$, % $C'_A > \% C'_N$, % $C'_N > 10$; naphthenic-aromatic, % $C'_P < 50$, % $C'_N > \% C'_A$; aromatic-naphthenic % $C'_P < 50$, % $C'_A > \% C'_N$. The subgroups are defined: waxy $C \geq 25\%$; nonwaxy $c < 2\%$; slightly resinous, $r < 10\%$; resinous $10\% \leq r < 25\%$;

³ Reprinted by permission from Chemical Abstracts, v. 56, 1962, p. 5011-5012.

asphaltic, $r \geq 25\%$; nonsulfurous, $s < 0.5\%$; sulfurous $s > 0.5\%$. A total of 12 subgroups has been established which is, however, not encountered in each major class.

SPECTRUM-TYPE CHARACTERIZATION

The author prefers to consider crude oils as a succession of compositions in which the consecutive compositions generally change only a little, but, because of the large number of oils, the differences between the extremes are very large.

Correlation Index System

The author's first attempt to devise another type of characterization factor led to the correlation index (166) in which the consecutive fractions for a Bureau of Mines routine analysis are represented by a number that is a function of specific gravity and boiling point. These data can be plotted and typical curves obtained that are more meaningful than is the base system. The index is best for two-component systems, such as paraffins plus naphthenes, but virtually all crude oils are at least three-component systems—aromatic, paraffinic, naphthenic—and under these conditions the index is not as factually descriptive as is desirable. This can be seen in figure 1, which shows typical correlation index curves for a paraffin base and two naphthene-intermediate base crude oils as classified by the Bureau system of 1935. It will be shown later that the high correlation indexes for the Conroe oil are caused by aromatics, not naphthenes, indicating one of the difficulties of this system.

Modified Correlation Index System

In 1960 Gruse and Stevens (77), following a suggestion by H. M. Smith and with his assistance, published a modification of the correlation index system which incorporated cloud point to indicate wax and carbon residue to indicate asphalt content. Such a system provides a somewhat better picture of the oil and approximates the spectrum approach when used in a graph, as presented in figure 2. The numbers and abbreviations in this figure refer to items in table I-2 in the referenced text (77).

Spectrum-Type Concept as Used in This Report

Perhaps crude oils can be thought of as an extremely long shelf of books where each book represents a crude oil, and these are arranged in order of increasing cyclization of the oil components. In these books each page represents a

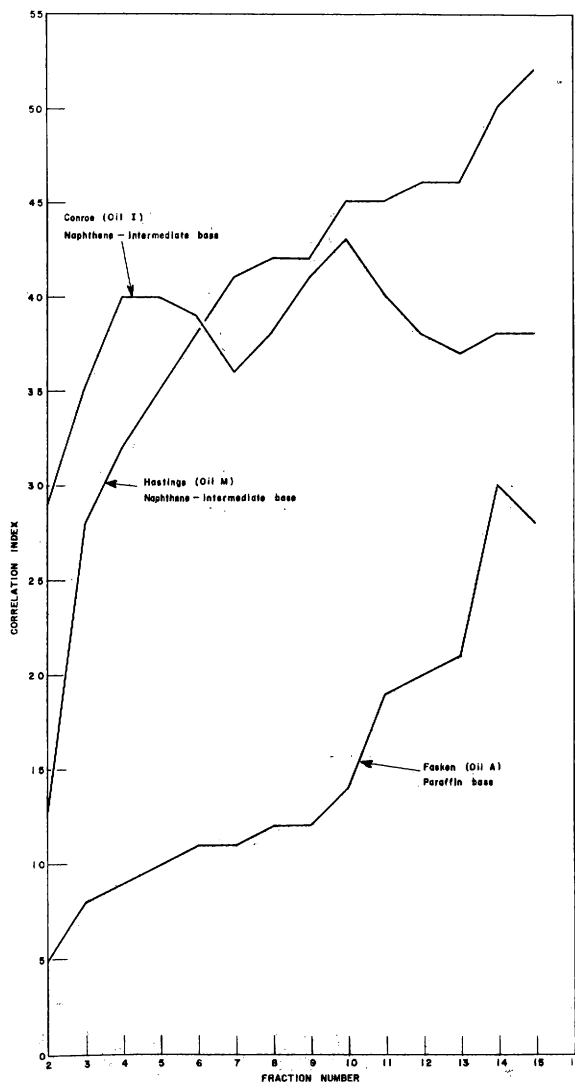


FIGURE 1.—Typical Correlation Index Curves.

single hydrocarbon or a sulfur, nitrogen, or oxygen compound that has been identified in petroleum; thus the total pages would represent all compounds thus far identified. Imagine that the extent of coloration of a given page was proportional to the quantity of the hydrocarbon or hetercompound represented that was present in a given oil. Further, assume that the color was symbolic of the type of compound: Black for hydrocarbons and yellow, red, and blue for sulfur, nitrogen, and oxygen compounds, respectively. Finally, assume that the pages representing these compounds are arranged in increasing order of boiling point. A great majority of the books would have most of their pages with some black—in the case of the heptane page for a Kawkawlin, Mich., crude oil to the extent of 2.46 percent. However, in certain books the pages for hydrocarbons or hetercom-

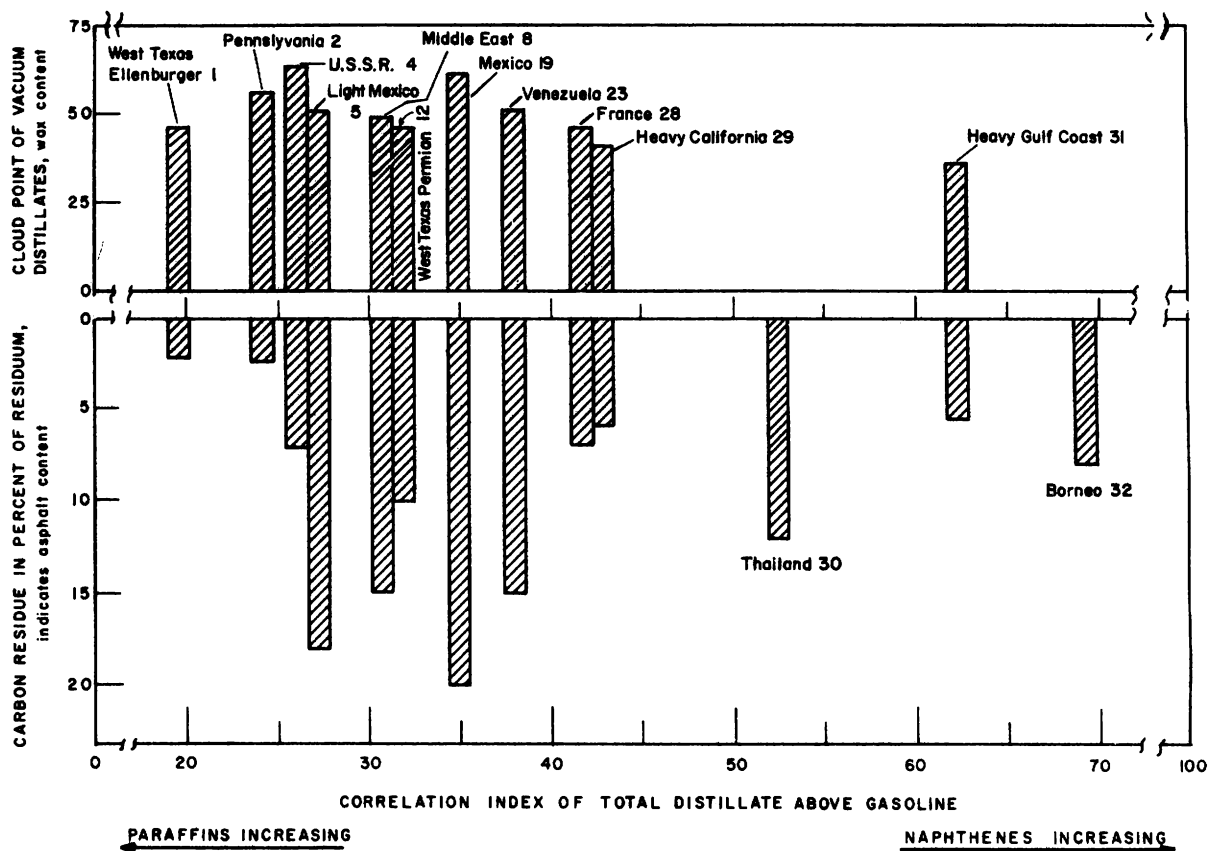


FIGURE 2.—Relation Between All Known Types of Crude Oils. (After H. M. Smith.) (From Gruse and Stevens (77), by permission.)

pounds known to be present in some crude oils would be white, indicating such compounds were missing or if present were below the limits of detection in that particular oil. There would invariably be pages with some yellow representing sulfur compounds. These would generally be more numerous and have more yellow near the end of the book, but some books would have several pages with yellow near the front or throughout the book. Red, signifying nitrogen compounds, would appear primarily in very small areas on pages near the back of the book, and in a very limited quantity elsewhere. Little is known about the quantity and occurrence of oxygen compounds denoted by blue; certainly there would be pages with blue on them near the

end of the book, and probably for some books such pages will be scattered throughout. Generally the difference between the extent and type of coloration in adjacent books would be small, yet large between books at opposite ends of the shelf. The difficulties of dividing such an array of books into a few groups having similar characteristics can be realized even using only the relatively limited number of the total compound in petroleum that have been identified. Obviously the books will become much thicker as research on composition continues, and grouping will become increasingly difficult. The use of a spectrum concept obviates the need for group classification.

REPRESENTATIVE CRUDE OILS FROM THE ENTIRE SPECTRUM

To present some idea of the range of crude oils and using the symbolism just described the author has considered two bookshelves, one for crude oils having 0.5 percent sulfur or less, and one for those having 1.35 percent sulfur or

more. From these collections of crude oils examples have been selected that show the wide variation in composition. The pertinent data are given in table 1 for low-sulfur oils and table 2 for high-sulfur oils.

TABLE 1.—Data on representative low-sulfur crude oils taken from routine analyses

Designation	Crude oil source, State or country and field	Geological data			General characteristics					Products, volume-percent			
		Era	Period	Producing horizon	°API	Weight-percent				Naphtha	Gas oil	Lube oil	Residuum
						Sulfur	Nitrogen	Carbon residue	Asphalt				
A	Texas: Fasken.....	Paleozoic.....	Ordovician.....	Ellenburger.....	48.5	<0.10	<0.10	0.4	2	39.7	38.8	10.4	10.0
B	New Mexico: Bagley.....	do.....	Siluro-Devonian.....	Dolomite.....	46.0	.34	.008	.1	1	36.4	39.2	16.7	7.6
C	Indonesia: Minas.....	Cenozoic.....	Miocene.....	Telisa.....	32.8	.10	.13	1.5	7	18.6	23.5	20.1	37.3
D	Michigan: Kawkawlin.....	Paleozoic.....	Devonian.....	Dundee.....	34.2	.45	.102	3.5	17	23.4	30.8	13.1	30.7
E	Pennsylvania: Bradford.....	do.....	do.....	do.....	41.1	.11	.010	.3	2	30.7	25.1	17.6	25.0
F	North Dakota: Beaver Lodge.....	do.....	Ordovician.....	Mission Canyon.....	46.0	.23	.022	.3	2	46.6	22.9	13.9	12.2
G	Louisiana: Charenton.....	Cenozoic.....	Miocene.....	do.....	36.8	.10	.02	.5	3	17.0	48.0	22.6	11.6
H	Louisiana: Gueydan, W.....	do.....	do.....	do.....	39.2	.10	.02	.3	2	20.7	41.6	23.3	10.6
I	Texas: Conroe.....	do.....	Eocene.....	Cockfield.....	37.4	.10	.027	.4	2	34.4	42.7	14.4	7.6
J	Borneo: Sanga Sanga.....	do.....	Miocene.....	do.....	31.9	.01	.07	.7	3	43.0	24.1	7.0	8.3
K	Louisiana: Main Pass (Block 69).....	do.....	do.....	do.....	30.6	.25	.098	2.0	10	16.0	32.3	21.3	29.6
L	California: Coalings (Nose).....	do.....	Eocene.....	do.....	30.4	.3	.260	4.2	21	23.8	28.2	19.3	27.7
M	Texas: Hastings.....	do.....	Oligocene.....	do.....	31.7	.21	.083	.7	3	21.1	36.2	22.9	19.6
N	Louisiana: South Pass (Block 27).....	do.....	Miocene.....	M2.....	24.0	.35	.103	1.8	9	3.1	33.6	18.3	44.3

	Correlation index		Cloud point, fractions 11-14, °F	Naphtha			Gas oil				Fraction 12						Fraction 14								
	Fractions 4-7	Fractions 8-15		Volume-percent			Aromatics volume percent	Paraffin-naphthenes		Volume-percent		Rings			Carbon atoms			Rings			Carbon atoms				
				Paraffins	Naphthenes	Aromatics		Volume-percent	Weight-percent		Aromatics	Paraffins-naphthenes	Total	Aromatic	Naphthene	Weight-percent			Total	Aromatic	Naphthene	Weight-percent			
									Rings	Chains						Aromatic	Naphthene	Paraffin				Aromatic	Naphthene	Paraffin	
A	10	20	45	93	1	6	9	91	10	90	11		89	1.0	0.1	0.9	6	22	72	1.9	0.0	1.9	1	43	56
B	10	23	48	83	16	1	6	94	24	76	10	90	1.1	.2	.9	5	29	66							
C	16	23	61	71	27	2	15	85	18	82	20	80	1.1	.2	.9	7	23	70							
D	18	32	39	66	29	5	16	84	22	78	22	78	1.1	.5	.6	13	22	65	1.9	.7	1.2	20	26	54	
E	22	23	49	59	34	7							1.1	.2	.9	6	26	68	1.4	.3	1.1	6	26	68	
F	28	35	42	59	31	10	22	78	27	73	26	74	1.7	.4	1.3	11	33	56	1.9	.6	1.3	16	29	55	
G	27	31	48	49	35	16	17	83	28	72	16	84	1.4	.2	1.2	7	33	60	1.8	.3	1.5	8	34	58	
H	27	28	56	57	23	20	19	81	23	77	13	87	1.2	.3	.9	9	26	65							
I	39	39	52	34	41	25	36	64	25	75	30	70	1.5	.5	1.0	16	27	57							
J	43	67	<5	26	35	39																			
K	29	38	32	38	52	10	18	82	38	62	20	80	1.5	.5	1.0	14	29	57	2.1	.6	1.5	14	35	51	
L	33	43	41	34	55	11	26	74	40	60	31	69	1.6	.6	1.0	20	30	50	1.8	.9	.9	23	24	53	
M	37	46	<5	16	77	7	22	78	50	50	16	84	1.9	.4	1.5	14	42	44	2.5	.5	2.0	13	47	40	
N	41	51	<5	0	97	3	19	81	61	39	28	72	2.2	.5	1.7	16	46	38							

1 Fraction 7 only.

TABLE 2.—Data on representative high-sulfur crude oils taken from routine analyses

Designation	Crude oil source, State or country and field	Geological data			General characteristics					Products, volume-percent			
		Era	Period	Producing horizon	°API	Weight-percent				Naphtha	Gas oil	Lube oil	Residuum
						Sulfur	Nitrogen	Carbon residue	Asphalt				
OS	Louisiana: Lisbon, W	Mesozoic	Lower Cretaceous	Pettit, Slego	28.2	1.33	0.129	0.7	3	20.9	24.2	13.1	40.3
PS	Kuwait: Burgan	do	Middle Cretaceous		31.0	2.54	.11	4.6	23	25.4	22.6	14.7	35.8
QS	New Mexico: Hobbs	Paleozoic	Permian	San Andres	37.4	1.41	.06	2.0	10	35.5	24.9	16.2	17.9
RS	Texas: Lee Harrison	do	do	Clear Fork	23.7	3.23	.04	3.6	18	26.1	23.0	15.0	35.1
TS	California: Richfield	Cenozoic	Miocene	Kraemer	22.6	1.86	.575	5.8	28	18.9	22.4	15.6	42.9
US	California: Wilmington				19.5	1.53	.662	7.3	36	11.6	21.1	16.9	49.2
VS	U.S.S.R. (Ural): Chusov	Paleozoic	Upper Carboniferous	Limestone	19.2	4.87		8.5	42	31.5	19.0	14.6	33.0

	Correlation index		Cloud point, fractions 11-14, °F	Naphtha			Gas oil			Fraction 12						Fraction 14								
	Fractions 4-7	Fractions 8-15		Volume-percent			Aromatic, volume percent	Paraffin-naphthenes		Volume-percent		Rings		Carbon atoms		Rings		Carbon atoms						
				Paraffins	Naphthenes	Aromatics		Volume-percent	Weight-percent		Aromatics	Paraffins-naphthenes	Total	Aromatic	Naphthene	Weight-percent			Total	Aromatic	Naphthene	Weight-percent		
									Rings	Chains						Aromatic	Naphthene	Paraffin				Aromatic	Naphthene	Paraffin
OS	10	24	41	81	17	2	11	89	20	80	19	81	1.1	0.4	0.7	11	22	67	1.7	0.5	1.2	15	26	59
PS	18	35	39	77	15	8	21	79	22	78	30	70	1.4	.5	.9	16	25	59	2.3	.7	1.6	19	29	52
QS	27	45	32	54	40	6	27	73	36	64	37	63	1.8	.6	1.2	16	27	57	2.4	.7	1.7	22	36	42
RS	34	50	46	50	24	26	42	58	27	73	57	43	1.9	.7	1.2	26	33	41	2.4	1.1	1.3	29	30	41
TS	31	45	29	30	61	9	23	77	45	55	27	73	1.7	.6	1.1	18	34	48	2.5	.7	1.8	22	36	42
US	33	51	<5	22	72	6	23	77	57	43	28	72	2.0	.6	1.4	17	36	47						
VS	46	70	44	30	24	46					54	46												

¹ For kerosine instead of fraction 12.

CRITERIA FOR SELECTION OF OILS

The following data were used in selecting these oils:

1. Volume-percent paraffins, naphthenes, and aromatics in the naphtha or the distillate obtained to a cut temperature of 200° C. The data necessary for these calculations are given in all recent Bureau of Mines crude oil analyses, but are not available generally for those oils analyzed before 1950. The analytical data used are volume-percent distillate, specific gravity, and refractive index for the sodium D and mercury g lines. The method of calculating the volume-percent of the three types of hydrocarbons is described by Smith and Hale (169). The compilation has been simplified by the use of computer calculated tables.

2. Volume-percent of aromatics of fraction 12, boiling between 200° and 225° C at 40 mm Hg pressure, calculated as previously described.

3. The average correlation index (unweighted) of fractions 4-7, as representative of the naphtha, and fractions 8-15 as representative of the gas oil and lubricating oil fractions. The correlation index is obtained from tables according to the equations in reference 166.

4. Average cloud point of fractions 11-14.

5. Weight-percent asphalt estimated by multiplying the Conradson residue value of the crude oil by 4.9.

6. Other data taken directly from the analysis report.

Complete analyses are given in the appendix.

In addition the following data are included:

1. Total aromatic and naphthenic rings per molecule for fractions 12 and 14. These are calculated from refractive index, density, and molecular weight data using the *n-d-M* method developed by Van Nes and Van Weston (192).

2. Weight-percent aromatic, naphthenic, and paraffinic carbon atoms per molecule for fractions 12 and 14. Refractivity intercept, density, and molecular weights are used according to a method developed by Kurtz, King, Stout, and Peterkin (106).

Relationships of General Characteristics for Each Oil

The following are considered as general characteristics pertaining to the whole oil: Volume-percent distillates and residuum; weight-percent sulfur, nitrogen, carbon residue, and asphalt; cloud point; and gravity in degrees API. The values for these characteristics are listed in tables 1 and 2 and their variations and interrelationships are discussed as follows.

The data for each oil are plotted (figs. 3 and 12) and distinct trends in most all properties

can be discerned. In general these can be related to chemical composition. Unfortunately, Bureau routine analyses do not provide the data needed to delineate more clearly the composition of gas oil and lubricating oil distillates and the residuum. The data in tables 1 and 2 are presented essentially in increasing order of cyclization of the oil, starting with the most paraffinic and ending with the least paraffinic. Because both aromatics and naphthenes contribute to cyclic hydrocarbons, some anomalies occur. For the high-sulfur oils the same general system is used.

Volume-Percent of Distillates and Residuum

The distillates considered are naphtha (defined in this report as the sum of fractions 1-7); gas oil (the sum of fractions 8-12); lubricating distillate (the sum of fractions 13-15); residuum, or the material remaining after the distillation is completed. The data used are the volume-percents for these portions of the crude oil, as shown in figure 3.

Naphthas

The variation shown in naphtha content ranges from about 3 percent to 47 percent; however, even greater extremes can be found from oils that do not contain any naphthas to those that contain 60 percent or more. Often these latter oils are considered as "distillates" or "condensates" by the industry and their designation depends upon legal definitions, because there is no clearly defined dividing point based on properties between ordinary crude oil and condensates. In 1952 the author published an extensive review of U.S. crude oils (164) and in another report (165) extended the presentation to include a number of Middle East, South American, and Canadian crude oils. It is believed that the general characteristics of crude oils from most sections of the oil-producing areas have not changed materially, although a number of new areas not covered by these reports have come into production. On this basis the figures used in the older reports represent the general distribution pattern for the United States; thus figure 4 shows the distribution of naphtha content in the U.S. crude oils.

Oils A, B, and F have the highest content of naphtha of the oils being considered, and of these oils A and F are of Cambro-Ordovician or Ordovician age, generally regarded as the oldest producing formations known, and oil B is of Siluro-Devonian age, probably representing the next oldest producing rocks. This tendency for the oils from the oldest producing formations to have a greater content of naphtha is generally acknowledged (127).

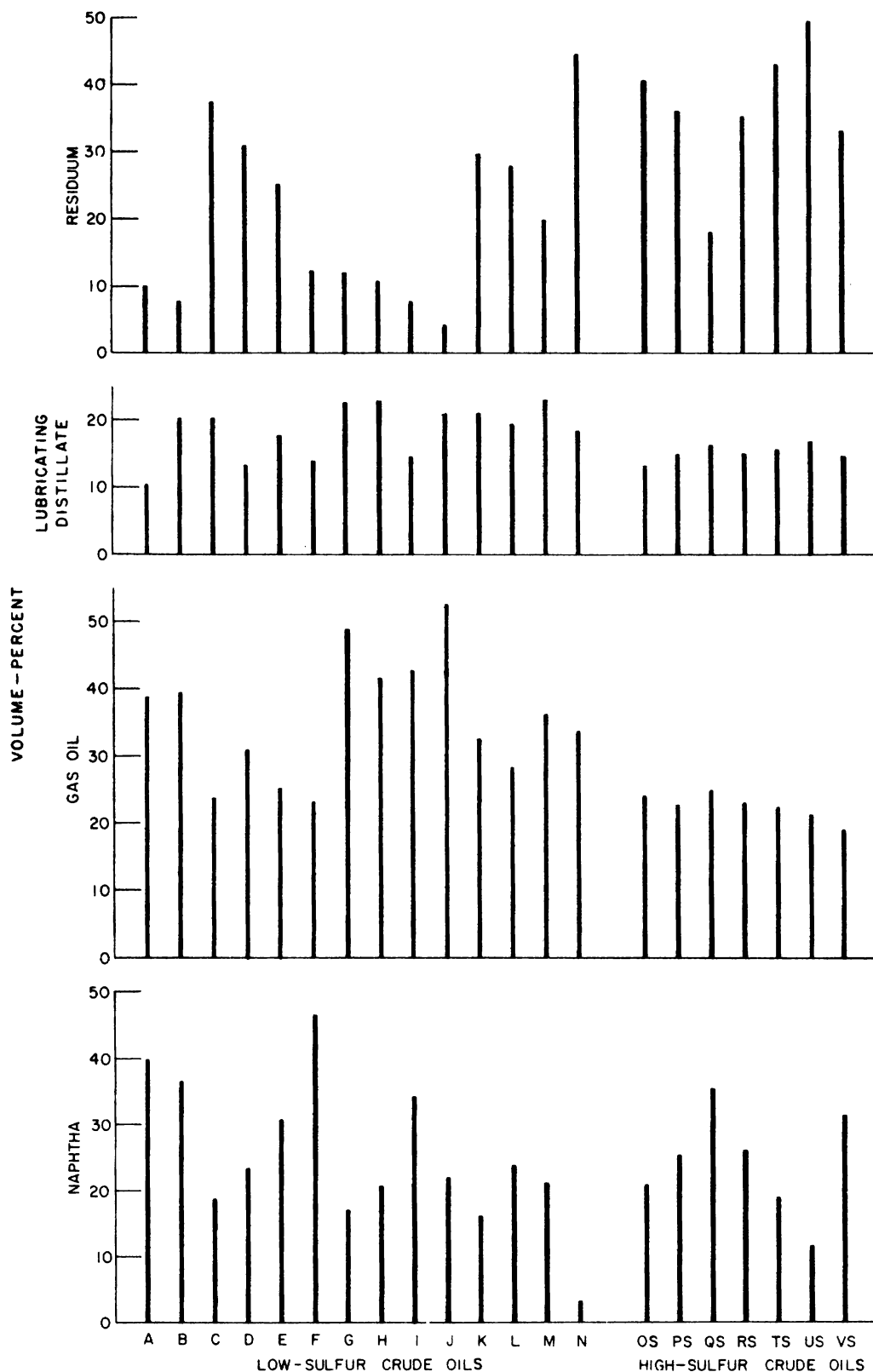


FIGURE 3.—Volume-Percent Distillates and Residuum for Low- and High-Sulfur-Content Crude Oils.

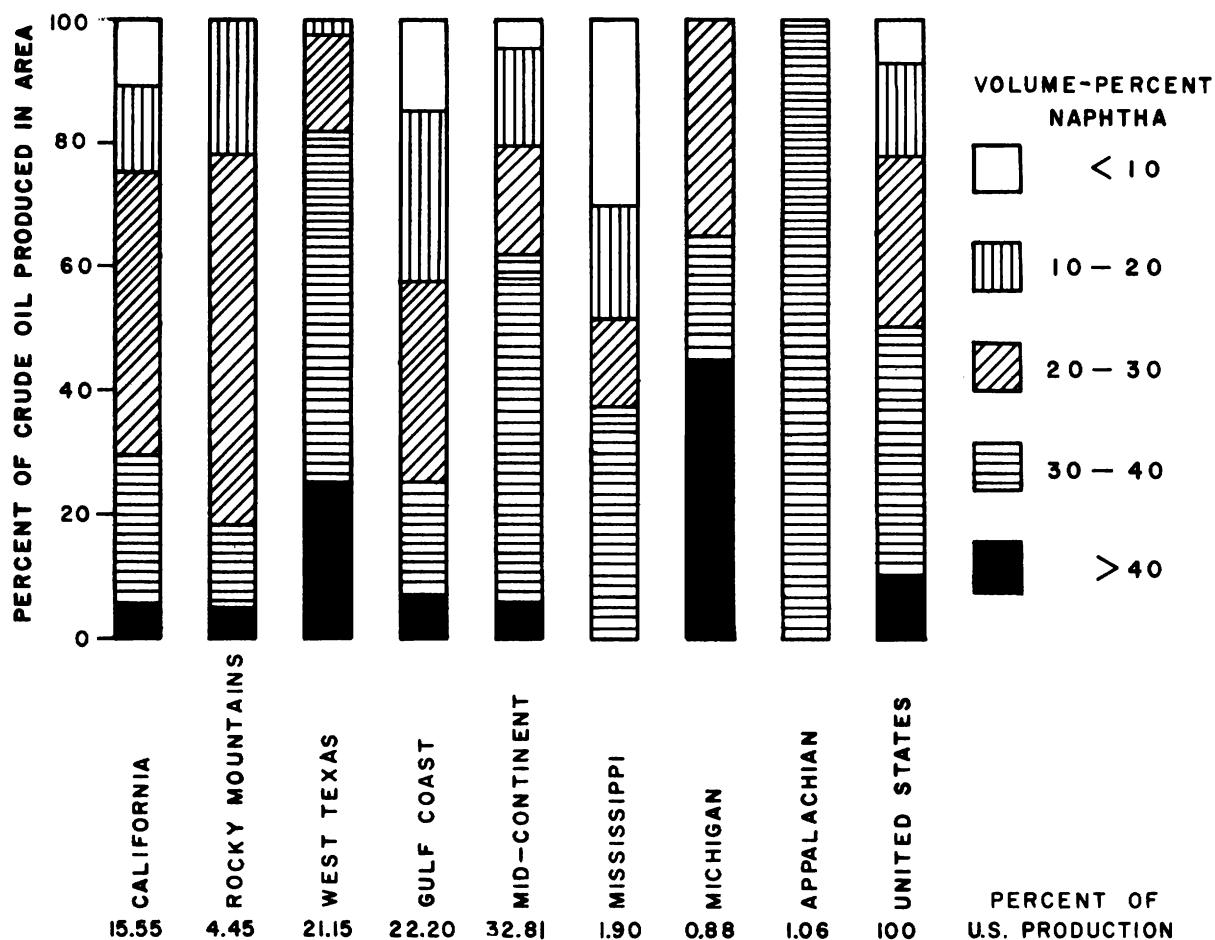


FIGURE 4.—Distribution of Naphtha in Crude Oils in the United States.

Biederman (14) has recently made an interesting analysis of the data reported by Martin and others (137) that presents substantial evidence of the maturing of crude oil as a result of both age and depth of burial. Bureau crude oil analyses can be used for this purpose also. In figure 5 panels A and B represent the distribution of the naphtha content for 2,804 post-Paleozoic oils and 3,640 Paleozoic oils portrayed as percent of samples in each geologic period according to content of naphtha. The histograms illustrate clearly that (1) the post-Paleozoic oils do not as a group attain well defined distribution curves, (2) the Tertiary oils show slightly saw-toothed distribution averaging about 11 percent in the range from 15 to 45 percent naphtha, (3) Cretaceous and Jurassic oils show maxima at 30-35 percent, with continuing contributions above this range, and (4) the Triassic oil data are erratic, presumably because of the small number. The Paleozoic oils in panel B all form well defined distribution curves with maxima at 35-40 percent. There appears to be some tendency for the oils from the older rocks to give more symmetrical

groups, with less concentration in the low naphtha content area. The author interprets this to indicate an approach to an equilibrium that would be represented by a gaussian distribution.

To emphasize the effect of depth of burial, a distribution analysis of the oils considered was made as follows:

- a —Oils from Paleozoic rocks (Permian, Pennsylvanian, Mississippian, Siluro-Devonian and Ordovician-Cambro-Ordovician);
- b —Oils from post-Paleozoic rocks (Tertiary, Cretaceous, Jurassic, Triassic).

Subgroupings of each were made as follows:

- (1) Oils produced from rocks 2,000 feet or less deep, and
- (2) Oils produced from rocks 10,000 feet or more deep.

In considering these depths of burial it should be recognized that present depths do not cover the complete geological history of the oil. It may have been accumulated at great depths and remained thus for many millions of years, and only comparatively

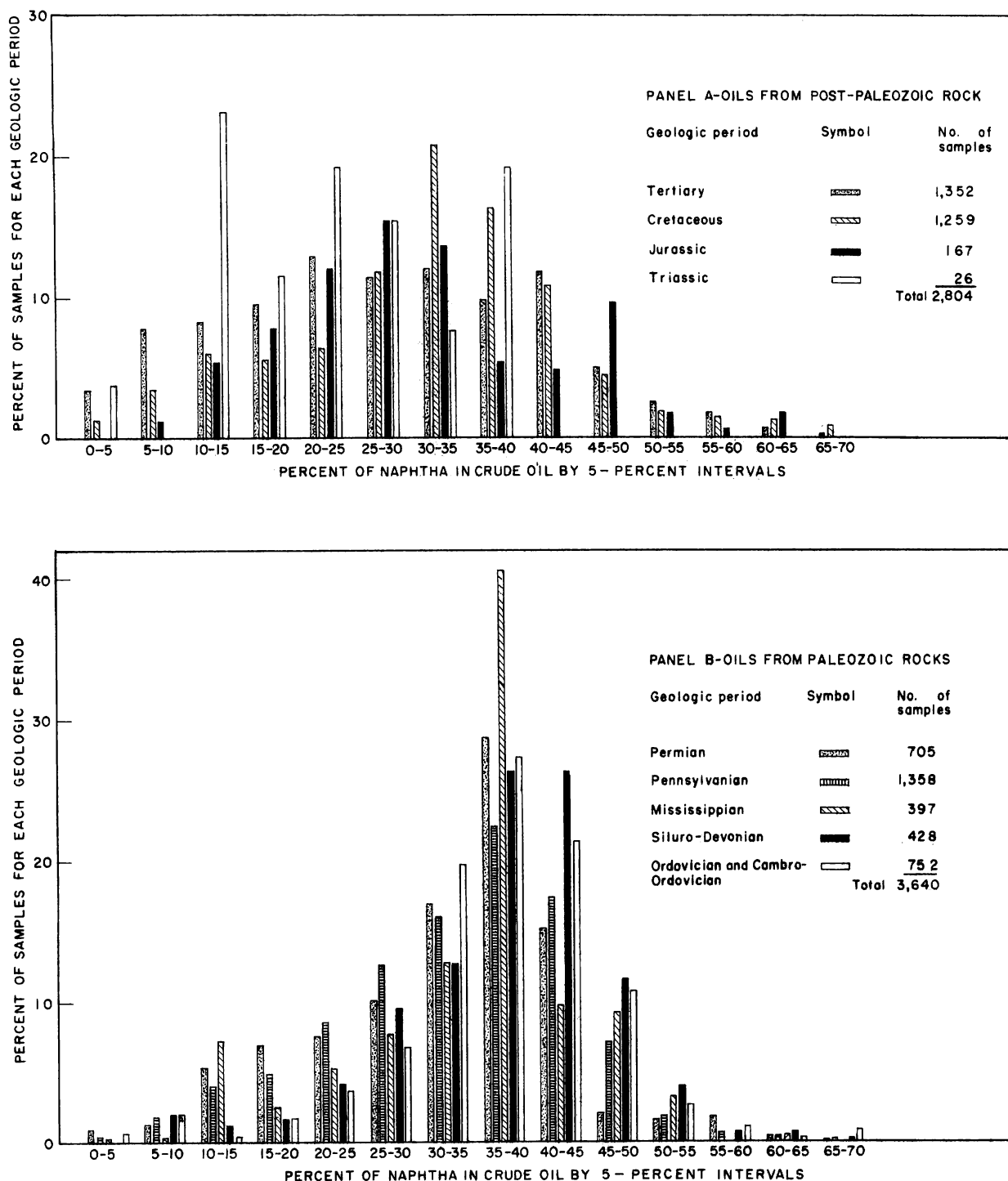


FIGURE 5.—Distribution of Naphtha Content of Crude Oil by Geological Period.

recently attained a shallow depth because of geological action. This is especially pertinent to Paleozoic rocks now found at 2,000 feet or less. The data for the Paleozoic oils are shown in figure 6 and for post-Paleozoic oils in figure 7. In panel A of figure 6 the oils from 2,000

feet or less do not as a group form the more normal distribution histogram shown in panel B. However, there are maxima that shift to the right with increase in age. Thus the Permian oils have a maximum at 20-25 percent, the Pennsylvanian oils also have a maximum at

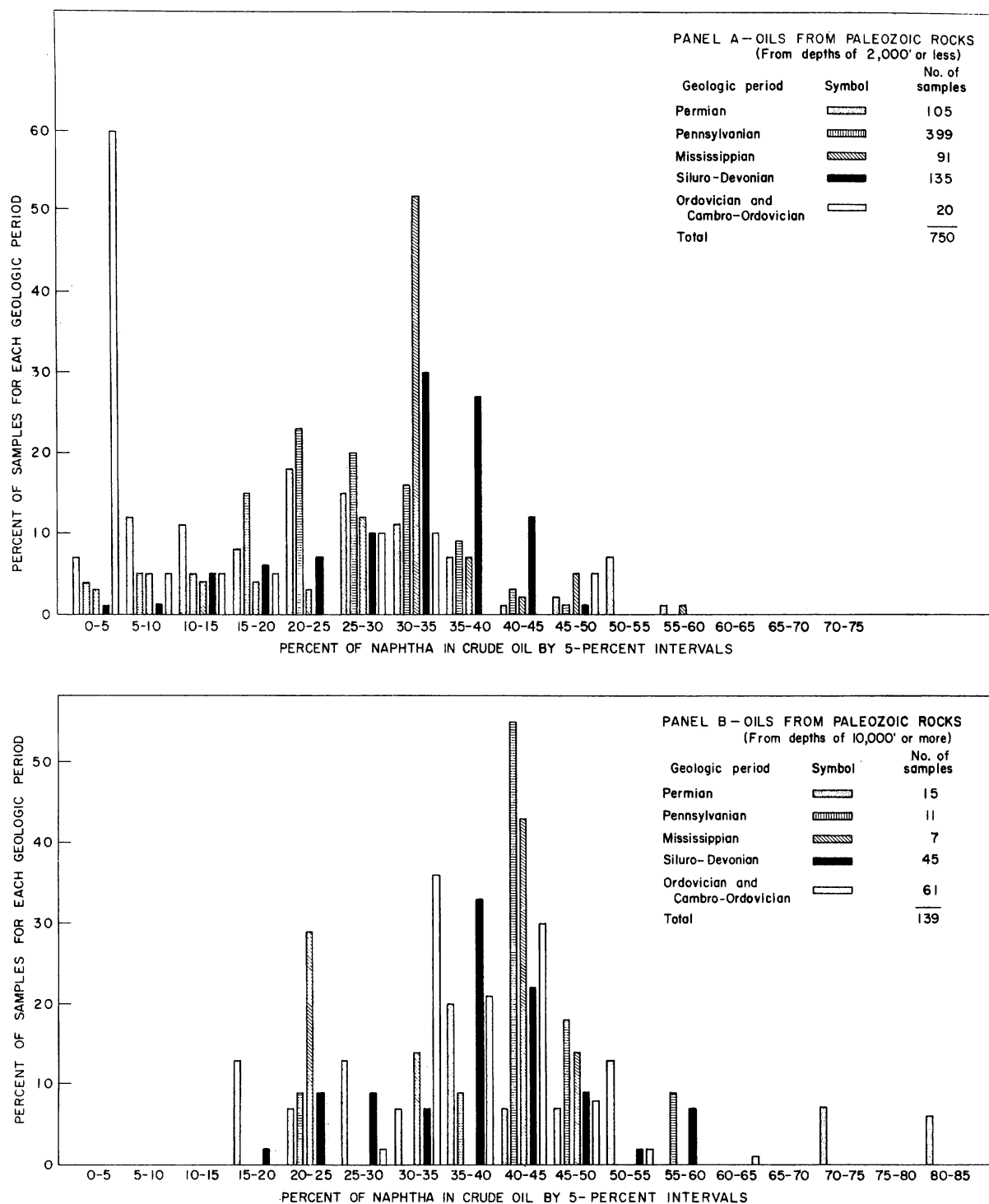


FIGURE 6.—Distribution of Naphtha Content of Crude Oil According to Depth of Burial in Paleozoic Rocks.

this same range, but are skewed toward the high content side. The Mississippian oils have a definite maximum at 20-25 percent, and the Siluro-Devonian oils have a maximum at 30-35 percent and are also skewed toward the high side. The few Ordovician oils, discounting those in the 0-5 percent range, are mostly in the 25-30 and 30-35 percent ranges. In contrast the oils from 10,000 feet or more shown in panel B show a definite maximum at 40 to 45 percent, and a distribution pattern only a little skewed to the low content side. It is of interest geologically that the high peak for Mississippian oils (panel A) at 30-35 percent naphtha is formed exclusively by oils from

four contiguous counties in Illinois, another group of seven almost contiguous counties in Illinois, Indiana, and Kentucky, and one stray Illinois county. The Ordovician oils with 0-5 percent naphtha (panel A) are from the Arbuckle Limestone in Montgomery and Labette Counties, Kans. and three separate counties in Oklahoma. It seems probable that these Kansas oils have been subject to "weathering" of some form. The geology of these Kansas oils is discussed by Neumann and others (144).

In panel A of figure 7 the data for oils from post-Paleozoic rocks 2,000 feet or less are presented. The large percentage of those oils having naphtha contents of 15 percent or

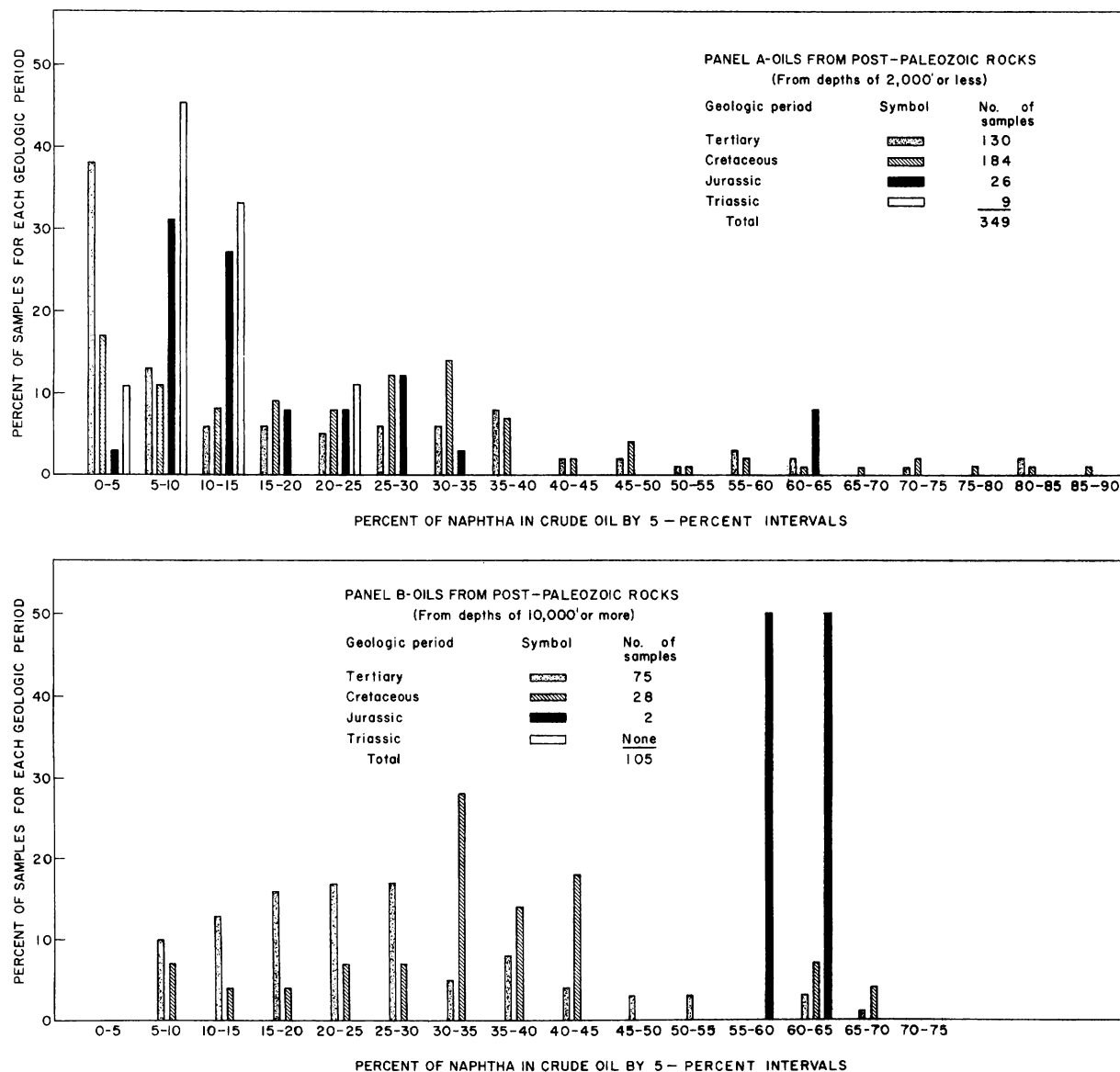


FIGURE 7.—Distribution of Naphtha Content of Crude Oil According to Depth of Burial in Post-Paleozoic Rocks.

below is marked. In contrast the data for oils from 10,000 feet or more shown in panel B show a distribution pattern with a maxima at 30 to 35 percent (excluding two Cretaceous oils that are essentially condensates). Although the distribution is still somewhat weighted on the low content side of the maximum the approach to a normal distribution curve is very apparent. These data, together with those of Phillipi (148) and of Biederman (14), make a rather strong case for the effect of age and depth of burial.

Many so-called naphthenic oils as found in the Gulf Coast area or in California have a low content of naphtha relative to oils from the Mid-Continent area. In general this seems to be because the paraffinic naphtha components are present in only small quantities. Sulfur content is sometimes associated with a small content of naphtha, but the author believes this is because sulfur became combined with a low-naphtha-content precursor of the oil, often or generally naphthenic, at some time during the genesis and accumulation of

the oil as we find it now. There are too many high-sulfur crude oils with considerable quantities of naphtha to establish a generality that sulfur content *per se* is consonant with a low-naphtha content. Oils TS and US are examples of high-sulfur, low-naphtha "naphthenic" crude oils relatively devoid of light paraffins; whereas oils PS, QS, and RS are examples of high-sulfur, high-naphtha-content crude oils, all of which contain a considerable quantity of paraffins in the naphtha.

Gas Oils

The content of gas oils generally shows less variation than does naphtha content, as the data (164) in figure 8 indicate. Oils G, H, I, K, M, and N are Gulf Coast petroleum that often contain more gas oil than do crude oils from other areas. This can be clearly seen in figure 8 and from table 1. The gas oil from oil I from Conroe has a high content of aromatics, whereas the others are primarily naphthenic. The gas oil contents of the high-sulfur oils are rather uniform at about 22 percent.

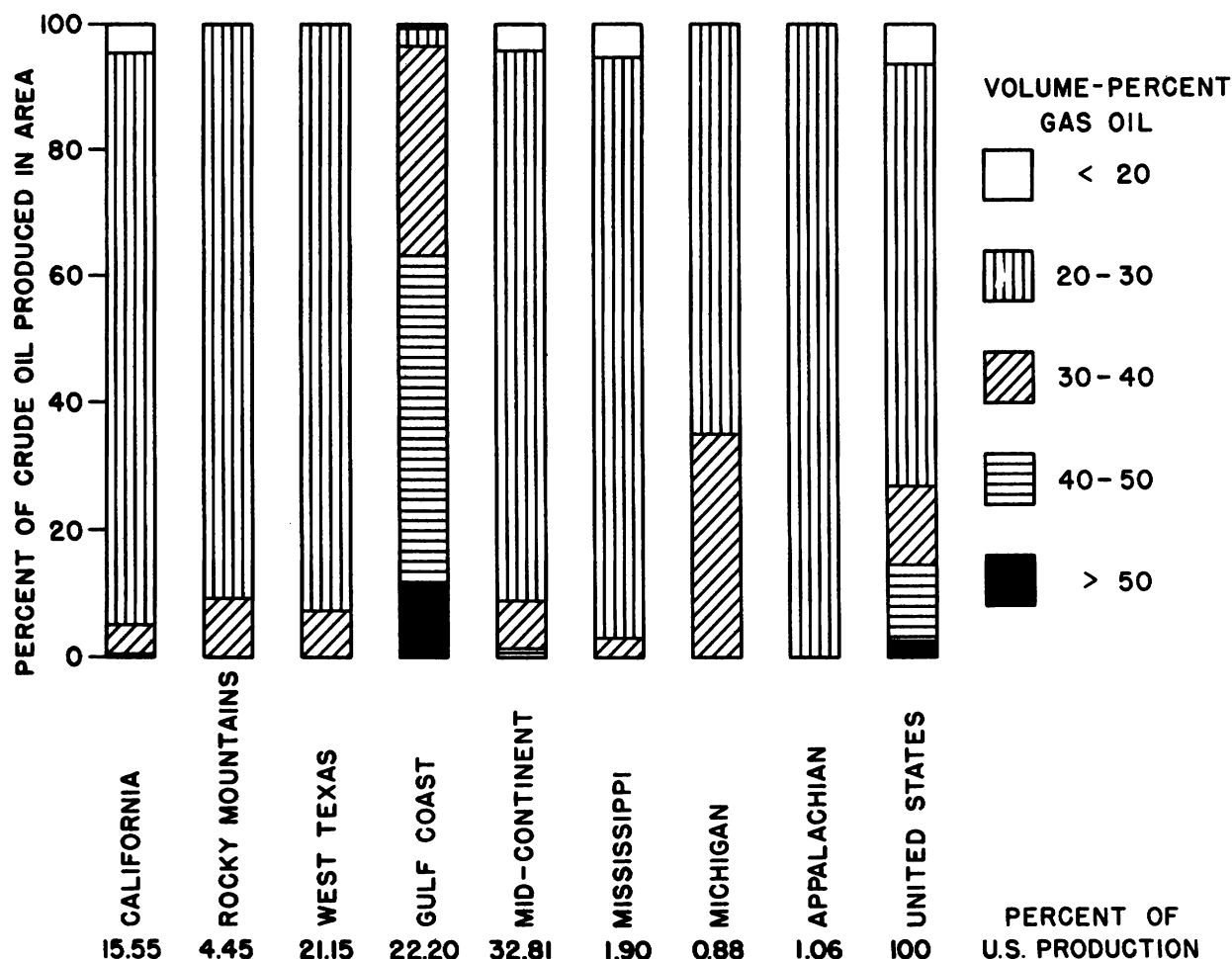


FIGURE 8.—Distribution of Gas Oil in Crude Oils of the United States.

A distribution analysis similar to that made for the naphthas was carried out for the gas oils and the data are shown in figure 9 for the effect of age. The results are the converse of those for the naphthas, as should be the situation if there is a long time effect of age. Panel A shows the distribution for the oils from post-Paleozoic rocks. The peak is in the range 25–30 percent, but the significant part is the weighting on the high content side of the maximum,

especially noticeable for Tertiary oils. Panel B showing data for oils from Paleozoic rocks is exceptionally restricted in range, the peak is at 25–30 percent, the next highest grouping is at 20–25 percent, and a third noticeable grouping at 30–35 percent—on either side of these there are very few oils. This is the most clearly restricted range of any of the naphtha or gas oil distribution histograms.

In figures 10 and 11 the same categories of

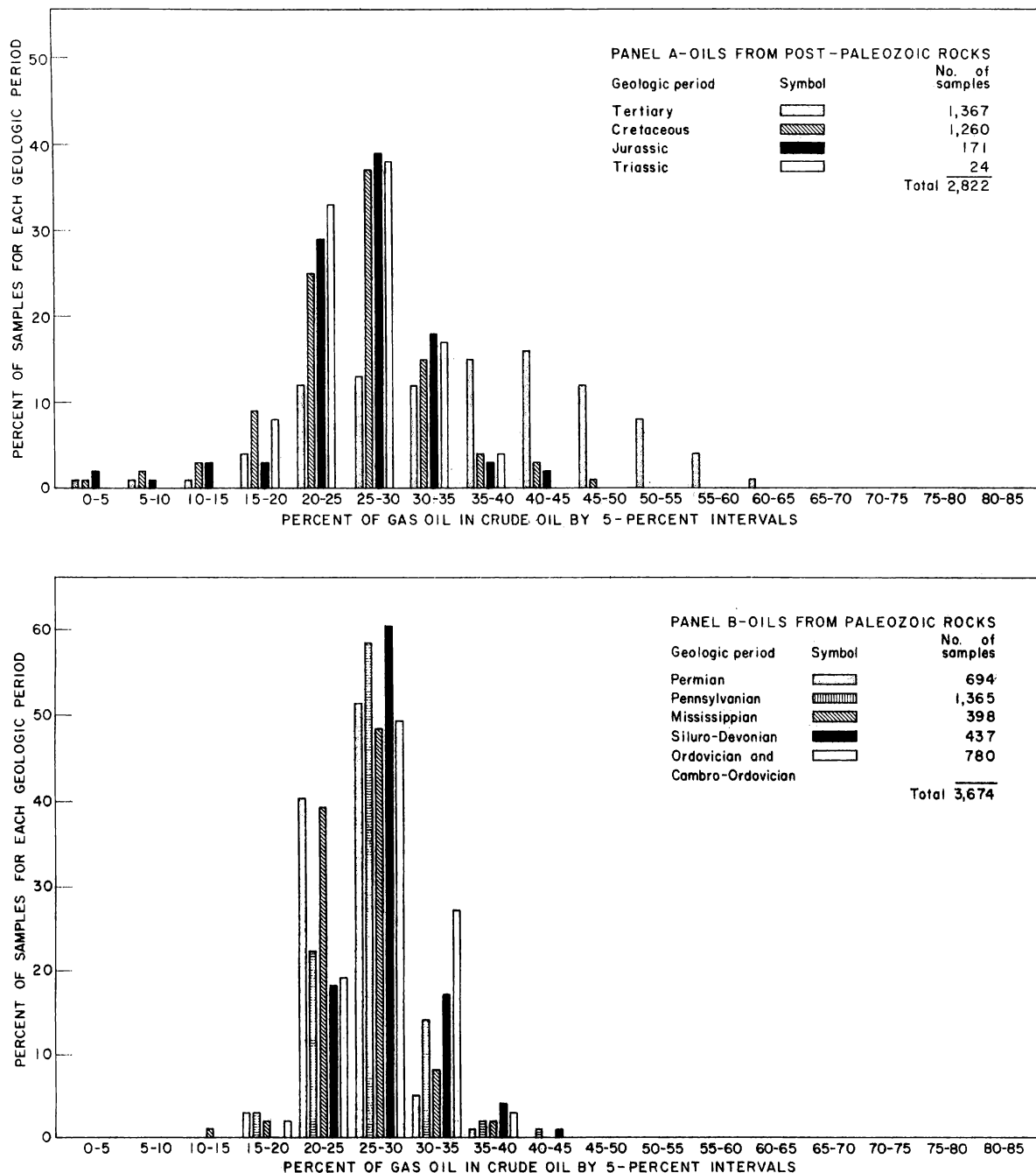


FIGURE 9.—Distribution of Gas Oil Content of Crude Oil by Geologic Period.

data are used to show the effects of depth of burial as were used for the naphtha content. The distribution graph in panel A of figure 10 for post-Paleozoic oils from 2,000 feet or less has a significantly greater proportion in the range above the maximum compared with similar data for oils from 10,000 feet or more in

panel B. The effect of depth of burial for Paleozoic oils shown in figure 11 is not clear. In fact there appears to be somewhat of a reversal in that the oils from 10,000 feet or more are weighted slightly on the high side. The high for the Ordovician oils at 30-35 percent is due exclusively to Ellenburger oils of the Permian

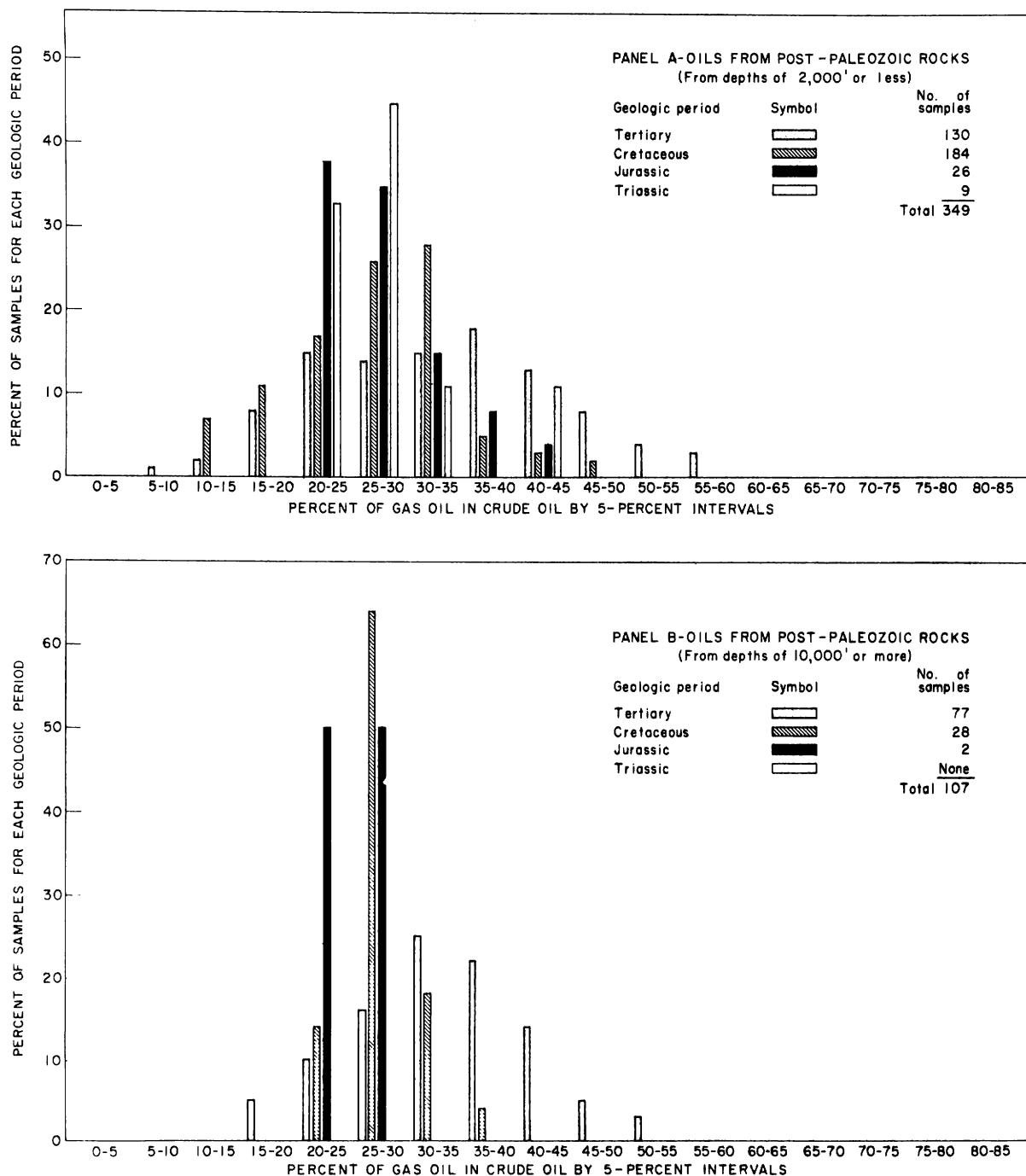


FIGURE 10.—Distribution of Gas Oil Content of Crude Oil According to Depth of Burial in Post-Paleozoic Rocks.

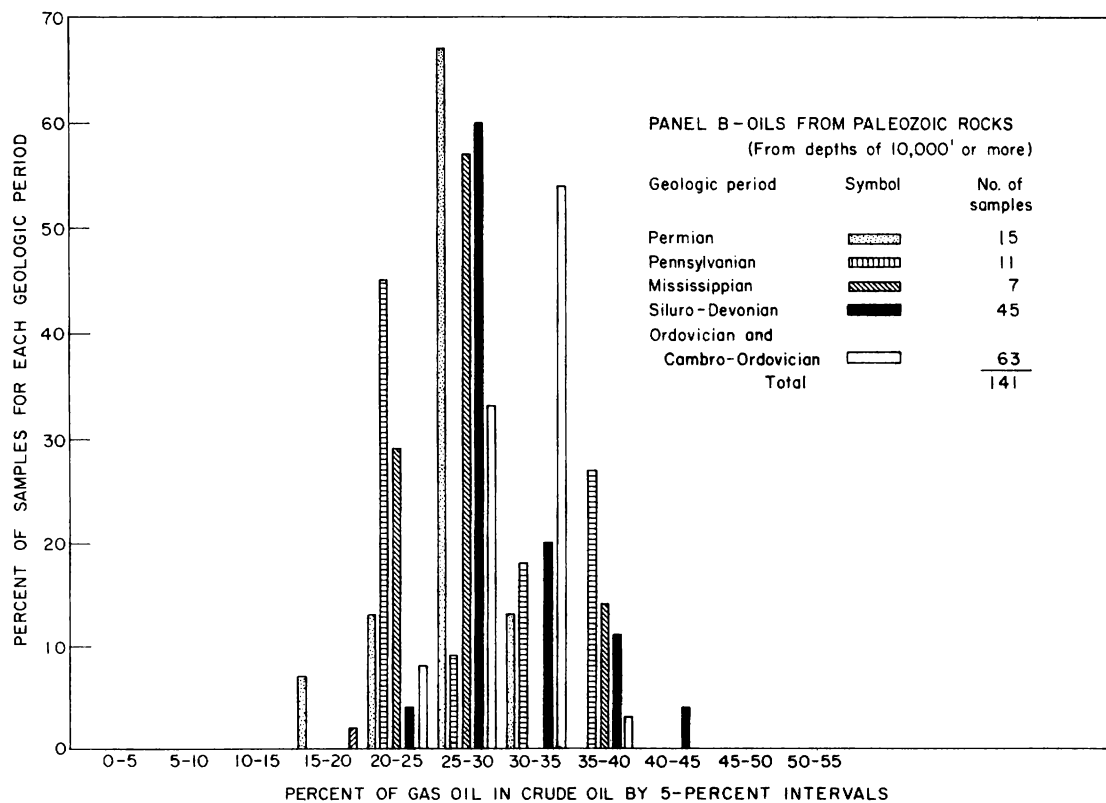
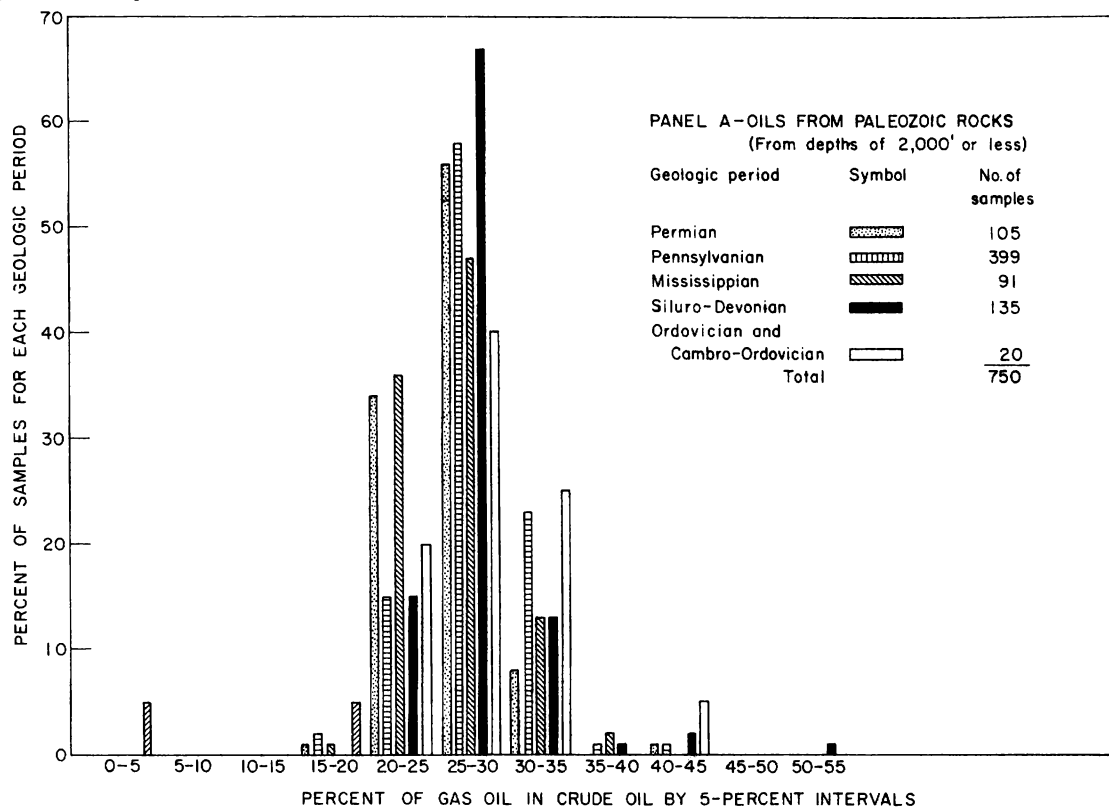


FIGURE 11.—Distribution of Gas Oil Content of Crude Oil According to Depth of Burial in Paleozoic Rocks.

Basin in West Texas and New Mexico. The similarity in distribution in panels A and B is evident, indicating that almost all oils from Paleozoic rocks fit this distribution pattern.

Lubricating Distillates

Theoretically it should be possible to treat the lubricating distillates similarly to the lighter distillates. However, in the case of the Bureau of Mines analyses these distillates are obtained under conditions that often lead to cracking for the final one or two fractions. Sometimes the distillation is actually stopped because of this before the final desired temperature is reached. Thus considerable uncertainty is introduced into the volume-percent of these fractions, and it seems doubtful if the data are dependable enough to use statistically. As a corollary the residua must also be placed in the unusable category statistically.

There is also another factor with regard to the larger molecules. They can lose one or more alkyl radicals, for example, without greatly affecting their volume as ordinarily measured. But these same alkyl radicals on hydrogenation or polymerization to a lighter hydrocarbon become immediately measurable. The percentage of lubricating distillates from high-sulfur oils are consistently slightly lower than the corresponding distillates from low-sulfur oils.

Residua

As noted previously there is considerable variation in the quantity of residuum of crude oils as obtained even by a standardized distillation procedure. In addition to distillation problems this would be expected because its constituents include such materials as resins; asphaltene; compounds with sulfur, nitrogen, and oxygen; heavy high-boiling hydrocarbons; and metallo-organic compounds. Some of these are thermally unstable, some are polar compounds and may react with the environment of the oil both in its early stages of formation and in its final accumulation, and there are probably interactions continually taking place. By reference to figure 12 and the panels on sulfur, nitrogen,

carbon residue, and asphalt some relationships can be pointed out. Table 3 presents data showing interrelationships of the content of residuum, nitrogen, sulfur, and asphalt among the low-sulfur oils.

A study of this table leads to the following conclusions:

1. The relatively high sulfur content of oil B appears to have caused no appreciable effect and one might conclude that most of the sulfur compounds are fairly volatile.

2. The high residuum and the asphalt content of oil C appears to be primarily caused by nitrogen.

3. The high residuum and high asphalt content of oil D seems related primarily to sulfur.

4. The residuum of oil E appears to consist of high-boiling hydrocarbons rather than asphaltic material—it seems doubtful if either nitrogen or sulfur had any appreciable effect.

5. The effect of sulfur and nitrogen for oil K seems to be similar to that for oil C, with not as much effect from sulfur as might be expected.

6. Comparison of oil L with oils B and K indicates that nitrogen may have played a prominent role in oil L.

7. In oil M one could assume that sulfur and nitrogen have been influential in forming high-boiling oils, but reactions have not proceeded to the asphalt stage to the extent they have in oil K.

8. Oil N seems to be similar to oil M, but with less effect of sulfur. The author realizes that these conclusions are predicated on an assumption that the original complex organic source material can change in two directions—toward a lighter product and through high-boiling oils to resinous (so-called) compounds to asphaltic material. In the course of this diagenesis nitrogen, sulfur, and probably oxygen play a part in determining the characteristics and quantity of the residuum and asphalt. How, we can only surmise at the moment. These data suggest that evidence for effects of sulfur and nitrogen are more easily discerned when their values are relatively low.

TABLE 3.—Data showing interrelationships of content of residuum, nitrogen, sulfur, and asphalt, weight-percent

Property	Oil designation							
	B	C	D	E	K	L	M	N
Residuum.....	7.6	37.3	30.7	25.0	29.6	27.7	19.6	44.3
Nitrogen.....	.008	.13	.102	.010	.098	.280	.083	.103
Sulfur.....	.34	.10	.45	.11	.25	.30	.21	.35
Asphalt.....	1.0	7.0	17.0	2.0	10.0	21.0	3.0	9.0

Similar data on the high-sulfur oils are more difficult to interpret because the extent of reaction is so great. However, of the oils in which the nitrogen content is known, the asphalt and residuum values are highest when the nitrogen values are high. Oil PS seems to be more appreciably affected by the sulfur content, and oil OS seems to be a resultant of both nitrogen and sulfur content in pro-

ducing a heavy oil with relatively small asphalt content, similar in this respect to oil E.

Sulfur

The sulfur contents of the 14 low-sulfur oils and the 7 high-sulfur oils are shown in panel D of figure 12. As stated previously the low-sulfur oils contain 0.50 percent sulfur or less, and the

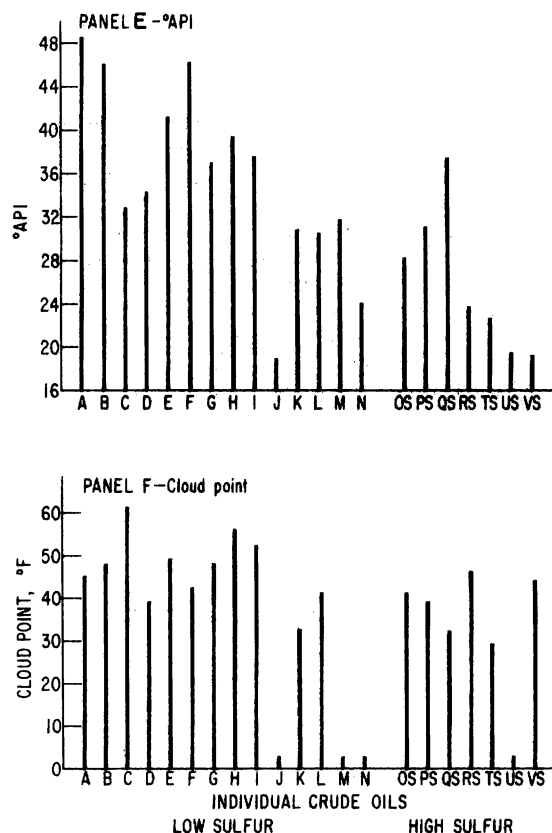
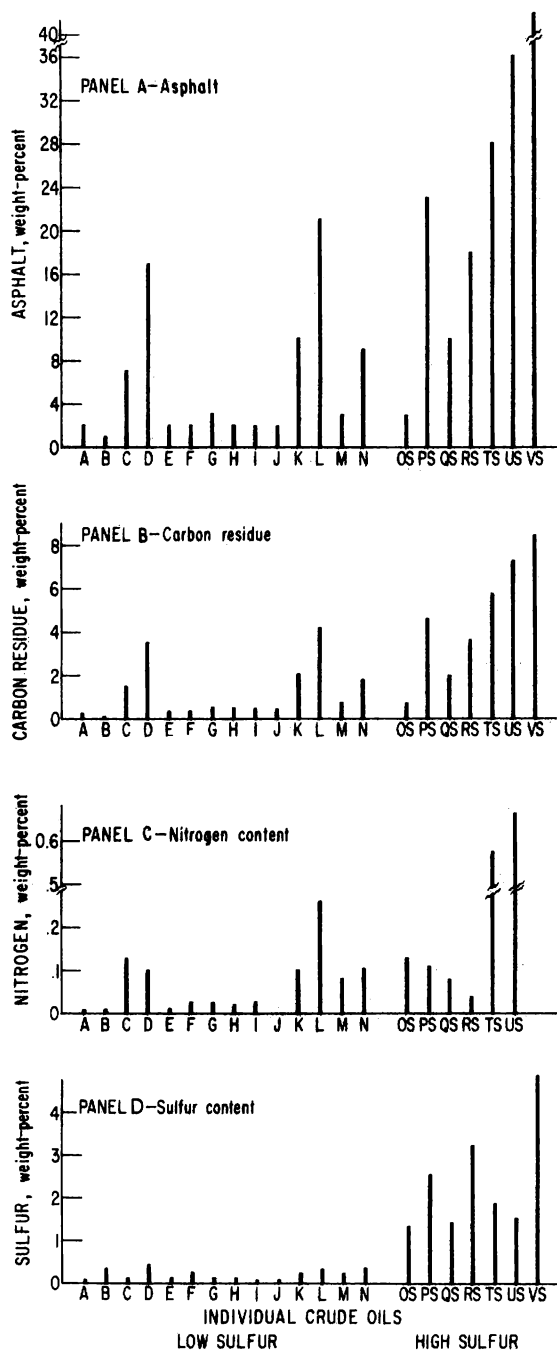


FIGURE 12.—Some Properties of Low- and High-Sulfur Crude Oils.

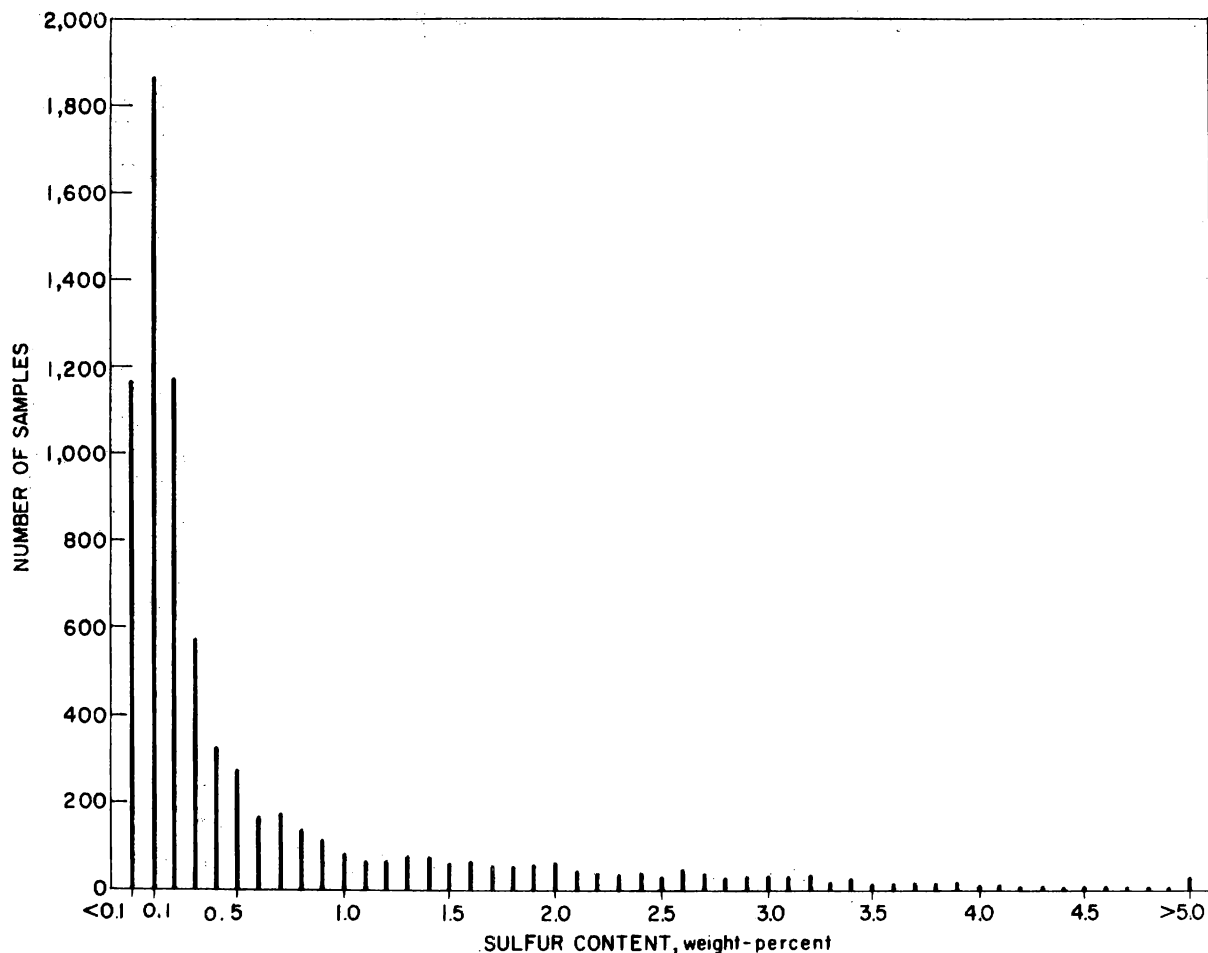


FIGURE 13.—Frequency Distribution of Sulfur Content of Crude Oils (7,273 Samples).

high-sulfur oils, 1.35 percent or more. Of course there are many petroleum having sulfur contents between 0.50 and 1.35 percent, but the two ranges shown are sufficient for illustrative purposes. The relationships of sulfur content and such properties as asphalt, residuum, and nitrogen have been pointed out in the discussion on residuum. Even API gravity (panel E) does not appear to be directly correlated with sulfur content. Figure 13 shows the frequency distribution of the sulfur content of 7,273 crude oils. This represents the occurrence, not the weighted quantity, of crude oils of different sulfur contents. Thus crude oils with a sulfur content of 0.10 to 0.20 percent are most common; there is a fairly high proportion with <0.10 percent; the occurrence of oils having >0.50 percent is relatively small. This would not be true on a production and reserve basis—one has only to consider the average sulfur content of fields in the Middle East (1.6 percent), Venezuela (1.1 percent), Colombia (0.9 percent), and Wets Texas Permian (1.6 percent), where there are

large reserves and large quantities of oil have been produced, to see that the distribution pattern on such a basis would probably show at least two maxima at about 1.0 and 1.6 percent sulfur.

The distribution of sulfur in crude oils is both important and interesting. In the majority of oils probably 75 percent or more of the sulfur will be found in the residual material left after removing the distillate through the lubricating oils. Thus the sulfur is usually a significant contributor to residual material, even though it seems to be less intimately related to quantity than is nitrogen. The types of sulfur compounds found in naphthas and gas oils will be discussed later.

Nitrogen

The nitrogen contents of the illustrative crude oils are shown in panel C of figure 12. The relationships of the nitrogen content to several other properties have been discussed as part of the residuum picture. There also appears to be

some correlation with API gravity, as would be expected because the nitrogen content of crude oil is definitely associated with the heavy ends—Ball (9) has postulated a relationship with the carbon residue of crude oil, which in turn is a rough measure of the asphalt content. Nitrogen content has been determined routinely by the Bureau only during the past few years, so that relatively few samples are available for distribution studies. The data presented in figure 14 are

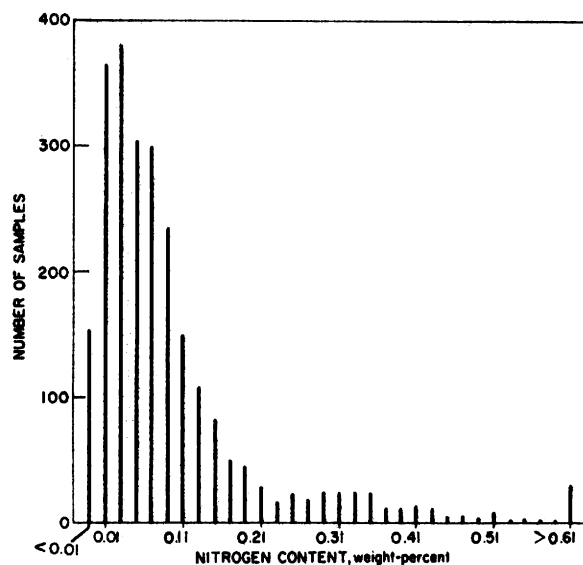


FIGURE 14.—Frequency Distribution of Nitrogen Content of Crude Oils (2,465 Samples).

based on 2,465 oils. The distribution graph shows that about 2 percent of the oils have a nitrogen content of <0.01 percent; 60 percent have between 0.01 and 0.09 percent; another 20 percent are between 0.09 and 0.15 percent; and the remaining 18 percent are above 0.15 to a maximum above 0.70 percent. Because nitrogen is associated with the heavy ends of crude oil, those oils having large contents of resins and asphalts would be expected to have the largest nitrogen contents. This is exemplified in California crude oils which in general have the highest content of nitrogen and also of asphaltic components. Many other asphalt-containing oils in Mississippi, Arkansas, and Wyoming fit this rule, but there are exceptions both ways; that is, asphaltic oils with low content of nitrogen, and relatively low-asphaltic-content oils with high contents of both nitrogen and sulfur.

Carbon Residue

Carbon residue values for the selected crude oils are shown in panel B of figure 12. Carbon residue is the material left after heating an oil

under carefully prescribed conditions as described by ASTM Method for Conradson Carbon Residue of Petroleum Products, D 189-64 (4) or ASTM Method for Ramsbottom Carbon Residue of Petroleum Products, D 524-64 (5). When the latter method is used for Bureau routine crude oil analysis the results are corrected to Conradson values. As mentioned previously, carbon residue correlates to some degree with the nitrogen content, to a somewhat lesser degree with the sulfur content, and quite nicely with the asphalt content. By multiplying the carbon residue value by 4.9 an approximation of 100-penetration asphalt yield can be obtained, based on work reported by Stanfield and Hubbard (173). Distribution of carbon residues for U.S. petroleum is shown in figure 15. The graph resembles the sulfur and nitrogen

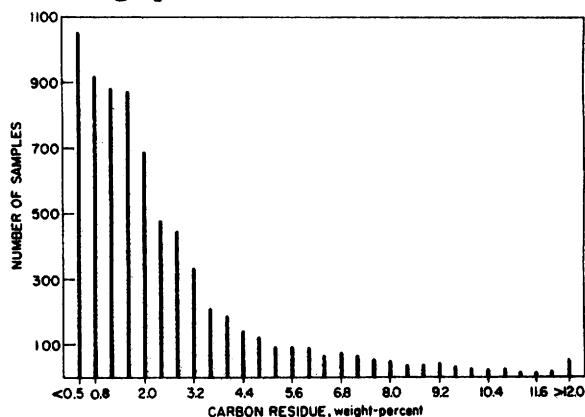


FIGURE 15.—Frequency Distribution of Carbon Residue of Crude Oils (7,228 Samples).

distribution graphs as might be expected. It does not resemble the degrees API distribution presumably because there are so many factors such as gasoline content and hydrocarbon type that affect gravity but do not enter directly into carbon residue values.

Asphalt

The asphalt content is a calculated figure, as referenced. Ball (8) has arrived at virtually the same figures by another calculation and presents asphalt contents of a number of crude oils, as well as other related properties. The relationship of the asphalt contents to sulfur and nitrogen has been discussed. The correlation of these data with degrees API is not without exceptions. For example, oils D and L have the highest asphalt contents of the low-sulfur group, and one might expect a lower API gravity than is found. Oil J has a low API gravity because of its aromatic nature. Oil OS might be expected to have a higher API gravity on the basis of its low asphalt content. The distribution of the asphalt content of 6,903

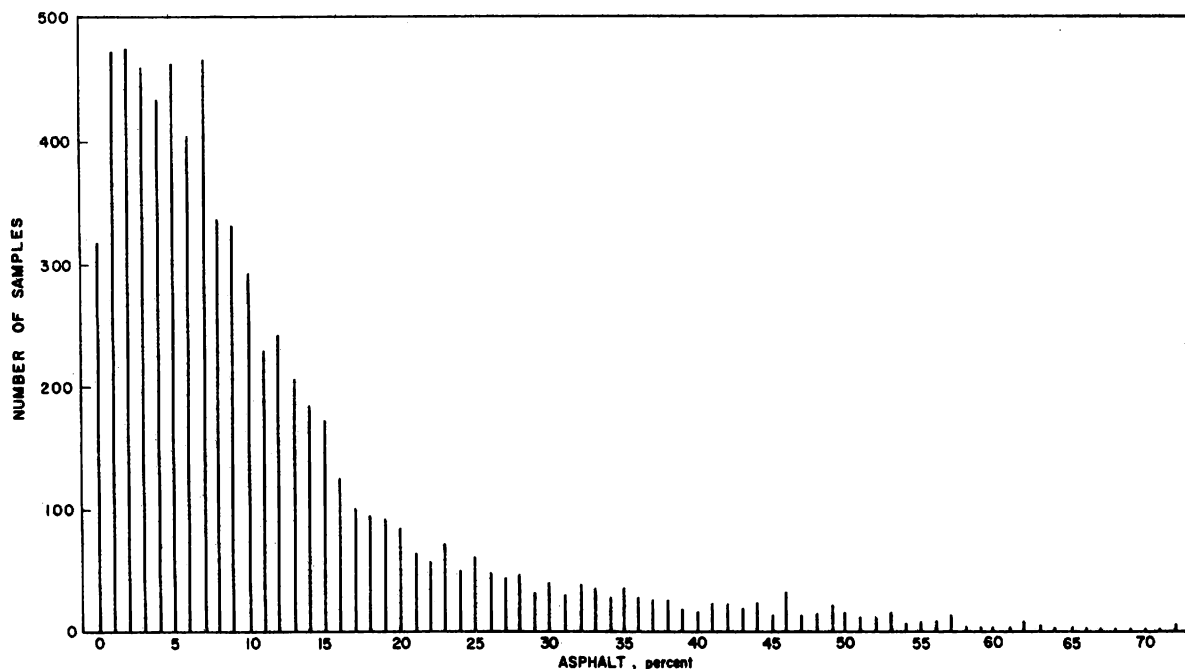


FIGURE 16.—Frequency Distribution of Asphalt Content of Crude Oils (6,903 Samples).

crude oils is shown in figure 16. As would be expected, it is similar to those for sulfur and nitrogen with certain exceptions that have been mentioned. Approximately 45 percent of the oils have an asphalt content of 7 percent or less. Again it is pointed out this is on an occurrence basis.

Cloud Points

The cloud point of an oil may be defined as the highest temperature at which the chilled oil will show a cloud of wax crystals under prescribed conditions (3). In this report the data in the tables and in panel F, figure 12, are the averages of the cloud points for fractions 11-14. This property is a rough indication of the quantity of waxy hydrocarbons present. The data are only reported for 5° F or above and in 5° F intervals. For oils showing no cloud at 5° F, the cloud point is reported as being "below 5° F". Many crude oils are in this category, and thus there are missing necessary data for a useful statistical study.

The usual reason for a distillate fraction to have a high cloud point is the content of paraffin wax, and this in turn will depend on the relative proportions of the normal paraffins present having from 20 to 40 or more carbon atoms. The higher molecular weight paraffins have higher freezing points and would therefore contribute to a higher cloud point. The cloud point data are used in this report as another means of distinguishing between crude oils, particularly those with cloud point of 30° F or

more as compared with those of less than 5° F. Three of the low-sulfur oils, J, M, and N, and oil US of the high-sulfur oils are in this latter category.

API Gravity

API gravities are used here because those persons likely to use this paper most probably use degrees API in their work (85) with crude oil.

The commercial segment of the petroleum industry characterizes the weight per unit volume of petroleum according to an arbitrary scale called degrees API or API gravity. The scientific segment of the industry uses either specific gravity or density. These have an inverse relationship to API gravity; when density or specific gravity are high, API gravity is low, and vice versa.

API gravities of crude oils differ greatly because

1. The proportions of various types of hydrocarbons, sulfur, nitrogen, and oxygen compounds differ appreciably from oil to oil.

2. API gravities of the different types of hydrocarbons differ considerably; paraffins have the highest values, followed by monocyclic cycloalkanes and aromatics. However, the API gravities of the alkylcycloalkanes and alkylaromatics increase with increase in length of the alkyl chain. Dicyclic and polycyclic cycloalkanes and aromatics have lower API gravities than the monocyclic compounds. The relationship of API gravity to structure is complex.

3. API gravities of sulfur and nitrogen compounds are less than those for hydrocarbons of corresponding boiling points.

Oils of low API gravity often have a small content of gasoline. However, this is not necessarily so, because if they happen to contain an unusual amount of cycloalkanes or especially aromatics, the API gravity can be low without a decrease in gasoline content. Oil J is an example of such an oil.

The API gravities of 7,386 crude oils have been separated into groups differing by 5° in API gravity. The frequency graph resulting is shown in figure 17. This is a fairly uniform distribution pattern, somewhat deficient on the high side, with some buildup in the region from 25° to 35° API. These distribution curves for API gravity, as is true for the other properties mentioned, reflect only the sampling of crude oils as they are distributed about the earth, and do not indicate how the property in question would be distributed on a weighted basis of total production and reserves. For example, the average API gravity of 12 Middle East crude oils is 33.2; as these represent a very large production and reserve, a distribution chart on this basis would probably show a peak or shoulder at that point. However, this report is concerned only with distribution based on occurrence.

RELATIONSHIPS OF HYDROCARBON TYPES FOR EACH OIL

Determined and Calculated Data

The naphthas are defined as the material distilled over in fractions 1-7 by the Bureau of Mines routine method of crude oil analysis, and the gas oil is the distillate contained in fractions 8-12. The gas oil thus may contain some kerosine as well as light gas oil. In figures 18 and 19 the composition of the naphthas and gas oils of the selected crude oils is shown according to the following hydrocarbon group or type classifications:

1. Volume-percent of aromatics in both naphtha and gas oil. This is a direct determination based on specific dispersion as described by Smith and Hale (169).

2. Volume-percent of naphthenes in naphtha. These are obtained by calculating the density of the paraffin-naphthene portion of each fraction by correcting its density for the contribution of aromatics, and using the new value on a specially prepared refractivity intercept-density chart (169).

3. Volume-percent of paraffins in naphtha. These are the differences between 100 and the sum of the aromatics and naphthenes.

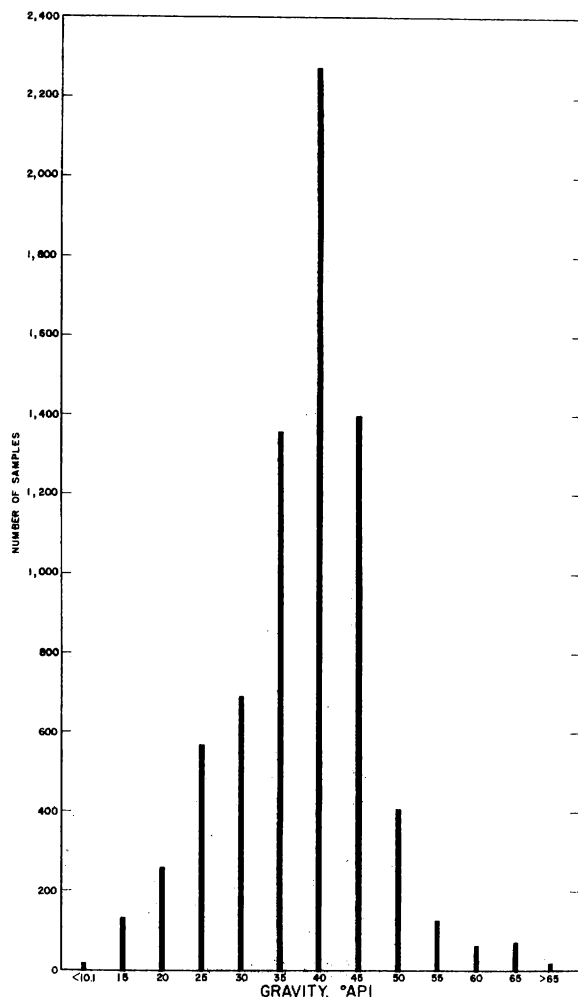


FIGURE 17.—Frequency Distribution of API Gravities of Crude Oils (7,386 Samples).

4. Volume-percent of paraffin-naphthenes in gas oils. This is 100 minus the volume-percent of aromatics in the gas oil.

5. Weight-percent naphthene ring in paraffin-naphthene portion of gas oils. This is calculated by using the density of the paraffin-naphthene portion as determined in paragraph 2 above to get a correlation index value. This can then be used on a plot of correlation index of paraffin-naphthene mixtures versus weight-percent naphthene ring to obtain a value for the latter property. This procedure is described and used in earlier reports (164-165).

6. The weight-percent of paraffins plus paraffin chain in the paraffin-naphthene portion is 100 minus weight-percent ring.

The data thus obtained are plotted in bar graphs for each oil showing the composition of each fraction in terms of volume-percent of aromatics, naphthenes, and paraffins totaling

100 percent for the naphthas. For the gas oils the composition of each fraction in terms of volume-percent of aromatics and paraffin-naphthenes is shown, and the paraffin-naphthene portion is further divided into weight-percent naphthene ring and weight-percent paraffins-plus-paraffin chain. The percent of paraffin chain on the aromatic rings is not determined.

Low-Sulfur Oils

Figure 18 presents data as described above for oils A through N (except J), and these are discussed individually as follows.

Oil A, Fasken, Tex.

This oil is produced from the Ellenburger Formation of Cambro-Ordovician rocks of the Paleozoic era in the western part of the Midland basin portion of the Permian Basin in West Texas and New Mexico. It is one of the most paraffinic oils known (Bureau 1935 classification, paraffin-paraffin). The bar graph shows a small but fairly constant content of aromatics, spotty and very small content of naphthenes, and 80 to 90 percent paraffins. A GLC analysis of fractions 1-7 shows that the paraffin portion of the naphtha distillate through heptane is composed of about 82 percent of normal paraffins and 18 percent of isoparaffins. These latter are predominately monomethyl paraffins such as methylpropane (isobutane), methylbutane (isopentane), 2- and 3-methylpentane, 2- and 3-methylhexane, and a much smaller quantity of 2,3-dimethylpentane. The paraffinicity extends into the gas oil, and there is not the increase in aromatics and naphthenes that will be usual in the other oils shown. Most of the Ellenburger production in the Permian Basin has similar characteristics. These oils are discussed in relation to the geology of the area in a paper by Jones and Smith (94).

Oil B, Bagley, N. Mex.

This oil is produced from the Siluro-Devonian dolomite of the Paleozoic era in the northernmost portion of the Permian Basin. The bar graph shows this is also a very paraffinic oil (Bureau 1935 classification, paraffin-paraffin). It has a lower aromatic content than Fasken oil even through the gas oil, but noticeably more naphthene content. Several fields in the same locality, Crossroads, Moore, and E. Caprock, and producing from the same formation

yield almost identical oils. Among other fields and formations producing similar oils are—

Location	Producing formation	Rock	Era
Haynesville, E., La.	Birdsong and Owens sands.	Upper Cretaceous.	Mesozoic.
Shongaloo, N.-Red Rock, La.	Tokio.....	do.....	Do.
Sligo, La.....	Paluxy.....	Lower Cretaceous.	Do.
Bled Khatara, Morocco.	Jurassic.....	Do.

As noted for oil OS (Lisbon, W., La.), these oils are from rock of the Mesozoic era, whereas many if not most paraffinic oils are reservoired in Paleozoic rock. Also the first three named have relatively shallow depths of burial, 5,000 feet or less.

Oil C, Minas, Indonesia

This oil is produced from the Telisa Formation of Miocene rock of the Cenozoic era. This is a less paraffinic oil than Fasken and Bagley oils, particularly in the naphtha portion, which is characterized by a very low aromatic content but a considerable increase in naphthene content (1935 Bureau classification, paraffin-paraffin). The aromatic content continues to increase in the gas oil, but the naphthenes are somewhat less than for the Bagley oil.

Oil D, Kawkawlin, Mich.

This oil is produced from the Dundee Formation of Devonian rocks of the Paleozoic era. Detailed analyses (73, 137) show that the naphtha from this oil has an unusually high content of *n*-alkanes and low content of isoalkanes and slightly more naphthenes than Minas oil (1935 Bureau classification, paraffin-intermediate). The gas oil has a considerable quantity of aromatics, as shown by 13 and 20 percent aromatic carbon atoms per molecule in fractions 12 and 14. This is in contrast to the Minas and Bradford oils on either side, and explains why it was classified as paraffin-intermediate.

Oil E, Bradford, Pa.

This oil is from an Upper Devonian Formation of the Paleozoic era. It represents an oil that at one time was considered the standard for paraffinic oils (1935 Bureau classification, paraffin-paraffin). Now oils that are more paraffinic are known, as this report shows. This oil is representative of much production in the Appalachian area, although there are other oils from that area that have a more paraffinic naphtha, and some that contain large quantities of cyclic compounds in the naphtha. The low

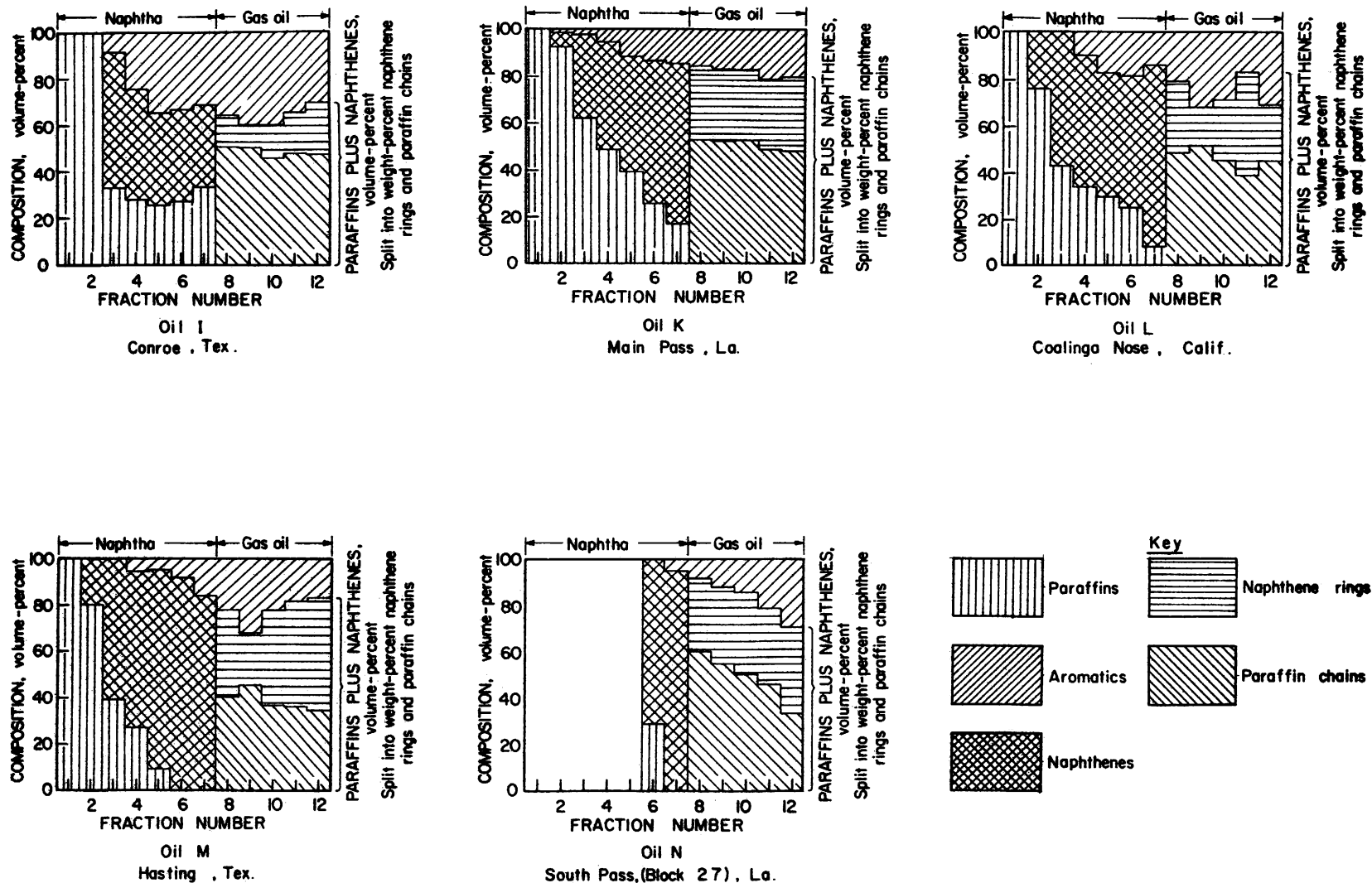


FIGURE 18-A.—Composition Diagrams for Low-Sulfur Crude Oils.

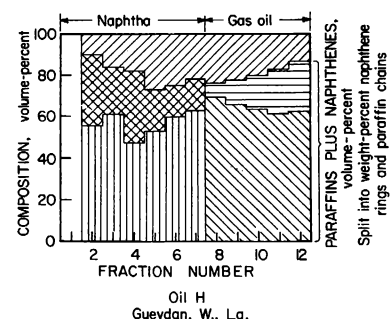
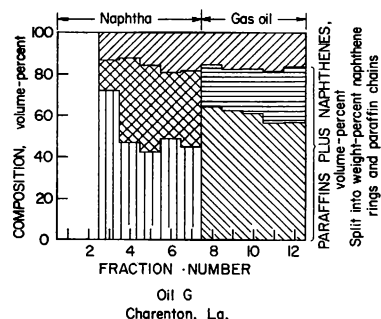
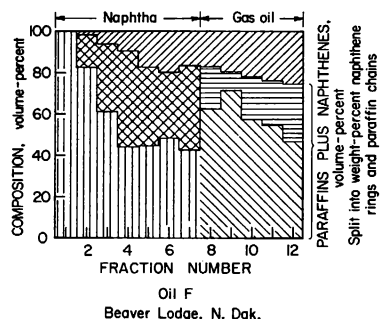
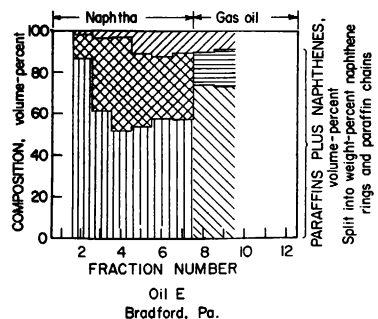
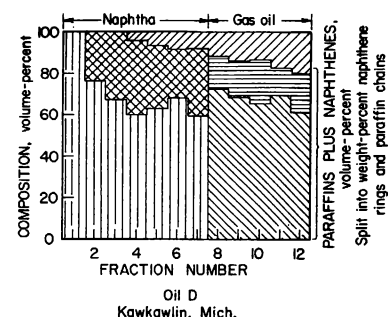
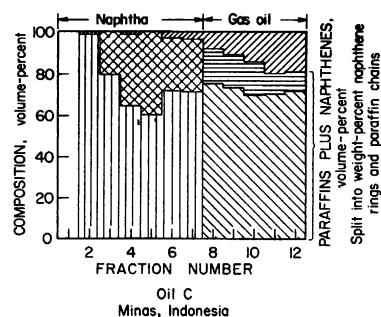
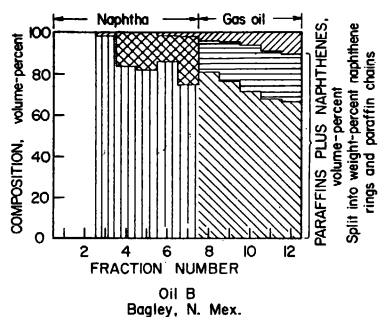
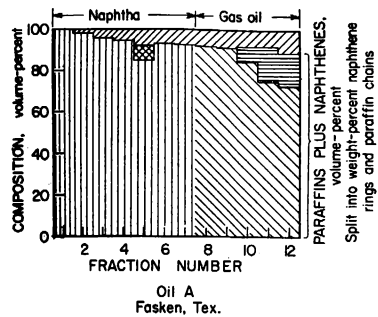


FIGURE 18-B.—Composition Diagrams for Low-Sulfur Crude Oils.

content of aromatic rings and percent of carbon atoms in fractions 12 and 14 explain why this was considered a typical paraffin-base oil.

Oil F, Beaver Lodge, N. Dak.

This oil is from the Mission Canyon Formation of Ordovician rocks of the Paleozoic era. It is the first (table 1) of five oils that would be considered intermediate-intermediate by the 1935 Bureau of Mines classification. The other oils are G, (Charenton, La.); H, (Gueydan, W., La.); K, (Main Pass, La.); and L, (Coalinga (Nose), Calif.). This Beaver Lodge oil is more naphthenic and aromatic than Bradford oil, as can be seen from both table 1 and the composition diagram. The difference in the naphtha is not great, but the cyclic compounds continue to increase in both naphtha and gas oil, and the percentages of aromatic carbon atoms in fractions 12 and 14 are among the highest. The gas oil has an average of 1.3 naphthene rings per molecule, indicating that possibly a third of the naphthenes are bicyclic.

Oil G, Charenton, La.

This oil is from a Miocene Formation of the Cenozoic era. It is typical of many oils from the Gulf Coast that have a high content of gas oil or lubricating oil fractions or both, and correspondingly less naphtha and residuum (1935 Bureau classification, intermediate-intermediate). The aromatic content of the naphtha is the highest of any oil yet discussed, but the increased aromatics do not carry into the gas oil. The naphthene content of the naphtha is about the same as for Bradford oil, and the paraffin-naphthene relationship for the gas oil appears to be very similar to that for oil F (Beaver Lodge) gas oil. The naphthenes in the gas oil appear to include a higher quantity of dicyclic naphthenes than any of the oils yet discussed except Beaver Lodge. There are many similar to Charenton on the Louisiana Gulf Coast, all of them having about the same aromatic content in naphthas and gas oils. It would be of much interest to prepare some model systems of an oil such as this with a variety of parameters such as pressure, temperature, moisture, and rock to see if discernible change toward a more paraffinic oil could be found as a function of time.

Oil H, Gueydan, W., La.

This oil is from a Miocene Formation of the Cenozoic era. It is also typical of many Louisiana Gulf Coast Miocene oils having generally low naphtha contents, high gas oil and lubricating oil contents, and small residua (1935 Bureau classification, intermediate-paraffin). It is distinguished from other Gulf Coast oils in table 1

by a somewhat higher content of paraffins and aromatics and a corresponding decrease in naphthenes in the naphtha. Although there are no detailed data for fraction 14 there are several indications as to why the old classification called this oil intermediate-paraffin (a rather unusual type). The average cloud points of fractions 11 to 14 is 56, higher than any other Gulf Coast oils; the weight-percent chain in the paraffin-naphthene portion of the gas oil and the weight-percent paraffinic carbon atoms in fraction 12 are also the highest of the Gulf Coast oils in table 1. Other crude oils of this nature are found in the following Louisiana fields: Eugene Island, Lake Salvador, LaRose, Sweet Bay Lake. There are many minor variations of this general type of crude oil; the Charenton oil just previously described is one and the Main Pass oil discussed later is a high-naphthene content variation.

Oil I, Conroe, Tex.

This oil is from the Cockfield Formation of Eocene rocks of the Cenozoic era. This is an unusually aromatic oil by almost any criteria (1935 Bureau classification, naphthene-intermediate). It is typical of Gulf Coast oils having a large content of gas oil, but it also has a naphtha content equivalent to many paraffinic oils; as a result the lubricating distillate is small and there is only 7.6 percent of residuum. The naphtha contains 25 percent of aromatics, including a high proportion of toluene, an unusually high content of naphthenes, and consequently a low content of paraffins. The aromaticity continues through the gas oil fractions. The number of rings per molecule and weight-percent aromatics and naphthenic carbon atoms point to the possibility of dicyclic aromatics, but possibly a somewhat greater content of monocyclic naphthenes than the West Gueydan oil.

Oil J, Sanga Sanga (Koetei District), Borneo

This oil is from a Miocene Formation of the Cenozoic era. The data are from two sources: The volume-percent paraffins, naphthenes, and aromatics are from a report by Kewley (102) in 1921; the rest of the data are from a 1937 report by the Bureau of Mines (105) (1935 Bureau classification, naphthene-naphthene). Of course the data are not for the same sample, but as nearly as can be determined from the reference, the type of oil was the same. Oil J is the first of three wax-free oils. This oil represents a maximum content of aromatics for naphtha for low-sulfur oils. (See oil VS.) In many respects it is similar to the Conroe oil. Data are not available to prepare a composition diagram.

Oil K, Main Pass, La.

This oil is from a Miocene Formation of the Cenozoic era. The composition diagram shows the greatly increased naphthene content of the naphtha, and the smaller overall increase in aromatics (1935 Bureau classification, intermediate-intermediate). The data in table 1 show that this trend continues for the gas oil, with 38 weight-percent naphthene ring in the paraffin-naphthene portion. The data for fraction 12 indicate one naphthene ring per molecule and 29 weight-percent carbon atoms in naphthene rings, both among the high values. In fraction 14 the naphthene rings per molecule are 1.5, indicating dicyclic naphthenes, and the weight-percent of carbon atoms in naphthene rings is 35, also one of the high values.

Oil L, Coalinga (Nose), Calif.

This oil is from an Eocene Formation of the Cenozoic era. This oil is not wax free although it is highly naphthenic—55 percent naphthenes 11 percent aromatics, and only 34 percent paraffins in the naphtha (1935 Bureau classification, intermediate-intermediate). The composition diagram and table 1 show that the aromatic content of the gas oil has increased markedly over that for the naphtha, but the paraffin chain content is lower than all of those having wax present except the Main Pass oil. This indicates that the paraffin chains present on the aromatics and naphthenes may be short but that *n*-paraffins are present, and hence the indication of wax. There are many oils produced in California very similar to the Coalinga oil. In all it appears that the content of alkyl-benzenes is relatively low, generally about 10 percent or less, but the content of aromatics increases rather rapidly in the boiling range of the alkyl naphthalenes, so that the gas oil contains about 30 percent of aromatics. The data for both fractions 12 and 14 on number of aromatic rings and weight-percent aromatic carbon atoms bear this out. So far as Bureau of Mines records show such oils seem to be rather unique among the crude oils of the world, excepting Soviet oils of which we do not have up-to-date analyses.

One U.S. oil from Red Wash field produced from Green River Shale of Tertiary series of Cenozoic era has distillates that appear to have similar properties, but the quantities of all distillates are much less and the residue is much greater.

Oil M, Hastings, Tex.

This oil is from the Frio Formation of Oligocene rock of the Cenozoic era. This is a wax-free oil characterized by a high naphthene

content throughout (1935 Bureau classification, naphthene-intermediate). The naphtha contains 77 percent naphthenes and only 7 percent aromatics and 16 percent paraffins; the paraffin-naphthene portion of the gas oil, which is 78 percent, is 50 percent rings and 50 percent chain, a much higher proportion of naphthene rings than in most other crude oils. This tendency continues into the higher boiling fractions: thus in fraction 14 there are 2.5 rings per molecule, of which 2.0 are naphthene rings; 47 percent of the carbon atoms are naphthenic, 40 percent paraffinic, and only 13 percent aromatic. There must be many dicyclic and probably polycyclic naphthenes in this oil. The composition diagram shows the essentially naphthenic characteristics of this oil. Oils having a high naphthene content are more common throughout the world than are aromatic oils like Conroe.

Oil N, South Pass (Block 27), La.

This oil is produced from Miocene Formation M2 of the Cenozoic era. It has the most naphthenic naphtha of any oil reviewed, but probably primarily because no material boiling below 143° C (289° F) is present, and the naphtha content is only 3.1 percent (1935 Bureau classification, naphthene-naphthene). Thus the lighter paraffinic hydrocarbons, which are those most likely to be present in a naphthenic naphtha, are entirely missing. The ratio of weight-percent naphthene ring and paraffin chain is such as to indicate a large quantity of dicyclic naphthenes. This conclusion is borne out by the data in fraction 12 showing 1.7 naphthene rings per molecule. There are several other oils that are similar to the South Pass oil, most of which are produced in Texas and Louisiana. However, the Miri field in Sarawak apparently produces a similar oil as described by Kewley (103). All of these oils are wax free, and all are produced from rocks of the Cenozoic era.

Comparisons Among Low-Sulfur Oils

An understanding of the many differences between oils that superficially appear to be alike is facilitated by various types of comparisons which are given in this part of the report. In making these comparisons oils other than the 14 basic oils just described have been used when it seemed they could add to the picture. They will be identified as additional oils.

Extremely Paraffinic Oils

There are a few oils that appear to be similar to oil A, the Ellenburger Fasken oil, but the necessary data to make direct comparisons

are not available, because these oils were analyzed many years ago and some of the properties necessary for such comparisons were not determined. The oil from the Carboniferous limestone of the Paleozoic era in Hardstoft, England, appears to be slightly more paraffinic especially in the lighter boiling fractions; another similar oil is from the Washington field in Pennsylvania and produced from Mississippian rocks of the Paleozoic era, oils from several fields (Martin, Warren, Jordan) of the Permian Basin in Texas and New Mexico producing from the Simpson Formation of Ordovician age of the Paleozoic era are also very like the Fasken oil. An oil from the Lisbon field in Louisiana is also very paraffinic, but in contrast to all of the other oils mentioned, which were from the early Paleozoic era, this oil is produced from the Smackover Formation from Jurassic rock of the Mesozoic era. It would be of interest to determine if this oil, which is very light, with an API gravity of 55.0 and a sulfur content of less than 0.10 percent, and thus approaches the characteristics of a condensate, may have originated in Paleozoic rock and migrated to its present position. However, if maturation is also a function of depth of burial as suggested by Philippi (148), then the Lisbon oil may have originated in Jurassic rock as it came from a depth of over 10,000 feet. It is also of interest that at a higher level at Lisbon, W., another paraffinic oil (oil OS) is found, but with a sulfur content of 1.33 percent. This oil has characteristics that one might expect from the sulfurization of the low-sulfur Lisbon oil. Here is an excellent opportunity to set up a model system of the Lisbon oil and several sulfurizing mediums and determine if reactions take place that might lead to the high-sulfur oil.

Bases for Comparisons

Consideration of the Minas oil affords an opportunity to discuss methods of comparing crude oils. The author has not found any oils that match the Minas oil closely, as was possible for the previous two oils. There are several oils however, that in some respects seem to be similar. For example in table 4 comparative data are presented on Minas crude oil and Beaver Lodge crude oil (not oil F) from a Silurian Formation of Paleozoic era in North Dakota. Analyses of naphthas for these crude oils by gas-liquid chromatography are available for Minas oil by Martin and Winters (136), and for Beaver Lodge oil by the same authors (135). Bureau of Mines analyses on oils from the same fields and formation are also available, and table 4 has been prepared from these three sources of data. Replicate samples were not analyzed by the Bureau and by Martin and Winters, but it is be-

TABLE 4.—Comparative composition data for naphthas from Minas and Beaver Lodge (Silurian) crude oils

Distillate or hydrocarbon	Minas ¹	Beaver Lodge ²
Volume-percent:		
Naphtha in crude oil.....	18.6	55.1
Residuum in crude oil.....	87.3	3.1
Paraffins in naphtha.....	71.0	75.0
Naphthenes in naphtha.....	27.0	12.0
Aromatics in naphtha.....	2.0	13.0
Volume-percent in crude oil:		
n-Pentane.....	.54	2.00
n-Hexane.....	.78	2.45
n-Heptane.....	.96	2.70
Isopentanes.....	.41	1.28
Isohexanes.....	.63	1.66
Isoheptanes.....	.63	1.49
Cyclopentane plus methylcyclopentane.....	.32	.75
Cyclohexane plus methylcyclohexane.....	.77	2.10
Benzene plus toluene.....	.05	.93
Volume-percent in naphtha:		
n-Pentane.....	2.90	3.63
n-Hexane.....	4.20	4.45
n-Heptane.....	5.16	4.90
Isopentanes.....	2.20	2.32
Isohexanes.....	3.39	3.02
Isoheptanes.....	3.39	2.71
Cyclopentane plus methylcyclopentane.....	1.72	1.36
Cyclohexane plus methylcyclohexane.....	4.14	3.81
Benzene plus toluene.....	.27	1.69
Ratio of volume-percents of hydrocarbons to n-hexane:		
n-Pentane.....	.69	.82
n-Hexane.....	1.00	1.00
n-Heptane.....	1.23	1.10
Isopentanes.....	.53	.52
Isohexanes.....	.81	.68
Isoheptanes.....	.81	.61
Cyclopentane plus methylcyclopentane.....	.41	.31
Cyclohexane plus methylcyclohexane.....	.99	.86
Benzene plus toluene.....	.06	.38
Correlation index: ³		
Fractions 4-7.....	16.0	20.0
Fractions 8-15.....	23.0	23.0

¹ Data from reference 136 converted to volume-percent.

² Data from reference 135 converted to volume-percent.

³ From Bureau of Mines routine analyses.

lieved that the samples were similar enough to justify the comparisons made.

On the basis of the correlation index these might be classed together although the correlation index of the Beaver Lodge naphtha is slightly higher. Both would be considered paraffinic-paraffinic by the 1935 Bureau of Mines method of classification. However, there are wide differences in the naphtha and residuum content, and there are differences in the relative proportions of naphthenes and aromatics in the naphtha.

Another method of comparison might be based on the volume percent of different hydrocarbons in the crude oil—here there is a wide difference. However, if these are calculated on the basis of their content in the naphtha, they are rather close except for the greater quantity of aromatics in Beaver Lodge naphtha. Also this same set of data show that there are more naphthenes in the Minas naphtha as was indicated by the paraffin-naphthene-aromatic split (table 1).

Still another method of comparison uses ratios of the volume-percent of each hydrocarbon to the volume-percent of n-hexane. When this is done the data show considerable similarity ex-

cept for benzene and toluene. This discussion raises the question as to what criteria must be met to decide that two oils are essentially the same. For one oil to be considered the same as another, there should be virtual equivalence in both the volume-percent and the composition of the distillate. On the other hand, the two examples just cited suggest that because of the similarity in the paraffin-naphthene relationships that the major part of the oil has undergone a similar sequence of reactions, or diagenesis, with the formation of aromatics a virtually random and independent process. The difference in volume of naphtha may be related to the extent to which the diagenesis has proceeded.

The data in table 5 further illustrate the difficulties of classification and the need to consider each oil individually. All of these oils except Minas (oil C) are additional oils as follows: Beaver Lodge, N. Dak., Silurian; Goodwill Hill, Pa., Devonian; Ossun, N., La., Cenozoic.

TABLE 5.—*Comparison of composition data for naphtha from four oils*

	Beaver Lodge	Goodwill Hill	Ossun, N.	Minas
Correlation index, fractions 4-7.....	20	17	19	16
Correlation index, fractions 8-12.....	23	21	22	23
Naphtha..... volume-percent.....	55.1	42.3	36.9	18.6
Residuum..... do.....	3.1	17.9	10.3	37.3
Paraffins..... volume-percent of naphtha.....	75	76	71	71
Naphthenes..... do.....	12	17	19	27
Aromatics..... do.....	13	7	10	2

For all of these oils the correlation index of fractions 4-7 is 18 ± 2 with one exception, and for fractions 8-15 it is 22 ± 2 . They would be paraffin-paraffin oils by the 1935 Bureau classification. Those characteristics that appear to differ significantly from the mean are underlined. Beaver Lodge (Silurian) oil has excess naphtha; Minas oil is deficient in naphtha; Beaver Lodge oil has a small quantity of residuum; Minas oil residuum is large; there are not wide differences in paraffin content, but the Ossun and Minas naphthas have slightly lower quantities; Beaver Lodge has the minimum content of naphthenes, whereas Minas naphtha has the most naphthenes; Coldwater and Minas naphthas are very deficient in aromatics; but only Coldwater gas oil is deficient in aromatics. Thus each of these oils that might be classed together has distinguishing characteristics that make each somewhat different.

Paraffinic Oils

Oils A (Fasken), C (Minas), D (Kawkawlin), E (Bradford), and Beaver Lodge, a Silurian

oil from North Dakota, all yield predominantly paraffinic naphthas. The naphthas from these oils are compared in table 6, where the contents of important hydrocarbons in the naphtha from each oil are given, and also the ratios of these hydrocarbons to *n*-hexane for each oil. Because of the rather wide differences in naphtha content the ratios give a better picture. They show that these ratios for *n*-pentane and *n*-heptane are essentially constant at about 1.20 for Minas, Kawkawlin, and Bradford oils, slightly lower for Beaver Lodge, and slightly higher for *n*-heptane for Fasken oil. Fasken and Kawkawlin oils have the lowest isoparaffin ratios and the lowest cyclopentane and cyclohexane ratios. All of the aromatic ratios are low, with Beaver Lodge having the highest. The Minas, Bradford, and Beaver Lodge oils are typified by high proportions of isoparaffins and naphthenes, and for the five oils considered there appears to be a correlation between isoparaffin and naphthene content. This will be discussed after further data have been presented. Also for these five oils the *n*-heptane/*n*-hexane ratio is always greater than 1.00; again for more naphthenic oils the converse, while not uniformly true, often is. All of these oils except Minas are from Devonian or older formations in the Paleozoic era. The author interprets the similarity in *n*-paraffin ratios probably as indication of source material having similar characteristics and of similar environmental conditions leading to diagenesis by similar mechanisms. The type of hydrocarbons found seem to indicate thermal cracking at low temperature over a long period of time.

All of these oils would have been classed as paraffin-paraffin except Kawkawlin paraffin-intermediate. The reason for the intermediate characteristics of the heavier fractions seems to be a rapid increase in the aromatic content with boiling point; thus Bagley has only 10 percent aromatics for fraction 12, whereas Kawkawlin has 22 percent.

Oils Having High Contents of Naphthenes and Aromatics

Oil I (Conroe) is noted for its aromatic content, but there are other oils similar to Conroe in aromatic content as shown in table 7. Detailed analyses of Maljamar and Conroe are available for the naphthas. They are summarized in table 8. For comparison a very naphthenic oil, oil M (Hastings) and a very paraffinic oil, oil A (Fasken), are also included, as well as a paraffinic oil, oil F (Beaver Lodge) also having an unusually high content of aromatics. All of these oils except Hastings have approximately the same content of naphtha so that direct comparison of quantities can be

TABLE 6.—*Comparative composition data for naphthas from paraffinic crude oils*

Hydrocarbon or hydrocarbon mixture	Volume-percent of crude oil					Ratio of volume-percent of hydrocarbon to percent <i>n</i> -hexane				
	Oil A, Fasken ¹	Oil C, Minas ²	Oil D, Kaw- kawlin ³	Oil E, Brad- ford ⁴	Beaver Lodge ⁵	Oil A, Fasken ¹	Oil C, Minas ²	Oil D, Kaw- kawlin ³	Oil E, Brad- ford ⁴	Beaver Lodge ⁵
<i>n</i> -Pentane.....	1.57	0.54	1.27	-----	2.00	0.52	0.69	0.61	-----	0.82
<i>n</i> -Hexane.....	3.00	.78	2.07	1.80	2.45	1.00	1.00	1.00	1.00	1.00
<i>n</i> -Heptane.....	4.43	.96	2.46	2.19	2.70	1.48	1.23	1.19	1.22	1.10
Isopentanes.....	.39	.41	.24	-----	1.28	.13	.53	.12	-----	.52
Isohexanes.....	.78	.63	.35	1.87	1.66	.26	.81	.17	1.04	.68
Isoheptanes.....	.87	.65	.39	2.34	1.49	.29	.83	.19	1.30	.61
Cyclopentane plus methylcyclopentane.....	.30	.32	.39	.53	.75	.10	.41	.19	.30	.30
Cyclohexane plus methylcyclohexane.....	1.17	.77	.92	2.34	2.10	.39	.99	.44	1.30	.86
Benzene plus toluene.....	.17	.05	.45	.53	.93	.06	.06	.22	.29	.37
Correlation index: ⁶										
Fractions 4-7.....	10.00	16.00	18.00	22.00	17.00	-----	-----	-----	-----	-----
Fractions 8-15.....	20.00	23.00	32.00	23.00	21.00	-----	-----	-----	-----	-----

¹ Unpublished data, Bureau of Mines.² Data from reference 136.³ Data from reference 137.⁴ Data from reference 73.⁵ Data from reference 135.⁶ Bureau of Mines data.TABLE 7.—*Comparative data on composition of five aromatic naphthas*

	Composition of naphtha, volume-percent		
	Paraffins	Naphthenes	Aromatics
Crowley, N., La.....	47	30	23
Hackberry, W., La.....	39	36	25
Maljamar, N. Mex.....	53	27	20
Conroe, Tex.....	34	41	25
Helen Goelke, Tex.....	49	26	25

made. On this basis they line up in the following order of decreasing paraffinicity: Fasken, Beaver Lodge, Maljamar, Hastings, Conroe. This is also in the order of decreasing geologic age. The oils with a high aromatic content in the naphtha are of three distinct types: The paraffinic-naphthenic Beaver Lodge oil with almost 1 percent benzene plus toluene in the naphtha,

with a ratio to *n*-hexane of 1.24; the less paraffinic but more naphthenic Maljamar naphtha with the benzene-toluene *n*-hexane ratio of 3.97; the low-paraffinic, high-naphthenic content Conroe oil with the benzene-toluene *n*-hexane ratio of 3.06. Hastings by comparison is essentially naphthenic, with the cyclohexane-methylcyclohexane *n*-hexane ratio being 5.14, and the benzene-toluene *n*-hexane ratio of 0.42. The benzene-toluene *n*-hexane ratio of Fasken oil is only 0.06. Hastings and to some extent Maljamar and Conroe are distinguished by the relatively large ratios of isoparaffins to *n*-hexane. There are data in the literature that indicate other oils that have above normal contents of isoparaffins in the gasoline range. Thus the oils from Winkler (73) and Yates fields in Texas (170), along with Monument oil from New Mexico were pointed out by Smith and Rall (170) as being unique in their high content of isoparaffins.

TABLE 8.—*Comparative composition data on naphthas from several types of crude oil*

Hydrocarbon or hydrocarbon mixture	Volume-percent of crude oil					Ratio of volume-percent of hydrocarbons to percent of <i>n</i> -hexane				
	Oil A, Fasken ¹ (Ordovician)	Oil F, Beaver Lodge ² (Devonian)	Maljamar ¹ (Permian)	Oil M, Hastings ³ (Tertiary)	Oil I, Conroe ⁴ (Tertiary)	Oil A, Fasken (Ordovician)	Oil F, Beaver Lodge (Devonian)	Maljamar (Permian)	Oil M, Hastings (Tertiary)	Oil I, Conroe (Tertiary)
<i>n</i> -Pentane.....	1.57	1.13	0.85	0.70	-----	0.52	0.73	0.84	1.40	-----
<i>n</i> -Hexane.....	3.00	1.55	1.01	.50	0.70	1.00	1.00	1.00	1.00	1.00
<i>n</i> -Heptane.....	4.43	2.16	.98	.28	.75	1.48	1.39	.97	.56	1.07
Isopentanes.....	.39	.65	.53	.75	-----	.13	.42	.52	1.50	-----
Isohexanes.....	.78	1.23	1.15	.84	.75	.26	.79	1.14	1.68	1.07
Isoheptanes.....	.87	1.65	1.06	.72	.68	.29	1.06	1.05	1.44	.97
Cyclopentane plus methylcyclopentane.....	.30	1.29	.94	1.40	.81	.10	.83	.93	2.80	1.16
Cyclohexane plus methylcyclohexane.....	1.17	3.28	3.22	2.57	3.53	.39	2.12	3.19	5.14	5.04
Benzene plus toluene.....	.19	1.92	4.02	.21	2.14	.06	1.24	3.97	.42	3.06

¹ Unpublished data, Bureau of Mines.² Data from reference 137.³ Data from reference 135.⁴ Data from reference 170.

There are also oils that are very naphthenic besides oil M (Hastings) and oil N (South Pass). A few are given in table 9.

TABLE 9.—*Data on some naphthenic naphthas*

	Volume-percent of naphtha		
	Paraffins	Naphthenes	Aromatics
Amelia, Tex.	10	84	6
Boling, Tex.	19	72	9
Sinton, W., Tex.	11	76	13
Binagadi, Baku, U.S.S.R. (105, 84, 194)	23	64	13
Sakhalin Island (Stratum), U.S.S.R. (105, 84, 194)	20	75	5

Other Illustrative Comparisons

In table 10 composition data on the naphthas^s of 11 crude oils are listed; these are as follows:

Field	Geologic period
Ponca City, Okla.	Ordovician.
West Edmond, Okla.	Devonian.
Redwater, Alberta, Canada.	Do.
Beaver Lodge (oil F), N. Dak.	Mississippian.
KMA, Tex.	Pennsylvanian.
North Smyer, Tex.	Do.
East Texas, Tex.	Cretaceous.
Swanson River, Alaska	Tertiary.
Segno, Tex.	Do.
Coalinga, Calif	Do.
Waha, Libya	Do.

Detailed composition data are available through C₇ hydrocarbons for these oils from the refer-

ences shown on the table. These oils are arranged in decreasing order of geologic age. The difficulty of classifying oils (as all of those would be intermediate-intermediate by the 1935 Bureau of Mines system) is well illustrated by the wide range covered in the content of the hydrocarbons listed, as well as considerable difference in ratios of these hydrocarbons to *n*-hexane. It is of interest that the *n*-heptane/*n*-hexane is less than 1.00 for 8 of the 11 oils, whereas for the paraffinic oils the ratio was always over 1.00. This and other ratios will be considered in another section of this report. Another fact of interest is the general increase in the value of the ratios for the cyclopentanes and cyclohexane to hexane with decrease in geologic age. This is especially true for the cyclohexanes. Also the difference in the actual percentages is of interest: For the Cretaceous and younger oils, the last five in the table, almost all values except some of those for Swanson River are less than one; in contrast for the first six oils that are Pennsylvanian or older almost all values except for benzene plus toluene are over one. This is in general agreement with the data presented earlier regarding increased naphtha content of older oils.

High-Sulfur Oils

Figure 19 presents data, as previously described, for the high-sulfur oils OS through VS, and these are discussed individually below.

TABLE 10.—*Composition data on naphthas from 11 crude oils*

Hydrocarbon or hydrocarbon mixture	Ponca City ²	West Edmond ¹	Redwater ²	Beaver Lodge ²	KMA ¹	North Smyer ²	East Texas ¹	Swanson River ²	Segno ¹	Coalinga ¹	Waha ²
VOLUME-PERCENT OF CRUDE OIL											
<i>n</i> -Pentane	1.38		1.58	1.13		2.16		0.85			0.21
<i>n</i> -Hexane	1.97	1.76	1.14	1.55	1.85	1.55	1.07	.91	0.88	0.57	.11
<i>n</i> -Heptane	2.21	1.74	1.04	2.16	1.64	1.34	.62	.98	.79	.44	.08
Isopentanes	.67		1.31	.65		1.72		1.66			.57
Isohexanes	1.53	1.01	1.45	1.23	1.46	2.59	.99	1.08	.85	.75	.78
Isoheptanes	1.48	1.38	1.04	1.65	1.53	2.01	.97	1.63	.87	.68	.77
Cyclopentane plus methylcyclopentane	1.32	.52	1.19	1.29	1.27	2.70	.87	1.35	.73	.89	.28
Cyclohexane plus methylcyclohexane	2.37	1.60	1.35	3.28	2.47	3.00	1.66	2.43	3.09	1.63	.46
Benzene plus toluene	.54	.42	.28	1.92	.46	.66	.37	.40	1.16	.77	.11
RATIO OF VOLUME-PERCENT OF HYDROCARBONS TO <i>n</i> -HEXANE											
<i>n</i> -Pentane	0.70		1.39	0.73		1.39		0.93			1.90
<i>n</i> -Hexane	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
<i>n</i> -Heptane	1.11	.99	.91	1.39	.89	.87	.58	1.18	.90	.77	.73
Isopentanes	.34		1.15	.42		1.12		1.81			5.19
Isohexanes	.77	.67	1.27	.79	.79	1.67	.92	1.19	.97	1.32	7.09
Isoheptanes	.75	.78	.91	1.06	.83	1.30	.91	1.79	.99	1.19	7.00
Cyclopentane plus methylcyclopentane	.67	.30	1.05	.83	.69	1.74	.81	1.48	.83	1.56	2.54
Cyclohexane plus methylcyclohexane	1.20	.91	1.18	2.12	1.33	1.94	1.55	2.67	3.51	2.86	4.18
Benzene plus toluene	.27	.24	.47	1.24	.25	.43	.35	.44	1.32	1.35	1.00

¹ Data from reference 170.

² Data from reference 187.

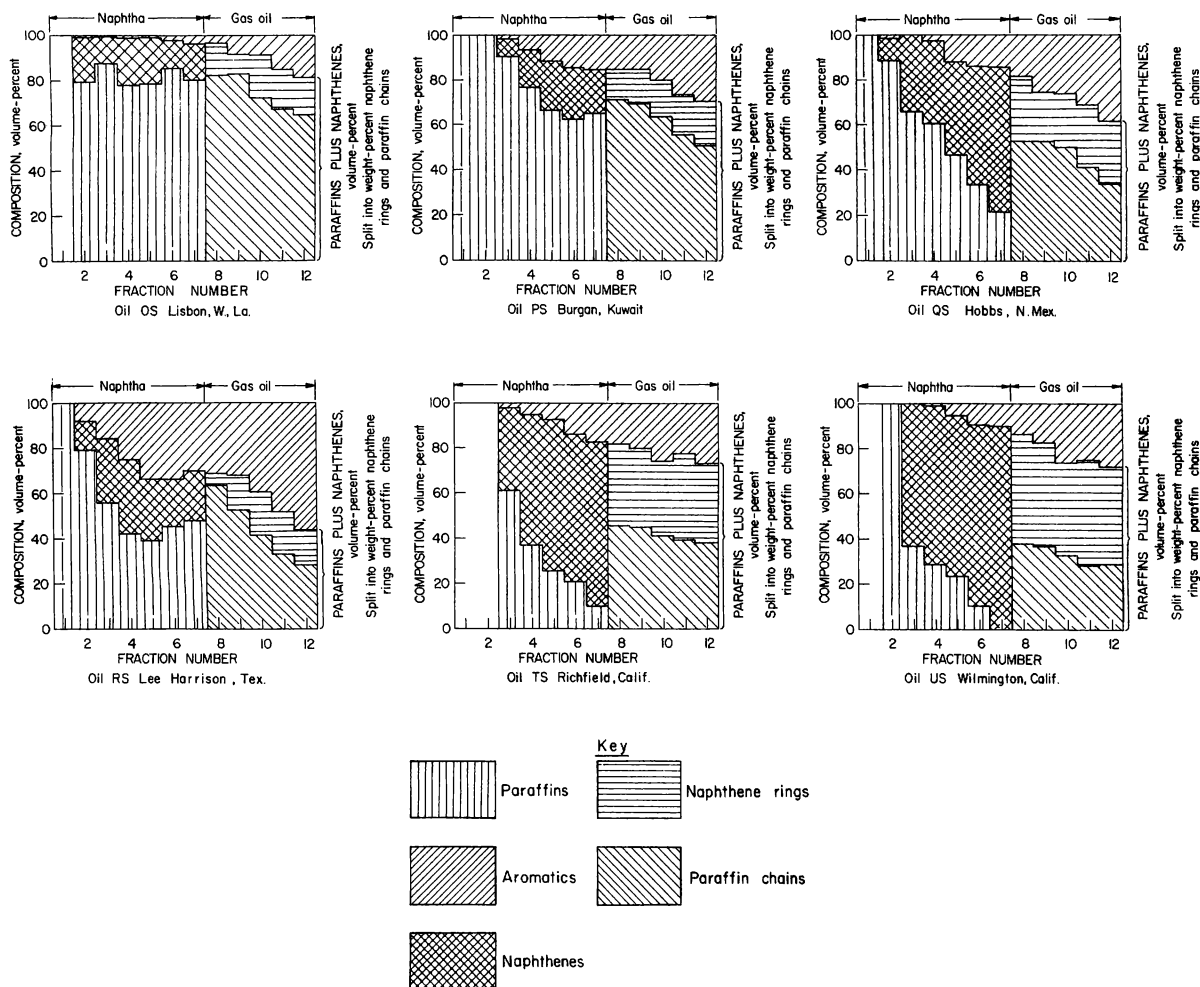


FIGURE 19.—Composition Diagrams for High-Sulfur Crude Oils.

Oil OS, Lisbon, W., La.

This oil is produced from the Pettit Formation of Lower Cretaceous rock of the Mesozoic era. This is a good example of a paraffinic crude oil with a high content of sulfur (1935 Bureau classification, paraffin intermediate). Generally oils of high-sulfur-content have considerable quantities of asphalt, but this oil has only 3.00 percent asphalt, yet it also has 0.13 percent nitrogen. Often this quantity of nitrogen will be accompanied by 10 to 12 percent asphalt. The oil is similar in the hydrocarbon composition of the naphtha and gas oil to that found for oil B (Bagley), except that the latter oil has a slightly higher naphthene content.

Oil PS, Burgan, Kuwait

This oil is produced from a Middle Cretaceous formation of the Mesozoic era. It is fairly typical of much of the Middle East production

(1935 Bureau classification, intermediate, intermediate). It has sulfur content of 2.54 percent, nitrogen of 0.11 percent, and asphalt of 23 percent. It can be compared with oil F, Beaver Lodge, except that the Burgan oil has a more paraffinic naphtha, the gas oils appear fairly similar in composition. The heavier part of the oil, judging by the number of aromatic and naphthene rings per molecule for fraction 14, has a definitely greater proportion of dicyclic compounds than does Beaver Lodge. This may be the affect of the presence of benzothiophene and dibenzothiophene compounds in the Burgan oil.

Oil QS, Hobbs, N. Mex.

This oil is produced from the San Andres Formation of Permian rock of the Paleozoic era. It is reasonably similar to Oil K (Main Pass) in the naphtha fractions, but has more aromatics in the gas oil fractions (1935 Bureau classification, intermediate-intermediate). Again

fraction 14 appears to have more dicyclic naphthenes and aromatics than the similar low-sulfur oil.

Oil RS, Lee Harrison, Tex.

This oil is produced from the Cedar Fork Formation of Permian rock of the Paleozoic era. This kind of oil is found only in the Permian Basin of West Texas so far as the author can determine. It is characterized by a high aromatic content of both the naphtha and gas oil, and by comparison a low naphthene content with a normal paraffin content (1935 Bureau classification, naphthene-naphthene). Fraction 14 has the highest number of aromatic rings per molecule of any oil shown in either table 1 or 2, and a correspondingly smaller number of naphthene rings per molecule. It can be compared in hydrocarbons to a low-sulfur oil from the Scharb, N. Mex., field, also of Permian production but from the Bone Spring Formation

A composition diagram is shown in figure 20. A comparison of the aromatic and naphthene ring content for fraction 14 of the two oils is given below:

	Total rings	Aromatic rings	Naphthene rings
Lee Harrison.....	2.4	1.1	1.3
Scharb.....	1.8	.8	1.0

Lee Harrison oil has 3.23 percent sulfur and only 0.14 percent nitrogen; obviously the asphalt, 18 percent, is in this case primarily a function of the sulfur content. The reverse is true of the next two oils, TS and US. So far as the author knows the highly aromatic west Texas Permian oils are unique whether high- or low-sulfur; all other high aromatic oils are found in rocks of the Cenozoic era with possible exception of oil VS from Chusov, U.S.S.R.

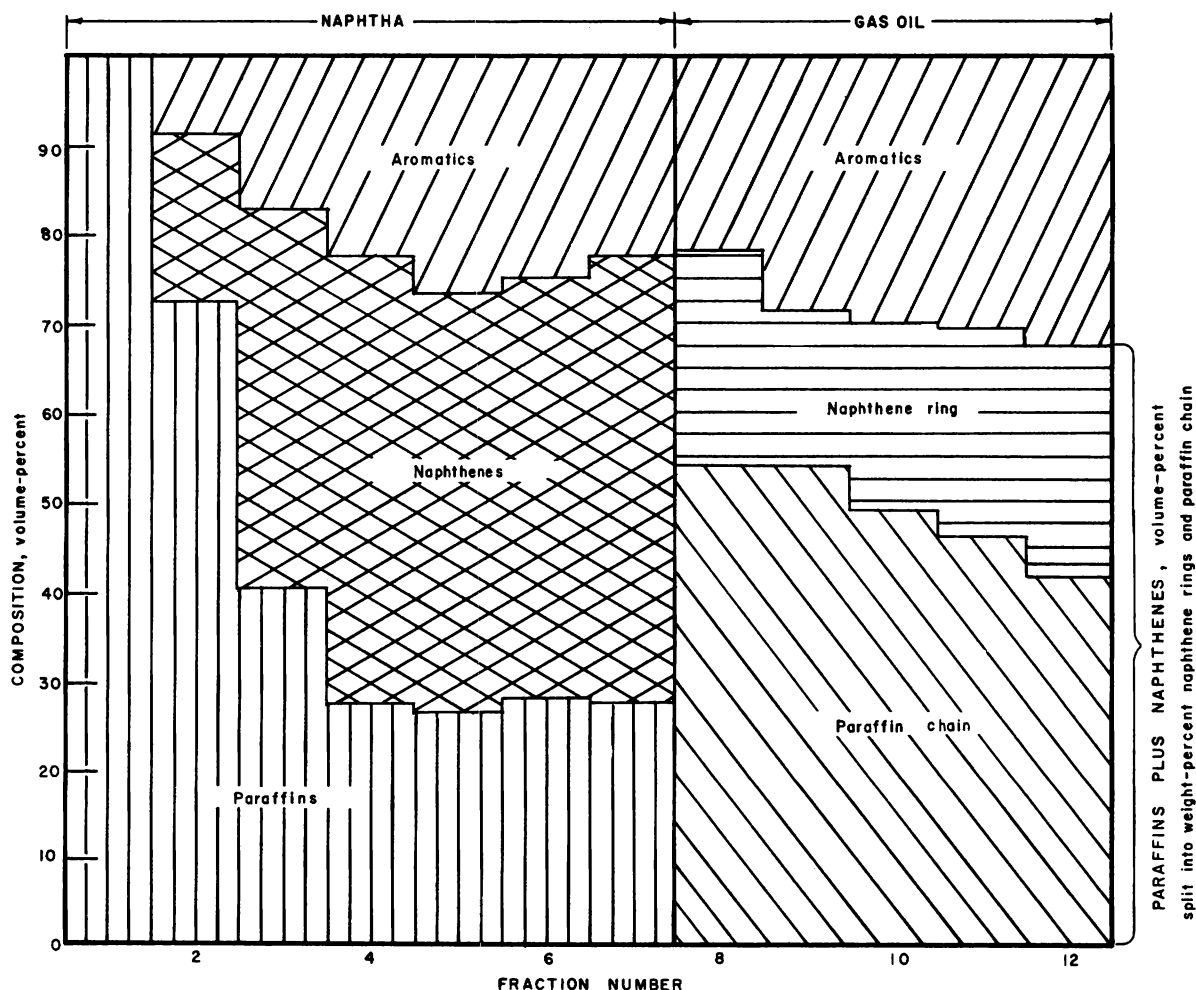


FIGURE 20.—Composition Diagram for Scharb Oil.

Oil TS, Richfield, Calif.

This oil is produced from the Kraemer Sandstone of Miocene rock of the Cenozoic era. It is typical of much California production with a naphtha having a low content of aromatics but rich in naphthenes (1935 classification, naphthene-naphthene). The gas oil is fairly aromatic. In fraction 14 the total rings are 2.5, which is high, and a naphthene ring content of 1.8 indicates dicyclic and possibly tricyclic naphthenes. It can be compared with the low-sulfur oil (Coalinga (Nose)). The naphtha is similar, but the Coalinga gas oil is somewhat more aromatic and less naphthenic. The nitrogen content is 0.575, the sulfur 1.86, and the asphalt 28.4 percent. The asphalt here appears to be related primarily to the nitrogen.

Oil US, Wilmington, Calif.

This oil is produced from a Miocene Formation of the Cenozoic era. It is the only wax-free, high-sulfur oil shown in this report, although there are similar oils in California (1935 classification, naphthene-naphthene). It, like oil TS (Richfield), has a high nitrogen content of 0.662 percent and has 35 percent asphalt, evidently related to the high nitrogen content. The composition diagram is similar in many respects to that for oil M, Hastings, Tex. Data on fraction 14 are not available, but those for fraction 12 show 2.0 total rings per molecule, with 1.4 of these attributed to naphthenes; in comparison Hastings shows 1.9 total rings and 1.5 due to naphthenes. Evidently both oils have dicyclic naphthenes.

In table 11 more detailed analyses of the naphtha to C_7 from Burgan (Kuwait), Lee Harrison, and Wilmington oils are given, together with similar data for Beaver Lodge and Hastings low-sulfur oils. The data in the table for Beaver Lodge and Burgan oils agree with the composition diagram in that the Burgan

naphtha is more paraffinic because of a lower content of both naphthenes and aromatics. The other comparison is between Wilmington and Hastings oils; here there is reasonably good agreement.

Oil VS, Chusov, U.S.S.R.

This oil is produced in the Ural region of the U.S.S.R. from Upper Carboniferous limestone of the Paleozoic era. There are no data to make a composition diagram. This oil has a very high content of sulfur, 4.87 percent, and 31.5 percent asphalt. It is a very aromatic oil (1935 classification, naphthene-naphthene). According to Velikovskiy (194) this is the most aromatic oil in the U.S.S.R. (as of 1938) and the aromaticity extends throughout the oil. The data from the Bureau of Mines analysis (105) confirms this. It is of interest that the oil is the only other Paleozoic oil with high content of aromatics except the Permian oils in west Texas and New Mexico. It would be interesting to compare this oil in detail with Lee Harrison oil, but neither the data nor the oil are available to do this.

Aromatic and Naphthene Profiles

Some of the same data just discussed plus additional data can be shown graphically in another manner that facilitates comparisons. The curves used for this purpose are termed aromatic and naphthene profiles, and are obtained as follows:

The *aromatic profile* is a plot of the volume-percent of aromatics, determined as previously described, for each fraction 2-12.

The *naphthene profile* is a plot of the correlation index for the paraffin-naphthene portion of each fraction 2-12. This figure is obtained by using the specific gravity of the paraffin-naphthene portion, calculated as described previously, to determine the correlation

TABLE 11.—Composition of naphthas to C_7 from several high- and low-sulfur crude oils

Hydrocarbon or hydrocarbon mixture	Volume-percent of crude oil					Ratio of volume-percent of hydrocarbons to percent <i>n</i> -hexane				
	Oil F, Beaver Lodge ¹	Oil PS, Burgan ²	Oil RS, Lee Harrison ¹	Oil US, Wilmington ¹	Oil M, Hastings ²	Oil F, Beaver Lodge	Oil PS, Burgan	Oil RS, Lee Harrison	Oil US, Wilmington	Oil M, Hastings
<i>n</i> -Pentane.....	1.13	0.56	1.08	0.25	0.70	0.73	0.44	1.02	1.25	1.40
<i>n</i> -Hexane.....	1.55	1.27	1.06	.20	.50	1.00	1.00	1.00	1.00	1.00
<i>n</i> -Heptane.....	2.16	1.51	.87	.18	.28	1.39	1.19	.92	.90	.56
Isopentane.....	.65	.23	1.15	.21	.75	.42	.18	1.08	1.05	1.50
Isohexane.....	1.23	.98	.35	.33	.84	.79	.77	.33	1.65	1.68
Isoheptane.....	1.65	1.22	2.01	.32	.72	1.06	.96	1.90	1.60	1.44
Cyclopentane plus methycyclopentane.....	1.29	.27	.73	.45	1.40	.83	.21	.69	2.25	2.80
Cyclohexane plus methylcyclohexane.....	3.28	.64	1.68	.47	2.57	2.12	.50	1.58	2.35	5.14
Benzene plus toluene.....	1.92	.20	2.46	.10	.21	1.24	.16	2.32	.50	.42

¹ Data from reference 137.

² Data from reference 135.

index from tables or by equation (166). Because the paraffin-naphthene portion is in one sense a two-component system in which the normal paraffins have an index of zero and the iso-paraffins of only about 5, compared to a range of 30 to 50 for the naphthenes in the naphtha, the index becomes a reasonably good representation of the naphthene content.

Low-Sulfur Oils

In figure 21 the aromatic profiles for all of the low-sulfur oils are plotted.

They show the same variations as did the composition charts, but comparison is somewhat easier. All of the oils that have naphthas with an aromatic content of less than 10 percent are shown in the left panel except oil N (South Pass). To avoid confusion oil N is shown on the right panel. Table 12 shows the distillation fractions in which certain hydrocarbons would be expected to be present if there were no azeotrope. This condition does not prevail completely, as for example the benzene/*n*-hexane azeotrope at 68.5° C. However, some

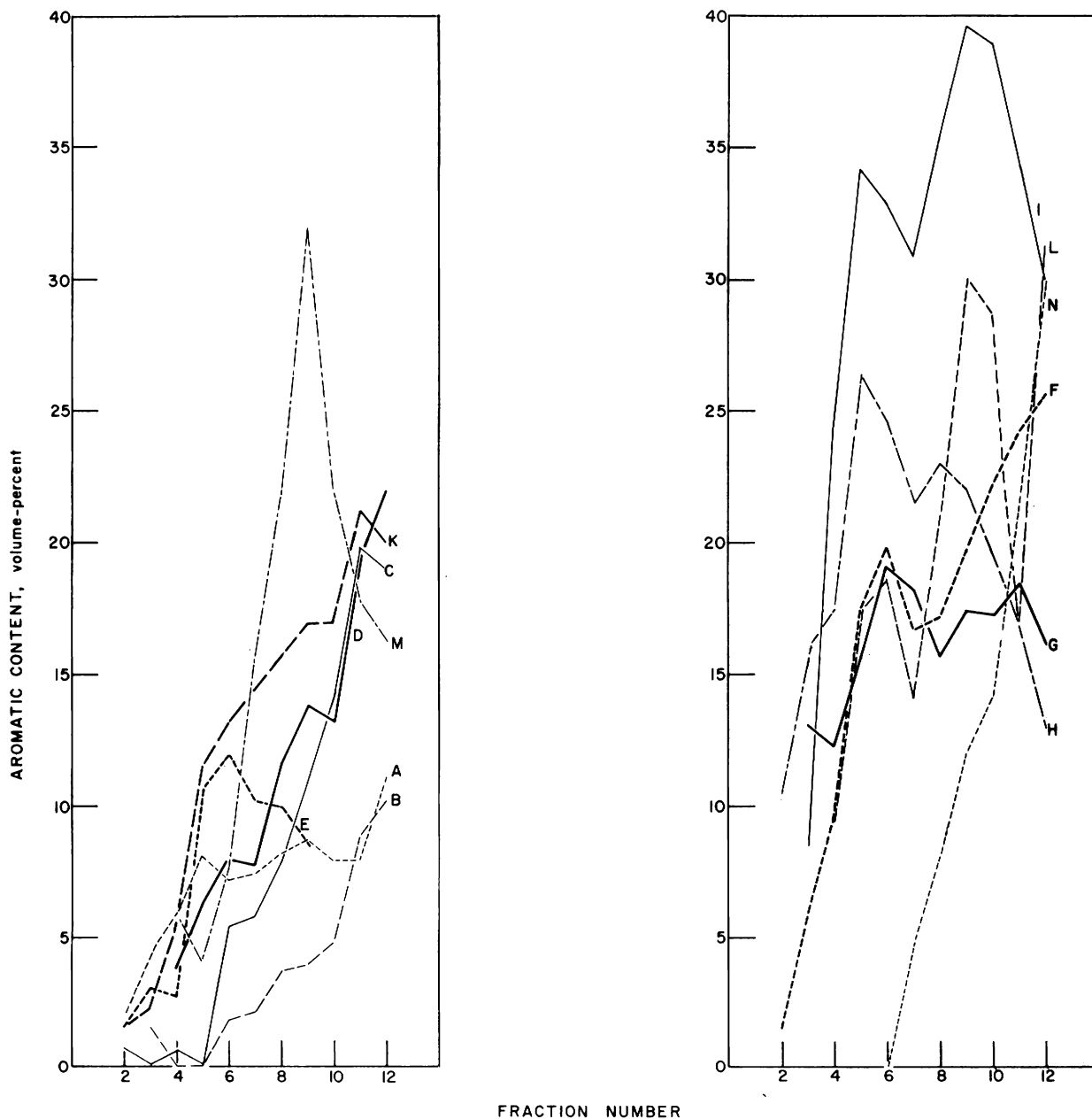


FIGURE 21.—Aromatic Profiles for Low-Sulfur Crude Oils.

of the humps in the aromatic and naphthene profiles can be labeled with different degrees of certainty. None of these oils with the exception of Bradford show any appreciable aromatic hump such as all except oil N do in the right panel. The aromatic content of Bradford is not high, but in the presence of a high paraffin content, which means a low profile, the hump may become prominent. As it occurs for fraction 6, it is presumably a trimethylbenzene and most probably the 1,2,4-derivative, as this often is the predominant isomer.

TABLE 12.—*Fractions in which certain hydrocarbons probably concentrate*

Fraction	Aromatics	Naphthenes
2.....	Benzene.....	Cyclopentane.
3.....	do.....	Methylcyclopentane; ¹ cyclohexane; dimethylcyclopentane. ¹
4.....	Toluene ¹	Ethylcyclopentane; methylcyclohexane. ¹
5.....	Ethylbenzene; xylenes ¹	<i>n</i> -Propylcyclopentane; isopropylcyclopentane; methylcyclohexane; trimethylcyclopentane; ethylcyclohexane; dimethylcyclohexane.
6.....	Butylbenzenes; trimethylbenzene; ¹ other alkylbenzenes.	C ₈ alkylcyclopentane; C ₈ alkylcyclohexane.

¹ Generally present in larger quantities than the others.

The profiles in the right panel show two prominent humps at fraction 5 for oils H (Gueydan, W.), and I (Conroe). These maxima are caused by the xylenes. The curves indicate a high content of aromatics for fraction 4, and this is most certainly toluene. Another set of maxima at fraction 6 for oils F (Beaver Lodge), G (Charenton), and L (Coalinga (Nose)) indicate trimethylbenzenes, probably the 1,2,4 isomer. This is not to imply that the trimethylbenzenes are missing in oils H and I, but rather that the xylenes are present to a lesser extent in oils F, G, and L, thus permitting maxima to show for the trimethylbenzenes. These latter are present in high content also in oils H and I. At fractions 8 and 9 the maxima are probably caused by naphthalene in the Conroe and Coalinga oils (right panel) and Hastings oil (left panel). Note that the content of monocyclic aromatics is apparently small in oil M, Hastings, at least to fraction 8.

Figure 22 shows the naphthene profiles. Cyclopentane that would be in fraction 2 seems to be present in most of the oils, but to a greater extent in the more aromatic oils in the right panel; methylcyclopentane and cyclohexane, the latter often to a lesser extent, are indicated in fraction 3 for all the oils except A, Fasken; B, Bagley; and possibly K, Main Pass. Methylcyclohexane is prominent in all oils except A

and B. C₈ alkylcyclopentanes or C₈ alkylcyclohexanes are probably the predominant naphthenes in fractions 6 and 7, and starting in fraction 7 the dicyclic naphthenes, such as the decalins, probably contribute materially.

High-Sulfur Oils

In figure 23 both the aromatic and naphthene profiles are shown for high-sulfur oils. The only oil showing a pronounced aromatic hump is RS (Lee Harrison). In all the other oils except (OS Lisbon, W.), the aromatic content is low in the naphthas but increases sharply and continuously. The Lisbon oil curve does not start to increase until about fraction 8 because of the high paraffin content of the light naphtha. The naphthene profiles are of a wide variety. Cyclopentane appears to be present in lesser quantities than in most of the low-sulfur oils, but the methylcyclopentane-cyclohexane mixtures in fraction 3 are evident, as is methylcyclohexane in fraction 4. Oils TS (Richfield) and US (Wilmington) appear to have rather large proportions of dicyclic and polycyclic naphthenes.

There is one very interesting aspect of the naphthene profile for both low- and high-sulfur-content oils—they all show a dip or an inflection at fraction 9 or occasionally at fraction 8 or 10. The average boiling points of these fractions—8, 205° C; 9, 231° C; 10, 257° C—each encompass a spread of about 40°. Thus they would include the isoprenoids 2,6,10-trimethylundecane, boiling point 231° C, and 2,6,10-trimethyldodecane (farnesane), boiling point 249° C. Both of these hydrocarbons have been found along with higher boiling isoprenoids in several crude oils in amounts exceeding those for most hydrocarbons. For example in East Texas crude oil they are present to the extent of 0.1 and 0.2 percent, respectively, according to Bendoraitis and coworkers (12). Table 13 shows the isoprenoids that have been found in East Texas oil and the quantities present together with their boiling points and distillate fraction in which they would probably occur. It is interesting to compare these data with the naphthene profile for East Texas oil, figure 24. The probable reason for the decrease from the maximum at fraction 4 due to methylcyclohexane is the presence of these isoprenoids in remarkable quantity in fractions 9–12. These isoparaffins have a correlation index value of approximately zero, compared with 20 to 30 for the naphthenes in fraction 9. Thus their presence in the quantities found could be a factor in the minimum values observed. Since this correlation was noticed the naphthene profiles of the oils studied in the

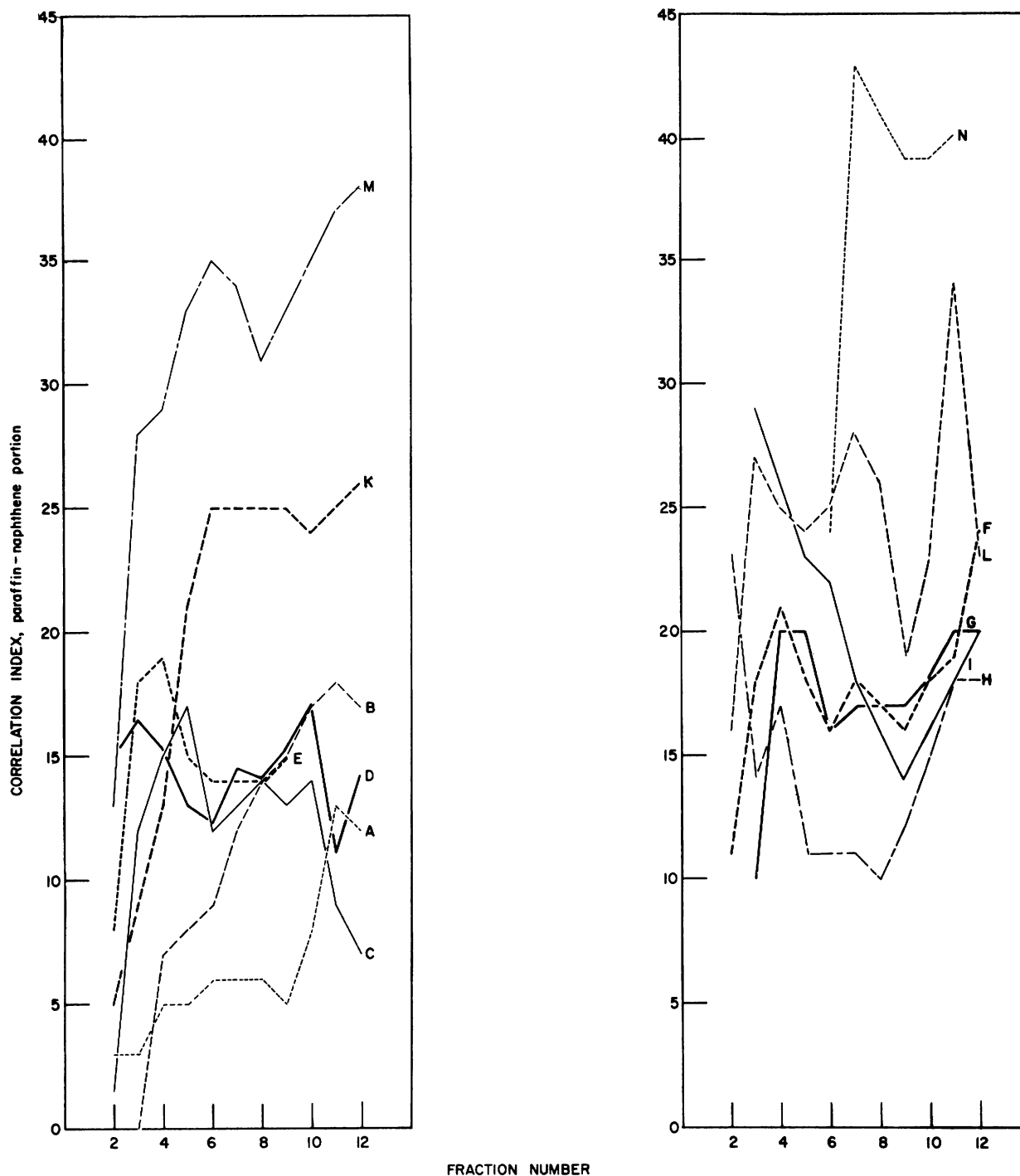


FIGURE 22.—Naphthene Profiles for Low-Sulfur Crude Oils.

Permian Basin report (94) have been reviewed and probably 90 to 95 percent of the oils show the decrease in correlation index for fraction 9 or occasionally 8.

This discovery, if it can be confirmed, will

offer an excellent guidepost to compare crude oils and even to trace their migration, for it is probable that such compounds will be among the liquids to migrate easily and will not be preferentially adsorbed by the rocks.

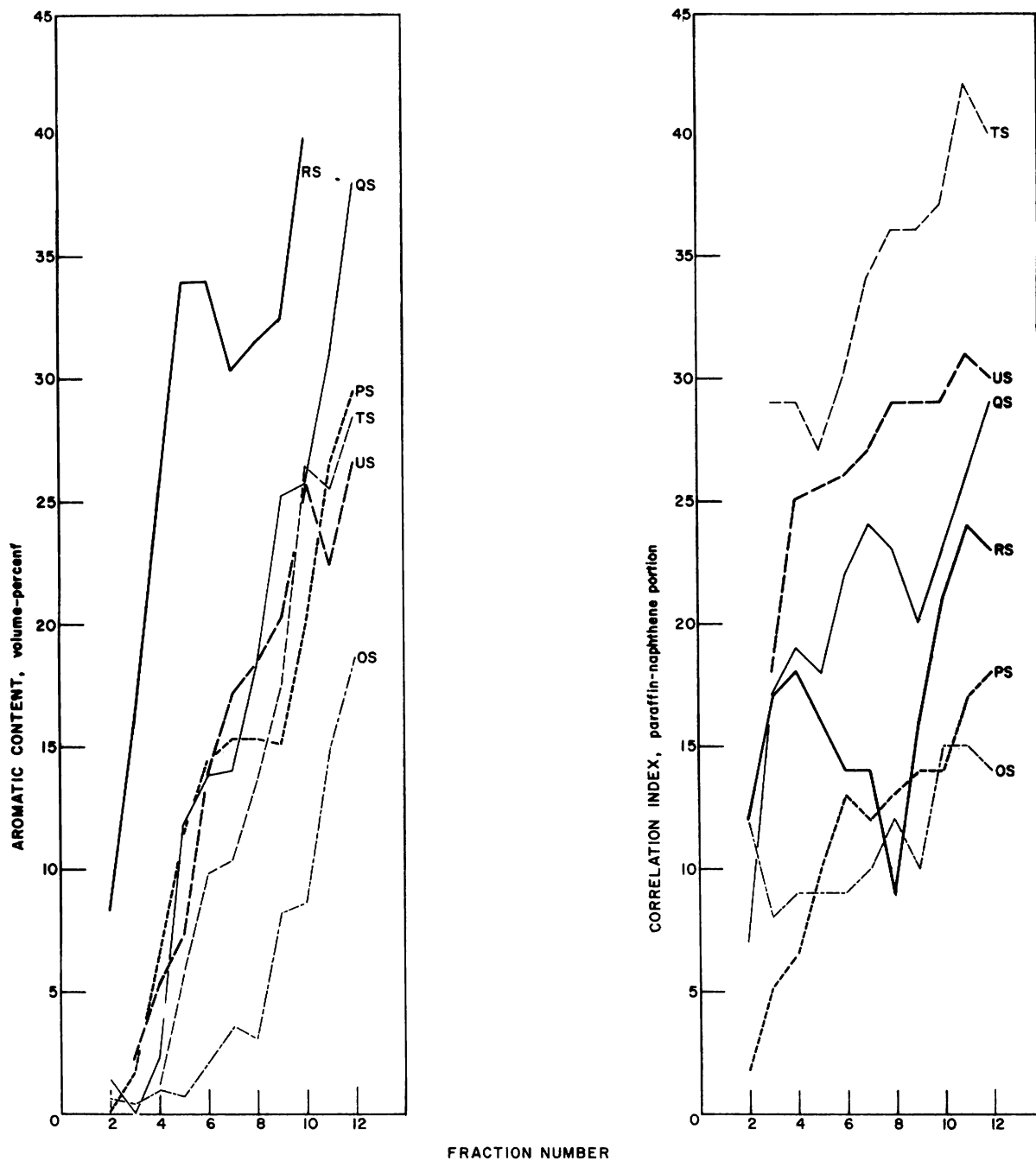


FIGURE 23.—Aromatic and Naphthene Profiles for High-Sulfur Crude Oils.

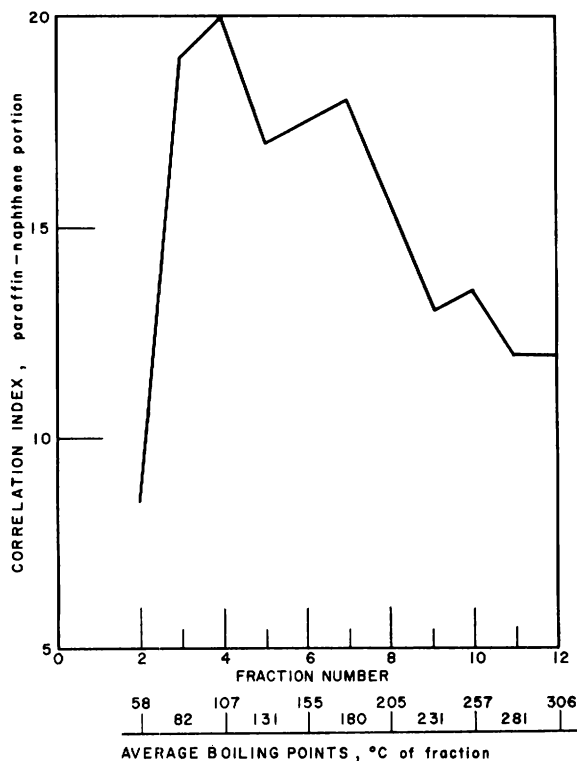


FIGURE 24.—Naphthene Profile for East Texas Oil.

TABLE 13.—Structure and content of isoprenoids isolated from East Texas crude oil (12)

(Hydrogen atoms omitted)

Name	Structure	Bolling point, °C	Fraction ¹	Estimated weight-percent in total crude
2,6,10-Trimethylundecane.....	$\begin{array}{ccccccc} & \text{C} & & \text{C} & & \text{C} & \\ & & & & & & \\ \text{C} & - \text{C} & - & \text{C}_2 & - & \text{C} & - \text{C}_2 - \text{C} \end{array}$	231	9	0.1
2,6,10-Trimethyldodecane (Farnesane).....	$\begin{array}{ccccccc} & \text{C} & & \text{C} & & \text{C} & \\ & & & & & & \\ \text{C} & - \text{C} & - & \text{C}_2 & - & \text{C} & - \text{C}_2 - \text{C} - \text{C} \end{array}$	249	10	.2
2,6,10-Trimethyltridecane.....	$\begin{array}{ccccccc} & \text{C} & & \text{C} & & \text{C} & \\ & & & & & & \\ \text{C} & - \text{C} & - & \text{C}_2 & - & \text{C} & - \text{C}_2 - \text{C} - \text{C} - \text{C} \end{array}$	270	10, 11	.2
2,6,10-Trimethylpentadecane.....	$\begin{array}{ccccccc} & \text{C} & & \text{C} & & \text{C} & \\ & & & & & & \\ \text{C} & - \text{C} & - & \text{C}_2 & - & \text{C} & - \text{C}_2 - \text{C} - \text{C}_2 - \text{C} - \text{C} \end{array}$	285	11	.06
2,6,10,14-Tetramethylpentadecane (Pristane).....	$\begin{array}{ccccccc} & \text{C} & & \text{C} & & \text{C} & & \text{C} \\ & & & & & & & \\ \text{C} & - \text{C} & - & \text{C}_2 & - & \text{C} & - \text{C}_2 & - \text{C} - \text{C}_2 & - & \text{C} - \text{C} \end{array}$	290	11, 12	.5
2,6,10,14-Tetramethylhexadecane (Phytane).....	$\begin{array}{ccccccc} & \text{C} & & \text{C} & & \text{C} & & \text{C} \\ & & & & & & & \\ \text{C} & - \text{C} & - & \text{C}_2 & - & \text{C} & - \text{C}_2 & - \text{C} - \text{C}_2 & - & \text{C} - \text{C} - \text{C} \end{array}$	325	13	.2
2,6,10,14-Tetramethylheptadecane.....	$\begin{array}{ccccccc} & \text{C} & & \text{C} & & \text{C} & & \text{C} \\ & & & & & & & \\ \text{C} & - \text{C} & - & \text{C}_2 & - & \text{C} & - \text{C}_2 & - \text{C} - \text{C}_2 & - & \text{C} - \text{C} - \text{C} - \text{C} \end{array}$	330	13	.1
Total.....				1.36

¹ Routine analysis fractions in which isoprenoids would most likely be found.

NAPHTHA HYDROCARBON COMPOSITION

The preceding section presented the overall picture of the naphthas and gas oils, with some interpretations of the differences as they relate to hydrocarbon groups or specific hydrocarbons. In this section the naphthas will be considered in more detail, first as a whole, and then by parts according to boiling point. Thus the material boiling to 100° C, between 100° and 150°, and 150° and 200° C will be discussed separately with emphasis on the quantitative factors.

GENERAL HYDROCARBON COMPOSITION OF FRACTIONS 1-7

The overall composition of the naphtha from the 21 representative crude oils previously discussed is described by the use of the correlation index and by the percentages of aromatic, naphthene, and paraffin hydrocarbons in the naphthas. These data are shown by bar graphs in figure 25.

Correlation Index Data for Naphtha Fractions 4-7, Panel A

The unweighted average correlation index values for fractions 4-7 are shown in panel A of figure 25 for both low- and high-sulfur oils. The low-sulfur oils start with values of 10 for the paraffinic naphthas from oils A and B (Fasken, Tex., and Bagley, N. Mex.). There is then a gradual increase with one minor interruption by oils ⁴ G and H (Charenton, and Gueydan, W., La.) to a high of 43 for oil J (Sanga Sanga, Borneo). This increase is caused primarily by increase in aromatics, as will be evident from the data in panel B. The bar for oil K (Main Pass, La.) drops somewhat because of a marked decrease in aromatics, but it has a high content of naphthenes and thus the correlation index values are still high. These values continue to increase in the next three oils to a maximum of 41 for oil N (South Pass, La.).

The high-sulfur oils show a very similar pattern, starting with a value of 10 for oil OS (Lisbon, W., La.) and increasing to a maximum of 46 for oil VS (Chusov, U.S.S.R.) with a slight break following oil RS (Lee Harrison, Tex.). Like the low-sulfur oils, the high values of the correlation index are caused in part by aromatics, but for oils TS and US (Richfield and Wilmington, Calif.) naphthenes

are the principal contributors to the index values.

The data in panels B, C, and D for content of naphthenes, aromatics, and paraffins, respectively, show the reasons for the correlation index values, and also indicate that the latter must be used with caution, because one cannot always tell if a high value is caused by aromatics, naphthenes, or a combination of both. To facilitate comparison with correlation index values these data are also shown in panels B, C, and D by dotted bars.

Volume-Percent Aromatics in Naphthas, Panel B

The aromatic content of the naphtha starts at 6 percent, drops to 1 percent for oil B (Bagley, N. Mex.), and then rises fairly uniformly to a maximum of 39 percent for oil J (Sanga Sanga, Borneo). This rise agrees well with the increase in index values, but there is the suggestion that naphthenes are also contributing to the values. There is a pronounced drop in aromatic content to 10 percent after the maximum, and the last four oils all have a low aromatic content, but high correlation index value, indicating a high naphthene content.

Of the high-sulfur oils only two have a high aromatic content, oils RS and VS (Lee Harrison, Tex., and Chusov, U.S.S.R.). From the correlation index it appears that of the remaining five oils, OS and PS (Lisbon, W., La., and Burgan, Kuwait) are probably primarily paraffinic, that oils TS and US, as mentioned previously, are naphthenic, and oil QS (Hobbs, N. Mex.) would appear to be naphthenic also, but the next two panels will show that it also contains a considerable quantity of paraffins in the naphtha.

Distribution Analysis of Aromatic Content

A distribution analysis of the aromatic content of the naphthas of 283 oils was made on the same geological basis as used previously for naphtha content, separating the aromatic content into the following percentage ranges: 0-5, 6-10, 11-15, 16-20, >20. The histogram in figure 26 supports the following points:

1. All the young Tertiary oils contain aromatics, and the percentages are fairly evenly divided over the entire range including >20 percent.

⁴ In this discussion the use of the term "oil" actually refers to the naphtha from that oil—this saves much repetition of the words "naphtha from."

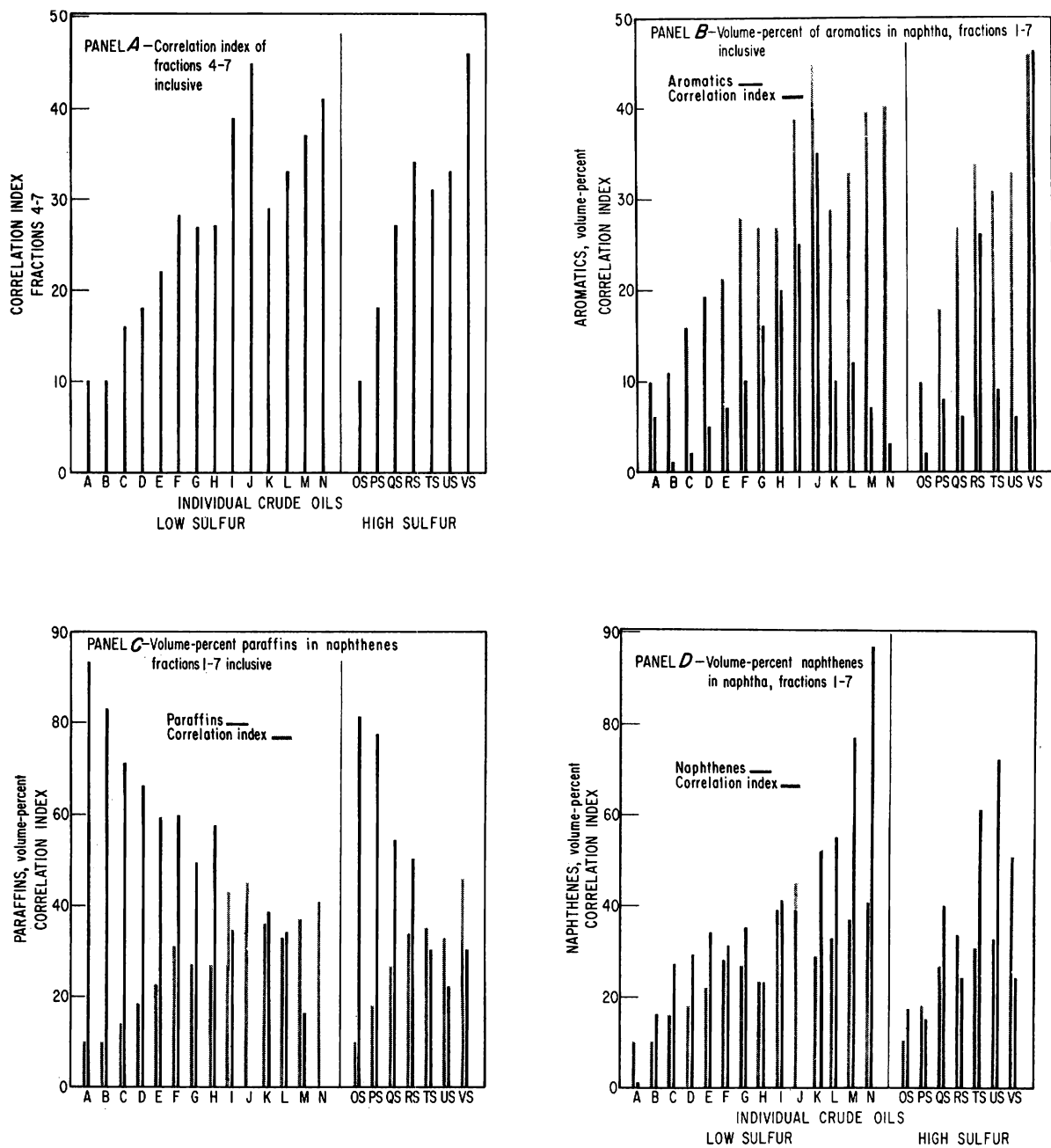


FIGURE 25.—Compositional Data on Low- and High-Sulfur Crude Oils.

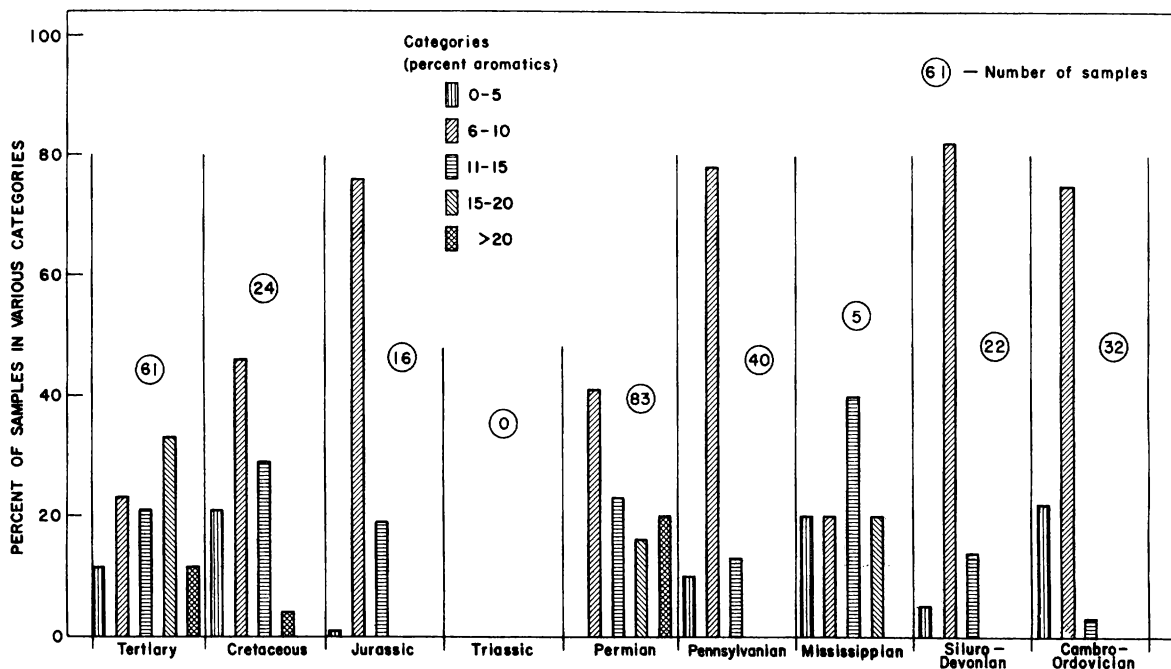


FIGURE 26.—Distribution of Aromatic Content of Naphtha by Geologic Period.

2. In the somewhat older Cretaceous oils the aromatic content seldom exceeds 15 percent, and is greatest at 6-10 percent.
3. The aromatic content of Jurassic oils is mostly in the 6-10 percent range with a much smaller proportion in the 11-15 percent range and none above this.
4. There were no Triassic samples.
5. The aromatic content of Permian oil shows none in the 0-5 percent ranges about 40 percent in the 6-10 percent range, and about 20 percent in each of the higher ranges including those >20.
6. Most of the Pennsylvanian, Siluro-Devonian, and Cambro-Ordovician oils have aromatic contents in the 6-10 percent range.
7. The five Mississippian samples were too few to provide useful data.

Three tentative general conclusions seem to stand out.

1. Naphthas from Tertiary oils contain the highest percentage of aromatics except for the Permian oils.
2. Permian oils from the Permian Basin of West Texas and New Mexico are unique in being the only oils of a period older than Tertiary and having a significant number of samples that have a high content of aromatics in their naphthas.

3. It appears that the normal expected aromatic content of a naphtha is 6-10 percent, other than the two exceptions noted.

Before sound conclusions regarding the aromatics can be reached, several studies should be made. A considerably larger sample selection covering all geologic periods should be studied. The question of why the younger oils have more aromatics should be considered. Is this caused by differences in the characteristics of the original source materials, by differences in diagenesis, difference in modes of accumulation and migration, by adsorption, or by a combination of these? Finally a plausible mechanism is needed to account for the high-aromatic, high-sulfur Permian oils of West Texas and New Mexico.

This distribution analyses technique offers interesting possibilities in studying the relationships of crude oil composition and the geological environment in which it is found. A number of properties of crude oil could be studied in this manner and probably some basic concepts could be developed.

Volume-Percent Paraffins in Naphthas, Panel C

The content of paraffins starts with 93 percent for oil A (Fasken, Tex.) and decreases with a few minor interruptions to a minimum of 7 percent for oil M (Hastings, Tex.). Data are not

available for oil J from Borneo, and oil N does not have a full boiling range naphtha; the distillate boiling to 150° C is entirely missing and this usually consists predominantly of paraffins. The correlation index values can be seen to increase with the decrease of paraffins and corresponding increase in cyclic hydrocarbons.

The paraffinic components of the naphtha for the high-sulfur oils OS and PS (Lisbon, W., La., and Burgan, Kuwait) are at once apparent, as is the low paraffin content for oils TS, US, and VS (Richfield, Calif., Wilmington, Calif., and Chusov, U.S.S.R.). As previously mentioned, oil QS (Hobbs, N. Mex.) has a considerable quantity of paraffins, 54 percent, and the Lee Harrison oil, RS, has 50 percent; in oil QS naphthenes are the next most abundant hydrocarbon type, but in oil RS aromatics are.

Volume-Percent Naphthenes in Naphthas, Panel D

Naphthenes are almost missing, 1 percent, in oil A (Fasken, Tex.), but increase to 16 percent in oil B (Bagley, N. Mex.) and then increase generally to a maximum of 97 percent for oil N (South Pass, La.), except for oil H (Gueydan, W., La.). Thus it seems that both paraffins and naphthenes cover almost the entire range from 0 to 100 percent in a reciprocal manner, with aromatics replacing one or the other to varying extents in most oils.

Among the high-sulfur oils the naphthas from oils QS, TS, and US stand out. Oil QS (Hobbs, N. Mex.) has appreciable naphthene content, and oils TS and VS (Richfield and Wilmington, Calif.) have high contents of naphthenes in the naphtha.

Ternary Diagram of Naphtha Compositions

The data just discussed are well summarized in figure 27 which is a ternary diagram showing the percentage of paraffins, naphthenes, and aromatics. The wide range in paraffin-naphthene content is clearly shown, and the rather random distribution of aromatics is noticeable. The majority of the naphthas have an aromatic content of 10 percent or less. One suggestion for this is that in the normal process of accumulating organic debris and its subsequent diagenesis and accumulation as petroleum only about 10 percent or less of aromatics occur in the naphtha. If there are unusual differences in source material, environmental conditions, or both, these may sometimes lead to greatly increased contents of aromatics. It would be very interesting and enlightening to know just how and when this occurs.

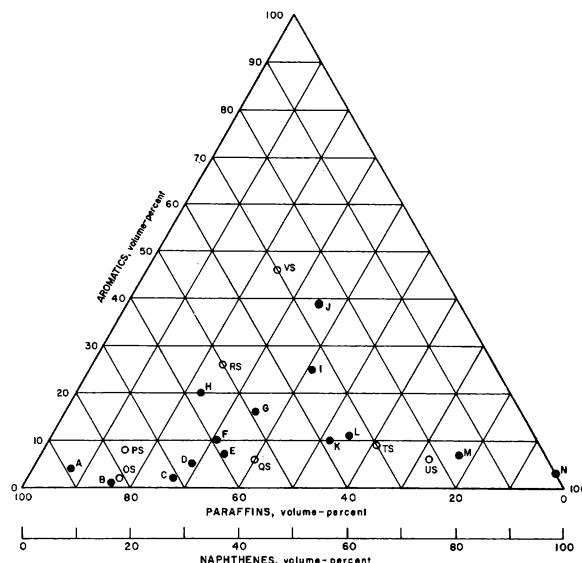


FIGURE 27.—Ternary Diagram of Volume-Percent Paraffins, Naphthenes, and Aromatics in Naphthas.

DETAILED HYDROCARBON COMPOSITION OF NAPHTHAS

In the next four parts of this report the individual hydrocarbons boiling to about 200° C are considered on a quantitative basis. Composition data are given in tables 14, 17, 20 and 21. On each of these tables is listed each of the hydrocarbons that have been identified in petroleum in the boiling range concerned. There is some overlapping of carbon numbers because of differences in boiling points for changes in structure for the same carbon numbers. This list is followed on all tables by the carbon number and boiling points of the compound. These listings are followed by one or more sections having the same general format but differing to accommodate the difference in the original data. The differences are found in the subheading under abundance, and these are as follows for the four tables:

Table 14	Section A	Weight-percent of crude oil.
Table 17	Section A	Volume-percent of crude oil.
	Section B	Weight-percent of distillate to 140° C.
	Section R1	Weight-percent of distillate to 150° C.
	Section R2	Weight-percent of distillate to 175° C.

Table 20	Section A	Volume-percent of crude oil.
	Section B	Weight-percent of distillate to 140° C.
	Section R1	Weight-percent of distillate to 150° C.
	Section R2	Weight-percent of distillate to 175° C.
Table 21	Section A	Volume-percent of crude oil.
	Section R1	Weight-percent of distillate to 150° C.
	Section R2	Weight-percent of distillate to 175° C.
	Section R3	Weight-percent of distillate to 150° to 200° C.

The section A data are entirely from U.S. publications, except the Dutch publication used for table 14. Sections B and R are based entirely on Soviet literature. Under all these section headings there are four columns: Minimum and maximum determined values, the calculated average for all data, and a ratio value for the average of each hydrocarbon relative to the average value for a single selected hydrocarbon in that section. The following hydrocarbons are used as the bases for the ratios:

n-Pentane for all hydrocarbons in table 14.

n-Hexane for all paraffins and cycloparaffins where an average *n*-hexane value can be determined in tables 17, 20, and 21.

Toluene for all aromatics in tables 17 and 20.

n-Propylbenzene for all aromatics in table 21.

Finally each section is completed by two columns of references, one each for the literature sources of the minimum and maximum values, and a column giving the number of oils represented in the average value. Often there is only a single reference to a hydrocarbon. In this event if quantitative data are available it is given under "calculated average" and a single sample is indicated in the maximum reference column.

The use of ratios instead of direct comparison is necessary because most of the Soviet data report only weight-percent of a distillate but do not give either the percent of the crude oil represented by the distillate or the specific gravity of the crude oil. Without these data volume-percent based on the crude oil cannot be calculated. However, the ratio of the weight-percent of the

individual hydrocarbon to that of *n*-hexane gives a figure that is suitable for comparison although not strictly identical to volume-percent ratio. For example: the following values for volume-percent—

$$\frac{\text{volume-percent 2-methylhexane}}{\text{volume-percent } n\text{-hexane}} = \frac{0.40}{1.37} = 0.292$$

would result in these figures for weight-percent—

$$\frac{\text{weight-percent 2-methylhexane}}{\text{weight-percent } n\text{-hexane}} = \frac{0.31}{1.03} = 0.301.$$

The differences are not significant in view of the uncertainty in analytical data. The minimum and maximum values give an idea of the range. The average value provides a norm or guideline, and significant deviations from this particularly for hydrocarbons in the same class, as between *n*-hexane and *n*-heptane, indicate crude oils that might be worthwhile studying in some detail and for which geological history and environment might be enlightening. This average value is not intended to mean that all crude oils should conform—the wide spread between most minima and maxima show this is not a fact. At the end of each section there are additional references, not shown in the table, which were used.

Composition of Naphthas, Hydrocarbons C_2-C_5

The data on the composition of the ethane through pentane portion of the naphtha are presented in table 14 on a weight-percent of crude oil basis. When dealing with such very volatile hydrocarbons as these there is always the problem of sampling and subsequent handling in such a manner that volatile material is not lost before analysis. None of the references used gave any indication of precautions to prevent such losses. Thus any conclusions drawn for these six hydrocarbons should always be considered with their volatility and loss possibilities in mind. None of the references gave data for methane. The average values show that the content of *n*-alkanes increases in the order ethane, propane, butane, pentane. However, the minimum and maximum values cover a rather wide range and table 15 shows that there are a number of samples where the *n*-butane content exceeds or equals that of *n*-pentane. The majority of the oils listed where this is true are from certain formations in Canada, and suggest that a study of this phenomenon for the area concerned might be useful. There is also a suggestion that possibly certain West Texas oils have this inverse relationship. With a few exceptions all of the oils where the abnormal *n*-butane/*n*-pentane relationship holds are produced from Paleozoic rock.

TABLE 14.—*Hydrocarbons identified in naphtha and their abundance, C₂–C₅, –86° to +36° C*

Hydrocarbon	Carbon number	Boiling point, °C	Abundance, weight-percent of crude oil				Reference ¹		No. of samples
			Determined		Average		Minimum	Maximum	
			Minimum	Maximum	Calculated	Relative to <i>n</i> -pentane			
Ethane.....	2	—86.6	0.004	0.15	0.053	0.047	135	193	66
Propane.....	3	—42.1	.01	1.64	.42	.38	158	193	89
Methylpropane.....	4	—11.7	.001	1.45	.29	.26	135	193	91
Butane.....	4	—5	.02	3.27	.90	.81	193	193	91
Methylbutane.....	5	+27.9	.06	2.18	.73	.66	193	193	91
<i>n</i> -Pentane.....	5	+36.1	.06	2.78	1.11	1.00	193	193	90

¹ Additional references used in compilation of data: 52, 136, 137.TABLE 15.—*Relative quantities of n-butane and n-pentane*

Country and State or province	Field	Formation	Geologic period
<i>n</i> -BUTANE GREATER THAN <i>n</i> -PENTANE			
United States:			
Texas.....	East Texas.....	Sabine riverbed ¹	Cretaceous.
Do.....	South Houston.....	Frio.....	Tertiary.
Do.....	South Ward.....	Permian.
Do.....	Wasson.....	Do.
Canada:			
Alberta.....	Bonnie Glen.....	D3.....	Upper Devonian.
Do.....	Campbell.....	Blairmore.....	Lower Cretaceous.
Do.....	Excelsior.....
Do.....	Fenn.....	D3.....	Upper Devonian.
Do.....	Leduc.....do.....	Do.
Do.....	do.....	D2.....	Do.
Do.....	Malmo.....	D3.....	Do.
Do.....	Redwater.....do.....	Do.
Saskatchewan.....	Midale.....	Midalebeds.....	Mississippian.
Do.....	do.....	Froissharbeds.....	Do.
Do.....	Wayburn.....do.....	Do.
Venezuela.....	San Joaquin.....
<i>n</i> -BUTANE EQUAL TO <i>n</i> -PENTANE			
United States:			
North Dakota.....	Beaver Lodge.....	Silurian.
Texas.....	North Smyer.....	Strawn.....	Permian.
Do.....	Teas.....	Ellenburger.....	Ordovician.
Canada:			
Alberta.....	Fairydell ²
Do.....	Joarcam.....	Viking.....	Lower Cretaceous.
Do.....	Malmo.....	D2.....	Upper Devonian.
Saskatchewan.....	Steelman.....	Midalebeds.....	Mississippian.
Colombia.....	Velasquez.....	Tertiary. ³

¹ Almost certainly Woodbine.² Produces from same formations as others listed.³ Known to produce from Tertiary.

With reference to methylpropane and methylbutane, methylpropane content is always less than that of *n*-butane, and the average ratio is about 3 to 1. In contrast there are several oils where the content of methylbutane exceeds that of *n*-pentane; this should clearly be considered abnormal. The oils showing this relationship are listed in table 16. The data for several are only 0.02 percent or less apart. Of the four that are left, three are Permian oils of west Texas, again indicating that these oils

are different; also three of these for which data are available show the content of isohexanes exceeding that of *n*-hexane by factors of 2 to 7.

Finally table 14 indicates that the content of methylpropane is decidedly less than that of methylbutane, and the individual analyses bear this out as only one sample shows the reverse, and this is probably within experimental error.

Composition of Naphthas, Hydrocarbons C₄–C₇

The data in table 17 cover the approximate boiling range of zero to 100° C, and include C₄–C₇ hydrocarbons. There is a small overlap with table 14 which is on a weight-percent basis and the data in table 17 section A based on crude oils which are in volume-percent. In section B where the data are from a distillate boiling to 140° C they represent 15 oils from Baku. A third section R1 presents Soviet data for distillates boiling to 150° C. Approximately 20 samples were used for this part of the compilation. Although the determined minimum, maximum, and average values are given, the only real comparison that can be made is by using the abundance relative to *n*-hexane for alkanes and cycloalkanes, or to toluene for aromatics. The final section R2 presents data from a single sample, but it is the only source of *n*-hexane for comparison with the other data in higher boiling ranges.

TABLE 16.—*Oils in which the content of methylbutane exceeds that of n-pentane*

Country and State	Field	Formation	Geologic period
Kuwait.....	Wafra.....	Eocene (Rad-huma).	Tertiary.
United States:			
Texas.....	Lee Harrison.....	Leonard.....	Permian.
Do.....	Hastings ¹	Frio.....	Tertiary.
Do.....	South Houston ¹	do.....	Do.
Do.....	South Ward.....	Permian.
Do.....	Winkler.....	Guadalupe.....	Do.
Wyoming.....	Wyoming composite ¹	Embar.....	Do.
Venezuela.....	Lagunillas.....	Tersleep.....	Pennsylvanian.
		Miocene and Eocene.	Tertiary.

¹ Methylbutane and *n*-pentane are 0.02 percent or less apart.

TABLE 17.—Hydrocarbons identified in naphtha and their abundance. C_4 – C_7 , 30°–100° C

Hydrocarbon	Carbon number	Boiling point, °C	Section A							Section B							Section R1							
			Abundance, volume-percent in crude oil				References ¹			Abundance, weight-percent of distillate to 140° C				References ¹			Abundance, weight-percent of distillate to 150° C				References ¹			
			Determined		Average		Minimum	Maximum	No. of samples	Determined		Average		Minimum	Maximum	No. of samples	Determined		Average		Minimum	Maximum	No. of samples	
			Minimum	Maximum	Calculated	Relative to <i>n</i> -hexane				Minimum	Maximum	Calculated	Relative to <i>n</i> -hexane				Minimum	Maximum	Calculated	Relative to <i>n</i> -hexane				
Paraffins:																								
<i>n</i> -Butane.....	4	—0.5	0.04	3.66	0.98	0.83	135	135	38	0.11	1.91	0.67	0.28	199	199	12	0.08	6.06	2.09	0.47	99	190	16	
2-Methylpropane.....	4	—11.7	.002	1.35	.29	.25	135	135	41								.10	5.36	1.65	.37	120	190	9	
<i>n</i> -Pentane.....	5	36.1	.14	3.06	1.15	.97	137	137	38	.48	2.66	1.04	.43	199	199	15	.08	10.74	3.69	.83	118	186	21	
2-Methylbutane (isopentane).....	5	27.9	.11	2.50	.86	.73	136	135	38	.35	5.16	1.39	.58	199	199	15	.13	4.53	2.37	.53	100	189	21	
2,2-Dimethylpropane (neopentane).....	5	9.5		.05	.008	.01	137	136	35								.13	.49	.31	.07	97	98	2	
<i>n</i> -Hexane.....	6	68.7	.04	3.10	1.18	1.00	170	73	77	.57	5.17	2.39	1.00	199	199	15	.09	8.43	4.44	1.00	118	98	21	
2-Methylpentane.....	6	66.3	.02	1.45	.55	.47	170	137	77	1.10	11.00	3.48	2.90	199	199	15	.43	4.78	2.88	.65	149	188	20	
3-Methylpentane.....	6	63.3	.01	1.02	.42	.36	170	137	77								.40	2.40	1.68	.38	120	98	20	
2,2-Dimethylbutane.....	6	49.7	.003	.12	.03	.03	137	135	80	.07	.84	.38	.16	199	199	15	.03	.55	.17	.04	190	97	18	
2,3-Dimethylbutane.....	6	58.0	.02	.32	.14	.12	170	170	77	.15	1.80	.73	.31	199	199	15	.06	1.31	.66	.15	100	186	20	
<i>n</i> -Heptane.....	7	98.4	.03	3.64	1.19	1.01	170	73	77	.64	5.96	3.04	1.27	199	199	15	.40	9.74	5.80	1.31	149	98	17	
2-Methylhexane.....	7	90.1	.05	.83	.35	.30	137	135	38								.50	6.55	2.19	.49	118	186	18	
3-Methylhexane.....	7	91.9	.02	.92	.39	.33	170	170	77	1.45	10.25	4.27	1.79	199	199	15	.64	3.65	2.64	.59	7	98	17	
3-Ethylpentane.....	7	93.5	.01	.13	.05	.04	137	136	38								.29	2.07	1.04	.43	199	199	7	.10
2,2-Dimethylpentane.....	7	79.2	.004	.09	.02	.02	137	136	41	.26	1.95	.75	.31	199	199	13	.09	1.07	.27	.06	118	101	16	
2,3-Dimethylpentane.....	7	89.8	.03	.37	.15	.13	136	137	38	.66	3.44	1.78	.74	199	199	14	.13	4.37	1.00	.23	182	97	13	
2,4-Dimethylpentane.....	7	80.5	.01	.14	.05	.04	136	136	38	.13	1.78	.72	.30	199	199	15	.10	1.32	.47	.11	188	101	16	
3,3-Dimethylpentane.....	7	86.1	.003	.05	.014	.01	137	135	41								.02	.68	.33	.07	186	99	7	
2,2,3-Trimethylbutane.....	7	80.9	.001	.024	.006	.005	136	136	38	.07	.42	.21	.09	199	199	11	.11	.28	.17	.04	99	99	4	
Olefins:																								
<i>i</i> -Heptenes.....	7	93.0																						
<i>i</i> -Octenes.....	8	121.0			.12	.10	153																	
Cyclobutanes:																								
Cyclobutane.....	4	12.5		.001			51																	
Cyclopentanes:																								
Cyclopentane.....	5	49.3	0.01	0.35	0.10	0.08	136	137	80	0.07	0.54	0.26	0.11	199	199	15	0.06	1.23	0.45	0.10	99	183	21	
Methylcyclopentane.....	6	71.8	.07	2.35	.53	.43	136	137	77	.48	5.10	3.79	1.58	199	199	15	.08	5.03	2.12	.48	101	182	21	
Ethylcyclopentane.....	7	103.5	.02	.53	.17	.14	136	171	38	.57	2.33	1.38	.58	199	199	15	.13	1.35	.63	.14	189	100	15	
1,1-Dimethylcyclopentane.....	7	87.8	.01	.25	.07	.06	136	137	72	.73	2.94	1.46	.61	199	199	15	.04	.96	.50	.11	186	99	10	
1,2-Dimethylcyclopentane.....	7	99.5		.23	.05	.04	135	137	51								.20	.97	.46	.10	100	187	12	
1,3-Dimethylcyclopentane.....	7	91.9	.03	1.45	.27	.23	136	137	21	.48	3.80	1.62	.68	199	199	10	.16	3.01	1.24	.28	118	99	18	
1,4-Dimethylcyclopentane.....	7	90.8	.02	.91	.17	.16	136	137	22	.77	1.83	1.37	.57	199	199	10	.08	2.16	.76	.17	118	183	14	
1,2,3-Dimethylcyclopentane.....	7	91.7	.02	1.38	.22	.19	136	73	24								.14	1.99	.73	.16	189	97	14	
Cyclohexanes:																								
Cyclohexane.....	6	80.7	.08	2.44	.46	.40	170	136	80	.41	8.50	5.46	2.28	199	199	15	.26	7.37	2.19	.49	149	99	20	
Methylcyclohexane.....	7	100.9	.24	3.90	1.15	.97	135	136	74	1.77	23.58	13.12	5.48	199	199	15	.53	20.05	6.14	1.38	118	99	20	
Aromatics:																								
Benzene.....	6	80.1	.001	1.57	.17	.35	137	170	78	.02	1.02	.38	.22	199	199	9	.02	3.45	.66	.39	118	53	18	
Toluene.....	7	110.6	.004	2.35	.49	1.00	137	73	67	.05	5.82	1.72	1.00	199	199	8	.11	6.60	1.71	1.00	101	53	18	

¹ Additional references used in compilation of data: 52, 191.² Relative to toluene.

Butanes

The methylpropane/*n*-butane situation was well covered in the discussion of table 14, but it is interesting to compare the Baku (section B) and miscellaneous Soviet data (section R1). The Baku data indicate a considerably smaller content of *n*-butane than was given in table 14. This is in keeping with the fact that most oils from the Baku region are comparatively deficient in light ends as shown by Velikovskiy (194) and Kraemer and Lane (105). Thus the low *n*-butane content is one indication of a different type of crude oil. The section R1 data of table 17 also indicate a lesser content of *n*-butane than the table 14 data. Presumably these must also include oils deficient in light ends. The ratio of methylpropane to *n*-butane is greater, partly because of the deficiency in *n*-butane and partly because of a greater proportion of isobutane. The higher ratio of methylpropane to *n*-butane suggests that the lower content of *n*-butane is real, because if there were losses of light ends methylpropane would be the hydrocarbon most likely to be lost.

Pentanes

2,2-Dimethylpropane data are available only for the oils in section A, and these show that this hydrocarbon even in its maximum content is present in very small quantities, about 1 percent of the *n*-hexane content. Presumably the same findings would apply to the oils in section B and R1.

The data for the oils in section A and R1 show that methylbutane content is from 65 to 75 percent of the *n*-pentane content, but for the Baku oils the reverse is true, *n*-pentane is 75 percent of the methylbutane content. A study of the individual Baku analyses indicate that this reversal is true for 9 of the 15 oils. A look ahead to the hexanes shows that this same preference for the branched compounds continues. For the same nine oils where methylbutane content exceeds *n*-pentane the ratio of the sum of 2- and 3-methylpentanes to *n*-hexane is 2.53 as compared to 0.85 for the remaining six oils. This implies that the source material or diagenesis or both are probably different for these two groups of oils. This accounts for the statement by Velikovskiy (194) that the Baku oils although paraffinic have good octane numbers, assuming that he was concerned mainly with these isoparaffinic oils.

Hexanes

Generally *n*-hexane is most abundant, followed by the methylpentanes, and finally the dimethylbutanes. However, as pointed out above the sum of the methylpentanes exceeds

the *n*-hexane for nine of the Baku oils by a factor of >2 , and since generally 2- and 3-methylpentane are present in only slightly different quantities, they both probably exceed the *n*-hexane content for these oils.

For the oils in section A 2-methylpentane is slightly more abundant on the average than 3-methylpentane, and this same relationship is more pronounced for the section R1 oils. A check of the individual analyses shows an interesting fact; in the following oils the 3-methylpentane content is higher than the 2-methylpentane:

Abqaiq	Central Area	Wade City
Abu Hadriya	Kirkuk	Wafra Eocene
Agha Jari	Qatif C	Winkler
Bahrein	Qatif D	

Nine of these are Middle East oils and all except one were analyzed or reported by Smith and Rall (170) and all except Wade City are high-sulfur oils. This raises the question as to whether there is a hidden analytical error in these results, possibly caused by the presence of sulfur compounds. The high-sulfur West Texas oils analyzed by the same method did not show this reversal, but the values for the two hydrocarbons were very close together. In contrast similar oils analyzed by GLC do not show this effect except for Wafra Eocene. At the time these analyses were made a report (75) on the method stated with regard to the effect of sulfur: "The conclusion reached is that 0.2 percent by weight of sulfur in a naphtha will not affect the final results of analyses for the three hydrocarbon types." It appears that further data on the relationship of 2- and 3-methylpentane in Middle East crude oils are needed.

Le (111) presents 2- and 3-methylpentane data for 14 crude oils, for 7 of which the sulfur content ranges from 0.97 to 2.86 (sulfur not given for the other seven oils), and in every case the 2-methylpentane is greater than the 3-methylpentane except in one instance where they are equal. The ratio of the 2- to the 3-isomer covers a range of 3.37 to 1.00. Thus it seems to be a rather well established fact that the 2- isomer is more abundant than the 3-isomer.

Heptanes

In virtually all cases for the oils in panels A and R1 the *n*-heptane content exceeds by a factor of 2 or more the content of any single isomer. In all cases the order of decreasing average concentration, with a few minor discrepancies, is *n*-heptane, 3-methylhexane, 2-methylhexane, 2,3-dimethylpentane, 3-ethylpentane, 2,4-dimethylpentane, 2,2-dimethylpentane, 3,3-dimethylpentane and 2,2,3-trimethylbutane. The decrease is an order of magnitude

between *n*-hexane and the methyl isomers, another order of magnitude from there to the dimethyl isomers, and still another order of magnitude to the trimethyl isomers. For the 15 oils from Baku 11 show a greater content of 2- plus 3-methylhexane than the total *n*-heptane; beyond this the average decreasing order of abundance was 2,3-dimethylpentane, 3-ethylpentane, 2,2-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, and 2,2,3-trimethylbutane. This is essentially like the panel A and R1 oils but at a higher quantitative level. The work of Le (111) reporting on 14 crude oils shows that 3-methylhexane is more abundant than 2-methylhexane in 10 oils, is the same for one oil, and the converse is true for 3 oils. Checking the individual analyses in section A of table 17 out of 39 oils, 37 have a higher content of 3-methylheptane than 2-methylheptane, in one oil there is no difference, and the converse is true in only one oil. Thus again a decided preference for one isomer over another is evidenced, but for those few where the 2-methylpentane is more abundant the range of ratio of 2-methylhexane to 3-methylhexane is much less, about 0.50 to 1.

Cyclopentanes

The apparent order of abundance of the cyclopentanes is methylcyclopentane, 1,*t*-2-dimethylcyclopentane; 1,*c*-3-dimethylcyclopentane; 1,*t*-3-dimethylcyclopentane; ethylcyclopentane; 1,1-dimethylcyclopentane; cyclopentane; 1,*c*-2-dimethylcyclopentane. This order of succession is based on section A and section R1 data; section B data show little variation among the dimethylcyclopentanes, but they are present to the extent of 2 to 10 times as much as in most of the oils in section A and R1. The ratio of methylcyclopentane to cyclopentane varies tremendously, from about 77 to 0.8 (one Soviet oil reported by Le (111) shows this reversal). The maximum value is also from Le.

Cyclohexanes

Only cyclohexane and methylcyclohexane are present in the boiling range being considered. Methylcyclohexane content is almost always greater than cyclohexane; only one reversal has been noted, that for Lee Harrison oil from West Texas. The ratio of methylcyclohexane to cyclohexane covers a range of roughly from 4.8 to 0.93. This is a much smaller range than for the corresponding cyclopentanes. As was true for the cyclopentanes, the content of the cyclohexanes in the Baku oils is 5 to 7 times that of the average for other oils based on ratios to *n*-hexane. Unfortunately, the absolute quantities cannot be determined; however, the ratio of methylcyclohexane to *n*-hexane is similar to

such Gulf Coast so-called naphthenic oils as South Houston, Conroe, Hastings, Saxet, Plymouth, and Tom O'Connor.

Aromatics

Benzene and toluene are the only aromatics in the boiling range in table 17. Toluene is usually present in the greater quantity but there are several exceptions; among the oils being considered here the following show more benzene than toluene: Wafra Eocene, Eola, Slaughter, Lee Harrison, and one Soviet oil. None of the Baku oils shows this reversal, nor are they abnormal in aromatic content as for the cycloalkanes and isoparaffins. Table 17 shows an average ratio of toluene to benzene of about 3 to 4; the smallest ratio noted is 0.58 for a Soviet oil.

Comparison of *n*-Paraffinic, Isoparaffinic, Naphthenic, and Aromatic Naphthas

In table 18 data on four types of naphthas are shown. These types are named *n*-paraffinic, isoparaffinic, naphthenic, and aromatic because one of those characteristics is outstanding, usually to the exclusion of the other three; this is not always true. In addition to these distinctions a Soviet and a U.S. oil have been shown for each class. Possibly better examples could be found, but only a limited number of oils have been analyzed in the required detail.

The data for the Soviet oils are presented as (1) the weight-percent of specific hydrocarbons of a gasoline (benzene) distillate boiling to 150° C (189) or 140° C (199) (2) the ratio of this weight-percent to the value for *n*-hexane. This enables comparison with the data for the U.S. oils. The data for the U.S. naphthas are (1) volume-percent of individual hydrocarbons based on the whole crude oil and (2) the ratio of this value for each hydrocarbon to that for *n*-hexane. It must be stressed that in this table the emphasis is on relative proportions of hydrocarbon classes rather than the total quantity present. For example some naphthas may have a high content of *n*-paraffins, but they may likewise have a high content of isoparaffins; thus they would be paraffinic naphthas, but not *n*-paraffinic.

n-Paraffinic Naphthas.—The Shugurovskoye oil (189) from the U.S.S.R. was chosen as a representative source for the *n*-paraffinic naphtha. Its contents of *n*-paraffins relative to *n*-hexane are all above 1.0 except *n*-nonane and this is probably not present in its full representative amount because of boiling point considerations. In contrast the content of isoparaffins is one or two magnitudes less, and the same observation

holds for the cyclopentanes, cyclohexanes, and aromatics. It seems clear this naphtha is dominated by the *n*-paraffins. The representative source for this U.S. naphtha is crude oil from Fasken, Tex. The same observations as made for the Soviet naphtha apply here also, but the contrast is even greater.

Isoparaffinic Naphthas.—Two isoparaffinic naphthas from Soviet oils were selected. The naphtha from Anastasievskoye oil not only has a high proportion of isoparaffins, but it has an equally high proportion of cycloparaffins, especially cyclohexanes. Normal paraffins are present in very insignificant quantities. The naphtha from Gyurgyanskoye crude oil (Baku region) is also decidedly isoparaffinic, but contains a much smaller proportion of cycloparaffins. The prevalence of multimethyl groupings in the Anastasievskoye naphtha is particularly noticeable—thus the larger quantities of dimethyl, dimethylethyl, and even trimethyl paraffins and the dimethyl, trimethyl, methylethyl, propyl, and isopropyl cyclohexanes. It is almost as if there were methyl, ethyl, and propyl radicals available to be attached to the paraffin chains or cycloparaffin rings. To a lesser extent, probably an order of magnitude less, the same general observation also applies to the Gyurgyanskoye naphtha. However, this latter Soviet naphtha compares more closely to the Winkler naphtha than to the Anastasievskoye naphtha. The Winkler naphtha isoparaffins are composed predominantly of the methyl isomer, the dimethyl compounds being present in small quantities only. This also appears to extend to the cyclopentanes; there are not enough data on the cyclohexanes to form a judgment. Later in this paper it will be pointed out that Winkler crude oil, along with those from the Yates, Tex., and Monument, N. Mex., fields are crude oils that deviate from the norm in several ways; their unusual high content of isoparaffins in the naphtha is one.

Naphthenic Naphtha.—The Soviet naphthenic naphtha is from Karachukhurskoye (upper formation) oil from the Baku region, and the U.S. naphtha is from the Saxet, Tex. oil. The Soviet oil contains more distillate, but the proportion of the *n*-paraffins, isoparaffins, and cycloparaffins are fairly similar throughout. In a number of instances the Saxet data are for two hydrocarbons combined, and this should be considered.

Aromatic Naphtha.—The Soviet aromatic naphtha from Karachukhurskoye (lower formation) oil from the Baku region is rather similar to the naphtha from the Conroe, Tex. oil. The nonaromatic portion of the naphtha is probably characterized by a somewhat greater content of cycloparaffins than a great many oils, but the distinguishing characteristic is the considerably

above normal content of benzene, toluene, and higher alkylated benzenes.

Distribution of Selected Hydrocarbons

There is another method of showing relationships of individual hydrocarbons or hydrocarbon types, and that is the percentage distribution of selected hydrocarbons within a given boiling range or carbon number limit. This is difficult to do successfully because analyses often do not report the full quota of compounds, and one does not know if the missing compounds should be considered as not present or just not determined. Through the reports of Martin and co-workers it is possible to make a limited analysis in this manner, and some of the Soviet reports can be used in a similar manner. In table 19 data for hydrocarbons in the C₅–C₈ range from nine crude oils are given. Not all hydrocarbons in the carbon number range are given because the complete data were not always available. The first nine columns of figures give the content in terms of volume-percent of the crude oil for items marked (a), in weight-percent of distillate for items marked (b). The second set of nine columns give the percentage distribution of each hydrocarbon or hydrocarbon type based on the total listed, so that the total of each column is 100 percent.

The data have been arranged in descending order of content of *n*-paraffins, starting with 64.65 percent for Fasken oil and ending with 0.93 percent for Anastasievskoye oil. The data are difficult to describe from a table, but when charted in bar graph form they are much easier to interpret. This has been done in figure 28. First glance shows the predominance of the *n*-paraffins and of paraffins with a single tertiary carbon atom. Fasken is outstanding for its content of *n*-paraffins, and Karachukhurskoye (upper) and Anastasievskoye oils have noticeably low contents of *n*-paraffins. Three oils stand out as having unusual content of paraffins with a single tertiary carbon atom—these are Swanson River, Wilmington, and Anastasievskoye. The latter is also distinguished by having a very unusual quantity of paraffins with two tertiary carbon atoms. With this exception the contents of paraffins with two tertiary carbon atoms, a quaternary carbon atom, or one quaternary and one tertiary carbon atom are uniformly very low. The cyclopentanes are remarkably constant, with cyclopentane and ethylcyclopentane present in very small quantities except for the ethylcyclopentane content of Karachukhurskoye (upper) oil. Methylcyclopentane and the dimethylcyclopentanes are present in about equal proportions except for the larger quantity of dimethylcyclopentanes in Wilmington oil.

Cycloparaffins:																			
Cyclopentanes:																			
Cyclopentane	.22	.04	.04	.01			.16	.12	.06	.19	.23	.15	.01	.25	.41	.14	.10	.14	
Methylcyclopentane	.82	.15	.26	.09	.65	7.22	.48	.36	.34	1.13	3.54	2.38	.11	2.75	2.74	.96	.71	1.01	
Ethylcyclopentane	.13	.03					1.02	.76	.10	.32	1.39	.93	.06	1.50	.57	.20	.22	.31	
1,1-Dimethylcyclopentane					.17	1.89	2.28	1.70	.09	.29	.91	.61	.02	.50	.53	.19	.04	.06	
1,2-Dimethylcyclopentane	.22	.04					1.34	1.00	.09	.29	2.26	1.52			1.06	.37			
1,3-Dimethylcyclopentane	1.03	.19	.11	.04	.16	1.78	.48	.36	.20	.65	1.68	1.13	.05	1.25					
1,4-Dimethylcyclopentane	.79	.14	.06	.02	.08	.89	.96	.72	.21	.68							.17	.24	
1,2,3-Dimethylcyclopentane	.14	.03	.05	.02	.21	2.33			.21	.68			.07	1.75	1.23	.43			
n-Propylcyclopentane	.86	.15															.28	.40	
Isopropylcyclopentane	.25	.05																	
1,1,2-Trimethylcyclopentane					.16	1.78											.40	.57	
1,1,3-Trimethylcyclopentane					.90	10.00													
1,2,3-Trimethylcyclopentane	.18	.03								.16	.52								
1,2,4-Trimethylcyclopentane																			
1,3,4-Trimethylcyclopentane	.46	.08			.88	9.78	7.28	5.43			5.56	3.73			2.47	.87			
1,2,4,4-Trimethylcyclopentane																			
1,3,4,4-Trimethylcyclopentane																			
1,2,3,4-Trimethylcyclopentane	.57	.10			.95	10.56													
Cyclohexanes:																			
Cyclohexane	.61	.11	.32	.11	.33	3.67	.41	.31	.27	.87	7.70	5.17	.22	5.50	3.19	1.12	1.13	1.61	
Methylcyclohexane	2.79	.50	.85	.28	.53	5.89	1.77	1.32	.55	1.77	22.47	15.08	.59	14.75	9.17	3.22	2.40	3.43	
Ethylcyclohexane	1.18	.21			2.46	27.33	.60	.45			4.82	3.23			3.80	1.33			
1,1-Dimethylcyclohexane	.16	.03			1.64	18.22	1.65	1.23			1.58	1.06			.56	.20			
1,2-Dimethylcyclohexane	.30	.05			3.80	42.22	.38	.28			1.14	.77	.19	4.75	.67	.24	.23	.33	
1,3-Dimethylcyclohexane							5.5	4.10			6.08	4.08			2.69	.94			
1,4-Dimethylcyclohexane	.87	.16			1.57	17.44	4.59	3.42			8.54	5.73	.23	5.75	2.58	.91	.59	.84	
1,2,3-Dimethylcyclohexane	.34	.06			5.31	59.00	4.38	3.27			3.29	2.21			1.76	.62			
Propylcyclohexane					2.59	28.78													
Isopropylcyclohexane					2.49	27.67													
1-Methyl-1-ethylcyclohexane																			
1-Methyl-2-ethylcyclohexane					.66	7.33													
1-Methyl-3-ethylcyclohexane					2.69	29.89													
1-Methyl-4-ethylcyclohexane					3.72	41.33													
1,1,2-Trimethylcyclohexane																			
1,1,3-Trimethylcyclohexane	2.68	.48			3.36	37.33													
1,2,4-Trimethylcyclohexane					2.71	30.11													
1,3,5-Trimethylcyclohexane					1.75	19.44													
Aromatics:																			
Benzene	.28	.05	.01	.003		.02			.01	.03	.03	.02	0	0	1.02	.36	.36	.51	
Toluene	.88	.16	.16	.05	0	0			.09	.29	.5	.34	0	0	5.82	2.04	1.78	2.54	
1,2-Dimethylbenzene	.18	.03	.13	.04							.11	.07	.01	.25	2.47	.87	.13	.19	
1,3-Dimethylbenzene	.83	.15									.23	.15	.03	.75	3.49	1.22	.80	1.14	
1,4-Dimethylbenzene	.28	.05	.39	.13	.85	9.44					.23	.15			.88	.31			
Ethylbenzene	.55	.10	.07	.02							1.19	.80	.03	.75	.87	.31	.08	.1	

¹ 2- and 3-Methylpentane combined.
² 2- and 3-Methylhexane combined.
³ 2,2- and 2,4-Dimethylpentane combined.
⁴ 2,3-Dimethylpentane and 2-methylhexane combined.

⁵ 2,4- and 2,5-Dimethylhexane combined.
⁶ All the dimethylheptanes.
⁷ All the methyl octanes.
⁸ Total trimethylcyclopentanes.

TABLE 19.—Distribution of selected hydrocarbons for nine crude oils

Hydrocarbon	Volume-percent of crude (a) or weight-percent of distillate (b)									Percent distribution based on hydrocarbons listed								
	(a) Fasken ¹	(a) Beaver Lodge ²	(a) Maljamar ¹	(a) Swanson River ²	(a) Hastings ³	(b) Karachukhur- koye Nizhnego ⁴	(a) Wilmington ²	(b) Karachukhur- koye Verkhnego ⁴	(b) Anastasievskoye ⁵	Fasken ¹	Beaver Lodge ²	Maljamar ¹	Swanson River ²	Hastings ³	Karachukhur- koye Nizhnego ⁴	Wilmington ²	Karachukhur- koye Verkhnego ⁴	Anastasievskoye ⁵
Paraffins C ₈ , C ₉ , C ₁₀ :																		
n-Paraffins.....	7.676	4.840	3.833	3.199	1.480	8.47	.819	2.62	0.17	64.45	27.37	22.91	21.50	18.45	17.52	16.30	4.89	0.93
Paraffins with one tertiary carbon atom.....	1.545	3.012	2.352	6.021	1.844	5.87	1.936	5.49	7.76	12.98	17.03	14.06	40.46	22.98	12.15	38.54	10.25	42.45
Paraffins with two tertiary carbon atoms.....	.179	.336	.363	.294	.340	.28	.032	2.42	6.12	1.60	1.90	2.17	1.98	4.24	.68	.64	4.52	33.48
Paraffins with one quaternary carbon atom.....	.016	.069	.025	.045	.165	.20	.010	.73	.97	.13	.39	.15	.30	2.06	.41	.20	1.36	5.31
Paraffins with one quaternary and one tertiary carbon atom.....		.005		.005	.024	.07	.004	.22	.26		.03		.03	.30	.14	.08	.41	1.42
Total.....	9.416	8.262	6.573	9.564	3.853	14.89	2.801	11.48	15.28	79.06	46.72	39.29	64.27	48.03	30.80	55.76	21.43	83.59
Cyclopentanes C ₅ , C ₆ , C ₇ :																		
Cyclopentane.....	.037	.110	.157	.140	.100	.41	.059	.23		.31	.62	.94	.94	1.25	.85	1.17	.43	
Methylcyclopentane.....	.253	1.180	.782	.740	.570	2.74	.390	3.17	.65	2.12	6.74	4.67	4.97	7.10	5.67	7.76	5.92	3.56
Dimethylcyclopentane.....	.213	1.028	.742	.796	.640	2.82	.927	1.39	.62	1.79	5.81	4.44	5.35	7.97	5.83	18.46	2.60	3.39
Ethylcyclopentane.....		.120		.096	.080	.57	.089	4.85			.68		.65	1.00	1.18	1.77	9.05	
Total.....	.503	2.438	1.681	1.772	1.390	6.54	1.465	9.64	1.27	4.22	13.85	10.05	11.91	17.32	13.53	29.16	18.00	6.95
Cyclohexanes C ₆ , C ₇ :																		
Cyclohexane.....	.322	1.210	.198	1.120	.830	3.19	.130	7.70	.33	2.70	6.84	1.18	7.53	10.35	6.60	2.58	14.37	1.80
Methylcyclohexane.....	.833	2.070	1.882	1.960	1.740	9.17	.340	22.47	.53	6.99	11.70	11.26	13.17	21.68	18.97	6.77	41.94	2.90
Total.....	1.155	3.280	2.080	3.080	2.570	12.36	.470	30.17	.86	9.69	18.54	12.44	20.70	32.03	25.57	9.35	56.31	4.70
Aromatics C ₈ , C ₇ , C ₆ :																		
Benzene.....	.010	.370	1.113	.039	.080	1.02	.016	.03	.02	.08	2.08	6.65	.26	1.00	2.11	.32	.05	.11
Methylbenzene.....	.176	1.550	2.809	.110	.130	5.82	.080	.50	.00	1.48	8.76	16.79	.74	1.62	12.04	1.59	.93	.00
Ethylbenzene.....	.075	.340	1.167	.054		.87	.037	1.19		.63	1.92	6.98	.36		1.80	.74	2.22	
Dimethylbenzenes.....	.577	1.440	1.304	.262		6.84	.155	.57	.85	4.84	8.13	7.80	1.76		14.15	3.08	1.06	4.65
Total.....	.838	3.700	6.393	.465	.210	14.55	.288	2.29	.87	7.03	20.90	38.22	3.12	2.62	30.10	5.73	4.26	4.76
Grand total.....	11.912	17.680	16.727	14.881	8.023	48.34	5.024	53.58	18.28	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

¹ Unpublished data, Bureau of Mines.² Data from reference 137.³ Data from reference 135.⁴ Data from reference 199.⁵ Data from reference 118.

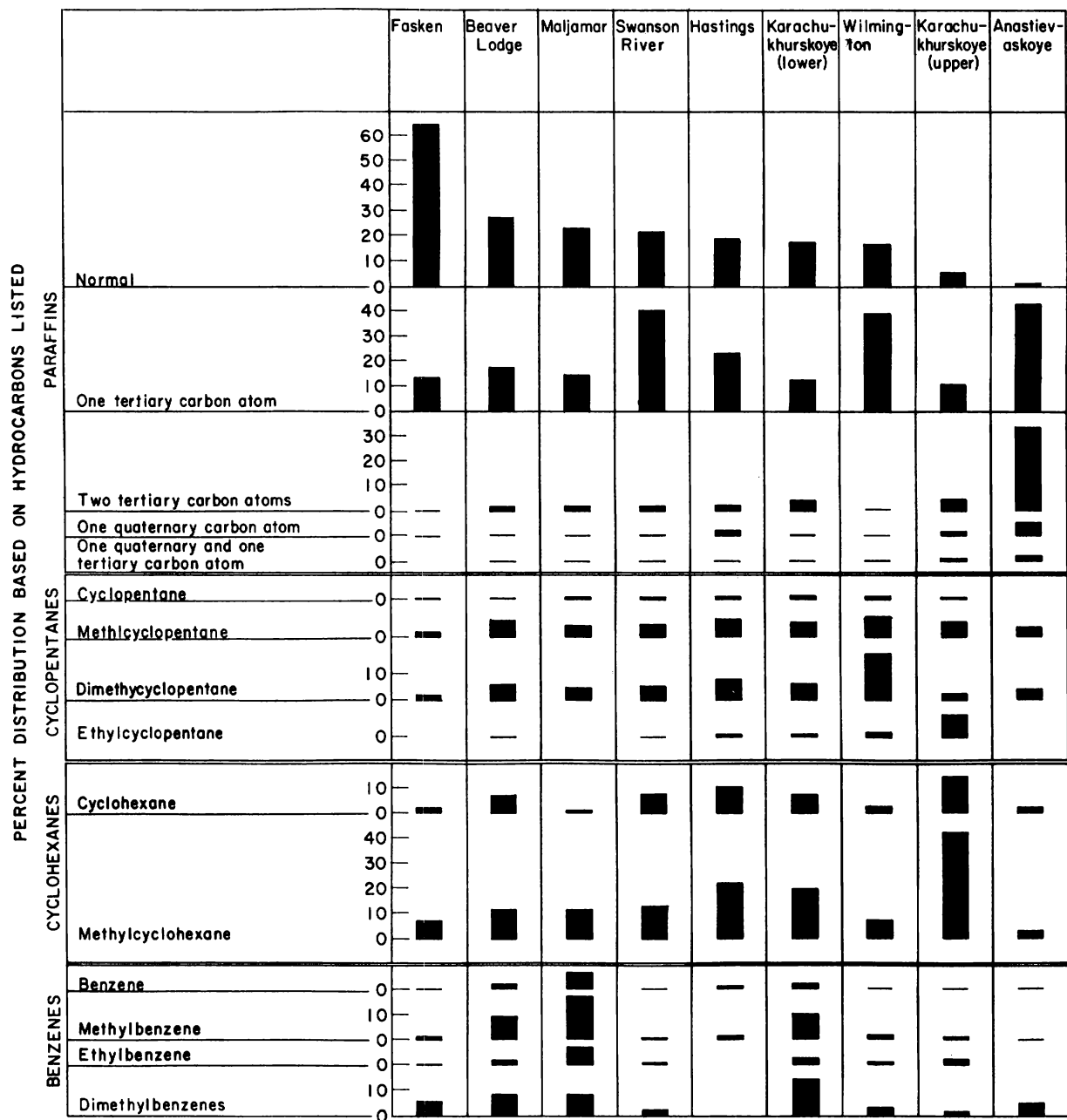


FIGURE 28.—Distribution of Selected Hydrocarbons for Nine Crude Oils.

Methylcyclohexane is always present in greater quantities than cyclohexane, although the difference is not large for a number of the oils. The one that is prominent is Karachukhurskoye (upper) with its very high methylcyclohexane content.

Of the aromatics benzene and ethylbenzene are present in the smallest quantities and in about equal proportions. Methylbenzene is present in three oils in relatively high content; namely, Beaver Lodge, Maljamar, and Kara-

chukhurskoye (lower). These same three oils also have the largest content of dimethylbenzenes.

Possibly the most interesting observation to be made from these data is the apparent independence of each type of hydrocarbon. Thus it is difficult to find any reflection of the large isoparaffin content of Anastasievskoye oil in the other groups, although one might expect larger quantities of other branched hydrocarbons. The large cyclohexane content

of Karachukhurskoye (upper) does not seem to be associated with any of the other composition data unless it is the ethylcyclopentane, also a C_7 cycloalkane. For this same oil there is a suggested relationship between the large content of paraffins with one tertiary atom and the dimethylcyclopentanes, but this is not continued into the cyclohexanes so far as the data go. Swanson River oil, also having a large content of paraffins with one tertiary atom, does not show a pronounced relationship with the other hydrocarbon groups. The three oils with highest aromatic content seem to be entirely independent and have no relationships with the other hydrocarbon groups.

This manner of portraying composition data lends itself well to making comparisons. It would be very desirable to carry such studies on through the C_8 , C_9 , and C_{10} hydrocarbons. Also the relative contents of the various isomers both structural and stereo could be isolated and studied.

Composition of Naphthas, Hydrocarbons C_8 - C_9

The data in table 20 cover the approximate boiling range 100° to 150° C and include C_8 and C_9 hydrocarbons. There are four sections to this table:

Section A.—This is the volume-percent of the crude oil the same as for table 17.

Section B.—This is the weight-percent of gasoline boiling to 140° C and covers the same Baku oils as did section B of table 17. Obviously with a 140° C limit these data do not give complete coverage.

Section R1.—This includes Soviet data from a number of Soviet reports outside Baku and report weight-percent of gasoline boiling to 150° C. This is based on the same analyses as section R1 of table 17. It is difficult to determine if such data include a full complement of hydrocarbons boiling at or near 150° C, such as *n*-nonane (150.8), *n*-propylcyclohexane (156.7), isopropylcyclohexane (154.8), and several methylethylcyclohexanes. The data have been included because they are reported and because they agree fairly well with data for the same hydrocarbons reported in gasoline boiling to 175° C.

Section R2.—This covers Soviet data from a number of reports giving weight-percent of gasoline boiling to 175° C.

Octanes

n-Octane is the most abundant hydrocarbon among the oils represented in sections A and R1, but is much less abundant than the 2- and 4-methylheptanes in the Baku oils (section B). Unfortunately there are only the data of Amer-

ican Petroleum Institute Research Project 6 (API RP 6) for one oil for the methylheptanes. Smith and Rall give data for the sum of the methylheptanes versus *n*-octane, and out of 32 oils 24 have *n*-octane content greater than combined content of methylheptanes; the 8 others where the reverse is true are oils where there is a greater proportion of isoparaffins and cycloparaffins. In this respect they resemble the Baku oils in section B. This continues the trend for such oils to have higher content of isoparaffins than *n*-paraffins. There seems to be little doubt that 2-methylheptane is present in larger quantities than either the 3- or 4-methylheptanes. (There is a suspicion that the 2- and 3-methylheptanes may have been reported together for the data in section B.) There are not enough data on ethylhexane to reach conclusions. The dimethylhexanes give divergent results: In section A the decreasing order of content is 2,3-, 2,2-, 3,4-; in section R1 it is 2,2-, 2,4-, 2,3-. However, there is agreement that the least abundant is the 3,3-dimethylhexane, and the next least abundant is the 2,5-dimethylhexane. In general methylethylpentane, trimethylpentane, and tetramethylbutane are present in significantly lesser quantities than the dimethyl compounds, although these are exceptions. There are too few data to reach general conclusions.

Nonanes

Data on the nonanes are primarily from Soviet sources as listed in section R1, and these data are mostly too few to arrive at sound conclusions. *n*-Nonane is the most abundant, and generally the methyloctanes and the dimethylheptanes are next, being for the most part one-quarter to one-half the *n*-nonane. However, it should be remembered that possibly all of the nonane in the oils studied was not included in the distillate to 150° C. The methylethylhexanes, trimethylhexanes, and tetramethylpentanes are definitely present in less amounts than other nonane isomers with the possible exceptions of the dimethylethylpentanes.

Cyclopentanes

Except for data on 1,1,3-trimethylcyclopentane all of the cyclopentane data are the single results reported by API RP 6 (129) or for the group of Soviet oils given in section R1. Propylcyclopentane appears to have a slightly greater abundance than isopropylcyclopentane, but both are present in quantities appreciably less than for methylcyclopentane or even ethylcyclopentane. Based on the data for the Soviet oils in panel R1 the order of magnitude for the abundance of the trimethylcyclopentanes is almost twice that for the methylethylcyclo-

pentane. Certain of the trimethylcyclopentanes, 1,*t*-2,*c*-3; 1,*c*-2,*t*-4-; 1,*t*-2,*c*-4-trimethylcyclopentanes, are present in larger quantities than the *n*-propylcyclopentane or isopropylcyclopentane. Some of the single values for Ponca City (129) oil in section A agree with these findings.

Cyclohexanes

The data on the C₆ cyclohexanes are difficult to interpret. Ethylcyclohexane is definitely less abundant than methylcyclohexane, and several of the dimethylcyclohexanes equal or exceed it in abundance, but there is not good agreement as to which ones these are except for 1,*t*-2-dimethylcyclohexane. The Baku oils have as a group an abundance in order of magnitude greater than the Ponca City oil (section A) or the Soviet oil (section R1). Possibly some of the difficulty is in the determination of the *cis*- and *trans*- isomers. Two of the methylethyl isomers are of the same order of magnitude as the dimethyl, and two have lower values: 1,1,3-Trimethylcyclohexane is the outstanding member of the trimethyl group, with the 1,2,4-isomer next.

Aromatics

A fair amount of data are available for the aromatics in the range under consideration for each of the four sections. Ethylbenzene does not vary greatly in proportion to the toluene present from 0.35 to 0.66. There are three Baku oils where ethylbenzene exceeds toluene. With regard to the xylenes, the *meta* isomer is the most abundant except for Winkler oil where the *meta-ortho* values are 0.04 and 0.05, respectively. As regards the *ortho-para* relationship, there are only three oils in which the *para* content exceeds the *ortho*, these are Winkler 0.06 vs. 0.015; Hendricks, 0.13 vs. 0.067; Moonie No. 2, 0.03 vs. 0.02. These are all oils that have been and will be pointed out as being "different" in other respects also.

Composition of Naphthas, Hydrocarbons C₉-C₁₁

The data in table 21 cover the approximate boiling range of 150° to 200° C and the carbon number range of C₉, C₁₀, C₁₁, and to a slight extent C₁₂. Sections A, R1, and R2 are the same as previously, representing volume-percent of the crude oil, and weight-percent of distillates boiling to 150° C and 175° C; a third section R3 covers the distillate 150° to 200° C. All of the references in sections R1, R2, and R3 are Soviet.

Paraffins

All of the data for paraffins comes from the report of AP1 RP 6. These are therefore data on a single crude oil, Ponca City, Okla. Whereas in most crude oils the *n*-paraffins decrease generally after *n*-heptane, in the Ponca City oil they remain remarkably near the same, thus in volume-percent of crude versus carbon number it looks like this:

Carbon No.	Volume-percent
C ₆ -----	1. 80
C ₇ -----	2. 3
C ₈ -----	1. 9
C ₉ -----	1. 8
C ₁₀ -----	1. 8
C ₁₁ -----	1. 6

Because there are no other data to modify these, the values for *n*-decane and *n*-undecane relative to *n*-hexane are large in contrast to previous data for *n*-paraffins where data for 30 or more oils was used. The 2-methyl isomer predominates over the 3- or 4-methyl isomers. One or two of the Soviet oils in section R1 show the presence of trimethylheptanes and tetramethylhexanes. The data in section R3 for *n*-decane and *n*-undecane cannot be determined on a comparative basis, since there is no appropriate *n*-hexane datum on which to base a ratio as used previously, and the article does not give the percentage relationships of the distillate to the crude oils. As most of the data on the cyclohexanes and benzenes are from this same article, one can obtain a comparison with them by comparing the calculated average values. On this basis the content of *n*-decane and *n*-undecane is roughly 10 to 20 times the content of most cyclohexanes and alkylbenzenes present in this boiling range. The one compound that is an exception is 1,2,4-trimethylbenzene.

Cyclohexanes

There are no cyclohexanes reported in section A except *n*-butylcyclohexane, also reported in section R3. For the rest of the cyclohexanes reliance is chiefly on the article by Le and Urmancheev (114) just discussed, because there are no data in section R1, and essentially only identification data in section R2. For the data in section R3 again no useful ratio can be calculated. Evidently *n*-butylcyclohexane is the most abundant of the C₁₀ cyclohexanes, *sec*-butylcyclohexane is more abundant than isobutylcyclohexane; and 1-methyl-3-*n*-propylcyclohexane, 1 - methyl - 4 - *n* - propylcyclohexane, and 1-methyl-3-isopropylcyclohexane are more abundant than either of these. 1,2-Dimethyl-4-ethylcyclohexane and 1,3-dimethyl-5-ethylcyclohexane are present in virtually the

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¹ Relative to toluene.

TABLE 21.—*Hydrocarbons identified in naphtha and their abundance, C₉–C₁₁, 150°–200° C*

[illegible]

AROMATICS																																	
<i>n</i> -Propylbenzene	9	159.2			.09	1.00	129		1								.03	.41	.23	1.00	30	187	4		.15	.48	.27	1.00	114	114	4		
Isopropylbenzene (cumene)	9	152.4			.07	1.78	129		1								.06	.12	.09	1.39	30	185	4	Trace	.38	.22	1.81	116	116	4	3		
1-Methyl-2-ethylbenzene (<i>o</i> -ethyltoluene)	9	165.2			.09	1.00	129		1								.14	.36	.22	1.96	187	31	5		.04	2.14	.59	1.2.18	116	96	5		
1-Methyl-3-ethylbenzene (<i>m</i> -ethyltoluene)	9	161.3			.17	1.89	129		1								.25	.48	.33	1.43	150	150	7		.41	.95	.72	1.2.67	96	113	5		
1-Methyl-4-ethylbenzene (<i>p</i> -ethyltoluene)	9	162.0			.06	1.67	129		1								.07	.27	.15	1.65	150	187	5		.19	.73	.49	1.81	96	114	5		
1,2,3-Trimethylbenzene (hemimellitene)	9	176.1			.19	1.2.11	129		1								.10	.49	.25	1.09	150	185	6		.29	1.53	.80	1.2.96	96	113	5		
1,2,4-Trimethylbenzene (pseudocumene)	9	169.4			.51	5.67	129		1								.33	1.09	.84	1.3.65	150	150	6		.97	2.89	1.98	1.7.33	96	114	5		
1,3,5-Trimethylbenzene (mesitylene)	9	164.7			.12	1.33	129		1								.17	1.09	.42	1.2.25	30	150	7		.34	1.01	.58	1.2.15	116	114	5		
<i>n</i> -Butylbenzene	10	183.3			.026	1.29	129		1																	.13	.49	.25	1.93	96	113	5	
Isobutylbenzene	10	172.8			.008	1.09	129		1			.14	101				1.04	.23	.12	1.52	185	187	3		.08	.12	.10	1.37	114	96	2		
<i>sec</i> -Butylbenzene	10	173.3			.017	1.19	129		1										.04	1.17	185		1		.06	.15	.11	1.41	114	114	4		
<i>tert</i> -Butylbenzene	10	169.1			.01	1.11	129		1								Trace							1			.15	1.55	96		1		
1-Methyl-2-propylbenzene	10	184.9			.046	1.51	129		1																	.04	.12	.09	1.33	116	96	4	
1-Methyl-3-propylbenzene	10	182.0			.060	1.67	129		1																	.04	.22	.09	1.33	116	114	4	
1-Methyl-4-propylbenzene	10	183.4			.027	1.30	129		1																								
1-Methyl-2-isopropylbenzene (<i>o</i> -cymene)	10	178.2			.009	1.10	129		1																								
1-Methyl-3-isopropylbenzene (<i>m</i> -cymene)	10	175.1			.08	1.89	129		1								.004	.03	.017	1.07	188	184	2		.03	.18	.09	1.33	116	114	4		
1-Methyl-4-isopropylbenzene (<i>p</i> -cymene)	10	177.1			.04	1.44	129		1										.004	1.02	187		1		.06	.21	.13	1.48	116	114	5		
1,2-Diethylbenzene	10	183.4			.005	1.06	129		1																	.17	.26	.18	1.67	114	114	4	
1,3-Diethylbenzene	10	181.1			.033	1.37	129		1																								
1,4-Diethylbenzene	10	183.8			.007	1.08	129		1																								
1,2-Dimethyl-3-ethylbenzene	10	193.9			.036	1.40	129		1																	.06	.17	.11	1.41	114	116	3	
1,2-Dimethyl-4-ethylbenzene	10	189.5			.057	1.63	129		1																	.34	.44	.38	1.41	116	113	3	
1,3-Dimethyl-2-ethylbenzene	10	190.0			.014	1.16	129		1																	.04	.12	.07	1.26	116	114	3	
1,3-Dimethyl-4-ethylbenzene	10	188.2			.050	1.56	129		1																			.06		.06	1.22	96	1
1,3-Dimethyl-5-ethylbenzene	10	183.6			.063	1.70	129		1																	.06	.34	.19	1.70	96	114	4	
1,4-Dimethyl-2-ethylbenzene	10	186.8			.041	1.46	129		1																	.12	.13	.12	1.44	112	113	2	
1,2,3,4-Tetramethylbenzene (prehnitene)	10	205.0			.2	1.2.22	129		1																	.18	.25	.23	1.85	114	116	4	
1,2,3,5-Tetramethylbenzene (isodurene)	10	198.0			.12	1.33	129		1																	.34	.83	.68	1.2.52	96	116	4	
1,2,4,5-Tetramethylbenzene (durene)	10	196.8			.052	1.58	129		1																		.23	1.85	96		1		
<i>n</i> -Pentylbenzene	11	205.3																															
2-Phenylpentane	11	193.0																															
3-Phenylpentane	11	191.0																															
Isopentylbenzene	11	198.5																															
1-Methyl-3- <i>n</i> -butylbenzene	11	204.1			.06	1.67	129		1																								
1-Methyl-4- <i>tert</i> -butylbenzene	11	192.8																															
1-Methyl-3,4-diethylbenzene	11	201.5																															
1-Methyl-3,6-diethylbenzene	11	200.0																															
1,2-Dimethyl-4- <i>n</i> -propylbenzene	11	208.5			.03	1.33	129		1																								
1,3-Dimethyl-4- <i>n</i> -propylbenzene	11	206.6			.03	1.33	129		1																								
Trimethylethylbenzene	11	212.3			.04	1.44	129		1																								
1,2-Diisopropylbenzene	12	204.0																								.03						1	
1,3-Diisopropylbenzene	12	203.0																								.03						1	
1,4-Diisopropylbenzene	12	210.0																															
Indane	9	177.8			.003		129		1																			.03	1.17	96		1	
1-Methylindane	10	190.6																															
2-Methylindane	10	191.4			.022		129		1																								
4-Methylindane	10	205.5			.03		129		1																								
5-Methylindane	10	201.5					129																										

¹ Relative to *n*-propylbenzene.

same amounts as the *sec*- and *iso* compounds. There are a considerable number of isomers present.

Aromatics

Because they are more reactive and can be more easily separated there is a slightly better story on the alkylbenzenes. Mair (129) reports the percent of a great number of these compounds as given in section A. Because toluene data for many of the oils were not available data have been calculated relative to *n*-propylbenzene to facilitate comparison. Iso-propylbenzene is always present in less quantity than the *n*-propylbenzene. Those alkylbenzenes that are present in quantities equal to or more than *n*-propylbenzene are 1-methyl-2-ethylbenzene, 1-methyl-3-ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,3,4-tetramethylbenzene, and 1,2,3,5-tetramethylbenzene. The data in section R2 and R3 are in excellent agreement for the C₉ alkylbenzenes. There is further agreement that the order of abundance of the methyl-ethylbenzene is 1,3-, 1,2-, 1,4-. This is in agreement with the abundance relationships for the dimethylbenzenes. Further, the trimethylbenzenes in sections R1 and R3 are in the abundance order 1,2,4-, 1,2,3-, 1,3,5-; in section R2 1,2,4- is the most abundant, but the other two

isomers are in reverse order. Williams (198) reports results similar to those in section R2 for the trimethylbenzenes, and in agreement with others on the relative proportions of the methylethylbenzenes. The predominance of the 1,2,4-trimethylbenzene is believed to be the usual finding and could be of significance in organic geochemical studies. Turning to the C₁₀ alkylbenzenes the predominant compounds found by Mair (129), Le and Urmancehev (114), and Kazanskii and coworkers (96) are tabulated below:

	Ratios relative to <i>n</i> -propylbenzene		
	(129)	(114)	(96)
1,2-Dimethyl-4-ethylbenzene.....	0.63	1.30	-----
1,2,3,6-Tetramethylbenzene.....	2.22	1.61	1.39
1,2,3,5-Tetramethylbenzene.....	1.33	2.63	1.89

It is probably significant that the trimethylbenzenes and tetramethylbenzenes appear in a number of oils to be the most abundant of the alkylbenzenes thus far determined quantitatively except toluene and possibly *m*- and *o*-xylene. It appears that allowing for some variations between oil those alkylbenzenes with the most methyl groups are the most abundant of the C⁸ and higher benzenes.

RELATIONSHIPS OF INDIVIDUAL HYDROCARBONS IN NAPHTHA

In 1943 Forziati and coworkers (73) studied in detail the gasoline fraction of seven crude oils and determined the major hydrocarbon components by silica gel separations, careful fractionation, and physical properties. From these data they reached four conclusions, the first three of which are as follows:

1. The gasoline fraction of different crudes may be characterized by specifying the relative amounts of the following five classes of hydrocarbons: * normal paraffins, isoparaffins, alkylcyclopentanes, alkylcyclohexanes, and aromatics.
2. The gasoline fraction of different crudes are composed of the same hydrocarbons, the differences from one crude to another being essentially in the relative amounts of the foregoing five classes of hydrocarbons.
3. Within each of these five classes, the individual hydrocarbons occur in proportions which are of the same order of magnitude for different naphthas.

The fourth conclusion concerned applicability of these findings to analytical uses. In 1953 Smith and Rall (170) reported the results of

analyses of naphthas from 32 crude oils in which the components were determined by fractionation and physical properties, primarily density and refractivity intercept. They stated that

... Forziati and coworkers . . . studying the components of straight-run naphthas from seven crude oils, observed that the ratios of the percentage of certain individual hydrocarbons and classes of hydrocarbons present in these naphthas showed surprising constancy. The present report presents data on naphthas from 21 domestic and 11 foreign crude oils that substantiate this observation.

In 1963 Martin and coworkers (137) presented an excellent study of the naphthas of 18 crude oils analyzed by gas chromatography supplemented by mass spectra. These new data, possibly because of a wider variety of crude oils and more accurate methods of analysis indicated some wider variations than had been previously noted. They state:

The generalizations of Rossini, Mair, and Streiff¹ (Author's note: These generalizations are essentially as quoted previously from Forziati) represented a significant advance in classifying the

* For the present, bicyclonaphthenes, the first of which is apparently encountered² at 147 deg C, are not considered in this classification.

² F. D. Rossini, *Petroleum Engr.* 14, 223 (1943).

¹ Rossini, F. D., Mair, B. J., and Streiff, A. J., "Hydrocarbons from Petroleum," Reinhold Corporation (New York), 1963.

TABLE 22.—Key to data shown on figures

Item No.	Reference	Field	State	Country	Geologic	
					Era	Period
1.	135.	Beaver Lodge.	North Dakota.	United States.	Paleozoic.	Silurian.
2.	135.	El Dorado.	Arkansas, Louisiana.	do.	Mesozoic.	Cretaceous.
3.	135.	Hastings.	Texas.	do.	Cenozoic.	Tertiary.
4.	135.	Kuwait.		Kuwait.	Mesozoic.	Cretaceous.
5.	135.	Lagunillas.		Venezuela.	Cenozoic.	Tertiary.
6.	135.	Saudi Arabian.		Saudi Arabia.	Mesozoic.	Jurassic.
7.	135.	Slaughter.	Texas.	United States.	Paleozoic.	Permian.
8.	135.	Tia Juana.		Venezuela.	Cenozoic.	Tertiary.
9.	135.	West Kansas.	Kansas.	United States.	Paleozoic.	Penn. or Miss.
10.	135.	Winkler.	Texas.	do.	do.	Permian.
11.	135.	Wyoming.	Wyoming.	do.	do.	Penn. or Permian.
12.	137.	Alida.	Saskatchewan.	Canada.	do.	Mississippian.
13.	137.	Beaver Lodge.	North Dakota.	United States.	do.	Do.
14.	137.	Darius.		Iran.	Mesozoic.	Cretaceous.
15.	137.	Eola (McLish).	Oklahoma.	United States.	Paleozoic.	Ordovician.
16.	137.	Eola (Oil Creek).	do.	do.	do.	Do.
17.	137.	Hendricks.	Texas.	do.	do.	Permian.
18.	137.	Kawkawlin.	Michigan.	do.	do.	Devonian.
19.	137.	Lee Harrison.	Texas.	do.	do.	Permian.
20.	137.	North Smyer.	do.	do.	do.	Pennsylvanian.
21.	137.	Pembina.	Alberta.	Canada.	Mesozoic.	Cretaceous.
22.	137.	Ponca City.	Oklahoma.	United States.	Paleozoic.	Ordovician.
23.	137.	Redwater.	Alberta.	Canada.	do.	Devonian.
24.	137.	South Houston.	Texas.	United States.	Cenozoic.	Tertiary.
25.	137.	Swanson River.	Alaska.	do.	do.	Do.
26.	137.	Teas.	Texas.	do.	Paleozoic.	Ordovician.
27.	137.	Uinta Basin.	Utah.	do.	Cenozoic.	Tertiary.
28.	137.	Wafra (Eocene).		Kuwait.	do.	Do.
29.	137.	Wilmington.	California.	United States.	do.	Do.
30.	138.	Comodoro.	Santa Cruz.	Argentina.	Mesozoic.	Cretaceous.
31.	138.	Minas.	Sumatra.	Indonesia.	Cenozoic.	Tertiary.
32.	138.	Moonie No. 2.	Queensland.	Australia.	Mesozoic.	Triassic.
33.	138.	Ranger Lake.	New Mexico.	United States.	Paleozoic.	Pennsylvanian.
34.	138.	Waha.		Libya.	Cenozoic.	Tertiary.
35.	138.	Wafra Ratawi.		Neutral Zone.	Mesozoic.	Cretaceous.
36.	170.	Abqaiq.		Saudi Arabia.	do.	Jurassic.
37.	170.	Abu Hadriya.		do.	do.	Cretaceous.
38.	170.	Agha Jari.		Iran.	Cenozoic.	Tertiary.
39.	170.	Bahrain.		Bahrain.	Mesozoic.	Cretaceous.
40.	170.	Central area.		Iran.	Cenozoic.	Tertiary.
41.	170.	Coalinga.	California.	United States.	do.	Do.
42.	170.	Conroe.	Texas.	do.	do.	Do.
43.	170.	Dammam.		Saudi Arabia.	Mesozoic.	Cretaceous.
44.	170.	East Texas.	Texas.	United States.	do.	Do.
45.	170.	Elk Basin.	Wyoming.	do.	Paleozoic.	Pennsylvanian.
46.	170.	Gach Saran.		Iran.	Cenozoic.	Tertiary.
47.	170.	Golden Meadow.	Louisiana.	United States.	do.	Do.
48.	170.	Hastings.	Texas.	do.	do.	Do.
49.	170.	Hull-Silk-Sikes.	do.	do.	Paleozoic.	Pennsylvanian.
50.	170.	Jennings.	Louisiana.	do.	Cenozoic.	Tertiary.
51.	170.	Kirkuk.		Iraq.	do.	Do.
52.	170.	KMA.	Texas.	United States.	Paleozoic.	Ordovician.
53.	170.	Monument.	New Mexico.	do.	do.	Permian.
54.	170.	Oklahoma City.	Oklahoma.	do.	do.	Ordovician.
55.	170.	Old Ocean.	Texas.	do.	Cenozoic.	Tertiary.
56.	170.	Plymouth.	do.	do.	do.	Do.
57.	170.	Qatif C.		Saudi Arabia.	Mesozoic.	Jurassic.
58.	170.	Qatif D.		do.	do.	Do.
59.	170.	Santa Barbara.		Venezuela.	do.	do.
60.	170.	Saxet.	Texas.	United States.	Cenozoic.	Tertiary.
61.	170.	Segno.	do.	do.	do.	Do.
62.	170.	Slaughter.	do.	do.	Paleozoic.	Permian.
63.	170.	Tom O'Connor.	do.	do.	Cenozoic.	Tertiary.
64.	170.	Wade City.	do.	do.	do.	Do.
65.	170.	Wasson.	do.	do.	Paleozoic.	Permian.
66.	170.	West Edmond.	Oklahoma.	do.	do.	Ordovician.
67.	170.	Yates.	Texas.	do.	do.	Permian.
68.	73.	Bradford.	Pennsylvania.	do.	do.	Devonian.
69.	73.	Conroe.	Texas.	do.	Cenozoic.	Tertiary.
70.	73.	East Texas.	do.	do.	Mesozoic.	Cretaceous.
71.	73.	Kawkawlin.	Michigan.	do.	Paleozoic.	Devonian.
72.	73.	Midway.	California.	do.	Cenozoic.	Tertiary.
73.	73.	Ponca City.	Oklahoma.	do.	Paleozoic.	Ordovician.
74.	73.	Winkler.	Texas.	do.	do.	Permian.
75.	(1).	Fasken.	do.	do.	do.	Ordovician.
76.	(1).	Keystone.	do.	do.	do.	Permian.
77.	(1).	Maljamar.	New Mexico.	do.	do.	Do.
78.	60.	Ponca City.	Oklahoma.	do.	do.	Ordovician.

¹ Unpublished Bureau of Mines data.

composition of crude oils. Generalization of a somewhat different form can now be reached.

Paraffins, cycloparaffins, and alkylbenzenes are the three main hydrocarbon classes in the naphtha fraction. Although there is no relationship between classes, certain composition patterns are followed within each of the classes. The ratio of structurally similar isomers will rarely vary by more than one order of magnitude. For structurally dissimilar isomers, the ratios can vary more, more widely the more dissimilar the structure. . . .

In approaching this subject the author has used the data of Forziati and coworkers (73), Smith and Rall (170), Martin and coworkers (135-137), a few Bureau of Mines data, and a few data by Desty (60). Some of the original data are in weight-percent; these have been converted to volume-percent and all data presented are on this basis. A key to all the data used is given in table 22.

The data are presented in a series of graphs of the volume-percents of one hydrocarbon plotted against those for another hydrocarbon. This serves several purposes. The nearness of the data to an average line gives a good indication of the randomness or cohesion of the data. The relative quantities of the compounds can be easily seen, and the variation with geological era noted. Certain data that do not conform to the general overall pattern can be easily located, and the oil sources studied for possible reasons for divergence of the data. There was not room to put names of all the oils discussed on the graph, so the oils mentioned in the text have been named on the charts so far as possible, and other oils are coded by number (table 22).

The following comparisons will be shown and discussed on a volume-percent of crude oil basis:

- n*-Hexane vs. *n*-heptane.
- n*-Hexane vs. *n*-pentane.
- n*-Hexane vs. *n*-octane.
- n*-Hexane vs. *n*-nonane.
- Isohexanes vs. isoheptanes.
- 2-Methylpentane vs. 3-methylpentane.
- 2-Methylhexane vs. 3-methylhexane.
- Cyclopentane vs. methylcyclopentane.
- Cyclohexane vs. methylcyclohexane (by individual points).
- Cyclohexane vs. methylcyclohexane (by zones and points).
- Toluene vs. benzene.
- Toluene vs. *n*-heptane.
- Toluene vs. methylcyclohexane.
- n*-Heptane vs. methylcyclohexane.

***n*-PARAFFINS**

***n*-Hexane vs. *n*-Heptane**

The data for *n*-hexane vs. *n*-heptane are presented in figure 29. It is apparent that there

is not a random distribution of data. Of the data 69 percent are within 20 percent of the average line. Many of those outside the dash lines, representing 20 percent error limits, based on *n*-heptane, are very close. In view of the fact that the data come from six sources, and were obtained by several methods, the agreement seems good. One sample, Ponca City crude oil, was analyzed in detail by three investigators (60, 73, 137). It is believed that Martin and Desty used encapsulated samples of the original oil studied by Forziati. The data, as shown below for Ponca City crude oil, give some idea of the sort of errors involved in these analyses:

	Volume-percent hydrocarbon	
	<i>n</i> -Hexane	<i>n</i> -Heptane
Desty (60).....	1.83	2.95
Forziati (73).....	1.89	2.38
Martin (137).....	1.97	2.21

The maximum difference for *n*-hexane is 7 percent, and for *n*-heptane 25 percent.

The author believes that those data that are within the 20 percent divergence limit probably represent origination from similar source material by analogous chemical routes in corresponding environments. Those data that fall outside the limits may be suspect of sampling or analytical error, or the conditions of similarity just mentioned were not met and geological conditions should be reviewed.

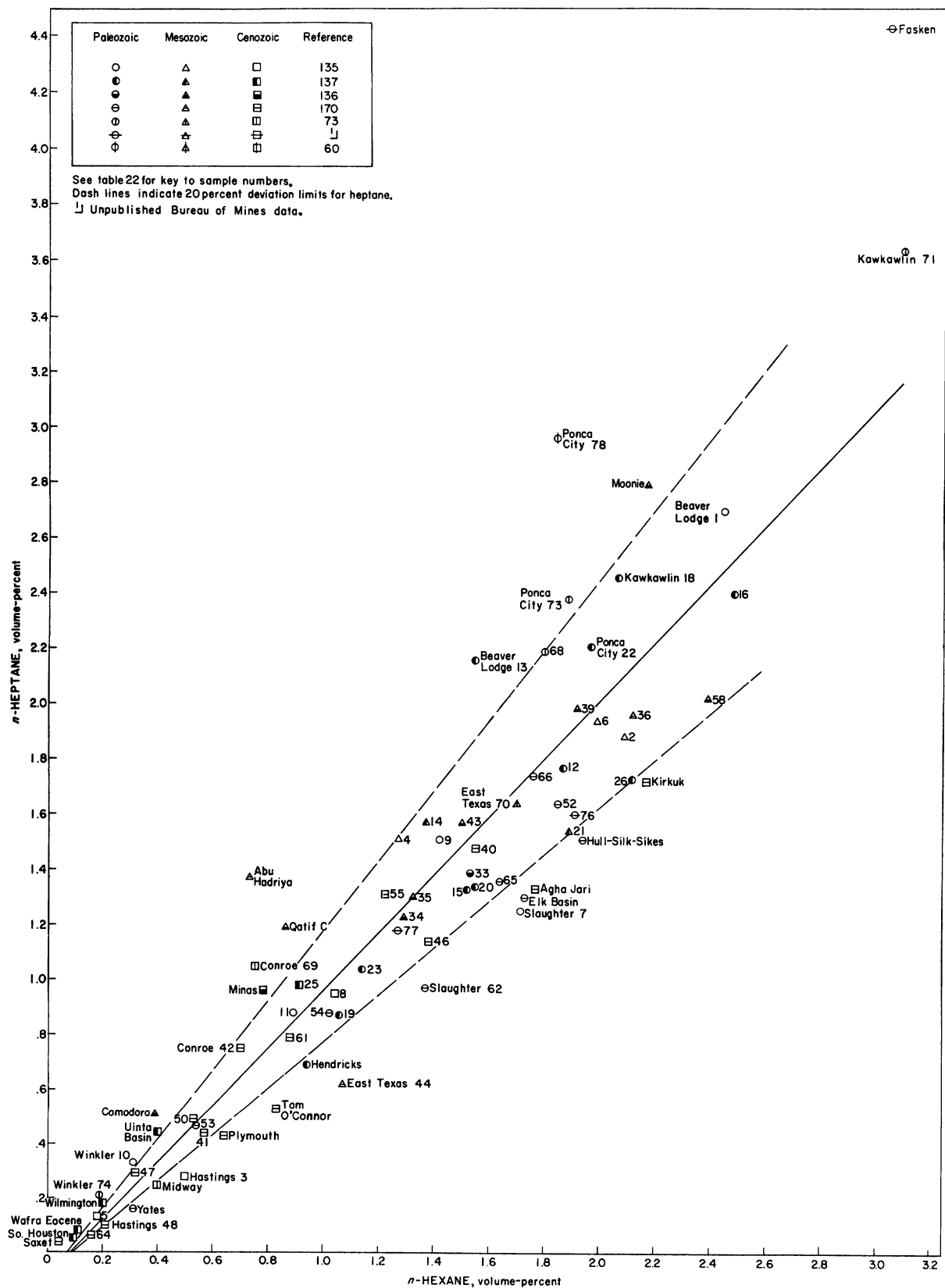
The data in figure 29 also show a decided difference in quantity of *n*-hexane and *n*-heptane with changes in geological era, as in table 23.

TABLE 23.—*Relationship of geological era and *n*-hexane and *n*-heptane content*

Geologic era	Percent of crude oils having—			
	<i>n</i> -Hexane		<i>n</i> -Heptane	
	≤1 percent	>1 percent	≤1 percent	>1 percent
Paleozoic.....	18	82	26	74
Mesozoic.....	18	82	12	88
Cenozoic.....	77	23	77	23

The data in this table and subsequent similar tables confirms in another way figures 5, 6, and 7 and associated statements that older and more deeply buried oils contained more light material.

It is interesting to consider the Paleozoic oils that constitute the 18 percent having less than one percent *n*-hexane. These oils are Hendricks, Monument, Winkler (two samples), Yates, and Wyoming composite. All of them are Permian

FIGURE 29.—Relationship of *n*-Hexane and *n*-Heptane.

oils except that the Wyoming has some Pennsylvanian oils admixed; all have a high sulfur content, one percent or more; all the five Permian oils have an unusually high content of isoparaffins in the naphtha, as shown by the data of Forziati and coworkers (73), Smith and Rall (170), and Martin and coworkers (137). Smith and Rall (170) pointed out that the Winkler, Yates, and Monument crude oils in comparison with the thermodynamic equilibrium data, more closely approached geologically acceptable temperature values than any of the other oils they studied. Martin and coworkers state: "Hendricks is an exception, but this probably is explained by the extraordinarily low formation temperature of only 30° C." Jones and Smith (94) point out that the loss of light naphtha may be the result of solution in fresher water than is normal for such reservoirs. The aromatics would be preferentially dissolved, and the aromatic content of the naphtha for all five Permian oils is lower than the normal content. There is geological evidence to support the presence of fresher water in these locations.

n-Hexane vs. *n*-Pentane

The data for *n*-hexane vs. *n*-pentane are presented in figure 30. Eight of the data points (Kuwait, Darius, Beaver Lodge (2), Kawkawlin, Ponca City, Moonie No. 2, Fasken) seem to be abnormally low in pentane content, and because this hydrocarbon is so volatile and easily lost, the writer has assumed that the data for these light samples do not represent the true pentane contents, and they have not been used in calculating the average line. If this assumption is not true, and the data are truly representative, then the geology of the producing formation should be studied.

Considering all the data, table 24 shows the relationship of geologic age and *n*-hexane and *n*-pentane content.

TABLE 24.—*Relationship of geological era and n-hexane and n-pentane content*

Geological era	Percent of crude oils having—			
	<i>n</i> -Hexane		<i>n</i> -Pentane	
	≤1 percent	>1 percent	≤1 percent	>1 percent
Paleozoic.....	15	85	10	90
Mesozoic.....	11	89	33	67
Cenozoic.....	89	11	89	11

As for the *n*-heptane/*n*-hexane graph, the larger quantities of both hydrocarbons are found in Paleozoic and Mesozoic oils, and conversely the lower quantities in Cenozoic oils. Further, two of the Paleozoic oils grouped with

the large group of Cenozoic oils are Winkler and Hendricks previously discussed.

Excluding the eight samples previously mentioned nine samples or 30 percent of the data are outside the 20 percent error limit based on *n*-pentane, and four of these are in the very low content range where larger errors would be expected.

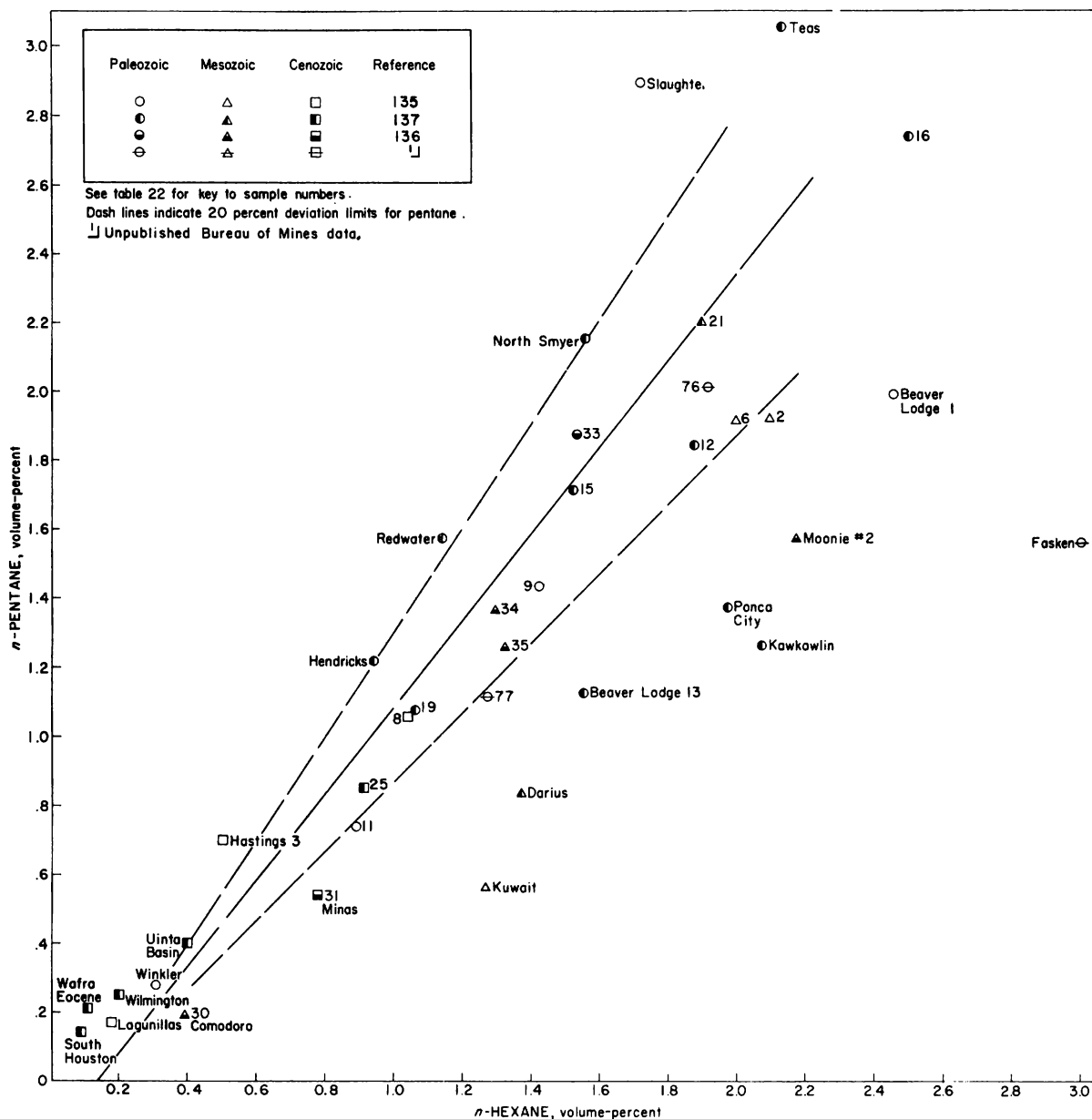
n-Hexane vs. *n*-Octane

There are less data available for *n*-octane, and none by the presumably more reliable gas chromatography method. The data available, all by Smith and Rall (170), are shown in figure 31. The Paleozoic and Mesozoic oils continue to have the greater number of samples with high contents of *n*-octane, but the differences are not as marked previously. Possibly this is because only one set of data is being used, and the samples represented were procured primarily in a reconnaissance to locate sources of aromatics, toluene particularly; hence there was specific selection of samples that probably has some effect on the results. Table 25 shows the distribution.

TABLE 25.—*Relationship of geological era and n-hexane and n-octane content*

Geological era	Percent of crude oils having—			
	<i>n</i> -Hexane		<i>n</i> -Octane	
	≤1 percent	>1 percent	≤1 percent	>1 percent
Paleozoic.....	22	78	33	67
Mesozoic.....	33	67	17	83
Cenozoic.....	63	37	63	37

Of those Paleozoic oils that appear with the large group of Cenozoic oils, Yates and Monument have already been discussed. The Oklahoma City distillate had a 90 percent point of 123° C compared with 125° C as the boiling point of *n*-octane, so it seems obvious that there was not a complete representative quota of *n*-octane in the sample analyzed. Samples Abu Hadriya and Qatif C consistently show high ratios for C₇, C₈, and C₉ with reference to *n*-hexane. This is consistent with the Bureau crude oil analyses of these oils, which show a marked deficiency of low-boiling material, so that the hexane content is low. This could be caused by surface treatment of the oil prior to sampling, improper sampling location, but more probably to a true deficiency of light ends in these oils. In this case then the geological history should be studied for reasons. In contrast to the Qatif C sample the Qatif D oil has an abundance of light hydrocarbons.

FIGURE 30.—Relationship of *n*-Hexane and *n*-Pentane.

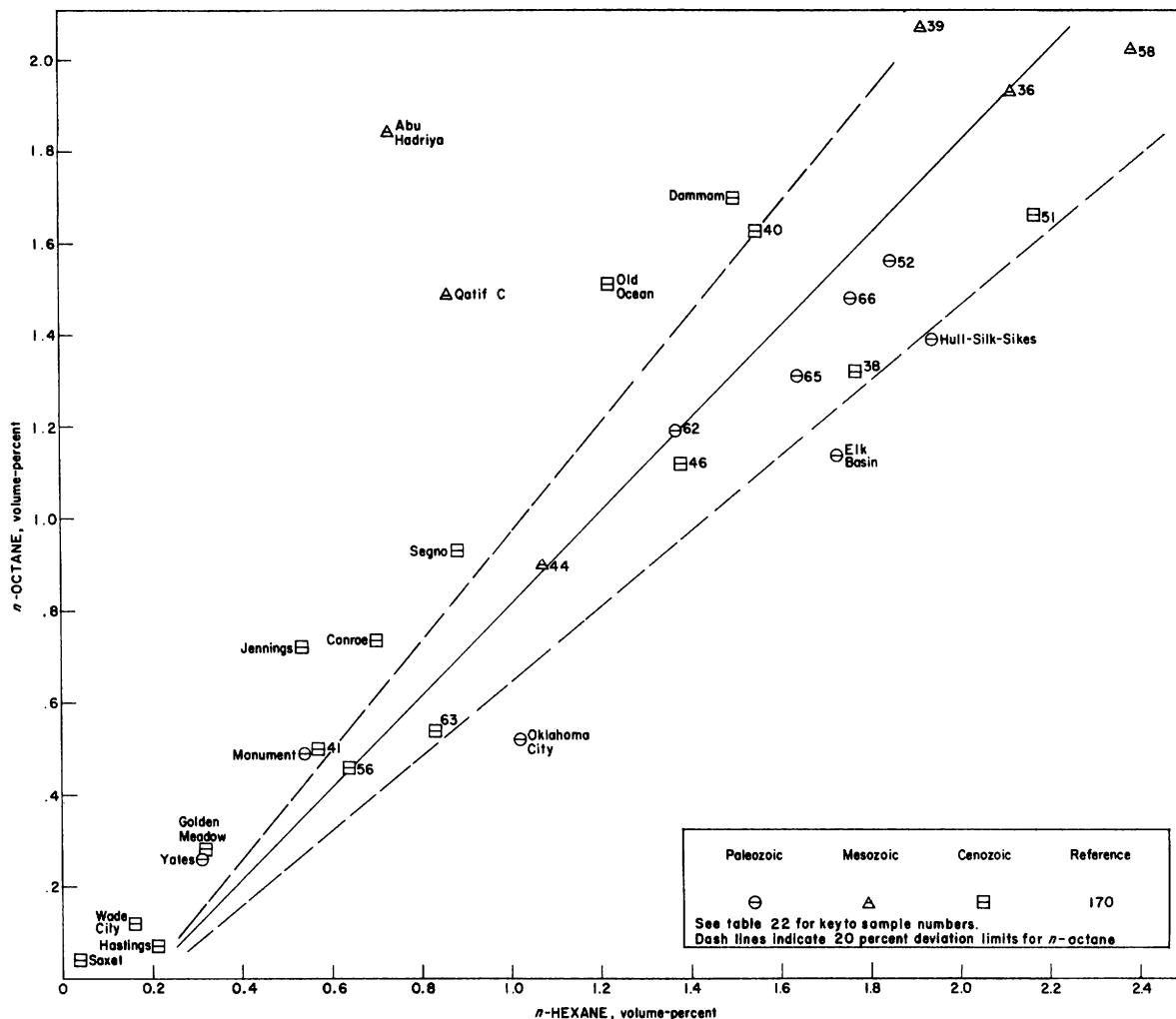
Only 52 percent of the samples fall within the 20 percent limit, but most of those outside the limit are reasonably close, and probably the limits of precision in this analysis are greater than 20 percent.

n-Hexane vs. *n*-Nonane

There are only 19 data points for *n*-nonane; these are shown in figure 32. Here again the same oils Abu Hadriya and Qatif C have a high nonane content relative to hexane. From the position of the remaining data again it would appear that the best curve would be at

about the position of the lower 20-percent-error limit. The data with regard to geological era and hydrocarbon content are given in table 26.

The trend is the same but less pronounced—presumably because of fewer and poorer data, but also because of the gradual change of proportion of light components with age or depth of burial. The oils that show a deficiency of *n*-nonane, Plymouth, Tom O'Connor, Elk Basin, and Hull-Silk-Sikes, are representative of crude oils that show a maximum *n*-alkane content at *n*-hexane and then decrease, somewhat similar to the Darius, Persian Gulf, crude

FIGURE 31.—Relationship of *n*-Hexane and *n*-Octane.TABLE 26.—Relationship of geological era and *n*-hexane and *n*-nonane content

Geological era	Percent of crude oils having—			
	<i>n</i> -Hexane		<i>n</i> -Nonane	
	≤1 percent	>1 percent	≤1 percent	>1 percent
Paleozoic.....	28	72	57	43
Mesozoic.....	67	33	25	75
Cenozoic.....	78	22	100	0

oil (fig. 49) as shown by Martin and coworkers (138).

ISOPARAFFINS

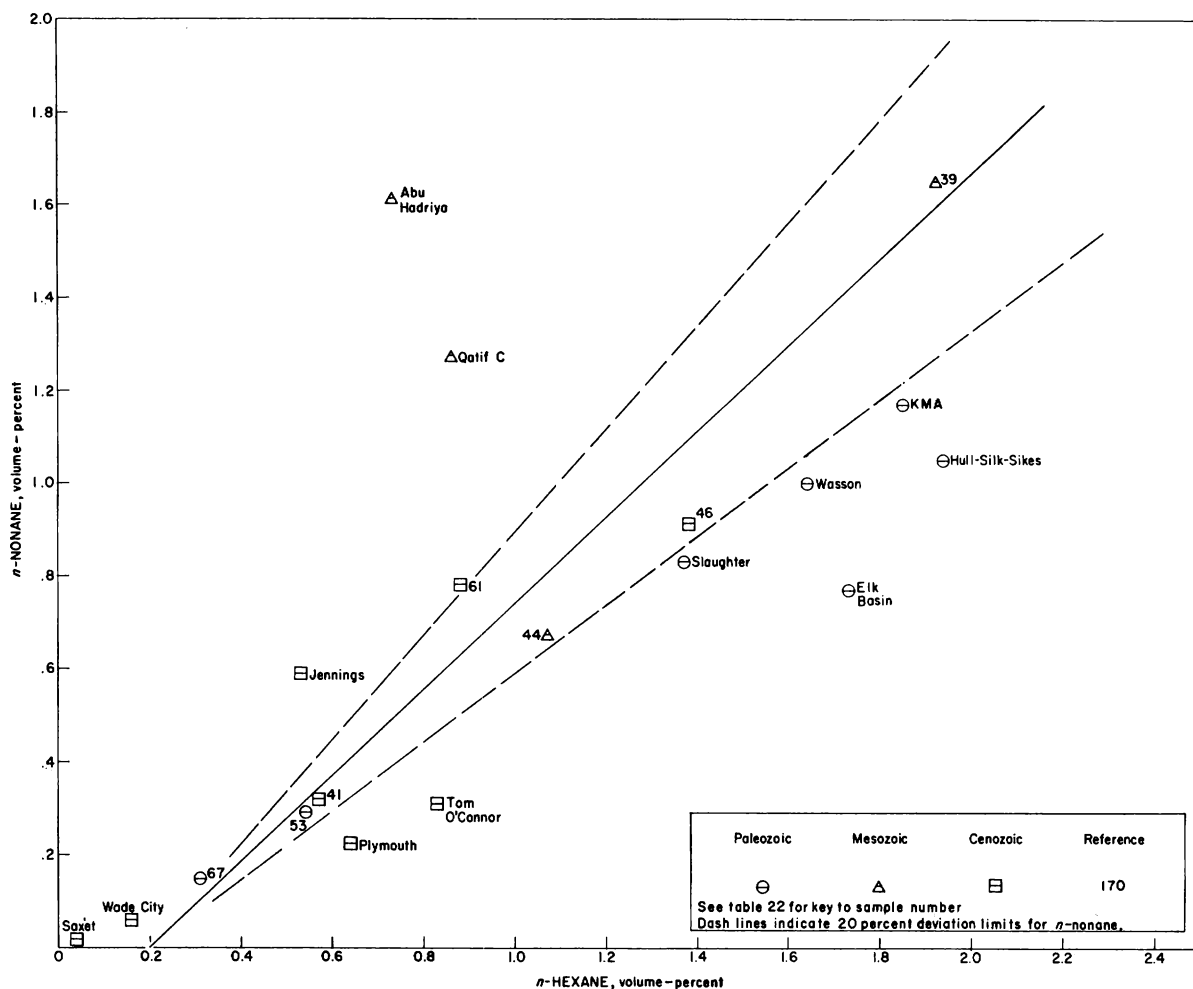
Isohexane vs. Isoheptane

The data for the relationship of total isohexanes to total isoheptanes is shown in figure 33. There seems to be more cohesiveness of

these data than for *n*-hexane and *n*-heptane. The reason for this is the excellent correlation between 2- and 3-methylhexane and 2- and 3-methylheptane. These particular isohexanes and isoheptanes constitute a large proportion of the total isohexanes and isoheptanes. Again considering the relationship of geological era and isohexane content table 27 shows the distribution.

TABLE 27.—Relationship of geological era and isohexane and isoheptane content

Geological era	Percent of crude oils having—			
	Isohexanes		Isoheptanes	
	≤1 percent	>1 percent	≤1 percent	>1 percent
Paleozoic.....	18	82	15	85
Mesozoic.....	41	59	29	71
Cenozoic.....	77	23	65	35

FIGURE 32.—Relationship of *n*-Hexane and *n*-Nonane.

These data are further confirmation of the fact that Paleozoic and Mesozoic oils have a higher content of light hydrocarbons at least through C_7 , and probably through C_8 .

The homogeneity of the data is shown by the occurrence of 78 percent of the data within the 20-percent-isohexane limits. The chief oils outside of the limits are Abu Hadriya and Qatif C, which seem to be short on isohexanes as they were on *n*-hexanes; as this has been attributed to lack of low boiling materials in the oil it would be even more likely for the isohexanes which all boil below the normal compound. Another group of oils that deviate are the previously discussed Yates and two Winkler samples. The Middle East oils appear to be centered in an area about one point: Isohexanes, 1.0; isohexanes, 1.2. Bureau routine crude oil analysis for these oils does not show any evidence that the light ends are deficient as for Abu Hadriya and Qatif C; therefore it is

concluded their higher ratio of isohexanes to isohexanes is typical of these oils. Two Ponca City data points are widely divergent, the third is almost in the curve; the reason for these deviations is not known. On the low isohexane side of the curve the West Texas Permian samples Slaughter and Lee Harrison deviate considerably and the Wasson sample much less. The author has for some time considered the high-sulfur, high-aromatic Permian oils of West Texas unique.

2-Methylpentane vs. 3-Methylpentane

The data for the relationship of 2-methylpentane and 3-methylpentane are shown in figure 34. These are very homogeneous except for one group of exceptions that all have a too high content of 3-methylpentane. These data points, which were not included in the calculation of the average line, all lie above the dash line which was drawn for an exclusion boundary.

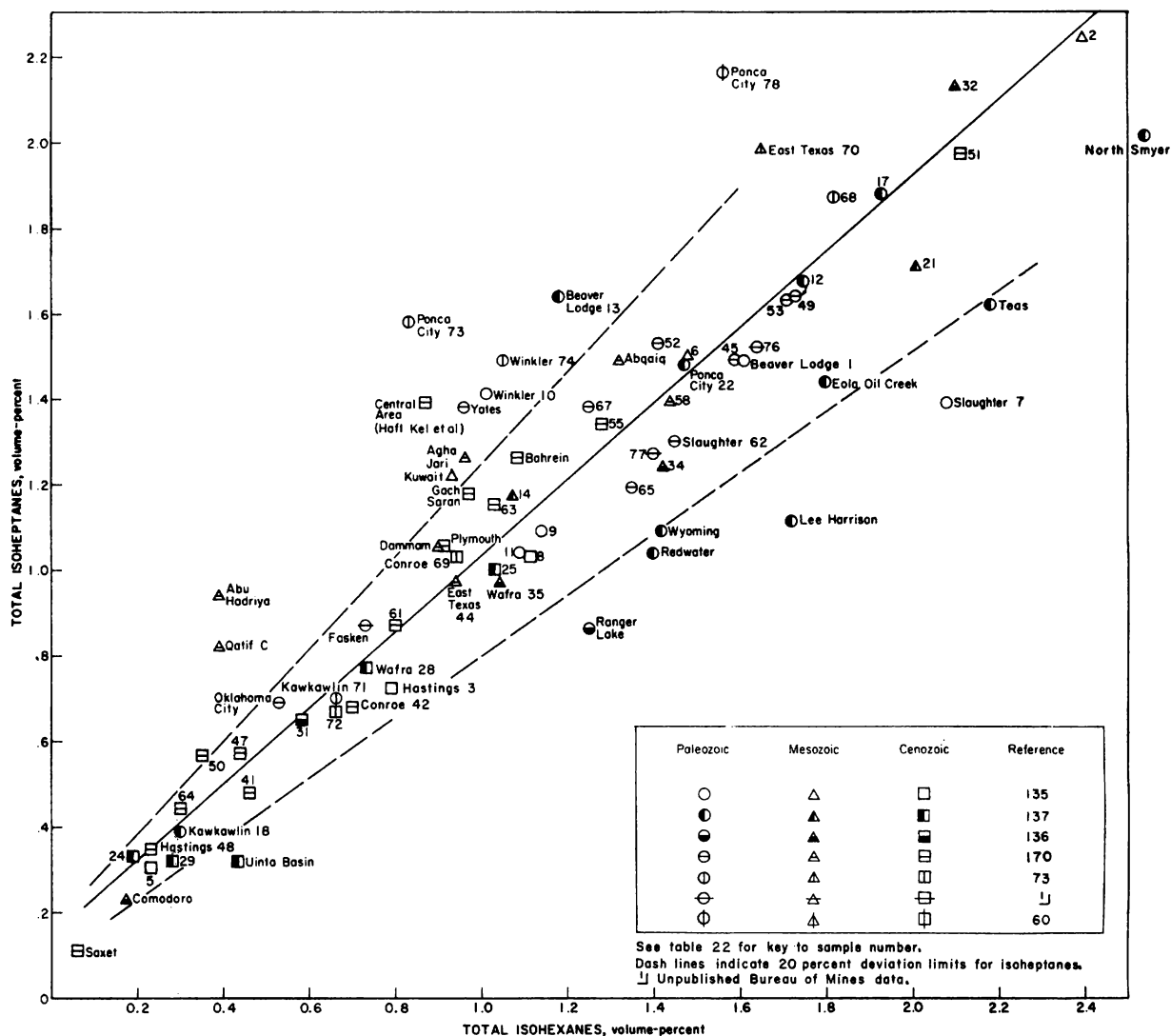


FIGURE 33.—Relationship of Total Isoheptanes and Isohexanes.

These oils are as follows:

Abqaiq (170)	Kirkuk	Slaughter
Abu Hadriya	Monument	Wafra (Eocene)
(170)	Ponca City (60)	(137)
Agha Jari (170)	Ponca City (73)	Winkler (73)
Bahrain	Qatif C	Winkler (135)
Central Area	Qatif D	Yates (170)
Gach Saran		

Most of the data excepted are from analyses made by Smith and Rall and first thought would be that there was an analytical bias; further study shows that all of the samples, except Ponca City, are of high-sulfur oils, and also mostly from the Middle East. On the other hand there are a few high-sulfur oils including some from the Middle East, that fall in with the other 60 samples; For example, Dammam, Elk Basin, and Wasson (170), Darius, Hend-

ricks, and Lee Harrison (137); Wafra Ratawi and Wilmington (136); Saudi Arabia, El Dorado, Kuwait, Wyoming Composite, Tia Juana, Lagunillas Quince, and Slaughter (135). Thus it appears not to be the sulfur *per se*; the best explanation appears to be that possibly the sulfur compounds affected the values of the refractive index determinations used in the Smith-Rall analytical method. Aside from the deviations the rest of the data exhibit very good correlation. It is of interest to speculate on the possible sources of these hydrocarbons. On a formula basis only it would be possible to form 2- and 3-methylpentane and two trimethyl isoprenoids that have been found in petroleum by splitting the C_{20} and C_{21} isoprenoids. It would be interesting to see if both the methylpentane and the isoprenoid contents

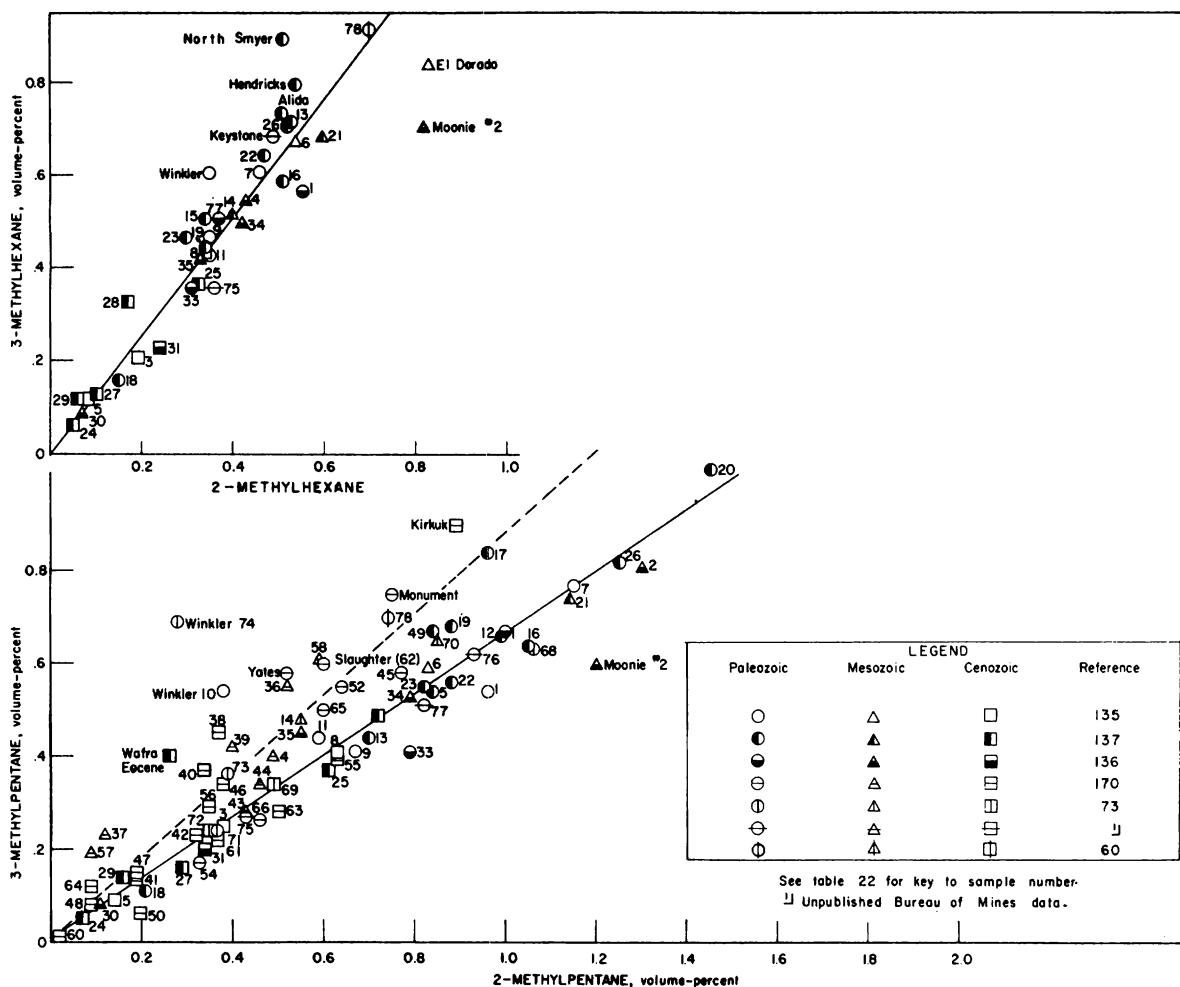
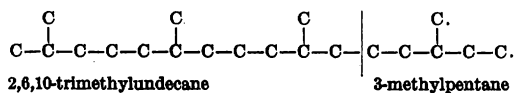
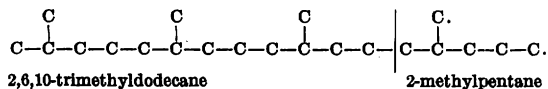


FIGURE 34.—Relationship of 2- and 3-Methylpentane, and of 2- and 3-Methylhexane.

increase and decrease together. Structurally phytane could split and after hydrogenation give 3-methylpentane and 2,6,10-trimethylundecane, as shown:



2,6,10,14-Tetramethylheptadecane could split to give 2-methylpentane and 2,6,10-trimethylundecane, as follows:



Whether there is any structural or energetic reason for such splitting is not known.

2-Methylhexane vs. 3-Methylhexane

The data for the relationship of the 2- and 3-methylhexanes are shown in figure 34. These

data are very homogeneous, and do not exhibit the exceptions just noted for the methylpentanes; perhaps it is significant that Smith and Rall did not determine those compounds separately, but as a sum so that their data are not used. There are only a few data that deviate widely: Winkler and Hendricks as might be expected, but unexpectedly North Smyer, El Dorado, and Moonie No. 2, although the latter showed considerable deviations for the methylpentanes. Similarly as for the methylpentanes, 2,6,10,14-tetramethylheptadecane could split to give 3-methylhexane and 2,6,10-trimethylundecane, but there seems to be no mechanism that will yield 2-methylhexane and any isoprenoid that has been found in crude oil.

CYCLOPENTANES

Cyclopentane vs. Methylcyclopentane

The data for the relationship of cyclopentane and methylcyclopentane are given in figure 35.

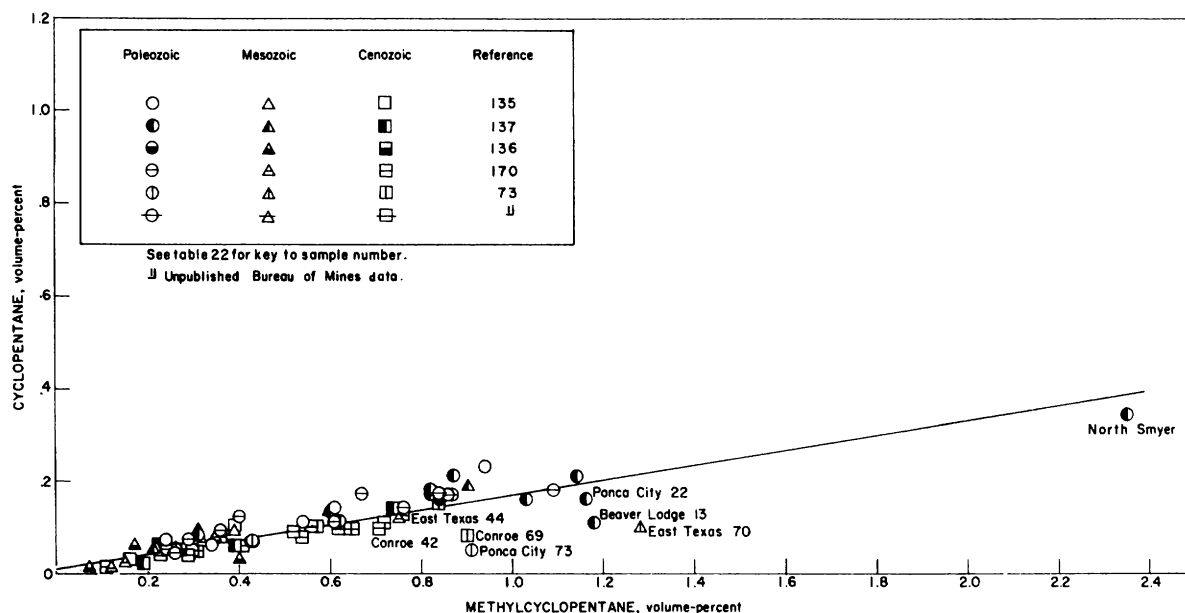


FIGURE 35.—Relationship of Cyclopentane and Methylcyclopentane.

The homogeneity is excellent—only 5 or 6 of the 77 samples deviate much from the average line. North Smyer has a very unusual content of both compounds. The GLC data (137) indicate that the preponderance of cyclopentanes in this oil over other oils continues for dimethylcyclopentane and trimethylcyclopentane. It also has a high cyclohexane and methylcyclohexane content but other oils have as high or higher content of cyclohexanes without having a concurrently high cyclopentane content. Here then is an oil that is unique in its high content of cyclopentanes. Would it be possible from geological study to understand why? These data relating methylcyclopentane content and geological era are given in table 28.

TABLE 28.—Relationship of geological era and methylcyclopentane content

Geological era	Percent of crude oil samples having methylcyclopentane	
	≤0.80 percent	>0.80 percent
Paleozoic.....	44	56
Mesozoic.....	12	88
Cenozoic.....	8	92

These show that Paleozoic oils are found throughout the range, but that the Mesozoic and Cenozoic oils are concentrated above 0.80 percent methylcyclopentane. The curve is so flat that it is difficult to get satisfactory corresponding data for cyclopentane, but it would be of the same general characteristics. The ratio of methylcyclopentane to cyclopentane is about

5.5. This is in good agreement with earlier data from table 17, except for the Baku crude oils.

CYCLOHEXANES

Cyclohexane vs. Methylcyclohexane

The data for the relationship of cyclohexane and methylcyclohexane are given in figure 36. These data with a few exceptions are coherent over a wide range. Two notable exceptions are the oils from Moonie No. 2 with an extremely high content of methylcyclohexane, and from Ranger Lake having an equally high content of cyclohexane. The relationships with geological era are given in table 29.

TABLE 29.—Relationship of geological era and cyclohexane and methylcyclohexane content

Geological era	Percent of crude oils having—			
	Cyclohexane		Methylcyclohexane	
	≤0.40 percent	>0.40 percent	≤1.0 percent	>1.0 percent
Paleozoic.....	33	67	29	71
Mesozoic.....	75	25	66	31
Cenozoic.....	56	44	52	48

These data show that there are twice as many Paleozoic oils with a content above the 0.40 or 1 percent limits as below. The Mesozoic oils are reversed in their relationship, and the Cenozoic oils are almost evenly divided. A study of the figure suggests that there may be zones according to oil type or geologic era. Accordingly the curves shown in figure 37

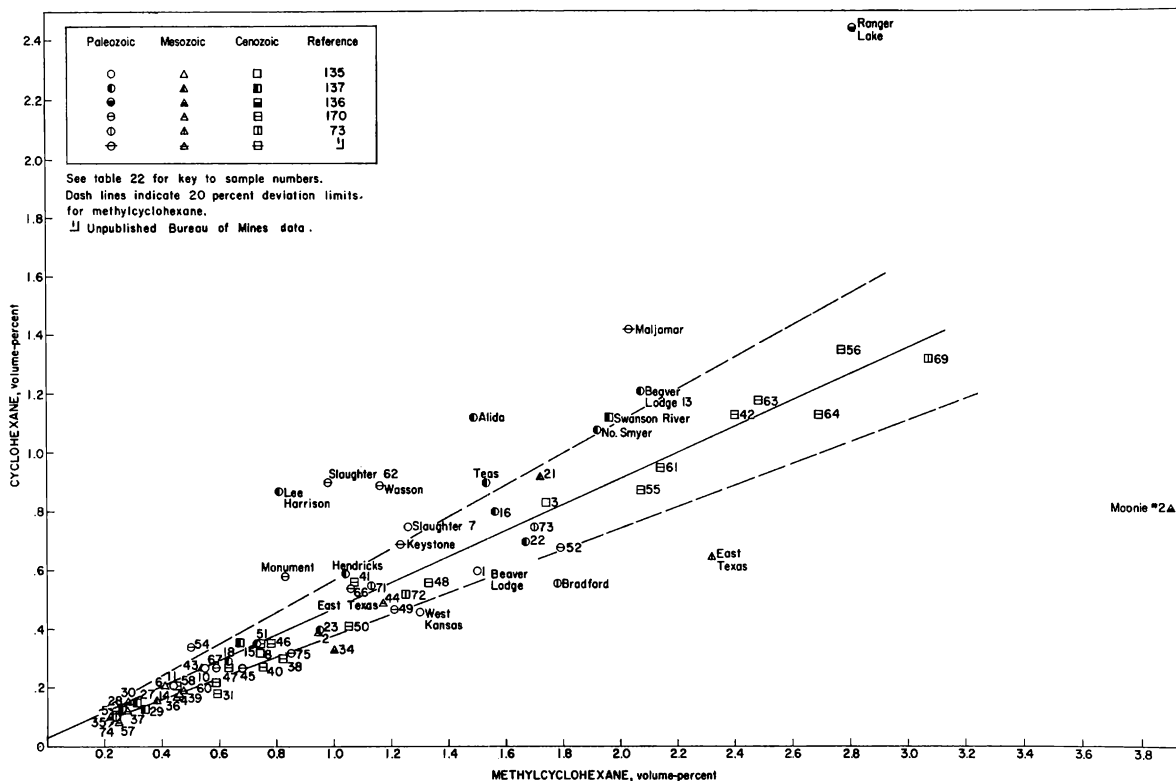


FIGURE 36.—Relationship of Methylcyclohexane and Cyclohexane.

were drawn. There are four curves: *a*, West Texas and New Mexico Paleozoic (Permian); *b*, Cenozoic; *c*, Paleozoic (except Permian); and *d*, Middle East Mesozoic-Cenozoic.

These curves define these areas fairly well, but there is very little difference between the Cenozoic curve and the Middle East Mesozoic-Cenozoic curve.

AROMATICS

Toluene vs. Benzene

The data for benzene and toluene are shown in figure 38. At first glance these seem to show considerable scatter; however, a closer inspection shows some order. Curve *a* is the average for all data points; curve *b* is the average curve with the data for Slaughter, Ranger Lake, Maljamar, Wasson, and Lee Harrison deleted. These all have a high toluene content but especially are noteworthy because of unusually high benzene content. All are Paleozoic oils; Slaughter, Wasson, and Lee Harrison have a sulfur content of over 1.0 percent, Maljamar 0.70 percent, and only Ranger Lake is low at 0.19 percent. This high aromatic content is in accord with the data given by Jones and Smith (94) on a large

number of high-sulfur Permian oils in west Texas and New Mexico. However, as yet it has been impossible to decide if the relationship of sulfur and aromaticity is fortuitous or causative. If these oils are not considered in calculating the average curve then curve *b* fits these data very nicely, with 76 percent within 20 percent deviation. Most crude oils do not exceed 0.80 percent toluene and 0.35 percent benzene. Those that do should be considered as worthy of further investigation, especially as to geological conditions. Above 0.40 percent toluene, disregarding the high-benzene-content Paleozoic oils, 59 percent of the oils are Mesozoic or Cenozoic, so that the bias in favor of those oils is small.

GENERALIZATION

All of the data presented on the relationships between hydrocarbons for those within a given class, such as *n*-paraffins, total or individual isoparaffins, cyclopentanes, and cyclohexanes or aromatics show in general there is much more coherence in the data than there is randomness. The author interprets this to indicate the probability for each specific pair considered to have had similar source materials, analogous diagenetic processes and corre-

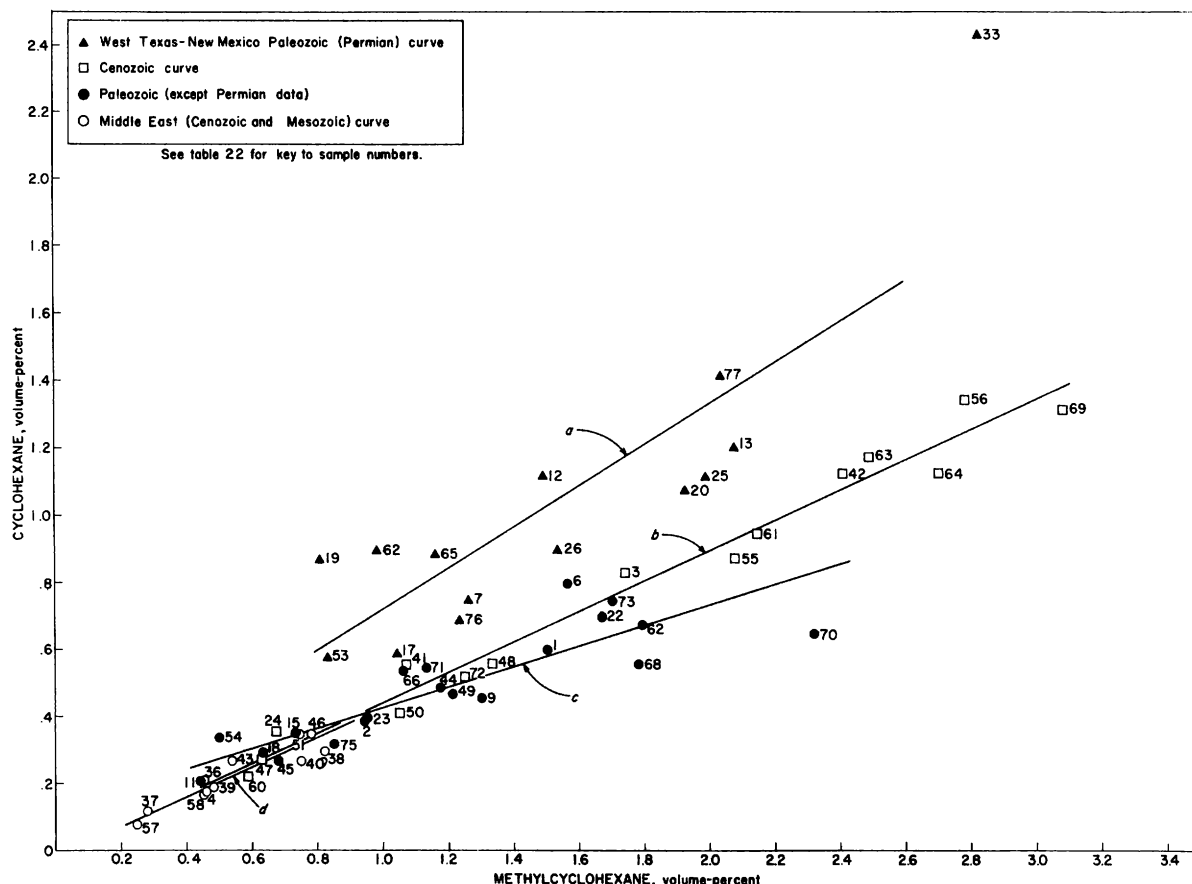


FIGURE 37.—Relationship of Methylocyclohexane/Cyclohexane Ratio to Stratigraphic Age.

sponding means of migration and accumulation. On the contrary those oils that fall out of the expected error in the determination involved should be the objects of further investigations. This might take the course of more detailed studies of other parts of the crude oil, but especially of as careful a study of geological conditions as possible, including the lithology of the reservoir and adjacent rock, consideration of possible source rocks and paths of migration, temperatures, salinity of associated water, possibility of meteoric water recharge, contamination of sample by oil from other producing horizons through faults and cracks, and selective adsorption of oil components on the rocks. By such studies the reasons for unusual oils may be searched out.

The west Texas Permian oils from the Glorieta, Clear Fork, and San Andres Formations of Permian age are good examples of unique oils. Their high aromatic content is not found in any other Paleozoic oils, yet there are a few Permian oils with a high aromatic content but with a low sulfur content. One

is almost forced to conclude that because of environment, such as anhydrite, sulfate water, and conditions suitable for development of bacteria capable of reducing sulfate to hydrogen sulfide, with subsequent formation of sulfur, the oils become highly sulfurized. Also that dehydrogenation of naphthenes to aromatics occurred, explaining the high aromatic content. In a few instances it appears that the sulfur compounds may have been removed by adsorption, giving the few high-aromatic, low-sulfur oils.

The intraclass relationships quite pointedly indicate that the older oils contain greater quantities of *n*-paraffins and isoparaffins. It would be of interest to see if the exceptions both ways could be related to difference in temperature, history, and pressure as well as age.

Possible sources of the methylpentanes and methylhexanes were suggested as being the low temperature cracking of phytane or pristane with concurrent formation of isoprenoids of 14 or 15 carbon atoms.

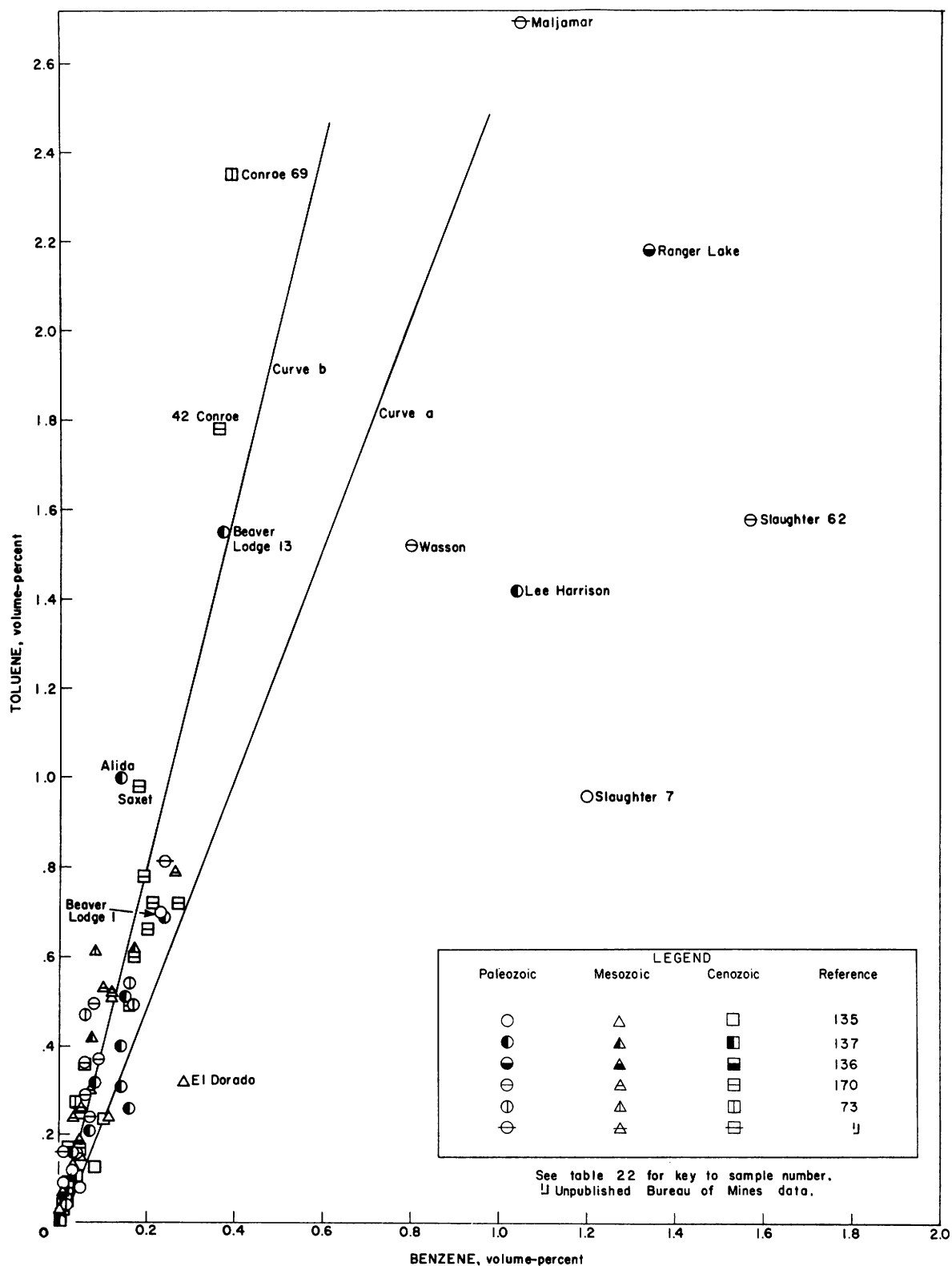


FIGURE 38.—Relationship of Benzene and Toluene.

MIXED CLASSES OF HYDROCARBONS

In contrast to the relationships presented above the next three to be considered are examples of interclass comparisons, all involving C_7 hydrocarbons.

n-Heptane vs. Methylcyclohexane

The data for *n*-heptane and methylcyclohexane are given in figure 39. The wide dispersion of these data in contrast to the homogeneity of the previous comparisons is evident. However, although there is not any linear relationship there is some segregation on primarily

geological considerations. All of the data that fall above the dashed line represent either Cenozoic oils or Paleozoic oils that have previously been mentioned as being deviates—namely, Yates, Winkler, and Monument. Maljamar and Ranger Lake are additional exceptions. All the data below the line represent Mesozoic or Paleozoic oils except Gach Saran, Agha Jari, Central Area, Kirkuk, Tia Juana, and Minas; these are all Cenozoic. All of the Middle East oils are rather closely grouped, including the Cenozoic oils. This suggests that regardless of the geological age of this present reservoir the oils in it may have had a common source.

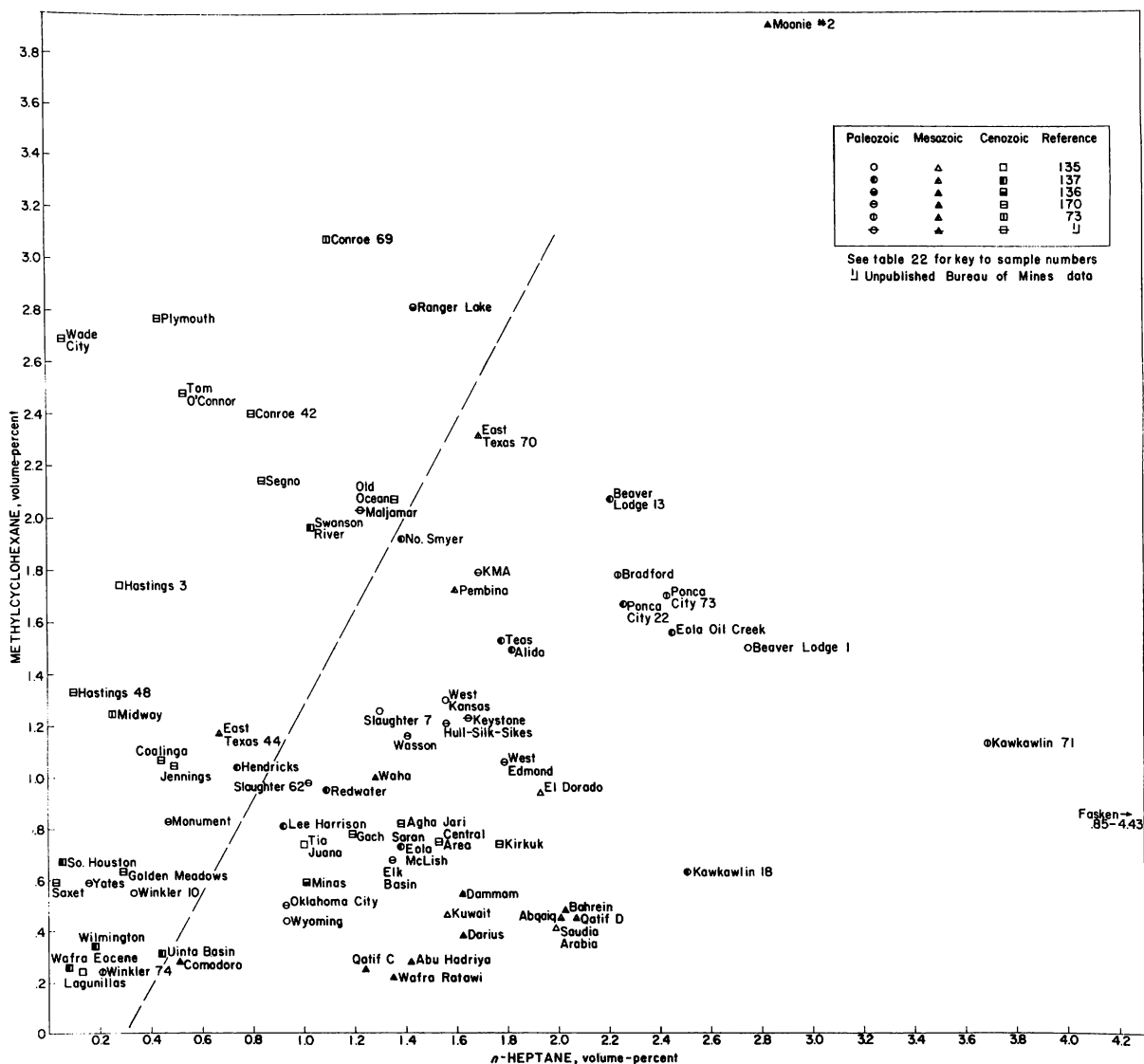


FIGURE 39.—Relationship of *n*-Heptane and Methylcyclohexane.

Toluene vs. Methylcyclohexane

The data for the relationship of toluene and methylcyclohexane are given on figure 40. Although not spread over as large an area these data are also well dispersed. The line has no significance except for reference. Three oils, Lee Harrison, Slaughter, and Wasson, show that a high toluene content does not mean a high content of methylcyclohexane, and the next figure will indicate that this is also true regarding *n*-heptane. Conversely, oils Moonie No. 2, Plymouth, Wade City, and Tom O'Connor show that there can be a high content of methylcyclohexane with only small amounts of toluene; this holds true for these same oils as regards *n*-heptane except for Moonie No. 2. This is a very exceptional oil and should be worthy of further study. Another group of oils, Maljamar, Ranger Lake, Conroe, and Beaver Lodge (13 in table 22) have high contents of both toluene and methylcyclohexane, and fairly normal quantities of *n*-heptane, except that Beaver Lodge has a rather high *n*-heptane content.

Toluene vs. *n*-Heptane

The data for the relationship of toluene and *n*-heptane are shown in figure 41. This figure is somewhat like figure 39 in that it can to a certain extent be separated into two groups. Thus the data above the line represent Cenozoic oils, high-sulfur West Texas Paleozoic oils, or recognized exceptions. The data below the line represent primarily Mesozoic and Paleozoic oils with a few exceptions: Kirkuk, Uinta Basin, Swanson River, Tia Juana, and Minas.

These last three figures demonstrate that there is not the degree of correlation interclass as there exists intraclass. The author believes that there is an approximate maximum limit of 0.80 percent toluene and 0.30 percent benzene that represents the content of these aromatics in many crude oils. When this limit is exceeded then one should look for reasons such as mentioned in the discussion of the intraclass relationships.

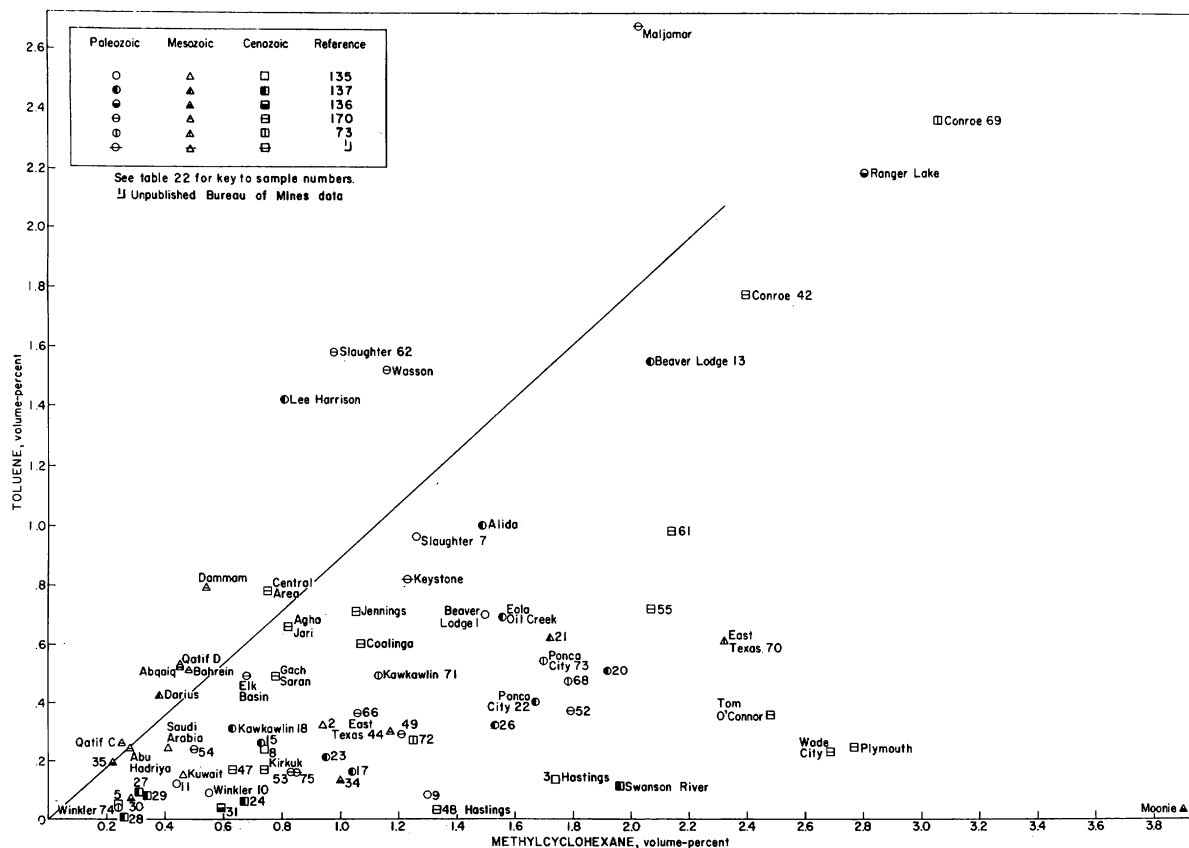
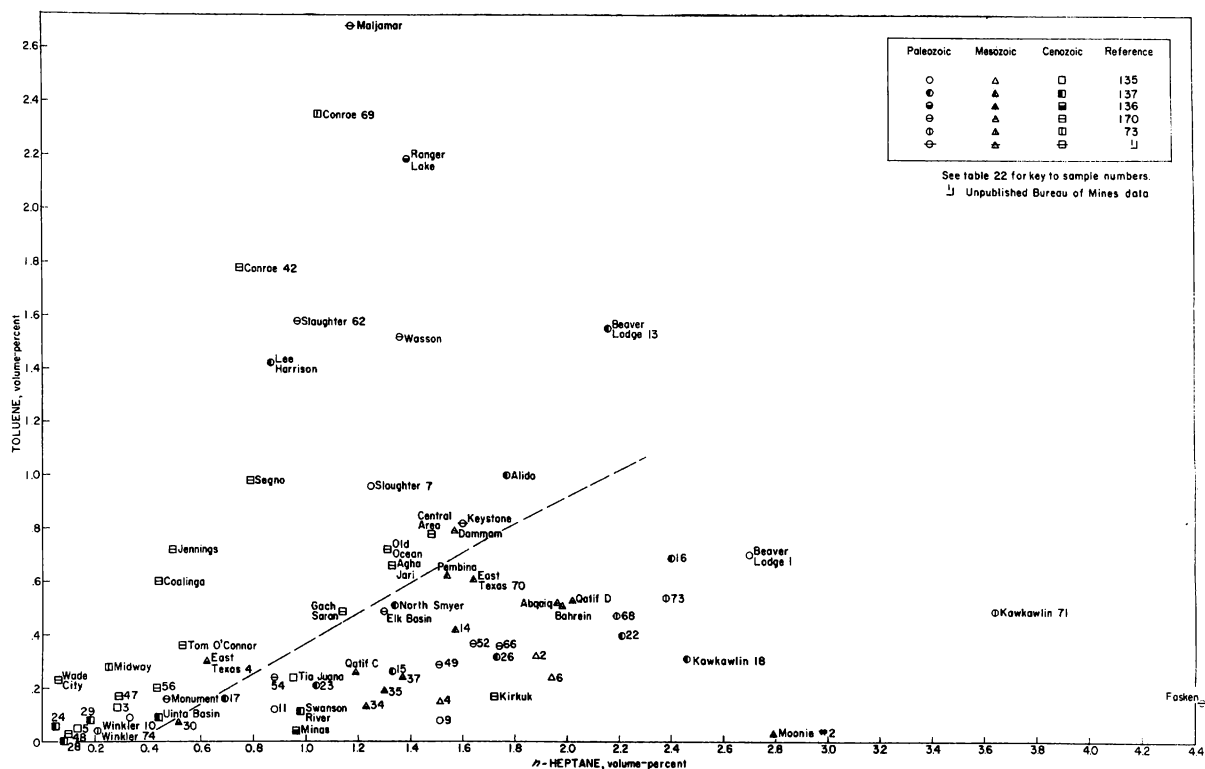


FIGURE 40.—Relationship of Toluene and Methylcyclohexane.

FIGURE 41.—Relationship of Toluene and *n*-Heptane.

COMPOSITION OF GAS OILS

Unfortunately it is not possible to present as complete a picture of gas oil composition as was possible for the naphthas, and quantitative data are particularly lacking. In the following discussion the general composition, as shown by the correlation index, the volume-percent of aromatics and paraffins plus naphthenes, the percent of carbon atoms in aromatic rings, naphthene rings and paraffin plus paraffin side chains and the number of aromatic and naphthene rings per molecule, will be presented first. This will be followed by an attempt to relate assumed model composition to actual data, and finally by a listing of the individual hydrocarbons that have been identified in the 200° to 300° C range.

GENERAL COMPOSITION OF FRACTIONS 8-12

The overall composition of the light gas oil fractions 8-12 is shown in figures 42-44. In these, besides the usual terms correlation index, and volume-percent of aromatics, naphthenes, or paraffins, several new terms are introduced. These are (1) percent of total carbon atoms in an average molecule that are in an aromatic

ring or rings, in naphthene rings, and percent of carbon atoms in individual paraffin hydrocarbons plus those in paraffin side chains; (2) total number of rings per average molecule, number of aromatic rings per molecule, and number of naphthene rings per molecule. These were reported in table 1 and methods used are referenced.

RELATIONSHIPS OF AROMATICS, NAPHTHENES, AND PARAFFINS

Panel A of figure 42 presents bar graphs of the average correlation index (unweighted) for fractions 8 through 15 of the same 14 low-sulfur and 7 high-sulfur crude oils previously discussed. These are arranged in the same order as in the previous discussion of naphthas. If the bar for oil J from Borneo is disregarded there is in general an increase in correlation index (CI) from 20 for oil A to over 50 for oil N. Reference to panel B showing the volume-percent of aromatics for fractions 8-12 indicates that through oil I this increase in CI is caused primarily by increase in aromatic content, but that for oils K, L, M, and N a considerable part of the CI

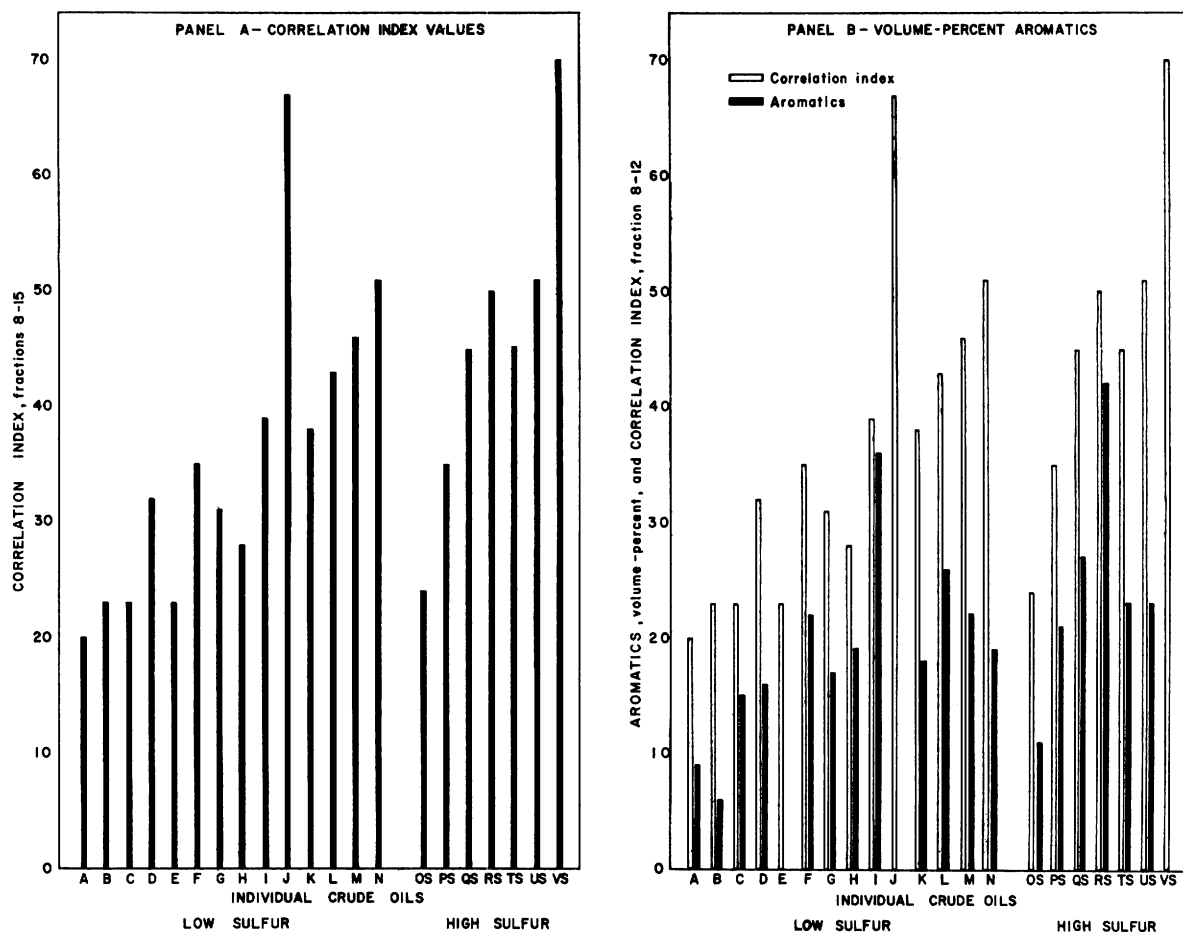


FIGURE 42.—Correlation Indexes for Fractions 8-15 and Volume-Percent Aromatics for Fractions 8-12.

increase is the result of increased content of naphthenes. This is borne out by panel A in figure 43, where the increase of naphthene rings for those four oils is apparent, as well as the percent of naphthenic carbon atoms shown in panel B of figure 43.

Numerous interesting observations can be deduced from the data in figures 42, 43, and 44 and the data in table 1; for example, (1) oil A, Fasken has the lowest CI values. This can be ascribed to the fact that it has the smallest number of aromatic rings per molecule, 0.1 and 0.0 for fractions 12 and 14 combined with a very low content of aromatics, and although the highest values for number of naphthene rings per molecule are 0.9 and 1.9 for fractions 12 and 14, these represent monocyclic and dicyclicalkynaphthenes having CI values of 10 to 20. Probably most of the aromatics present are alkylbenzenes. (2) Oil D, Kawkawlin, although it has a very paraffinic naphtha, has a high CI for the gas oil portion. This can be attributed primarily to a considerable increase in the average number of rings per molecule, 0.5 and 0.7

for fractions 12 and 14, combined with a fairly high volumetric content of aromatics. (3) Oils L and M, Coalinga (Nose) and Hastings, present some interesting differences. Both have about the same volume-percent of aromatics, 26 and 22 respectively, and about the same percent of carbon in aromatic rings, but the Coalinga oil has a noticeably higher number of aromatic rings per molecule 0.6 to 0.4 for fraction 12, and 0.9 to 0.5 for fraction 14. This would indicate a preference for naphthalene compounds in the Coalinga oil. In contrast to this, the Hastings oil has a much high number of naphthene rings per molecule pointing to saturated fused cyclohexane or cyclopentane rings. (4) With one exception, oil A (Fasken), for both high and low-sulfur content the number of aromatic rings per molecule increases in going from fraction 12 to fraction 14. (5) This same finding also applies to the number of naphthene rings, only in this case oil F (Beaver Lodge) shows no change. Both of these last items indicate the increase in cyclic compounds with increase in boiling point or molecular weight of the

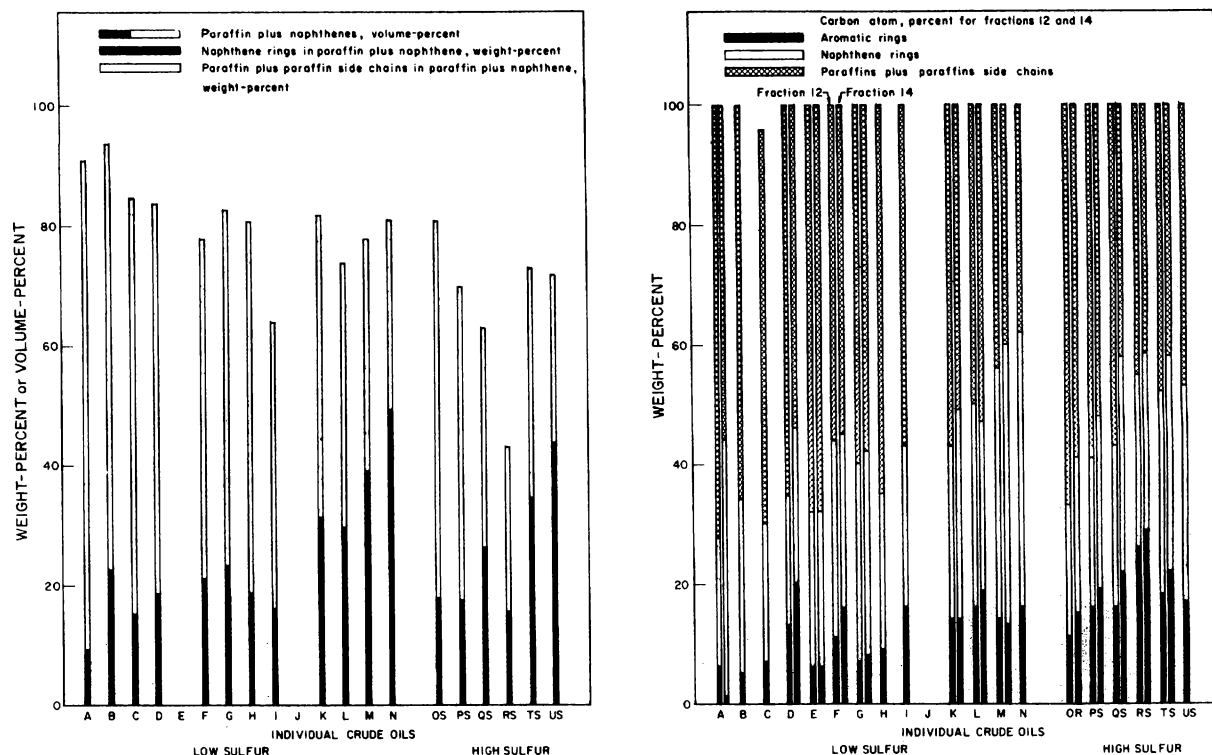


FIGURE 43.—Volume-Percent Paraffins Plus Naphthenes in Fractions 8-12 and Distribution of Carbon Atoms for Fractions 12 and 14.

crude oil fractions. (6) It appears that there is a tendency for the high-sulfur oils to contain a high proportion of aromatics except for oil OS (Lisbon, W.). They also seem to contain a greater portion of the carbon in aromatic rings, and to contain a slightly greater number of aromatic rings per molecule again with the exception of oil OS. It would be interesting to know if this is actually true, or can be ascribed to the fact that the sulfur compounds contribute to the physical properties used in these calculations in such a way as to cause an apparent increase in aromatics. The author believes that most of the sulfur compounds concerned are benzothiophenes or dibenzothiophenes and thus have an aromatic character inherently that is reflected in the data used. (7) Oil RS, Lee Harrison, probably deserves a special note, since it represents a unique group of oils, the west Texas and New Mexico high-sulfur, high-aromatic oils from the Permian Basin. The CI for fractions 8-15 is high; the volume-percent of aromatics in fractions 8-12 is very high; the percent of carbon in aromatic rings is the highest of all 21 oils; the number of aromatic rings per molecule is also the highest of any of the oils, with a value of 1.1 for fraction 14. In contrast the number of naphthene rings per molecule is somewhat less than comparison

with the other oils would indicate. Several possible explanations for these oils have been suggested; but none are entirely satisfactory. Jones and Smith (94) discuss the situation in their paper on the composition and stratigraphy of Permian Basin crude oils.

RELATIONSHIPS OF AROMATIC CARBON ATOMS, AROMATIC RINGS, AND VOLUME-PERCENT OF AROMATICS

In figures 45 and 46 an attempt has been made to show how the determined values for percent of aromatic carbons per molecule, number of aromatic rings per molecule and volume-percent of aromatics in fraction 12 relate to hypothetical mixtures of several aromatic compounds. The compounds selected were decylbenzene, hexyltetrahydronaphthalene, pentyl-naphthalene, and methylphenanthrene. The percent of aromatic carbon atoms and number of aromatic rings were calculated for each of these hydrocarbons and for several mixtures. These data form a series of fan-shaped straight lines originating at zero when plotted against assumed values for the volume-percent of aromatics. For example, methyl-

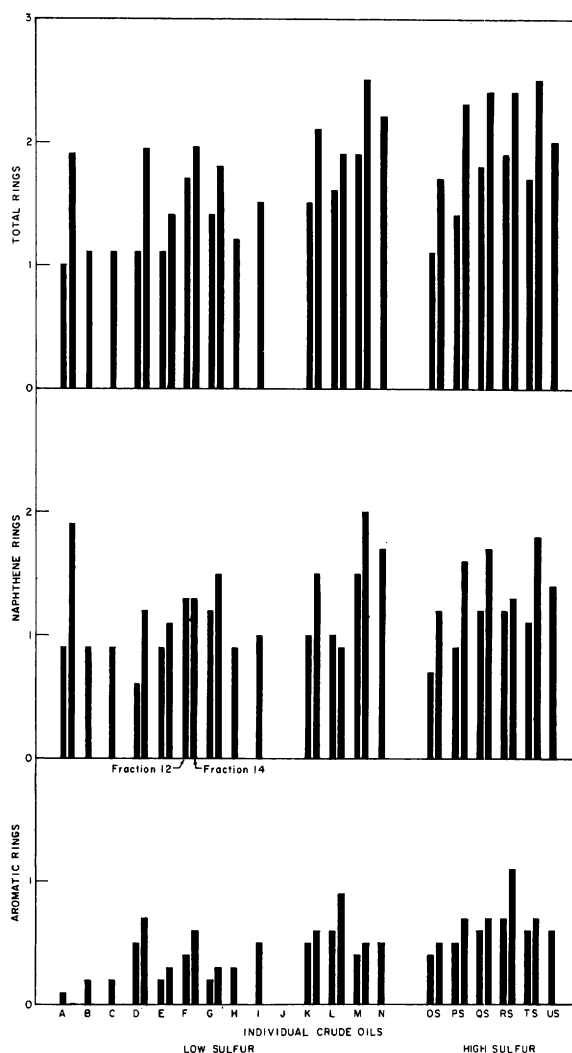


FIGURE 44.—Number of Aromatic, Naphthene and, Total Rings per Molecule for Fractions 12 and 14.

phenanthrene has three rings per molecule. If these aromatics were present to the extent of 10, 20 or 30 percent in a fraction of which the balance were nonaromatic, then the number of rings per molecule for the fraction would be 0.3, 0.6, and 0.9, respectively. Similar calculations can be made for various mixtures of the aromatic components. When these data are calculated and the lines drawn then the observed data can be placed on the diagram. When this is done it appears from figure 45 that (1) The aromatic components of oil A (Fasken), C (Minas), and G (Charenton) must be largely either alkylbenzene, alkyltetrahydronaphthalene, or both. (2) The aromatic component of oil F (Beaver Lodge) is probably about 50 percent of monocyclic aromatics and 50 percent naphthalenes. (3) The aromatic content of oils B (Bagley), N (South Pass), I (Conroe), and L (Coalinga) has a major

portion of alkyl-naphthalene, with small portions of monocyclic and possibly tricyclic aromatics. (4) The aromatic content of oils H (Gueydan), M (Hastings), K (Main Pass), and O (Kawkawlin) all have from 10 to 50 percent of tricyclic aromatics present with the balance probably alkyl-naphthalenes.

The corresponding data in figure 46 showing the percent of aromatic carbons per molecule correlates well with the conclusion just given based on figure 45. However, a few of the data points are not in agreement. Thus oil A (Fasken) shows 70 percent of monocyclic aromatics as compared to 100 percent in figure 45. For estimated data of this kind this amount of disagreement is not unusual. Oil B (Bagley) is indicated as being either about 50-50 monocyclic and dicyclic aromatics, or possibly a mixture with a small proportion of tricyclic aromatics. Oil H (Gueydan), M (Hastings), and K (Main Pass) are still indicated as having tricyclic aromatics. Oil D (Kawkawlin) falls below the 100 percent line for the dicyclic aromatics, and thus figure 46 indicates a smaller content of tricyclic aromatics than does figure 45. However, the point of interest here is that an oil with a very paraffinic naphtha appears to have tricyclic aromatics in the light gas oil. The remaining oils agree within the limitations of the methods used.

Another interesting and possibly useful exercise is to make a model construction for fraction 12 using an *n*-paraffin (*n*-heptadecane); a monocyclic cyclohexane (cyclohexylundecane); a dicyclic naphthene (heptylbicyclodecane); a monocyclic aromatic (hexyltetrahydronaphthalene) and a dicyclic aromatic (pentyl-naphthalene). Table 30 gives the basic information on each of these hydrocarbons. In table 31 the calculated properties of certain mixtures are compared with the determined properties of fraction 12 for an essentially paraffinic oil, oil A (Fasken); a less paraffinic more aromatic oil, oil I (Conroe); an oil with still less paraffins, more naphthalenes and aromatics, oil L (Coalinga); and a very naphthenic oil, oil N (South Pass). In general the calculated values agree fairly well, and the different assumed compositions are in agreement with present conceptions of these oils. Of course, this is a greatly simplified model for illustrative purposes only and should not be construed as representing the actual composition.

HYDROCARBONS IDENTIFIED IN GAS OIL AT 200° TO 300° C

Table 32 gives a listing of hydrocarbons identified in gas oil, the crude oil in which they were identified, and the pertaining references.

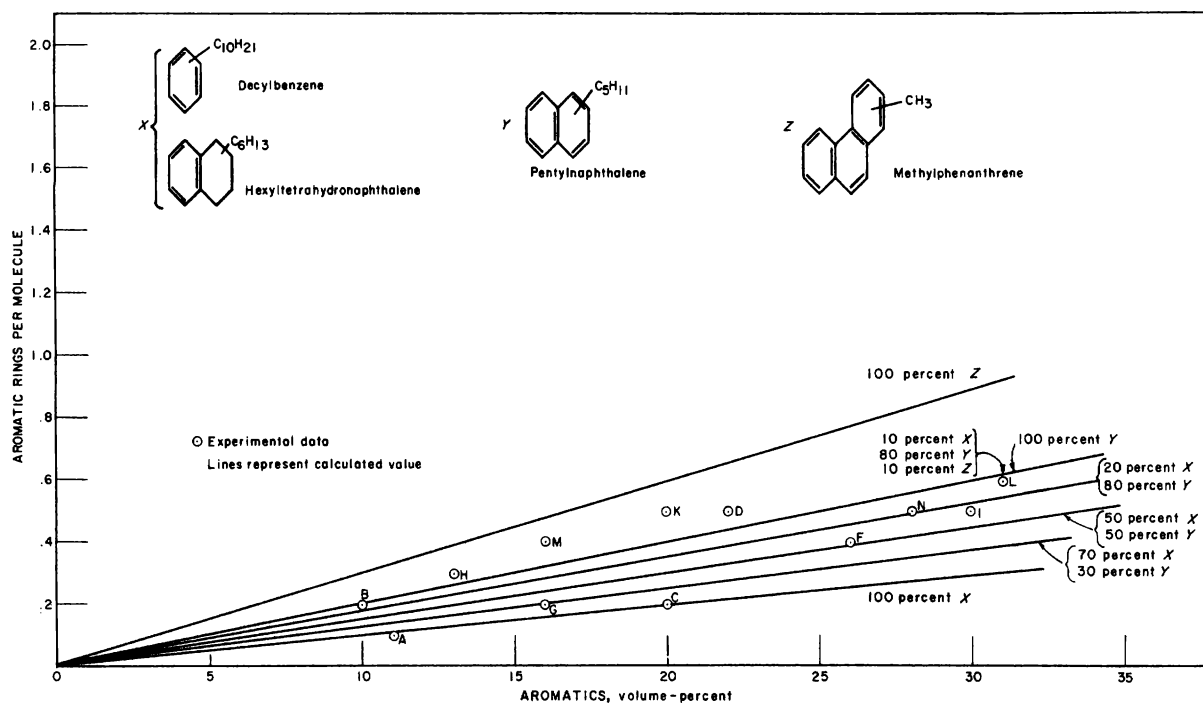


FIGURE 45.—Experimental and Calculated Relationships of Aromatic Rings per Molecule and Volume-Percent Aromatics Based on Fraction 12.

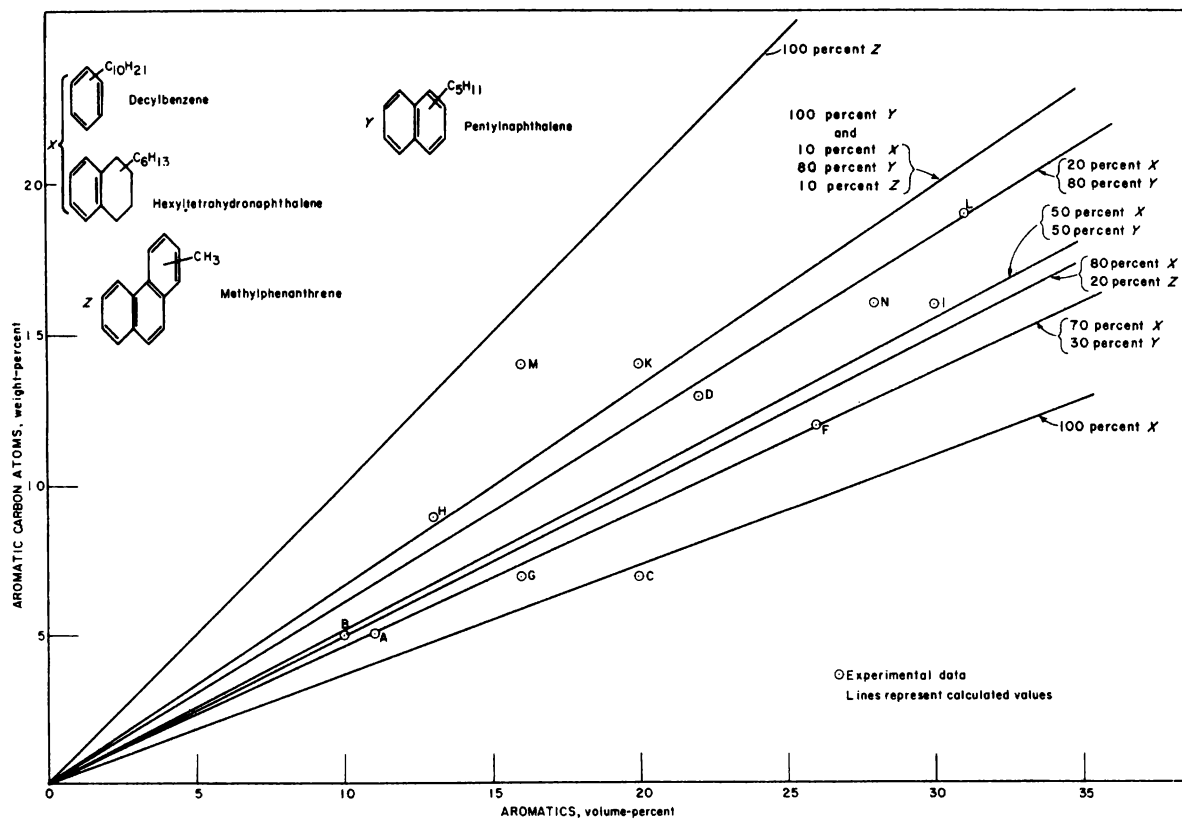


FIGURE 46.—Experimental and Calculated Relationships of Aromatic Carbon Atoms and Volume-Percent Aromatics Based on Fraction 12.

TABLE 30.—Source of calculated data used in table 31

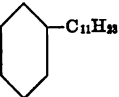
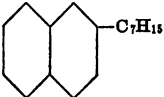
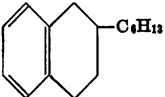
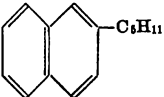
	Hydrocarbon				
	<i>n</i> -Heptadecane	Cyclohexylundecane	Heptylbicyclodecane	Hexyltetrahydronaphthalene	Pentynaphthalene
Structural formula.....	$\text{CH}_3(\text{CH}_2)_{15}\text{CH}_3$	 $\text{C}_{11}\text{H}_{23}$	 C_7H_{15}	 C_6H_{13}	 C_5H_{11}
Empirical formula.....	$\text{C}_{17}\text{H}_{35}$	$\text{C}_{17}\text{H}_{31}$	$\text{C}_{17}\text{H}_{31}$	$\text{C}_{16}\text{H}_{21}$	$\text{C}_{15}\text{H}_{18}$
Paraffinic carbon atoms	100	64.7	41.2	37.5	33.3
Naphthenic carbon atoms, weight-percent.....	0	35.3	58.8	25.0	0
Aromatic carbon atoms, weight-percent.....	0	0	0	37.5	66.7
Total rings.....	0	1	2	2	2
Naphthenic rings.....	0	1	2	1	0
Aromatic rings.....	0	0	0	1	2

TABLE 31.—Comparison of determined and calculated data

	Oil A		Oil I		Oil L		Oil N	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
<i>n</i> -Heptadecane.....percent.....		45		30		0		0
Cyclohexylundecane.....do.....		20		10		40		20
Heptylbicyclodecane.....do.....		20		30		30		60
Hexyltetrahydronaphthalene.....do.....		10		20		10		10
Pentynaphthalene.....do.....		5		10		20		10
Paraffinic carbon atoms.....weight-percent.....	72	72	57	60	50	49	43	47
Naphthenic carbon atoms.....do.....	22	21	27	26	30	34	42	45
Aromatic carbon atoms.....do.....	6	7	16	14	20	17	14	10
Total rings per molecule.....	1.0	1.1	1.5	1.3	1.6	1.6	1.9	1.8
Naphthenic rings per molecule.....	.9	.9	1.0	.9	1.0	1.1	1.5	1.5
Aromatic rings per molecule.....	.1	.2	.5	.4	.6	.5	.4	.3
Aromatics.....volume-percent.....	11	15	30	30	31	30	16	20

¹ Determined from table 1.² Calculated. See table 30.

TABLE 32.—Hydrocarbons identified in 200°–300° C range

Type, subtype, and compound	Formula	Boiling point or range °C	Crude oil source ¹	Reference
Paraffins:				
Normal:				
<i>n</i> -Dodecane.....	$\text{C}_{12}\text{H}_{26}$	216	1	129
<i>n</i> -Tridecane.....	$\text{C}_{13}\text{H}_{28}$	235	1	129
<i>n</i> -Tetradecane.....	$\text{C}_{14}\text{H}_{30}$	253	1	129
<i>n</i> -Pentadecane.....	$\text{C}_{15}\text{H}_{32}$	271	1	129
<i>n</i> -Hexadecane.....	$\text{C}_{16}\text{H}_{34}$	287	1	129
<i>n</i> -Heptadecane.....	$\text{C}_{17}\text{H}_{36}$	302	1	129
Branched:				
2,6,10-Trimethylundecane.....	$\text{C}_{14}\text{H}_{30}$	231	1	129
2,6,10-Trimethyldodecane (Farnesane).....	$\text{C}_{15}\text{H}_{32}$	249	1	129
2,6,10-Trimethyltridecane.....	$\text{C}_{16}\text{H}_{34}$	270	2	12
2,6,10-Trimethylpentadecane.....	$\text{C}_{18}\text{H}_{38}$	285	2	12
2,6,10,14-Tetramethylpentadecane (Pristane).....	$\text{C}_{19}\text{H}_{40}$	290	2	12
2,6,10,14-Tetramethylhexadecane (Phytane).....	$\text{C}_{20}\text{H}_{42}$	325	2	12
2,6,10,14-Tetramethylheptadecane.....	$\text{C}_{21}\text{H}_{44}$	330	2	12
Cycloalkanes:				
Cyclohexanes:				
1,2-Diisopropylcyclohexane.....	$\text{C}_{12}\text{H}_{24}$	225–230	3	113
1,3-Diisopropylcyclohexane.....	$\text{C}_{12}\text{H}_{24}$	225–230	3	113
Bicyclodecenes:				
<i>t</i> -Decahydronaphthalene.....	$\text{C}_{10}\text{H}_{18}$	187	1	129
<i>c</i> -Decahydronaphthalene.....	$\text{C}_{10}\text{H}_{18}$	196	1	129
1-Methyldecahydronaphthalene.....	$\text{C}_{11}\text{H}_{20}$	205–215	4	6
1,6-Dimethyldecahydronaphthalene.....	$\text{C}_{12}\text{H}_{22}$		4	6
1,7-Dimethyldecahydronaphthalene.....	$\text{C}_{12}\text{H}_{22}$		4	6
Tricyclodecane:				
Tricyclo[3,3,1,1 ^{2,7}] decane (Adamantane).....	$\text{C}_{10}\text{H}_{16}$	190	1	129
Indans:				
Indan.....	C_9H_{10}	170	1	129
1-Methylindan.....	$\text{C}_{10}\text{H}_{18}$	191	1	129
2-Methylindan.....	$\text{C}_{10}\text{H}_{18}$	191	1	129
4-Methylindan.....	$\text{C}_{10}\text{H}_{18}$	205	1	129
5-Methylindan.....	$\text{C}_{10}\text{H}_{18}$	202	5	198

See footnote at end of table.

TABLE 32.—Hydrocarbons identified in 200°–300° C range—Continued

Type, subtype, and compound	Formula	Boiling point or range °C	Crude oil source ¹	Reference
Aromatics:				
Alkylbenzenes:				
1,2,3,4-Tetramethylbenzene	C ₁₀ H ₁₄	205	1	129
1,2,3,5-Tetramethylbenzene	C ₁₀ H ₁₄	198	1	129
1,2,4,5-Tetramethylbenzene	C ₁₀ H ₁₄	197	1	129
n-Pentylbenzene	C ₁₁ H ₁₆	205	6	143
2-Phenylpentane	C ₁₁ H ₁₆	193	6	143
3-Phenylpentane	C ₁₁ H ₁₆	191	6	143
Isopentylbenzene	C ₁₁ H ₁₆	199	6	143
1-Methyl-3-n-butylbenzene	C ₁₁ H ₁₆	204	1	129
1-Methyl-4-tert-butylbenzene	C ₁₁ H ₁₆	193	6	143
1-Methyl-3,4-diethylbenzene	C ₁₁ H ₁₆	202	-----	133
1-Methyl-3,6-diethylbenzene	C ₁₁ H ₁₆	200	-----	65
1,2-Dimethyl-4-n-propylbenzene	C ₁₁ H ₁₆	209	1	129
1,3-Dimethyl-4-n-propylbenzene	C ₁₁ H ₁₆	207	1	129
Trimethylethylbenzene	C ₁₁ H ₁₆	212	1	129
1,2-D isopropylbenzene	C ₁₂ H ₁₈	204	3	113
1,3-D isopropylbenzene	C ₁₂ H ₁₈	203	3	113
1,4-D isopropylbenzene	C ₁₂ H ₁₈	210	3	113
1,2-Dimethyl-4-tert-butylbenzene	C ₁₂ H ₁₈	215	6	143
Aromatics: (Continued)				
Tetrahydronaphthalenes:				
1,2,3,4-Tetrahydronaphthalene	C ₁₀ H ₁₂	208	1	129
2-Methyl-[1,2,3,4-tetrahydronaphthalene]	C ₁₁ H ₁₂	221	1	129
5-Methyl-[1,2,3,4-tetrahydronaphthalene]	C ₁₁ H ₁₂	234	1	129
6-Methyl-[1,2,3,4-tetrahydronaphthalene]	C ₁₁ H ₁₂	229	1	129
Naphthalenes:				
Naphthalene	C ₁₀ H ₈	218	1	129
1-Methylnaphthalene	C ₁₁ H ₁₀	245	1	129
2-Methylnaphthalene	C ₁₁ H ₁₀	241	1	129
1-Ethynaphthalene	C ₁₂ H ₁₂	259	1	129
2-Ethynaphthalene	C ₁₂ H ₁₂	258	1	129
1,2-Dimethylnaphthalene	C ₁₂ H ₁₂	268	1	129
1,3-Dimethylnaphthalene	C ₁₂ H ₁₂	265	1	129
1,4-Dimethylnaphthalene	C ₁₂ H ₁₂	268	1	129
1,5-Dimethylnaphthalene	C ₁₂ H ₁₂	265	1	129
1,6-Dimethylnaphthalene	C ₁₂ H ₁₂	263	1	129
1,7-Dimethylnaphthalene	C ₁₂ H ₁₂	263	1	129
1,8-Dimethylnaphthalene	C ₁₂ H ₁₂	270	7	152
2,3-Dimethylnaphthalene	C ₁₂ H ₁₂	269	1	129
2,6-Dimethylnaphthalene	C ₁₂ H ₁₂	262	1	129
2,7-Dimethylnaphthalene	C ₁₂ H ₁₂	263	1	129
1-n-Propylnaphthalene	C ₁₃ H ₁₄	272	1	129
2-n-Propylnaphthalene	C ₁₃ H ₁₄	273	1	129
1-Methyl-1-ethylnaphthalene	C ₁₃ H ₁₄	270	1	129
2-Methyl-6-ethylnaphthalene	C ₁₃ H ₁₄	270	1	129
1,2,4-Trimethylnaphthalene	C ₁₃ H ₁₄	261	7	152
1,2,5-Trimethylnaphthalene	C ₁₃ H ₁₄	283	7	152
1,2,6-Trimethylnaphthalene	C ₁₃ H ₁₄	280	1	129
1,2,7-Trimethylnaphthalene	C ₁₃ H ₁₄	280	1	129
1,2,8-Trimethylnaphthalene	C ₁₃ H ₁₄	295	7	152
1,3,6-Trimethylnaphthalene	C ₁₃ H ₁₄	280	7	152
1,3,7-Trimethylnaphthalene	C ₁₃ H ₁₄	280	1	129
1,3,8-Trimethylnaphthalene	C ₁₃ H ₁₄	280	1	129
1,3,7-Trimethylnaphthalene	C ₁₃ H ₁₄	280	1	129
1,3,8-Trimethylnaphthalene	C ₁₃ H ₁₄	280	1	129
1,4,6-Trimethylnaphthalene	C ₁₃ H ₁₄	289	7	152
1,4,7-Trimethylnaphthalene	C ₁₃ H ₁₄	278	1	129
1,6,7-Trimethylnaphthalene	C ₁₃ H ₁₄	280	1	129
2,3,6-Trimethylnaphthalene	C ₁₃ H ₁₄	277	1	129
2-tert-Butylnaphthalene	C ₁₄ H ₁₆	275	6	143
2-Methyl-6-propylnaphthalene	C ₁₄ H ₁₆	280	1	129
Methylisopropylnaphthalene	C ₁₄ H ₁₆	280	1	129
1,4,5,7-Tetramethylnaphthalene	C ₁₄ H ₁₆	303	6	107
2,3,6,7-Tetramethylnaphthalene	C ₁₄ H ₁₆	302	1	129
Biphenyls:				
Biphenyl	C ₁₂ H ₁₀	255	1	129
2-Methylbiphenyl	C ₁₃ H ₁₂	255	1	129
3-Methylbiphenyl	C ₁₃ H ₁₂	273	1	129
4-Methylbiphenyl	C ₁₃ H ₁₂	270	1	129
2,5-Dimethylbiphenyl	C ₁₄ H ₁₄	267	1	129
Trimethylbiphenyl	C ₁₄ H ₁₄	267	1	129
Tetramethylbiphenyl	C ₁₄ H ₁₄	267	1	129
1,2-Diphenylethane	C ₁₄ H ₁₄	285	6	143
Acenaphthenes:				
Acenaphthene	C ₁₂ H ₁₀	277	6	143
Methylacenaphthene	C ₁₃ H ₁₂	275	1	129
Fluorenes:				
Fluorene	C ₁₃ H ₁₀	297	6	143
Monomethylfluorene	C ₁₄ H ₁₂	319	1	129

¹ 1. Ponca City, Okla. 2. East Texas. 3. Bavy, U.S.S.R. 4. Mirzaak, U.S.S.R. 5. Texas. 6. Romashkino, U.S.S.R. 7. Chongelekak, U.S.S.R.

n-Paraffins and Isoparaffins

All of the *n*-paraffins have been found, but the only isoparaffins reported are the series of seven isoprenoids found in East Texas oil (table 13) and a number of other crude oils. These are of considerable interest because they are present in larger quantities than most individual hydrocarbons except the *n*-paraffins. In East Texas oil the contents range from 0.06 percent of the crude oil for 2,6,10-trimethylpentadecane to 0.5 percent for 2,6,10,14-tetramethylpentadecane (pristane). Phytane and the others are presumed to have been derived in one or more ways from phytol which is esterified to a carboxyl group on the chlorophyll molecule.

Cycloalkanes

Apparently no cyclopentanes have been identified in this boiling range, but two diisopropylcyclohexanes have been found. Decalin or decahydronaphthalene and several methyl derivatives are known and one tricyclic, adamantane. Indan and its methyl derivatives have also been found. In general our knowledge of the cycloalkanes in this boiling range is very meager.

Aromatics

The most progress has been made in identifying aromatics because they are more reactive and can be more readily separated and identified. Alkylbenzenes are prominent, as are tetrahydronaphthalenes, and especially naphthalenes. Dimethylnaphthalenes, trimethylnaphthalenes, tetrahydronaphthalenes, and decahydronaphthalenes are among the most abundant types of hydrocarbons found in the gas oil boiling range. Biphenyl and its alkylated substitute products are present in small quantities, but only diphenylethane has been identified, no diphenylmethane. Two fluorenes have also been found.

As a whole relatively little is known about the individual components of gas oil, with the possible exception of the alkylbenzenes and the alkylnaphthalenes. The paraffin-naphthene portion is generally in the range of 60 to 80 percent, yet aside from the *n*-paraffins, the isoprenoids, and possibly the decalins virtually nothing is known. However, the knowledge gained from the data on table 1 suggested the compounds to use in the model mixture shown on table 31.

SULFUR COMPOUNDS IN NAPHTHAS AND GAS OILS

Virtually every petroleum distillate contains sulfur in the form of sulfur compounds. These are restricted to compounds of carbon, hydrogen, and sulfur except possibly in the very heavy portion of crude oil where nitrogen and oxygen or both may be present along with the sulfur atom. However, as yet very few identifications (48, 108) of such compounds have been published, and these are in the over 450° C boil ng range. In light gasoline from some crude

oils the sulfur content may be only in thousandths of a percent, whereas from a high-sulfur crude oil it may be several tenths of a percent.

Table 33 is a list of all the sulfur compounds known to have been identified in crude oil. It includes those extending beyond the boiling range of gas oils because it seemed desirable to make the list complete and these were relatively few in the range above 200° C.

TABLE 33.—*Sulfur compounds in crude oils*

Type, subtype, and compound	Formula	Boiling point, °C	Crude oil source							
			Wasson		Wilmington		Agha Jari		Miscellaneous	
			Status ¹	Reference	Status ¹	Reference	Status ¹	Reference	Source ²	Reference
Thiols:										
Alkyl:										
Methanethiol.....	CH ₃ SH	5.9	0.00240	44					1	1
Ethanethiol.....	C ₂ H ₅ SH	35.0	.00530	44					1	15
1-Propanethiol.....	C ₃ H ₇ SH	67.8	.00199	44			t	45	1	15
2-Propanethiol.....	C ₃ H ₇ SH	52.6	.00041	44			i	45	1	15
1-Butanethiol.....	C ₄ H ₉ SH	98.4	Trace	44					1	15
2-Butanethiol.....	C ₄ H ₉ SH	85.0	.00386	44			i	45	1	15
2-Methyl-1-propanethiol.....	C ₄ H ₉ SH	85.5	.00003	44			t	45	1	15
2-Methyl-2-propanethiol.....	C ₄ H ₉ SH	64.2	.00055	44			i	45	1	55
1-Pentanethiol.....	C ₅ H ₁₁ SH	126.6	i	44						
2-Pentanethiol.....	C ₅ H ₁₁ SH	112.4	.0014	44						
3-Pentanethiol.....	C ₅ H ₁₁ SH	113.9	.00057	44						
2-Methyl-1-butanethiol.....	C ₅ H ₁₁ SH	118	i	44						
2-Methyl-2-butanethiol.....	C ₅ H ₁₁ SH	99.2	.00064	44						
3-Methyl-1-butanethiol.....	C ₅ H ₁₁ SH	118	i	44						
3-Methyl-2-butanethiol.....	C ₅ H ₁₁ SH	109.8	i	44						

See footnotes at end of table.

TABLE 33.—*Sulfur compounds in crude oils*—Continued

Type, subtype, and compound	Formula	Boiling point, °C	Crude oil source							
			Wasson		Wilmington		Agha Jari		Miscellaneous	
			Status ¹	Reference	Status ¹	Reference	Status ¹	Reference	Source ²	Reference
Thiols—Continued										
Alkyl—Continued										
2,2-Dimethyl-1-propanethiol	C ₄ H ₁₀ SH	103.7	i	44			t	46		
1-Hexanethiol	C ₆ H ₁₄ SH	152.6	i	44						
2-Hexanethiol	C ₆ H ₁₄ SH	138.9	i	0.0028						
3-Hexanethiol	C ₆ H ₁₄ SH	157	i	44						
2-Methyl-1-pentanethiol	C ₆ H ₁₄ SH	≈142	i	44						
2-Methyl-2-pentanethiol	C ₆ H ₁₄ SH	124.0	i	44						
2-Methyl-3-pentanethiol	C ₆ H ₁₄ SH	134.5	i	44						
3-Methyl-1-pentanethiol	C ₆ H ₁₄ SH		i	44						
3-Methyl-2-pentanethiol	C ₆ H ₁₄ SH		i	44						
3-Methyl-3-pentanethiol	C ₆ H ₁₄ SH		i	44						
4-Methyl-1-pentanethiol	C ₆ H ₁₄ SH		i	44						
4-Methyl-2-pentanethiol	C ₆ H ₁₄ SH		i	44						
2,2-Dimethyl-1-butanethiol	C ₆ H ₁₄ SH		i	44						
2,3-Dimethyl-1-butanethiol	C ₆ H ₁₄ SH		i	44						
2,3-Dimethyl-2-butanethiol	C ₆ H ₁₄ SH		i	44						
3,3-Dimethyl-1-butanethiol	C ₆ H ₁₄ SH		i	44						
3,3-Dimethyl-2-butanethiol	C ₆ H ₁₄ SH		i	44						
2-Ethyl-1-butanethiol	C ₆ H ₁₄ SH		i	44						
1-Heptanethiol	C ₇ H ₁₆ SH	176.9	i	44						
2-Heptanethiol	C ₇ H ₁₆ SH	163.6	i	44						
3-Heptanethiol	C ₇ H ₁₆ SH		i	44						
4-Heptanethiol	C ₇ H ₁₆ SH		i	44						
2-Methyl-2-hexanethiol	C ₇ H ₁₆ SH		i	44						
2-Octanethiol	C ₈ H ₁₈ SH	186.4	t	154						
Cycloalkane:										
Cyclopentanethiol	C ₅ H ₉ SH	132.1	i	44						
1-Methylcyclopentanethiol	C ₆ H ₁₁ SH		i	44						
c-2-Methylcyclopentanethiol	C ₆ H ₁₁ SH		i	44						
t-2-Methylcyclopentanethiol	C ₆ H ₁₁ SH		i	44						
c-3-Methylcyclopentanethiol	C ₆ H ₁₁ SH		t	44						
t-3-Methylcyclopentanethiol	C ₆ H ₁₁ SH		t	44						
Cyclohexanethiol	C ₆ H ₁₁ SH	158.7	t	0.0012	44					
Sulfides:										
Alkyl:										
2-Thiopropane	C ₃ H ₆ S	37.4		0.0088	176		i	45	1	15
2-Thiobutane	C ₄ H ₈ S	66.7		0.0222	176		i	45		
2-Thiapentane	C ₅ H ₁₀ S	95.6		0.0030	176		i	45		
3-Thiapentane	C ₅ H ₁₀ S	92.1		0.0075	176		i	45	1	15
3-Methyl-2-thiobutane	C ₅ H ₁₀ S	84.8		0.0064	176					
2-Thiahexane	C ₆ H ₁₂ S	123.5		0.00077	176					
3-Thiahexane	C ₆ H ₁₂ S	118.5		0.0012	176				1	15
3-Methyl-2-thiapentane	C ₆ H ₁₂ S	112	i		176					
2-Methyl-3-thiapentane	C ₆ H ₁₂ S	107.4	i		176		i	45		
3,3-Dimethyl-2-thiobutane	C ₅ H ₁₀ S	99.0	i		176					
2-Thiaheptane	C ₇ H ₁₄ S	145	i		176					
3-Thiaheptane	C ₇ H ₁₄ S	144.2		0.00078	176					
4-Thiaheptane	C ₇ H ₁₄ S	142.7	i		176					
3-Methyl-2-thiahexane	C ₇ H ₁₄ S	139	i		176					
2-Methyl-3-thiahexane	C ₇ H ₁₄ S	132		0.00078	176				1	15
4-Methyl-3-thiahexane	C ₇ H ₁₄ S	133.6		0.00050	176					
5-Methyl-3-thiahexane	C ₇ H ₁₄ S	134.2	i		176					
3,3-Dimethyl-2-thiapentane	C ₆ H ₁₂ S	131	i		176					
3,4-Dimethyl-2-thiapentane	C ₆ H ₁₂ S		i		176					
3-Ethyl-2-thiapentane	C ₆ H ₁₂ S		i		176					
2,2-Dimethyl-3-thiapentane	C ₆ H ₁₂ S	120.4		0.00058	176					
2,4-Dimethyl-3-thiapentane	C ₆ H ₁₂ S	120		0.00053	176					
2-Methyl-3-thiaheptane	C ₇ H ₁₆ S		t	a	176					
3-Methyl-4-thiaheptane	C ₇ H ₁₆ S		t	a	176					
2-Methyl-4-thiaheptane	C ₇ H ₁₆ S		i		176					
4-Methyl-3-thiaheptane	C ₇ H ₁₆ S		t	a	176					
4-Ethyl-3-thiahexane	C ₇ H ₁₆ S		t	a	176					
2,2-Dimethyl-3-thiahexane	C ₇ H ₁₆ S		i		176					
2,4-Dimethyl-3-thiahexane	C ₇ H ₁₆ S	142.3	i		176					
2,5-Dimethyl-3-thiahexane	C ₇ H ₁₆ S		i		176					
4,4-Dimethyl-3-thiahexane	C ₇ H ₁₆ S		i		176					

See footnotes at end of table.

TABLE 33.—*Sulfur compounds in crude oils*—Continued

Type, subtype, and compound d	Formula	Boiling point, °C	Crude oil source							
			Wasson		Wilmington		Agha Jari		Miscellaneous	
			Status ¹	Reference	Status ¹	Reference	Status ¹	Reference	Source ²	Reference
Sulfides—Continued										
Alkyl—Continued										
4,5-Dimethyl-3-thiahexane	C ₇ H ₁₆ S	-----	i	176	-----	-----	-----	-----	-----	-----
3,5-Dimethyl-4-thiaheptane	C ₈ H ₁₈ S	165	i	176	-----	-----	-----	-----	-----	-----
2,4-Dimethyl-3-thiaheptane	C ₈ H ₁₈ S	-----	i	176	-----	-----	-----	-----	-----	-----
2-Methyl-4-ethyl-3-thiahexane	C ₈ H ₁₈ S	-----	i	176	-----	-----	-----	-----	-----	-----
3-Ethyl-4-thiaheptane	C ₈ H ₁₈ S	-----	i	176	-----	-----	-----	-----	-----	-----
4-Ethyl-3-thiaheptane	C ₈ H ₁₈ S	-----	i	176	-----	-----	-----	-----	-----	-----
5-Methyl-4-thiaoctane	C ₉ H ₂₀ S	-----	i	176	-----	-----	-----	-----	-----	-----
4-Methyl-3-thiaoctane	C ₉ H ₂₀ S	-----	i	176	-----	-----	-----	-----	-----	-----
3-Methyl-4-thiaoctane	C ₉ H ₂₀ S	-----	i	176	-----	-----	-----	-----	-----	-----
2-Methyl-3-thiaoctane	C ₉ H ₂₀ S	-----	i	176	-----	-----	-----	-----	-----	-----
Cyclic:										
Thiacyclopentane	C ₄ H ₈ S	132.1	.000077	177	-----	-----	i	55	1	15
2-Methylthiacyclopentane	C ₅ H ₁₀ S	133.2	.0023	177	i	43	i	17	1	15
3-Methylthiacyclopentane	C ₅ H ₁₀ S	138.7	.00046	177	i	43	i	17	1	15
Thiacyclohexane	C ₆ H ₁₂ S	141.8	.00032	177	i	43	i	17	1	-----
2,2-Dimethylthiacyclopentane	C ₆ H ₁₂ S	138	i	177	i	43	i	17	-----	-----
3,3-Dimethylthiacyclopentane	C ₆ H ₁₂ S	~145	i	177	-----	-----	-----	-----	-----	-----
c-2,3-Dimethylthiacyclopentane	C ₆ H ₁₂ S	-----	ta	177	i	43	i } ^b	17	-----	-----
t-2,3-Dimethylthiacyclopentane	C ₆ H ₁₂ S	148	ta	177	i	43	i } ^b	17	-----	-----
c-2,4-Dimethylthiacyclopentane	C ₆ H ₁₂ S	148	i	177	i	43	i } ^b	17	-----	-----
t-2,4-Dimethylthiacyclopentane	C ₆ H ₁₂ S	148	i	177	i	43	i } ^b	17	-----	-----
c-3,4-Dimethylthiacyclopentane	C ₆ H ₁₂ S	156	ta	177	i	43	-----	-----	-----	-----
t-3,4-Dimethylthiacyclopentane	C ₆ H ₁₂ S	156	ta	177	i	43	-----	-----	-----	-----
c-2,5-Dimethylthiacyclopentane	C ₆ H ₁₂ S	142.3	.0024	177	i	43	-----	-----	-----	-----
t-2,5-Dimethylthiacyclopentane	C ₆ H ₁₂ S	142	.0025	177	i	43	-----	-----	-----	-----
2-Ethylthiacyclopentane	C ₆ H ₁₂ S	-----	i	177	i	43	i	17	-----	-----
2-Methylthiacyclohexane	C ₇ H ₁₄ S	153	.0029	177	i	43	i	17	-----	-----
3-Methylthiacyclohexane	C ₇ H ₁₄ S	158	.000024	177	i	43	i	17	-----	-----
4-Methylthiacyclohexane	C ₇ H ₁₄ S	158.6	.000048	177	i	43	i	17	-----	-----
2-n-Propylthiacyclopentane	C ₇ H ₁₄ S	179	i	177	-----	-----	-----	-----	-----	-----
2,2,5-Trimethylthiacyclopentane	C ₇ H ₁₄ S	158	i	177	.000070	43	i	17	-----	-----
2,3,5-Trimethylthiacyclopentane	C ₇ H ₁₄ S	157	-----	-----	-----	-----	i	17	-----	-----
2,3,4-Trimethylthiacyclopentane	C ₇ H ₁₄ S	164	-----	-----	-----	-----	i } ^a	17	-----	-----
3,4-Dimethylthiacyclohexane	C ₇ H ₁₄ S	164	-----	-----	-----	-----	i } ^a	17	-----	-----
2,6-Dimethylthiacyclohexane	C ₇ H ₁₄ S	164	-----	-----	-----	-----	i } ^a	17	-----	-----
2-Ethyl-5-methylthiacyclopentane	C ₇ H ₁₄ S	164	-----	-----	-----	-----	i } ^a	17	-----	-----
3-Isopropylthiacyclopentane	C ₇ H ₁₄ S	180	-----	-----	-----	-----	i } ^a	17	-----	-----
3-Methyl-4-ethylthiacyclopentane	C ₇ H ₁₄ S	180	-----	-----	-----	-----	i } ^a	17	-----	-----
2,4-Diethylthiacyclopentane	C ₈ H ₁₆ S	180	-----	-----	-----	-----	i } ^a	17	-----	-----
2,3,5-Dimethyl-5-ethylthiacyclopentane	C ₈ H ₁₆ S	180	-----	-----	-----	-----	i } ^a	17	-----	-----
2,3,6-Trimethylthiacyclohexane	C ₈ H ₁₆ S	180	-----	-----	-----	-----	i } ^a	17	-----	-----
2,3-Diethylthiacyclopentane	C ₈ H ₁₆ S	180	-----	-----	-----	-----	i } ^a	17	-----	-----
2,6-Dimethyl-3-ethylthiacyclopentane	C ₈ H ₁₆ S	180	-----	-----	-----	-----	i } ^a	17	-----	-----
c-2,5-Diethylthiacyclopentane	C ₈ H ₁₆ S	-----	t	154	-----	-----	-----	-----	-----	-----
t-2,5-Diethylthiacyclopentane	C ₈ H ₁₆ S	184	t	154	-----	-----	-----	-----	-----	-----
2,2,5,5-Tetramethylthiacyclopentane	C ₈ H ₁₆ S	-----	t	154	.000085	43	-----	-----	-----	-----
Alkyl-cycloalkyl:										
(1-Thiapropryl)cyclohexane	C ₈ H ₁₆ S	204	i	176	-----	-----	-----	-----	-----	-----
(2-Methyl-1-thiapropryl)cyclohexane	C ₉ H ₁₈ S	214	i	176	-----	-----	-----	-----	-----	-----

See footnotes at end of table.

TABLE 33.—*Sulfur compounds in crude oils*—Continued

Type, subtype, and compound	Formula	Boiling point, °C	Crude oil source							
			Wasson		Wilmington		Agha Jari		Miscellaneous	
			Status ¹	Reference	Status ¹	Reference	Status ¹	Reference	Source ²	Reference
Sulfides—Continued										
Alkyl-cycloalkyl—Continued										
(2-Methyl-1-thiabutyl) cyclopentane.	C ₉ H ₁₈ S	207	i	176						
(3-Methyl-1-thiabutyl) cyclopentane.	C ₉ H ₁₈ S	207	i	176						
(2,2-Dimethyl-1-thiapropryl)cyclohexane.	C ₁₀ H ₂₀ S	230	i	176						
Alkyl-aryl:										
(2-Methyl-1-thiabutyl) benzene.	C ₁₀ H ₁₄ S		i	154						
3-Methyl-1-(2-methyl-1-thiapropryl)benzene.	C ₁₀ H ₁₄ S		i	154						
4-Methyl-1-(2-methyl-1-thiapropryl)benzene.	C ₁₀ H ₁₄ S		i	154						
Thienyl:										
Methyl,3,4,5-trimethyl-2-thienylsulfide.	C ₈ H ₁₂ S ₂	~250			i	19				
Dithiaalkyl:										
2,3-Dithiabutane.	C ₂ H ₆ S ₂	115	t	3						
2,3-Dithiapentane.	C ₃ H ₈ S ₂	135	t	3						
3,4-Dithiahexane.	C ₄ H ₁₀ S ₂	152.6	t	3						
Bicyclic:										
2-Thiabicyclo[2,2,2]octane.	C ₇ H ₁₂ S	~191			i	16				
c-2-Thiabicyclo[3,2,1]octane.	C ₇ H ₁₂ S	~190			i	16				
c-3-Thiabicyclo[3,2,1]octane.	C ₇ H ₁₂ S	~191			i	16				
c-3-Thiabicyclo[3,3,0]octane.	C ₇ H ₁₂ S	~191					i	15		
c-6-Thiabicyclo[3,2,1]octane.	C ₇ H ₁₂ S	~191					i	15		
c-8-Thiabicyclo[3,2,1]octane.	C ₇ H ₁₂ S	~189					i	15		
x-Methyl-8-thiabicyclo[3,2,1]octane.	C ₈ H ₁₄ S	~189					i	15		
3-Methyl-2-thiabicyclo[3,3,0]octane.	C ₈ H ₁₄ S	195					i	15		
4-Methyl-2-thiabicyclo[3,3,0]octane.	C ₈ H ₁₄ S	202					i	15		
4-Ethyl-2-thiabicyclo[3,3,0]octane.	C ₉ H ₁₆ S	210					i	15		
2-Thiabicyclo[4,3,0]nonane.	C ₉ H ₁₆ S	208					i	15		
2-Methyl-2-thiabicyclo[3,3,0]octane.	C ₈ H ₁₆ S	195					i ^a	15		
6-Thiabicyclo[4,3,0]nonane.	C ₉ H ₁₆ S	195					i ^a	15		
c-7-Thiabicyclo[4,3,0]nonane.	C ₉ H ₁₆ S								1	55
4-7-Thiabicyclo[4,3,0]nonane.	C ₉ H ₁₆ S								1	55
9-Thiabicyclo[3,3,1]nonane.	C ₉ H ₁₆ S	~230					i	16		
c-1-Thiahydrindane.	C ₉ H ₁₆ S	214					i	17		
4-1-Thiahydrindane.	C ₉ H ₁₆ S	213					i	17		
3,4-Dimethyl-2-thiabicyclo[3,3,0]octane.	C ₉ H ₁₆ S	210					i ^a	15		
9-Methyl-6-thiabicyclo[3,4,0]nonane.	C ₉ H ₁₆ S	210					i ^a	15		
1-Thiaindan.	C ₈ H ₈ S	236	i	178						
2-Methyl-1-thiaindan.	C ₉ H ₁₀ S	232	i	178						
3-Methyl-1-thiaindan.	C ₉ H ₁₀ S		t	178						
5-Methyl-1-thiaindan.	C ₉ H ₁₀ S		t	178						
7-Methyl-1-thiaindan.	C ₉ H ₁₀ S		t	178						
2,2-Dimethyl-1-thiaindan.	C ₁₀ H ₁₂ S		t ^a	178						
3,3-Dimethyl-1-thiaindan.	C ₉ H ₁₀ S		t	178						
2,3-Dimethyl-1-thiaindan.	C ₉ H ₁₀ S		t	178						
3-Ethyl-1-thiaindan.	C ₉ H ₁₀ S		t ^a	178						
3,5-Dimethyl-1-thiaindan.	C ₉ H ₁₀ S		t	178						
3,7-Dimethyl-1-thiaindan.	C ₉ H ₁₀ S		t ^a	178						
3,6-Dimethyl-1-thiaindan.	C ₉ H ₁₀ S		t	178						
2,5-Dimethyl-1-thiaindan.	C ₉ H ₁₀ S		t ^a	178						
2,7-Dimethyl-1-thiaindan.	C ₉ H ₁₀ S		t ^a	178						
2-Ethyl-1-thiaindan.	C ₉ H ₁₀ S		t	178						
2,6-Dimethyl-1-thiaindan.	C ₉ H ₁₀ S		t	178						
2,4-Dimethyl-1-thiaindan.	C ₁₁ H ₁₂ S		t	178						
2-Ethyl-1-thiaindan.	C ₁₁ H ₁₂ S		t ^a	178						
2-Methyl-3-ethyl-1-thiaindan.	C ₁₂ H ₁₄ S		t ^a	178						
2,2,5-Trimethyl-1-thiaindan.	C ₁₂ H ₁₄ S		t ^a	178						
2,2,7-Trimethyl-1-thiaindan.	C ₁₃ H ₁₆ S		t ^a	178						
2-Methyl-6-dimethyl-3-thiabicyclononane.	C ₁₁ H ₂₀ S	~250					i	19		

See footnotes at end of table.

TABLE 33.—*Sulfur compounds in crude oils*—Continued

Type, subtype, and compound	Formula	Boiling point, °C	Crude oil source							
			Wasson		Wilmington		Agha Jari		Miscellaneous	
			Status ¹	Reference	Status ¹	Reference	Status ¹	Reference	Source ²	Reference
Sulfides—Continued										
Tricyclic:										
Thiaadamantane.....	C ₈ H ₁₄ S	227					i	18		
Thiophenes:										
Alkyl:										
Thiophene.....	C ₆ H ₆ S	84.1			i	180				
2-Methylthiophene.....	C ₇ H ₈ S	112.5			i	180				
3-Methylthiophene.....	C ₇ H ₈ S	115.4			i	181				
2-Ethylthiophene.....	C ₈ H ₁₀ S	134.0			0.000080	42				
3-Ethylthiophene.....	C ₈ H ₁₀ S	136			.000027	42				
2,3-Dimethylthiophene.....	C ₈ H ₁₀ S	141.6			.000094	42				
2,4-Dimethylthiophene.....	C ₈ H ₁₀ S	140.7			.000058	42				
2,5-Dimethylthiophene.....	C ₈ H ₁₀ S	138.7			.000061	42				
3,4-Dimethylthiophene.....	C ₈ H ₁₀ S	145			.000028	42				
2-Isopropylthiophene.....	C ₇ H ₁₀ S	142			.000006	42				
2- <i>n</i> -Propylthiophene.....	C ₇ H ₁₀ S	158.5			.000009	42	i	17		
2,3,4-Trimethylthiophene.....	C ₉ H ₁₂ S	175					i	17		
2-Ethyl-3,4-dimethylthiophene.....	C ₉ H ₁₂ S	190					i	17		
3-Ethyl-2,4-dimethylthiophene.....	C ₉ H ₁₂ S	190					i	17		
4-Ethyl-2,3-dimethylthiophene.....	C ₉ H ₁₂ S	193					i	17		
2,3,4,5-Tetramethylthiophene.....	C ₉ H ₁₂ S	195					i	17		
2-Ethyl-3,4,5-trimethylthiophene.....	C ₉ H ₁₄ S	205					i	17		
Bicyclic:										
2-Methylthieno[3,2- <i>b</i>]thiophene.....	C ₇ H ₆ S ₂	~215	i	87						
3-Methylthieno[2,3- <i>b</i>]thiophene.....	C ₇ H ₆ S ₂	~215	i	87						
Benzothiophenes:										
Benzo[<i>b</i>]thiophene.....	C ₈ H ₆ S	219.9	i	41						
2-Methylbenzo[<i>b</i>]thiophene.....	C ₉ H ₈ S	243	i	41						
3-Methylbenzo[<i>b</i>]thiophene.....	C ₉ H ₈ S	240	i	41						
4-Methylbenzo[<i>b</i>]thiophene.....	C ₉ H ₈ S		t	155						
7-Methylbenzo[<i>b</i>]thiophene.....	C ₉ H ₈ S	264	i	154						
2-Ethylbenzo[<i>b</i>]thiophene.....	C ₁₀ H ₁₀ S								1	55
3-Ethylbenzo[<i>b</i>]thiophene.....	C ₁₀ H ₁₀ S								1 ^a	55
2,3-Dimethylbenzo[<i>b</i>]thiophene.....	C ₁₀ H ₁₀ S	250	i	155					1 ^a	55
2,4-Dimethylbenzo[<i>b</i>]thiophene.....		255	i	155						
2,5-Dimethylbenzo[<i>b</i>]thiophene.....			t	155						
2,7-Dimethylbenzo[<i>b</i>]thiophene.....			t ^a	155						
2,6-Dimethylbenzo[<i>b</i>]thiophene.....			i						1	55
3,6-Dimethylbenzo[<i>b</i>]thiophene.....			i							
3,7-Dimethylbenzo[<i>b</i>]thiophene.....			i							
4,7-Dimethylbenzo[<i>b</i>]thiophene.....			i							
3- <i>n</i> -Propylbenzo[<i>b</i>]thiophene.....									1	55
Dibenzothiophenes:										
Dibenzothiophene.....		295	i	154					5	68
2-Methyldibenzothiophene.....		310	t	154						
4-Methyldibenzothiophene.....		341	t ^a	154					2,5	68, 132
1,6-Dimethyldibenzothiophene.....		340							1	56
4,6-Dimethyldibenzothiophene.....		~350							2,3,1	33, 55, 132
3,4,6,7-Tetramethyldibenzothiophene.....		>350							3	35
3,4,7,8-Tetramethyldibenzothiophene.....		>350							3	34
2,4,7,8-Tetramethyldibenzothiophene.....		>350							3	34
3,4,6,7-Tetramethyldibenzothiophene.....		>350							3	34

See footnotes at end of table.

TABLE 33.—*Sulfur compounds in crude oils*—Continued

Type, subtype, and compound	Formula	Boiling point, °C	Crude oil source							
			Wasson		Wilmington		Agha Jari		Miscellaneous	
			Status ¹	Reference	Status ¹	Reference	Status ¹	Reference	Source ²	Reference
Thiophenes—Continued										
Tricyclic thiophenes:										
Indanothiophenes:									4	125
Indenothiophenes:									4	125
Acenaphenothiophenes:									4	125
Benzodithiophenes:									4	125
Benzo[<i>b</i>]naphtho[2,1- <i>d</i>]thiophene.		408							2, 3	34, 132
Methylbenzonaphthothiophene.		422							2	132
3-Ethyl-8,8-dimethylnaphtho-(1: 2- <i>b</i>)thiophene.		>350							3	34

¹ Figures are weight-percent of crude oil:

i positively identified.

t tentatively identified.

| a any one or any combination may be present.

b indicates cis and trans forms not differentiated.

² Crude oil source:

1. Iran.

2. Ponca City, Okla.

3. Kuwait.

4. Probably United States.

³ Unpublished Bureau of Mines data.

There have been two major studies of sulfur compounds in crude oil: (1) That by American Petroleum Institute Research Project 48 (API RP 48) on the Synthesis, Properties, and Identification of Sulfur Compounds in Petroleum conducted at the Bureau of Mines Research Centers at Bartlesville, Okla., and Laramie, Wyo. (2) A similar research project carried out over a number of years by the British Petroleum (BP) Company. The work of API RP 48 was concentrated on crude oil from the Wasson field in Texas with additional data on a few other crude oils, chiefly Wilmington, Calif., oil. The BP effort has concerned primarily Middle East crude oil, especially that from the Agha Jari field. Because there are only these two main sources of data, and because most of the effort was toward identification with relatively little quantitative data, it is not possible to present an abundance picture as for the hydrocarbons. However, a few salient points can be gleaned from the data.

A comparison of the thiol, sulfide, thiophene, benzothiophene, and dibenzothiophene data make possible the following conclusions:

1. Wasson naphtha boiling to 200° C contains alkyl and cycloalkyl thiols, and alkyl, alkyl-cycloalkyl, alkyl-aryl, and cyclic sulfides, but no thiophene or alkylthiophenes.
2. Wilmington naphtha boiling to 150° C contains thiophene and alkylthiophenes and cyclic sulfides, but no thiols or alkyl sulfides.
3. Agha Jari naphtha boiling to 200° C contains alkyl and cycloalkyl thiols, alkyl and cyclic sulfides, and alkyl thiophenes.
4. Wasson, Iranian, Lacq, Kuwait, and Ponca City distillates over 200° C all contain benzothiophenes, dibenzothio-

phenes, and higher molecular weight polycyclic aromatic thiophenes. It appears almost certain that in Wilmington and Agha Jari crude oils the major sulfur compounds of the heavy distillates are also benzothiophenes and polybenzothiophenes.

5. Agha Jari distillate in the vicinity of 200° C contains bicyclic sulfides. It seems probable that these are also present in other crude oils, but no search has been made for them in Wasson and Wilmington oils.
6. Thiaindanes were found in Wasson distillate, but were not searched for in Wilmington, and were not reported in Agha Jari or Middle East oils. They are present in relatively small quantities compared with the cyclic sulfides, so they may have been overlooked, particularly since these investigations were made on acid sludge.
7. Alkyl-cycloalkyl and alkyl-aryl sulfides were found in Wasson distillate, but have not been reported for any other oil.
8. Compounds with two sulfur atoms, but not of the disulfide type, were found in Wasson and Agha Jari distillates. No search was made for them in Wilmington oil.
9. Alkyl disulfides in trace amounts were found in a sample of crude oil from Deep River, Mich., that was sampled and processed carefully to prevent oxidation of thiols to disulfides.
10. Compounds with sulfur and nitrogen, thianaphthoquinoline and thioquinolone, have been found in California crude oils.

The studies made by BP were on acid sludge and consequently compounds present in very small quantity may have been lost in the processing. The API RP 48 work was carried out by processes applied to the whole crude oil designed to minimize loss and change.

Only a few quantitative data are available—these are for a few thiols and sulfides in Wasson distillates, and thiophene in Wilmington distillate. Smith and others (168) have presented curves showing the trends for thiol and sulfide distribution, and Thompson and others (179) have similar curves for the thiophenes. These are reproduced in figure 47. These show that the proportion of 1-alkanethiols decreases in an alternating manner relative to carbon number with increase in molecular weight and becomes negligible at approximately six or seven carbon atoms. The 2-alkanethiols are the most abundant of all alkanethiols, and on the basis of present data appear to alternate in abundance between odd- and even-numbered carbon atom molecules, the even-numbered being the most abundant. Their content should become negligible at approximately 12 to 15 carbon atoms. Tertiary mercaptans are present only in small quantities. The curve for the sulfides shows that the 2- and 3-methylthiaalkanes and 2-methyl-3-thiaalkane all decrease in abundance with increase of molecular weight and apparently will disappear at approximately 8 to 10 carbon atoms. Sulfides with tertiary carbon-sulfur linkages are present only in very small quantities.

The curves for thiophenes in figure 47 show that the 2-methyl compounds are more abundant than the 3-methylthiophenes. Also that as the chain length increases the amount of the compound present decreases, and the 2-methylthiophenes would seem to disappear at about C_{10} , or a pentylthiophene. This would be at the point where benzothiophene makes its appearance.

The available data on sulfur compounds can be summarized as follows:

1. The gasoline fractions may contain one or more of the following:
 - a. Alkyl and cycloalkyl thiols and sulfides (decreasing)⁵
 - b. Alkyl, alkyl-cycloalkyl, alkyl-aryl sulfides (decreasing)
 - c. Cyclic sulfides (increasing?)
 - d. Alkylthiophenes (decreasing)
2. The kerosine-light gas oil may contain one or more of the following:
 - a. Cyclic sulfides (decreasing)
 - b. Bicyclic sulfides (increasing)
 - c. Thiaindanes(?)
 - d. Alkylthiophenes (decreasing)

- e. Benzothiophenes (increasing)
3. The medium to heavy gas oil may contain one or more of the following:
 - a. Benzothiophenes (decreasing)
 - b. Dibenzothiophenes (increasing)
 - c. Tricyclobenzothiophenes (increasing)
 4. The apparently universal presence of the benzothiophenes and polybenzothiophenes and the occasional presence of the simple alkylated thiophenes suggest that these two types of thiophenic compounds have different origins.

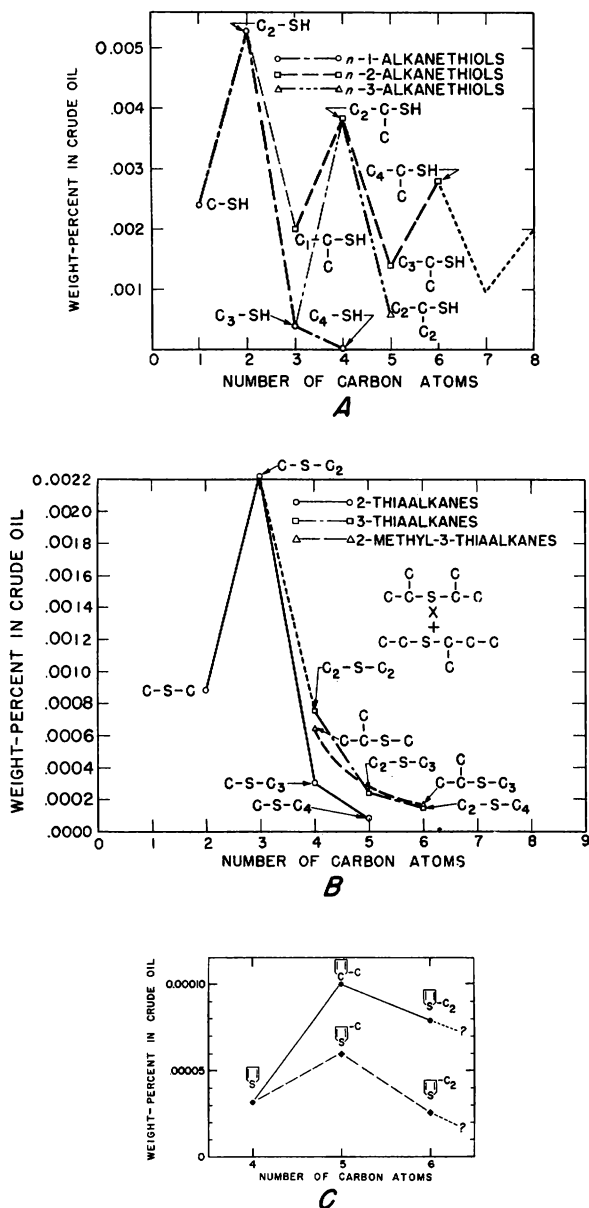


FIGURE 47.—Quantitative Relationships of Thiols (A), Sulfides (B), and Thiophenes (C).

⁵ The words "decreasing" and "increasing" refer to the relative change in abundance with increase in boiling point.

NITROGEN COMPOUNDS IN NAPHTHAS AND GAS OILS

As for the sulfur compounds, all nitrogen compounds identified in crude oil are listed in table 34. The nitrogen content of crude oils ranges from virtually nil to about 1.0 percent. The distribution was discussed in table 3 and under "Residua." Ball (9) has presented data on the distribution of nitrogen in the distillate and residuum of Wilmington crude oil that contains 0.65 percent nitrogen. These data, given below, show that even in a high-nitrogen crude

oil the content of nitrogen in the distillate boiling to 300° C is very small:

Boiling range, ° C	Nitrogen, weight-percent
Up to 130.....	0.00
130-250.....	.0027
250-300.....	.028
300-350.....	.10
350-400.....	.25
400-500.....	.48
Residuum.....	.97

TABLE 34.—Nitrogen compounds in crude oil

Type, subtype, and compound	Formula	Boiling point or range, ° C	Crude oil source ¹	Reference
Pyridines:				
Alkyl:				
3-Methylpyridine.....	C ₆ H ₇ N	170-200	1	122
2, 3-Dimethylpyridine.....	C ₇ H ₉ N	170-200	1	122
3, 5-Dimethylpyridine.....	C ₇ H ₉ N	170-200	1	122
3-Methyl-6-ethylpyridine.....	C ₈ H ₁₁ N	170-200	1	122
2,3,4-Trimethylpyridine.....	C ₈ H ₁₁ N	170-200	1	122
2,3,5-Trimethylpyridine.....	C ₈ H ₁₁ N	210-220	1	122
3-Ethyl-5-methylpyridine.....	C ₈ H ₁₁ N	170-200	1	122
2,3-Dimethyl-6-isopropylpyridine.....	C ₁₀ H ₁₅ N	170-200	1	122
di-2-sec-Butyl-4,5-dimethylpyridine.....	C ₁₁ H ₁₇ N	200-210	1	122
Pyridines:				
Dihydro:				
2-Methyl-6,7-dihydro-1,5-pyridine.....	C ₆ H ₁₁ N	209-211	1	124
5-Methyl-6,7-dihydro-1,5-pyridine.....	C ₆ H ₁₁ N	209-211	1	123
Bicyclic:				
Dinaphthenopyridine.....	R-C ₁₂ H ₁₇ N	350-375	4	108
Thianaphthapyridine.....	R-C ₁₂ H ₁₇ N	ca400	4	108
Quinolines:				
Alkyl:				
Quinoline.....	C ₁₀ H ₈ N	230-240	1	122
2-Methylquinoline.....	C ₁₁ H ₁₀ N	230-240	1	122
2,3-Dimethylquinoline.....	C ₁₂ H ₁₂ N	260-270	1	122
2,4-Dimethylquinoline.....	C ₁₂ H ₁₂ N	260-270	1	122
2,6-Dimethylquinoline.....	C ₁₂ H ₁₂ N	240-260	1	122
2,3,5-Trimethylquinoline.....	C ₁₃ H ₁₄ N	270-280	1	122
2,4,8-Trimethylquinoline.....	C ₁₃ H ₁₄ N	270-280	1	122
2-Methyl-8-ethylquinoline.....	C ₁₄ H ₁₆ N	250-260	1	122
2,3,4,8-Tetramethylquinoline.....	C ₁₇ H ₁₇ N	290-300	1	122
2,3-Dimethyl-8-ethylquinoline.....	C ₁₇ H ₁₇ N	280-290	1	122
2,4-Dimethyl-8-ethylquinoline.....	C ₁₇ H ₁₇ N	290-300	1	122
2,3,4-Trimethyl-8-ethylquinoline.....	C ₁₈ H ₁₈ N	300-330	1	122
2,3,8-Trimethyl-4-ethylquinoline.....	C ₁₈ H ₁₈ N	300-310	1	122
2,3-Dimethyl-8-n-propylquinoline.....	C ₁₈ H ₁₈ N	290-300	1	122
2,4-Dimethyl-8-n-propylquinoline.....	C ₁₈ H ₁₈ N	290-300	1	122
2,3,4-Trimethyl-8-n-propylquinoline.....	C ₁₉ H ₂₀ N	310-320	1	122
2,3,4-Trimethyl-8-isopropylquinoline.....	C ₁₉ H ₂₀ N	310-320	1	122
2,3-Dimethyl-4,8-diethylquinoline.....	C ₁₉ H ₂₀ N	310-320	1	122
2,4-Dimethyl-8-sec-butylquinoline.....	C ₁₉ H ₂₀ N	310-320	1	122
2,3-Dimethyl-4-ethyl-8-n-propylquinoline.....	C ₂₀ H ₂₂ N	310-320	1	122
Tetrahydro:				
5,6,7,8-Tetrahydroquinoline.....	C ₉ H ₁₀ N	220-240	1	122
Benzo:				
2,3-Dimethylbenzo[a]quinoline.....	C ₁₁ H ₁₂ N	>350	1	122
2,4-Dimethylbenzo[a]quinoline.....	C ₁₁ H ₁₂ N	>350	1	122
Hydroxybenzoquinoline.....	C ₁₀ H ₁₀ NO		2	92
Naphtheno:				
Mononaphthenoquinoline.....	R-C ₁₂ H ₁₅ N	350-375	4	108
Dinaphthenoquinoline.....	R-C ₁₇ H ₁₉ N	400	4	108
Thianaphthoquinoline.....	C ₁₃ H ₁₃ NS	450-500	4	108
Miscellaneous:				
Carbazoloquinolines.....				
Indoloquinoline.....	C ₁₀ H ₈ N ₂	315-540	2	92
1,10-Penanthroline.....	C ₁₁ H ₈ N ₂	315-540	2	92
Alkyltetrahydrocarbazolenine.....	R-C ₁₂ H ₁₅ N	315-540	2	92
Carbazoles:				
Carbazole.....	C ₁₂ H ₉ N	354	1	108
Alkylcarbazoles.....	R-C ₁₂ H ₁₅ N	350-375	4	108
Mononaphthenocarbazoles.....	R-C ₁₆ H ₁₇ N	ca400	4	108
Dinaphthenocarbazoles.....	R-C ₂₀ H ₂₀ N	450-500	4	108
Quinolones:				
2-Quinolone.....	R-C ₉ H ₇ NO	340-450	3	48
Benz-2-quinolone.....	R-C ₁₀ H ₉ NO	340-450	3	48
2-Thioquinolone.....	R-C ₉ H ₇ NS	340-450	3	48

¹ 1. Unidentified California distillates. 2. Unidentified heavy gas oil. 3. Heavy gas oils from Ventura Basin, Calif. 4. Unidentified oil.

The most extensive study of nitrogen compounds, all classified as basic nitrogen compounds, is that conducted over a period of years by Professor J. R. Bailey and associates of the University of Texas starting as API RP 20 from 1927 to 1931. Professor Bailey continued these studies until his death in 1940, and Professor H. L. Lochte at the same university has continued the studies up to the present. The work is reported in a book by Lochte and Littman (122). The source of the nitrogen compounds isolated was on Edleanu liquid sulfur dioxide extract at a kerosine distillate from California crude oils.

The only compounds that have been isolated in the naphtha-gas oil range are pyridines and quinolines. The quinolines isolated by Bailey all have a methyl substitution in the 2-position, and usually only methyl groups in the 3- and 4-positions. These data are given in table 35. Larger substituents are found in the 8-position. These structural factors may be related to the origin of these compounds, or may simply indicate that these compounds are more amenable to the separation processes used.

TABLE 35.—*Structural relationships of quinolines found in petroleum*

Compound	2-Position	3-Position	4-Position	8-Position
1.....	Methyl.....
2.....	do.....	Methyl.....
3.....	do.....	Methyl.....
4.....	do.....	Methyl.....
5.....	do.....	Methyl.....	Do.....
6.....	do.....	Methyl.....	Do.....
7.....	do.....	Ethyl.....
8.....	do.....	Methyl.....	Methyl.....	Methyl.....
9.....	do.....	do.....	Ethyl.....
10.....	do.....	Methyl.....	Do.....
11.....	do.....	Methyl.....	do.....	Do.....
12.....	do.....	do.....	Ethyl.....	Methyl.....
13.....	do.....	do.....	n-Propyl.....
14.....	do.....	Methyl.....	Do.....
15.....	do.....	Methyl.....	do.....	Do.....
16.....	do.....	do.....	do.....	Isopropyl.....
17.....	do.....	do.....	Ethyl.....	Ethyl.....
18.....	do.....	Methyl.....	sec-Butyl.....
19.....	do.....	Methyl.....	Ethyl.....	n-Propyl.....

There are no quantitative data on these compounds so relative abundances cannot be discussed. The compounds in the latter part of table 34 are high boiling and are found in the heavy gas oil or material boiling in general above 300° C; therefore, they have not been discussed in this section.

OXYGEN COMPOUNDS IN NAPHTHAS AND GAS OILS

Our knowledge of the oxygen content of crude oils and its fractions is meager, and in some respects we know less than about nitrogen in crude oil. Oxygen indigenous to crude oil or its fractions is formidable to determine: (1) Unless activation analysis can be used it is a difficult determination, and is often arrived at by difference; (2) There is no easy way to distinguish between dissolved oxygen, oxygen that may have reacted since the sample was obtained, and the oxygen of compounds originally present in the sample; (3) The quantities of oxygen containing compounds are very small. For these reasons, and also because oxygen compounds have not been known to cause the difficulties in refining and utilization that sulfur and nitrogen compounds do, there has been no concerted effort to study them comparable to API RP 48 and API RP 52 on sulfur and nitrogen. There is considerable evidence that, like nitrogen, oxygen is present in greater quantities as the boiling point increases, but this has not been as well documented as for nitrogen. The trend is clearly seen in the data shown on table 36, where most of the compounds shown boil above 200° C, and many above 300° C. Some asphalts have been shown to have oxygen contents of several percent.

Quantitative data on the oxygen content of crude oils or distillates is very difficult to find. As most of the compounds are acidic, some scattered data are available on naphthenic

acids of which those given in table 37 taken from an article by Shipp (163) give some idea of the quantitative picture.

These data show two points clearly: (1) the increase of naphthenic acids with increase in boiling point; (2) the much higher content of naphthenic acids in the naphthenic and asphaltic crude oils. Reference to table 36 shows that a number of naphthenic acids in the boiling range covered have been identified, primarily by Bailey, Lochte, and others (122) at the University of Texas working mostly on extracts from Signal Hill crude oil. However, they also found a series of aliphatic saturated fatty acids, and this was recently confirmed by Graham (76) working on a naphthenic acid concentrate from San Joaquin Valley, California, crude oil. Thus the data in table 37 may include saturated fatty acids, especially in the kerosine boiling range. The San Joaquin Valley fatty acids, extracted by conversion to esters, were present in the crude naphthenate and the crude oil to the extent given in table 38. These data would indicate the maximum content of these saturated fatty acids were in the gas oil fraction.

In addition to the aliphatic saturated straight-chain acids several other acid types have been found. Among the most interesting are four isoprenoid acids found by Cason and Graham (37) as given in table 39.

TABLE 36.—*Oxygen compounds in crude oils*

Type, subtype, and compound	Formula	Boiling point or range, ° C	Crude oil source ¹	Reference
Saturated fatty acids:				
Formic.....	HCOOH	101	1	122
Acetic.....	CH ₃ COOH	118	1	122
Propionic.....	C ₂ H ₅ COOH	141	1	122
Isobutyric.....	C ₄ H ₇ COOH	154	1	122
Butyric.....	C ₃ H ₇ COOH	163	1	122
Isovaleric.....	C ₅ H ₉ COOH	175	1	122
<i>n</i> -Pentanoic (valeric).....	C ₄ H ₉ COOH	185	1	122
<i>n</i> -Hexanoic.....	C ₅ H ₁₁ COOH	206	1	122
2-Methylpentanoic.....	C ₅ H ₁₁ COOH	193	1	122
3-Methylpentanoic.....	C ₅ H ₁₁ COOH	197	1	122
4-Methylpentanoic.....	C ₅ H ₁₁ COOH	200	2	122
<i>n</i> -Heptanoic.....	C ₆ H ₁₃ COOH	223	1	122
3-Ethylpentanoic.....	C ₆ H ₁₃ COOH	212	2	122
2-Methylhexanoic.....	C ₆ H ₁₃ COOH	210	1	122
3-Methylhexanoic.....	C ₆ H ₁₃ COOH	227	1	122
4-Methylhexanoic.....	C ₆ H ₁₃ COOH	217	1	122
5-Methylhexanoic.....	C ₆ H ₁₃ COOH	216	1	122
<i>n</i> -Octanoic.....	C ₇ H ₁₅ COOH	237	1, 11	76, 122
<i>n</i> -Nonanoic.....	C ₈ H ₁₇ COOH	254	1, 11	76, 122
<i>n</i> -Decanoic.....	C ₉ H ₁₉ COOH	270	11	76
<i>n</i> -Undecanoic.....	C ₁₀ H ₂₁ COOH	280	11	76
<i>n</i> -Dodecanoic.....	C ₁₁ H ₂₃ COOH	294	11	76
<i>n</i> -Tridecanoic.....	C ₁₂ H ₂₅ COOH	305	11	76
<i>n</i> -Tetradecanoic (myristic).....	C ₁₃ H ₂₇ COOH	317	3, 4, 11	27, 76
<i>n</i> -Pentadecanoic.....	C ₁₄ H ₂₉ COOH	348	11	76
<i>n</i> -Hexadecanoic (palmitic).....	C ₁₅ H ₃₁ COOH	338	3, 4, 5, 6, 11	27, 76, 122
<i>n</i> -Heptadecanoic.....	C ₁₆ H ₃₃ COOH	348	11	76
<i>n</i> -Octadecanoic (stearic).....	C ₁₇ H ₃₅ COOH	359	3, 4	122
<i>n</i> -Eicosanoic (arachidic).....	C ₁₉ H ₃₉ COOH	378	3, 4	122
Isoprenoid acids:				
2,6,10-Trimethylundecanoic.....	C ₁₄ H ₂₇ COOH	-----	11	37
3,7,11-Trimethyldodecanoic.....	C ₁₄ H ₂₉ COOH	-----	11	37
2,6,10,14-Tetramethylpentadecanoic.....	C ₁₉ H ₃₉ COOH	382	11	37
3,7,11,15-Tetramethylhexadecanoic.....	C ₂₀ H ₄₁ COOH	409	11	37
Cycloalkanecarboxylic acids:				
Cyclopentane acids:				
Cyclopentanecarboxylic.....	C ₆ H ₉ COOH	215	1	122
2-Methylcyclopentanecarboxylic.....	C ₆ H ₁₁ COOH	220	1	122
3-Methylcyclopentanecarboxylic.....	C ₆ H ₁₁ COOH	235	1	122
2,2-Dimethylcyclopentanecarboxylic.....	C ₇ H ₁₃ COOH	-----	7	27
1,2,2-Trimethylcyclopentanecarboxylic.....	C ₈ H ₁₅ COOH	-----	1	122
Cyclohexane acids:				
Cyclohexanecarboxylic.....	C ₇ H ₁₁ COOH	232	1	122
4-Methylcyclohexanecarboxylic.....	C ₇ H ₁₃ COOH	-----	1	27
<i>c</i> -2,2,6-Trimethylcyclohexanecarboxylic.....	C ₈ H ₁₇ COOH	-----	1, 11	76, 122
<i>t</i> -2,2,6-Trimethylcyclohexanecarboxylic.....	C ₈ H ₁₇ COOH	-----	1, 11	76, 122
Cycloalkaneacetic acids:				
Cyclopentane acids:				
Cyclopentylacetic.....	C ₆ H ₁₁ COOH	230	1	122
3-Methylcyclopentylacetic.....	C ₇ H ₁₃ COOH	-----	1	122
2,3-Dimethylcyclopentylacetic.....	C ₈ H ₁₅ COOH	-----	1	122
3,3,4-Trimethylcyclopentylacetic.....	C ₉ H ₁₇ COOH	-----	7	122
2-Methylcyclopentylpropionic.....	C ₉ H ₁₇ COOH	-----	7	27
Ketones:				
Alkyl ketones:				
Methyl.....	C ₂ H ₅ CO	56	8	122
Methylethyl.....	C ₃ H ₇ CO	80	8	122
Methyl- <i>n</i> -propyl.....	C ₄ H ₉ CO	102	8	122
Methylisopropyl.....	C ₄ H ₉ CO	93	8	122
Methyl- <i>n</i> -butyl.....	C ₅ H ₁₁ CO	127	8	122
Ethyl-isopropyl.....	C ₅ H ₁₁ CO	115	8	81
Cyclic:				
Acetyl-isopropyl-methylcyclopentane.....	C ₁₁ H ₂₀ O	130-250	9	25
Alkylfluorenones.....	R-C ₁₅ H ₈ O	320-330	9, 10	56, 109
Phenols:				
Phenol.....	C ₆ H ₅ OH	181	8	27
<i>o</i> -Cresol.....	C ₇ H ₇ OH	181	3, 4, 7	27
<i>m</i> -Cresol.....	C ₇ H ₇ OH	201	3, 4, 7, 8	27
<i>p</i> -Cresol.....	C ₇ H ₇ OH	201	3, 4, 7	27
1,2,3-Xylenol.....	C ₈ H ₉ OH	218	3, 7	27
1,2,4-Xylenol.....	C ₈ H ₉ OH	225	4, 8	27
1,3,4-Xylenol.....	C ₈ H ₉ OH	209	3, 4	27
1,3,5-Xylenol.....	C ₈ H ₉ OH	-----	4, 7	27
β -Naphthol.....	C ₁₀ H ₇ OH	295	8	27
Miscellaneous:				
Dimethylmaleic anhydride.....	C ₈ H ₆ O ₃	-----	1, 8	122
Dimethylmaleic acid.....	C ₈ H ₆ (COOH) ₂	-----	8	27
Phthalic acid.....	C ₈ H ₆ (COOH) ₂	-----	-----	27
Diethylphthalate.....	C ₁₂ H ₁₈ O ₄	-----	12	27
Oxyallobetui-2-ene.....	C ₂₈ H ₄₆ O ₂	-----	12	11

¹ 1. Signal Hill, Calif. 2. U.S.S.R. 3. Japan. 4. Poland. 5. Borneo. 6. California. 7. Rumania. 8. Texas. 9. Wilmington, Calif. 10. Agha Jari. 11. San Joaquin Valley, Calif. 12. United States.

TABLE 37.—*Naphthenic acid content of distillates from U.S. crude oils*

Source	Boiling range		Naph- thenic acids, percent
	° F	° C	
Kerosine:			
Pennsylvania.....	350-530	177-277	0.00
East Texas (mixed).....	360-520	182-271	.009
Mid-Continent pipeline (mixed).....	330-535	166-279	.009
Cuyaga, Tex. (mixed).....	335-540	168-282	.011
Luling, Tex. (mixed).....	300-560	149-293	.027
California (mixed asphaltic).....	350-550	177-288	.06
Texas heavy (naphthenic).....	400-500	204-260	.078
Gas oil:			
Pennsylvania.....	570-660	290-349	.016
Mid-Continent pipeline (mixed).....	575-665	302-352	.018
Texas light (mixed).....	375-740	302-393	.04
California (mixed asphaltic).....	500-700	260-371	.36
Texas heavy (naphthenic).....	490-670	254-354	.35

TABLE 38.—*Fatty acid ester content of crude methylnaphthenate*

Carbon atoms in ester	Boiling point of acid, ° C	Volume-per cent of crude naphthenate	Volume-per cent of crude oil
8.....	237	0.6	0.006
9.....	254	1.9	.019
10.....	270	6.3	.063
11.....	280	11.3	.113
12.....	294	17.0	.170
13.....	305	14.5	.145
14.....	317	18.2	.182
15.....	328	12.0	.120
16.....	338	13.2	.132
17.....	348	3.8	.038
18.....	359	1.3	.013

¹ Calculated from extrapolated curve.

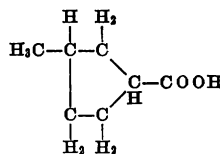
TABLE 39.—*Isoprenoid acids identified in California petroleum*

<i>Compound</i>	<i>Structure</i>
2,6,10-Trimethylhendecanoate.	$ \begin{array}{ccccccc} & \text{C} & & \text{C} & & \text{C} & \\ & & & & & & \\ \text{C} & - \text{C} - \text{C}_2 & - & \text{C} - \text{C}_3 & - & \text{C} - \text{C} & \text{O O H} \end{array} $
3,7,11-Trimethyldodecanoate.	$ \begin{array}{ccccccc} & \text{C} & & \text{C} & & \text{C} & \\ & & & & & & \\ \text{C} & - \text{C} - \text{C}_2 & - & \text{C} - \text{C}_3 & - & \text{C} - \text{C} & - \text{C} - \text{O O H} \end{array} $
2,6,10,14-Tetramethylpentadecanoate.	$ \begin{array}{ccccccc} & \text{C} & & \text{C} & & \text{C} & & \text{C} \\ & & & & & & & \\ \text{C} & - \text{C} - \text{C}_2 & - & \text{C} - \text{C}_3 & - & \text{C} - \text{C}_2 & - & \text{C} - \text{C} - \text{O O H} \end{array} $
3,7,11,15-Tetramethylhexadecanoate.	$ \begin{array}{ccccccc} & \text{C} & & \text{C} & & \text{C} & & \text{C} \\ & & & & & & & \\ \text{C} & - \text{C} - \text{C}_2 & - & \text{C} - \text{C}_3 & - & \text{C} - \text{C}_2 & - & \text{C} - \text{C} - \text{C} - \text{O O H} \end{array} $

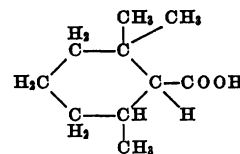
If the author has correctly interpreted the figures in the referenced report the acids are present to the following approximate percents in the crude oil: C_{15} , 0.002; C_{19} , 0.0989; C_{20} , 0.1935. Relative to the content of many hydrocarbons certainly the C_{19} and C_{20} acids are not minor constituents.

The naphthenic acids are found as both the simple carboxylic acids and the slightly more complex acetic or propionic acids. The latter

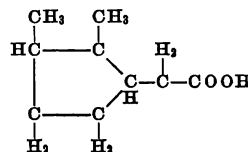
two types have been found only with the cyclopentyl ring. Typical forms reported by Lochte (122) are as follows:



3-Methylcyclopentanecarboxylic acid

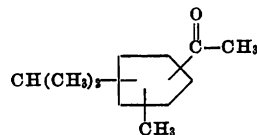


**2,2,6-Trimethylcyclohexane-
carboxylic acid**



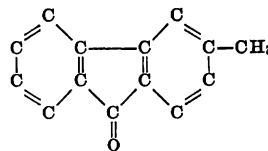
2,3-Dimethylcyclopentylacetic acid.

Several ketones have been reported in condensate fractions, along with the lower members of the saturated fatty acid series in material boiling up to about 150° C. There seem to be no data to indicate if these will be found in the light naphtha fractions from ordinary crude oil. Several cyclic ketones have been found in Wilmington crude oil:



Acetyl-isopropyl-methyl-cyclopentane

in the gasoline boiling range and alkyl fluorenones such as



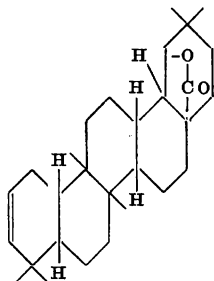
4-methylfluorenone in the kerosine boiling range.

Phenols are usually found in petroleum distillates, and phenols with the monomethyl and dimethyl substituted compounds have been identified. Until there is proof of the occurrence of phenols in crude oil one may question as to whether the compounds found were indigenous or artifacts. Data on such compounds in crude oil as against cracked products are scarce.

Field, Dempster, and Tilson (71) are authors of an excellent article on this subject, but it appears to be based on analyses of phenols extracted from cracked naphtha.

Several other unexpected oxygen compounds such as maleic and phthalic acid compounds and a lactone have been reported as shown in table 36.

The lactone (11)



oxyallobetul-2-ene may be related to natural products.

POSSIBLE PETROLEUM PRECURSORS

One cannot contemplate the large and varied array of hydrocarbons and their heteroatomic counterparts that form petroleum without being curious as to how such a complex mixture originates. This question has plagued chemists and geologists for many years and still is not solved, although within the last decade a much better understanding of some of the possible routes has been reached and considerable progress made toward a consensus. Although at first thought a section on the origin of petroleum may seem out of place in a paper devoted primarily to the composition of naphtha and light gas oil, it will be shown shortly that the boiling range of these products includes compounds for which scientists are still searching for an adequate and acceptable explanation as to source. This also is the only part of petroleum for which reasonably good knowledge of the individual constituents exists qualitatively and to some extent quantitatively. It is this writer's belief that much of the progress that has occurred in recent years has stemmed from increased knowledge of the presence of individual compounds or series of compounds and the possible linking of these to certain precursors. Therefore it seems in keeping with this paper to present very briefly the current thinking in regard to the origin of petroleum with special emphasis as to possible precursors of the several types of compounds that have been found.

Almost since petroleum was discovered there have been two major theories as to origin—

In summary saturated fatty acids from C_1 to C_{20} , isoprenoid acids C_{14} to C_{21} , cyclopentane and cyclohexane carboxylic acids C_5 to C_{10} , cyclopentyl acetic acids C_8 to C_{10} , aliphatic ketones C_3 to C_8 , phenols C_6 to C_8 , and a number of more or less exotic oxygen containing compounds have been identified in crude oil, but quantitative data are almost entirely missing. The content of all these compounds, based on scanty data, appear to increase with increase in boiling range of the petroleum fraction. The naphthenic type crude oil appears to have a greater content of naphthenic acids, but there does not appear to be any data to show that paraffinic crude oils have more saturated fatty acids. Some of the compounds could be derived from natural products and thus may be important in organic geochemistry. The 200° to 300° C fraction of crude oil has been subject to the most study, and while a little is known regarding material boiling below 200° C, almost nothing is known about the portion above 300° C.

these were generally referred to as "inorganic" and "organic." Today the words "abiotic" and "biogenic" are used to describe similar processes. There have been several abiotic processes, starting with the concept of Berthelot (13) involving the formation of acetylene and other hydrocarbons by reduction of carbon dioxide in ground water by alkali metals, to the formation of so-called "primitive" molecules from the actions of various forms of energy on a primeval atmosphere of hydrogen, oxygen, carbon, and nitrogen in a fully reduced state. This latter theory is well exemplified by the work of Eck and others (63). There are several good statements regarding the biogenic origin of petroleum and the reader is referred to Gruse and Stevens (77, pp. 228-254), Degens (58), and particularly to Calvin (32) in his Bakerian Lecture "Chemical Evolution." Robinson (156) suggests a combination of both theories. The writer also can see that both theories have a place. There seems little doubt that organic compounds at least the simpler ones, must have had an abiotic origin. However, it seems even more certain that petroleum as it occurs in sediments is the end result of biogenic processes on earth, followed by diagenesis of the organic debris deposited in the sediments. Thus abiotic processes well may have been, eons ago, the original source of living organic matter in which in turn underwent biogenetic development and in a much more ocomplex form was ultimately deposited in sediments. Calvin (32) refers to this biogenesis when he says:

. . . within the not too distant future I believe we will be able to reconstruct this chlorophyll-containing structure . . . from its component molecular parts. When we can do that we will have carried out the whole structural evolution from the atoms of which the molecules are made up, to the visible, biological functioning structure.

In general it appears that many of the hydrocarbon types identified in petroleum are more complex than the primitive type compounds and most probably are arrived at through biogenic processes. A recent article by Ponnamperuma and Pering (151) shows that the hydrocarbons produced by a simulated abiotic process in the laboratory do not reproduce in any way the isoprenoids that are found in rocks over 2 billion years old.

The biogenic theory for the origin of petroleum has two concepts: one is the direct alteration of the individual constituents of the organic debris by chemical action or thermal degradation; the other proposes a material variously called micropetroleum, protopetroleum or neopetroleum which is, to quote Degens (58):⁶

. . . regarded as an organic extract from the organic debris embedded in the sediments. It is assumed to be a complex mixture of high-molecular weight organic compounds and, as such, only a petroleum precursor, inasmuch as petroleum is made up of about 50 percent of light hydrocarbons . . . Accordingly, the generation of the gas and gasoline fractions is largely accomplished *after migration* (Smith's italics) by thermal decomposition of the heavy hydrocarbons. The inference is that petroleum and its precursor concentrate is a dynamic mixture of chemical constituents that are subject to change throughout its post-depositional history.

This author can agree with the last statement, but feels that the most likely hypothesis is a combination of both concepts, the extent of one or the other at a given time or place being dependent upon both the source material and the environment. Any theory of petroleum origin, to be fully acceptable, must explain certain geochemical findings satisfactorily. These, as so well stated by Degens,⁷ are as follows:

- (1) Formation of light hydrocarbons in the C_3 to C_{14} range which are absent from present day organisms and recent sediments; they occur in ancient sediments and constitute about 50 percent of the average crude oil.
- (2) Greater abundance of hydrocarbons in ancient sediments, when compared to recent sediments of the same lithology.
- (3) General chemical similarities between all petroleum systems independent of their geological age; observed fluctuations in chemistry (ratio of paraffins to naphthenes to aromatics) are of the same order of magnitude in crude oils taken from the same formation as they are between formations.

- (4) Preference of odd- or even-numbered paraffins (C_{16} and up) in recent and, to a lesser degree, in ancient sediments, in contrast to petroleum paraffins that exhibit no preference.
- (5) Formation of hydrocarbons under both fresh water and marine conditions.
- (6) C^{12} enrichment in both marine kerogen and crude oil by about 6 to 10 per mil relative to living organisms with no apparent difference between the kerogen and the associated petroleum.
- (7) C^{12} enrichment in the light hydrocarbon fractions up to the pentanes, and C^{13} enrichment in the benzenoid hydrocarbon fraction when compared to the σC^{13} of the whole crude oil.
- (8) Identification of the biochemical composition of the source materials and simple outline of the pathway of their low temperature transformation to hydrocarbons.
- (9) Time and place of hydrocarbon formation.
- (10) Oil droplet formation and final accumulation of petroleum.

To these this author would add:

- (11) A maximum n -alkane content at C_6 - C_8 in most oils, but in others it may be at C_{15} - C_{18} or occasionally at C_{25} - C_{30} .
- (12) Certain structures, such as for isoprenoid hydrocarbons, porphyrins, and a number of polycyclic hydrocarbons (cyclopentanophenanthrenes, benzofluorens) that have close resemblance to naturally occurring compounds.

Adherence to the biogenic theory, regardless of which of its two concepts is accepted, implies belief in low-temperature thermal degradation as part of the diagenesis mechanism. Geological and chemical facts relating to the organic matter in sediments have strongly indicated a low temperature history for the sediments that seldom exceed 200° C, and more often was well below this figure, in the vicinity of 100° to 125° C. In some thermodynamic considerations farther on these temperatures should be kept in mind.

ORGANIC PRECURSORS AND THEIR ORIGINS

With the preceding admittedly too short condensation of current thinking on the origin of petroleum the next factor to be considered is the organic debris: What does it consist of and what are the end products that are deposited in the sediments?

Most organic geochemists are in agreement that the five principal classes of organic compounds that reach the sediments are proteins, carbohydrates, lignins, pigments and lipids. The geochemists disagree mildly on the exact components to place under each class, but they would probably agree that they would include the organic constituent end-members found in sediments given by Degens (58)⁸: "amino compounds; carbohydrates and derivatives, lipids,

⁶ Egon T. Degens, *Geochemistry of Sediments, A Brief Survey*, © 1965. Reprinted by permission of Prentice-Hall, Inc., Englewood Cliffs, N.J.

⁷ Work cited in footnote 6.

⁸ Work cited in footnote 6.

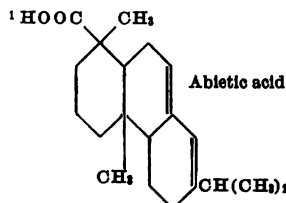
isoprenoids and steroids; heterocyclic compounds; phenols, quinones and humic compounds; hydrocarbons; asphalts." Most of these, with the exception of derived hydrocarbons and asphalt, are the building blocks that must be converted into the derived hydrocarbons and to asphalt.

This author has always considered that source material must play an important part in the ultimate composition of petroleum. Certainly from the many and varied sources of organic debris there exists as wide a spectrum in com-

position as found in crude oil. Table 40 presents the major components of the oils or extracts of a random selection of seeds, leaves, wood, and spores. The variety of compounds even from these few sources covers a wide range, and offers many possible avenues for hydrocarbon generation. When one considers the literally millions of species of flora and fauna that can contribute, the variety of compounds that will be found, and the possibilities for certain species to concentrate over a period of years in some particular location, either by direct growth

TABLE 40.—Compounds found in various seed, leaf, and wood oils and extracts

Source	Compound	Comments
Seed oils (36):		
Valerianaceae:		
(Kentranthus macrosiphon).....	α -Eleostearic acid.....	Three conjugated double bonds.
Compositae:		
Osteospermum hyoseroides (DC).....	<i>t</i> -8, <i>t</i> -10, <i>c</i> -12-Octadecatrienoic acid.....	Do.
Osteospermum ecklonis (DC).....	Dimorphecolic (9-hydroxy-4-10, <i>t</i> -12-octadecadienoic acid).....	Do.
Tagetes erecta L.....	9-Hydroxy-10,12-octadecadienoic acid.....	Two conjugated double bonds.
	13-Hydroxy-9,11-octadecadienoic acid.....	Do.
	Limonene.....	Terpene.
	Isopipertanol.....	Do.
Oil of gingergrass (145).....	<i>c</i> - <i>p</i> -Menthadiene-1(7),8-ol-2.....	Do.
	Perillyl alcohol.....	Do.
	<i>d</i> -Sabinene.....	Do.
	<i>d</i> -Limonene.....	Do.
Oil of juniperus horizontalis Moench (49).....	<i>n</i> -Heptane.....	<i>n</i> -Paraffin.
Pinus jeffreyi } Pinus sabiniana/		
Cucurbitaceae seed oils (40):		
Ecballium elaterium } Trichosanthes anguina/	Punicic acid.....	Three conjugated double bonds.
Cucumis dipsaceus } Cucurbita ficifolia/	Palmitic acid.....	Saturated.
	Oleic acid.....	One double bond.
	Linoleic acid.....	Two double bonds.
	α -Eleostearic acid.....	Three conjugated double bonds.
	Oleic acid (both free and combined).....	One double bond.
	Linoleic acid (both free and combined).....	Two double bonds.
	Isopimaric acid (free).....	Diterpenic acid.
	Dehydroabietic acid (free).....	C ₂₀ H ₃₀ O ₂ diterpenic acid.
	Abietic acid (free) ¹	Diterpenic acid.
Momordica charantia.....		
Pinus resinosa Ait. extract of heartwood (159).....		
Leaf oils of Sitka and Englemann spruce (194):		
Sitka spruce oil.....	<i>d</i> -Myrcene.....	Acyclic terpene.
	<i>l</i> -Piperitone.....	Cyclic terpene.
	<i>d</i> -Camphor.....	Do.
	<i>c</i> -Hex-3-en-1-ol.....	
Englemann spruce oil.....	<i>d</i> -Camphor.....	Do.
	<i>d</i> -Bornyl acetate.....	Do.
	<i>d</i> -Linalool.....	Acyclic hydroxyterpene.
Cholesterol in higher plants (39):		
Solanum tuberosum.....	Cholesterol.....	
Dioscorea spiculiflora.....	Cholesterol.....	
Pollen of Coniferous species (39):		
Douglas fir.....	Palmitic acid.....	Saturated.
	Oleic acid.....	One double bond.
	Linoleic acid.....	Two double bonds.
Formosan Douglas fir.....	Palmitic acid.....	Saturated.
	Oleic acid.....	One double bond.
	Linoleic acid.....	Two double bonds.
	Palmitic acid.....	Saturated.
Big-cone Douglas fir.....	Stearic acid.....	Do.
	Oleic acid.....	One double bond.
	Palmitic acid.....	Saturated.
	Stearic acid.....	Do.
Ponderosa pine.....	Oleic acid.....	One double bond.
	Linolenic acid.....	Three double bonds.
	Lauroic acid.....	Saturated.
	Palmitic acid.....	Do.
Lodgepole pine.....	Stearic acid.....	Do.
	Oleic acid.....	One double bond.
	Linolenic acid.....	Three double bonds.



at that point, or by some distribution and concentration system it seems very probable that the composition of the resultant petroleum will be governed in part, and the author believes to a considerable part, by the nature of the deposited organic debris.

PRECURSORS FOR HYDROCARBONS

n-Alkanes

The *n*-alkanes that have been identified (129) range from methane with 1 carbon atom to *n*-tritetracotane with 43 carbon atoms. There is considerable variability in the content of the normal paraffins in crude oil. Some Michigan oils contain large quantities of the normal paraffins, but relatively small quantities of isoparaffins. In contrast many gulf coast oils have only traces of normal paraffins. Some idea of the variation is given by the data in figure 48. Two researchers have reported *n*-paraffins of 74 carbon atoms (78) and of 78 carbon atoms (59). Headlee (78) reported additional *n*-paraffins in the range C_{54} – C_{74} in West Virginia crude oil. Although positive identification in these ranges is very difficult, compounds boiling to about

500° C have been definitely identified, with probable isolation of even higher boiling paraffins. Recent data (56) indicate that the high melting waxes containing 24 to 25 carbon atoms are not composed entirely of *n*-paraffins, but it is not known if the remainder of the waxes are alkyl paraffins with only a few small branches, possibly in the 2-position, or alkylcycloparaffins with a long paraffin chain.

The distribution for *n*-alkanes in crude oils of different ages is extremely interesting to the geochemist. Martin and coworkers (138) give an excellent exposition of this distribution, and figure 49, taken from their report, illustrates the following facts:

1. The most common distribution shows no pronounced odd or even carbon atom predominance, a maximum at C_7 , and no sharp decrease near C_{18} . This is typified by the Darius curve.
2. The distribution maximum may be at a higher carbon number, such as C_{11} . There may be marked predominances of odd-numbered carbon atoms, and the *n*-alkane content may decrease sharply at C_{18} . The Pine Unit and John Creek curves illustrate this situation.
3. An unusual distribution is shown by the Uinta Basin crude oil with a maximum at C_{27} .

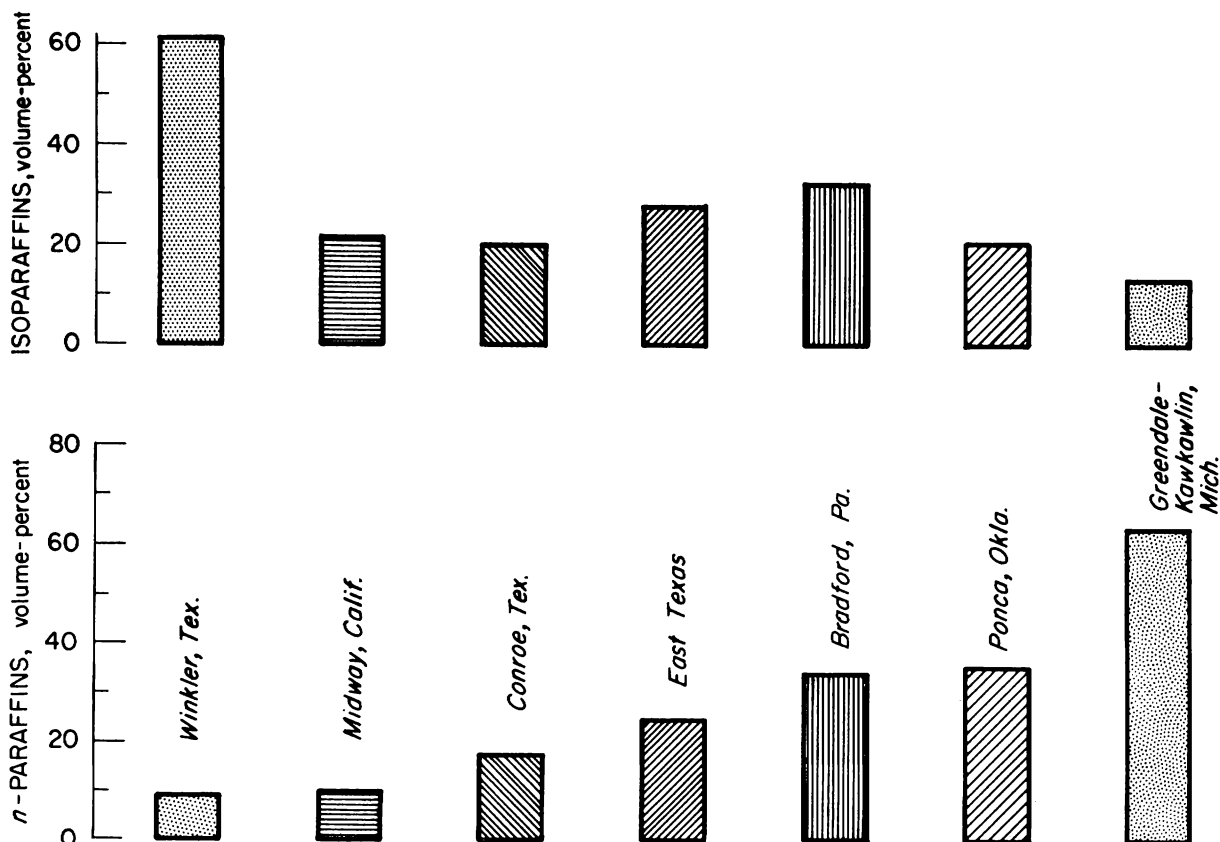


FIGURE 48.—Relationships of *n*-Alkanes and Isoalkanes in 40°–102° C Paraffin-Naphthene Portions of Naphthas From Seven Crude Oils. (From data in Reference 73.)

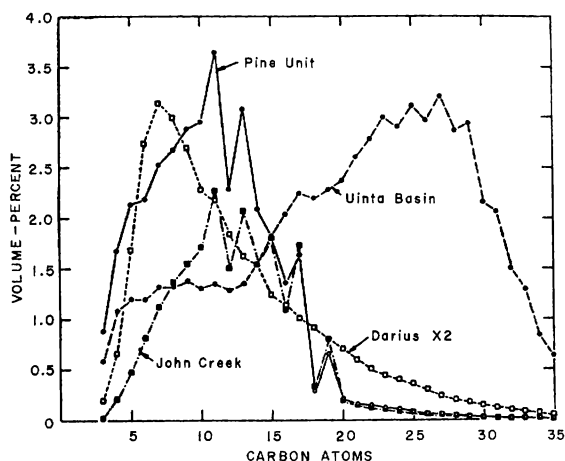


FIGURE 49.—Distribution of *n*-Paraffins in Four Crude Oils. (From Martin, Winters, and Williams (138), by permission.)

and a slight odd-numbered predominance from from C_{23} to C_{32} .

4. Other crude oils may show other variations, such as having the maximum *n*-alkane content at C_{17} or having odd-numbered predominance at different carbon number positions.

n-Alkane Sources

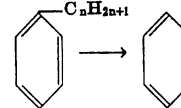
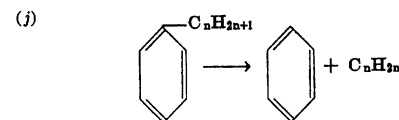
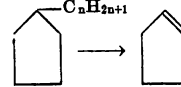
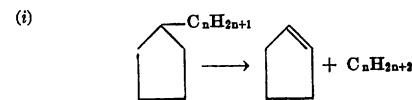
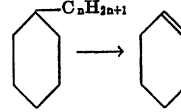
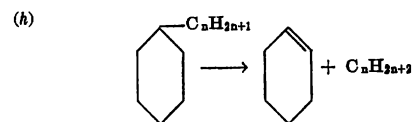
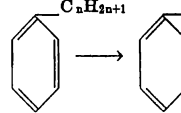
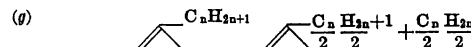
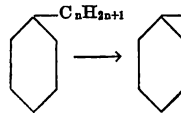
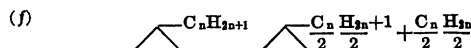
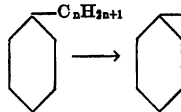
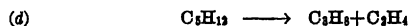
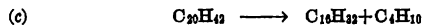
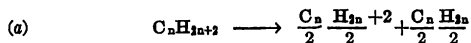
Hydrocarbons

Naturally occurring hydrocarbons seem an obvious source (171). Gerarde and Gerarde (74), in an excellent summary of hydrocarbons in nature, show that hydrocarbons from C_7 to C_{37} are found in the leaves and fruits of plants and in some insects, and the terpentine of the Jeffrey and Digger pines is almost pure heptane. However, most of the *n*-alkanes in natural products are in the C_{20} to C_{30} range and show a decided predominance for odd-numbered *n*-alkanes. This is contrary to the data for most crude oils which usually have a considerable quantity of hydrocarbons from C_2 upward and show little predominance for either odd or even carbon atom compounds. This does not preclude naturally occurring hydrocarbons as contributors. Thus Koons and coworkers (104) have recently shown that in marine organisms as typified by sponges and coral there are hydrocarbons present in the range C_{24} – C_{34} and they show no odd or even preference similar to most crude oils.

Thermal Cracking

This is an appropriate place to discuss thermal cracking. Phillipi (148) in a recent excellent article makes a strong case for thermal formation of petroleum from sediment organic mat-

ter. Erdman (66), Degens (58), and others have pointed to low-temperature pyrolysis as a predominant factor and an earlier statement indicated 100° to 200° C (373° to 673° K) as being the range envisioned. Thermodynamics may be of aid here. The following reactions involving only *n*-paraffin chains were used as models for applying thermodynamic data.



The values used were those reported as the free energy of formation in the ideal gas state, ΔF_f° in the API RP 44 compilation (2). In this paper the term ΔF_f° has been replaced by the term ΔG_f° , the gibbs energy of formation, but with the same numerical values. The gibbs energy of reaction, ΔG° for each reaction *a* through *j* at several different temperatures were calculated from the formula $\sum \Delta G_f^\circ$ (products) – $\sum \Delta G_f^\circ$ (reactants) = ΔG° (reaction). From a plot of ΔG° (reaction) versus the absolute temperature, $^\circ$ K, a temperature was interpolated for ΔG° (reaction) equal to zero. A typical graph is shown in figure 50 for the median splitting of *n*-alkanes, reaction *a*. When the gibbs energy of the reaction is zero the equilibrium constant, *K*, at the corre-

sponding absolute temperature, T , is one, since $\Delta G^\circ = -RT \ln K$, where R is the gas constant. For the isolated reaction used of the type $A = B + C$, the reaction constant would be

$$K = \frac{B \times C}{A} = 1.$$

where A , B and C are concentrations expressed in mole fractions. For $K=1$, B and C must in all cases equal 0.4142 mole fraction and $A=0.1716$, and the percent of A decomposed is approximately 83. Thus in effect the temperature at which the equilibrium constant equals unity has been determined for the purpose of using this temperature to show the feasibility of thermal cracking under geological conditions. It is realized that many of the data are for the gas phase—but good consistent data for the liquid phase, especially for a series of compounds, are difficult to find; further if all data are for the gas phase the differences are minor. Also the data used for the higher molecular weights were obtained by the method of increments, not experimentally. Finally, and most important, these data are for a single isolated reaction that probably could not occur as an isolated reaction under geologic conditions. It is also equally true that it is impossible to make any useful assumption regarding the conditions or environment, both chemical and physical, that might prevail if such a reaction initiated. However, the thermodynamic data as used in this paper will indicate the degree of possibility of a given reaction occurring over a range of temperatures, but the direction and extent of subsequent related reactions will be governed by existing, but unknown conditions. For example, in the splitting of an n -paraffin an n -olefin is formed, but olefins in crude oil are very rare. This implies that among several possibilities hydrogenation, polymerization, or attachment to another active molecule may have occurred, but there is no basis for selection of a preferred reaction.

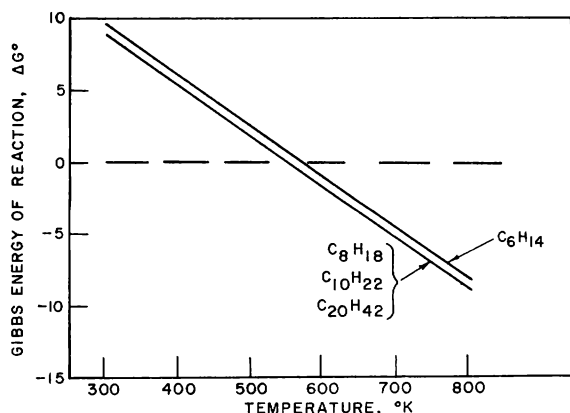


FIGURE 50.—Median Splitting of n -Alkanes.

With these admitted deficiencies in mind the data in figure 51 are presented, and several observations can be made, the validity of which must be tempered by the previous comments regarding the data. *It should be remembered that the temperatures referred to are those for which $\Delta G^\circ=0$ and $K=1$, at which points about 83 percent of the reactant A has reacted.* Obviously at lower temperatures smaller quantities will have reacted, but in terms of geologic time very small quantities of reaction products per unit time are permissible, *in fact necessary*, because it has been shown many times that petroleum is *not* an equilibrium mixture for any of the various components for which analyses have been made.

- Curve *a*. About 550° K is required to cause median splitting of n -paraffins of C_8 or more. Below C_8 the temperature rises abruptly.
- Curve *b*. The temperature required to split off ethane from n -paraffins of C_8 or more is about 15° K above that for median splitting. The shapes of the two curves are almost identical and they meet at the point for C_4H_{10} .
- Point *c*. At a chain length of C_{20} the temperature required to split off butane is the same as that to split off decane, 550° K.
- Point *d*. The temperature required to split C_8H_{18} into C_3H_8 and C_2H_4 is the same as for splitting C_4H_{10} into C_2H_6 and C_2H_4 .
- Curves *e, f, g*. About 550° K is required for median splitting of n -paraffin chains of C_8 and above on alkylcyclopentanes, alkylcyclohexanes, or alkylbenzenes. This is the same temperature required for median splitting of n -paraffins of C_8 or more. For chains of less than C_8 there is the typical rapid rise in temperature.
- Curve *h*. About 495° K is required to split off the entire n -paraffin chain from the cyclohexane ring for chains of C_4 and more. This temperature is 55° K lower than the median splitting of n -paraffins. Shorter chains require a higher temperature.
- Curve *i*. About 530° K is required to split off the entire n -paraffin chain from the cyclopentane ring for chains of C_6 and more. Shorter chains require a higher

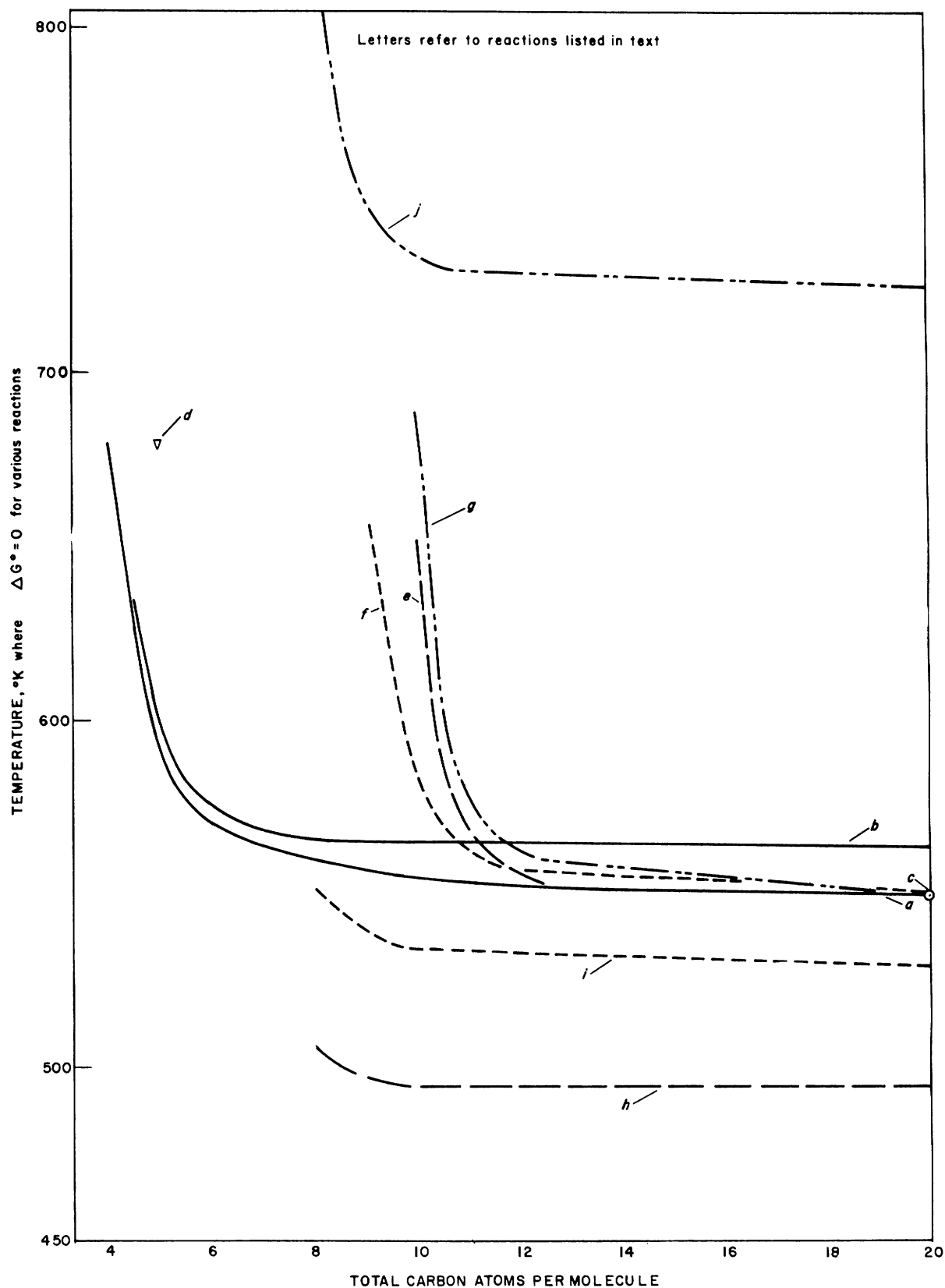


FIGURE 51.—Gibbs Energy of Reaction Data for Hydrocarbon Splitting Reactions.

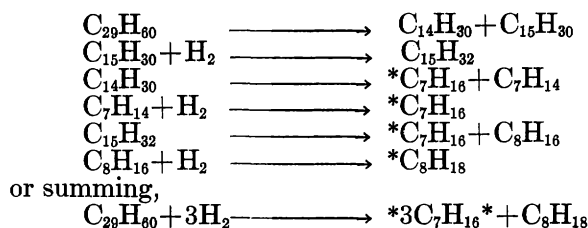
temperature. This temperature is intermediate between that for the total chain removal from the cyclohexane ring, but still 20° K below the median splitting for *n*-paraffins.

Curve *j*.

About 725° K is required to split off the entire *n*-paraffin chain from the benzene ring for chains of C₄ or more. Shorter chains require a higher temperature.

The general conclusion from these observations is that at geologically acceptable temperatures most of these reactions could initiate with an entirely plausible percent reacted value provided conditions and environment permit continuation of the reaction. The possible exception is the aromatics, especially those with chains shorter than C₄. Earlier in this paper the prevalence of short chain (C₁-C₃) polyalkylbenzenes was mentioned, a fact in harmony with these thermodynamic observations.

A theoretical application of these data is made to the *n*-paraffin C₂₉H₆₀ that is very commonly found in a wide variety of leaves and fruits. For example, assume median splitting of nonacosane and of its primary products, plus the necessary hydrogenation without specifying the source of the hydrogen:



* Final products.

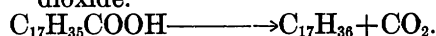
This could explain the lack of *n*-paraffins below C₁₄-C₁₅ in recent sediments, their presence in ancient sediments, and also the common phenomena of the predominance of C₇ and C₈ *n*-paraffins in crude oils.

It is beyond the scope of this paper to consider such problems as sources of hydrogen and disappearance of olefins. However, over the long time involved the quantity of hydrogen required at any given time would be very small and could be supplied by several sources. One example would be by irradiation, such as by gamma rays, and another would be cyclization of a paraffin with release of hydrogen. Further in this report the reaction of olefins with hydrogen sulfide is discussed. This would be an easy means of removing olefins. These examples do not exhaust the possible solutions of the hydrogen and olefin problems.

Saturated Fatty Acids

Martin and coworkers (138) suggest saturated fatty acids as precursors for the C₁₁-C₁₈ *n*-alkane range. This view is substantiated by the work of Cooper (46) and by Lawlor and Robinson (110) and concurred in by Mair (130) among others. Saturated C₁₂-C₁₈ fatty acids are major constituents of many natural vegetable and animal fats. Cooper has shown that fatty acids survive in sediments (46) and has proposed a mechanism for the decarboxylation reaction (47). Jurg and Eisma (95) have shown that thermal cracking of higher molecular weight fatty acids in the presence of bentonite must not be overlooked both as a decarboxylation reaction and as a means of forming *n*-paraffins with smaller carbon numbers:

Stearic acid \longrightarrow Heptadecane + carbon dioxide.



The basic data (from Parks and Huffman (147) except as noted) are

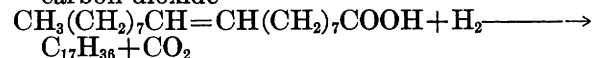
- ΔG°_{298} Palmitic acid (solid): -80.00 kcal
 ΔG°_{298} Liquefaction: -1.44 kcal
 ΔG°_{298} Addition of two CH₂ groups (l): +1.30 kcal
 a. ΔG°_{298} Stearic acid (l): -80.14 kcal
 b. ΔG°_{298} Heptadecane (l):
 -9.0 + 1.3 × 17 = 13.1 kcal
 c. ΔG°_{298} Carbon dioxide (g) -93.96 kcal (196)
 $\Delta G^\circ = (B + C) - (A) = -0.72 \text{ kcal}.$

The result does not indicate a very large driving force for the reaction; however, the basic data on stearic acid may be in error by 2 or 3 kcal, and there are no other data on which to determine the direction of change with increase in temperature.

Unsaturated Fatty Acids

Martin and coworkers (138) suggest unsaturated fatty acids as precursors particularly in the C₁₈-C₂₀ range. Most unsaturated fatty acids are C₁₈ compounds with different degrees of unsaturation and accordingly different reactivities. Here again it is possible to make an approximation of the gibbs energy data. Assume the unsaturated acid is oleic acid, C₁₈H₃₆, commonly found in many natural products:

Oleic acid + hydrogen \longrightarrow Heptadecane + carbon dioxide



The basic data (from Parks and Huffman (147) except as noted) are

- ΔG°_{298} Stearic acid (l): -80.14 kcal
 ΔG°_{298} Introduction of double bond: 20.00 kcal

- a. $\Delta G_f^\circ_{298}$ Oleic acid (1): -60.14 kcal
 b. $\Delta G_f^\circ_{298}$ Heptadecane (1): 13.10 kcal
 c. $\Delta G_f^\circ_{298}$ Carbon dioxide (g) -93.96 kcal
 (196)
 $\Delta G^\circ = (B + C) - (A) = -21.72 \text{ kcal.}$

This indicates more favorable conditions for the formation of the *n*-paraffin than did the data for stearic acid. In 1927 Marks and Howard (134) pyrolyzed oleic acid at 235° to 490° C in the presence of nickel and decided the principle reaction was $2nC_{17}H_{33}COOH \longrightarrow nC_{17}H_{34} + (C_{17}H_{32})_2 + 2nH_2 + 2nCO$. There are no data that will permit thermodynamic evaluation of this reaction.

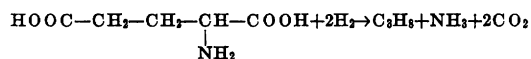
Waxes

Waxes are esters of fatty acids and complex alcohols and thus could be precursors of *n*-alkanes in the C_{23} and higher range as suggested by Martin and coworkers (138) and Lawlor and Robinson (110).

Amino Acids

Erdman (67) has suggested that simple amino acids, hydrolysis products of proteins, may be the precursors for both normal and isoalkanes in the C_2 - C_8 range. Limited thermodynamic data are available on the amino acids. For glutamic acid the data would be

Glutamic acid plus hydrogen \rightarrow Propane + ammonia + carbon dioxide



The basic data are from Parks and Huffman (147) except as noted.

- A. $\Delta G_f^\circ_{298}$ Glutamic acid(s): -170.40 kcal
 B. $\Delta G_f^\circ_{298}$ Propane (g): -5.61 kcal (2)
 C. $\Delta G_f^\circ_{298}$ Ammonia (g): -3.94 kcal (91)
 D. $\Delta G_f^\circ_{298}$ Carbon dioxide (g): -93.96 kcal (196)
 $\Delta G^\circ = (B + C + D) - A = -27.08 \text{ kcal.}$

This value appears as favorable as for the fatty acids. Additionally, this is a dicarboxylic acid, and an amino acid with only one carboxyl group should result in a greater negative value for ΔG° .

Odd-Even Preference

No special attention has been given to the difference in odd-even preference as for *n*-alkanes in petroleum and those in recent and ancient sediments. It seems obvious that the several sources suggested and the various reactions that convert them to *n*-alkanes will eventually result in neither odd nor even preference, but that oils not sufficiently mature may show odd preference at certain molecular weight ranges, depending upon the source material.

Blumer (21) in discussing the transformation of saturated straight-chain fatty acids in sediments suggests that a wide-range mixture of fatty acids and paraffin hydrocarbons is produced with an average molecular weight lower than that of the starting material.

Summary

Figure 52 shows the major sources for *n*-alkanes that have been suggested in relation to the size of the *n*-alkane molecule. All sources except the amino acids are lipids.

Isoalkane Sources

A discussion of the relationship of the isoalkanes to source materials should start with the statement that no one has pointed out any odd or even carbon number predominances for isoalkanes. For discussion purposes it is convenient to divide the isoalkanes into nonisoprenoid and isoprenoid types primarily because of possibly different origins.

Nonisoprenoid Isoalkanes

Fatty Acids.—Branched chain fatty acids are very rare in nature, particularly those with an alkyl substituent (Fieser and Fieser (72)). The Biology Data Book (1) indicates that the principal known source of naturally occurring branched fatty acids is wool grease, and Weitkamp (197) identified 10 methyl-substituted acids in wool grease including all the even-numbered ones from C_{10} to C_{28} . Almost all of the acids found have only one methyl group, and almost invariably it is in the 2- or 3-position. Recently Leo and Parker (117) reported finding iso (2-methyl) and anteiso (3-methyl) branched chain acids in recent sediments. The substitution of a methyl group for a hydrogen on a fatty acid makes only a small change in $\Delta G_f^\circ_{298}$, so the same conclusions reached regarding the *n*-fatty acids would also apply to those that have only a few methyl substitutions. Because of the apparent scarcity of these branched acids in nature one must

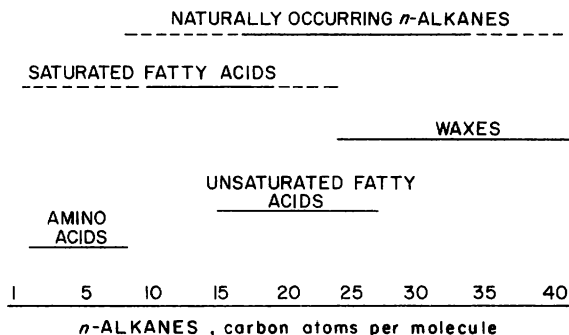


FIGURE 52.—Sources of *n*-Alkanes.

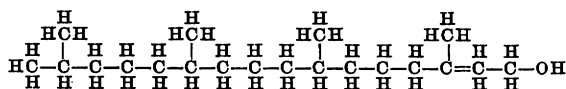
look elsewhere for precursors unless one accepts Mair's suggestion (130) that ancient fatty acids possibly contained a greater proportion of branched-chain acids. However, there seems to be no proof of this thus far; the acids that have been isolated from ancient sediments are normal (46).

Terpenoids.—As an alternative Mair suggests that the acyclic terpenoids by different degrees of degradation and presumably hydrogenation evolve into isoalkanes. Bendoraitis and co-workers (12) suggest mechanisms whereby such compounds as lycopene an acyclic tetraterpenoid, and squalene, an acyclic tetraterpenoid, may be broken down to branched alkanes of both isoprenoid and nonisoprenoid types. Meinschein (139) says, "It is probable that a major portion of the branched-paraffins and cycloalkanes in sediments and in crude oils are compounds derived from, or related to, isoprenoid by-products formed in the biogenesis of compounds such as steroids."

Amino acids.—Finally, Erdman (67) suggests that the proteins hydrolyze to provide a variety of amino acids that through decarboxylation and reductive deamination can yield branched chain alkanes. If the thermodynamic conclusion presented for the formation of *n*-alkanes from amino acids is acceptable then the same conclusions should hold for the branched alkanes. However, it is evident the source or sources of the nonisoprenoid isoalkanes is obscure.

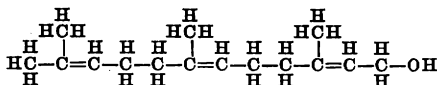
Isoprenoid Alkanes

Seven isoprenoids that have been isolated from petroleum are listed in table 13. Virtually all geochemists agree that probably these compounds are derived from phytol, in turn a saponification product of chlorophyll, but also a chemical entity in some living organisms,



Phytol

or from farnesol



Farnesol

Phytol is an acyclic diterpenoid and farnesol an acyclic sesquiterpenoid. Both come under the classification of lipids. Interestingly isoprenoid acids with the carbon skeleton of phytane, pristane, and farnesane have been isolated from a California petroleum (37). Blumer (21) discusses the possible reactions phytol and fatty acids may undergo to yield hydrocarbons.

Recent analytical developments have made it possible to analyze very ancient rocks, 1 to 2 billion years old, and determine their content of specific hydrocarbons. Meinschein and coworkers (140) and Eglinton and coworkers (64) have identified *n*-alkanes in the C₂₃-C₃₁ range and pristane and phytane in billion-year-old Nonesuch shale. Oro and coworkers (146) have identified *n*-alkanes (C₁₆-C₃₂) pristane, and phytane in Gunflint iron formation 1.9 × 10⁹ years old. These reports all indicate biological processes involving lipids billions of years ago. Blumer and coworkers (22-23) report pristane is present in quantities of 1 to 3 percent in the body fat of certain zooplankton, from whence it is deposited in the liver oils of whales and sharks. The pristane of petroleum may be derived directly from zooplankton. Finally in an excellent article on chemical evolution Calvin (32) discusses the isolation of isoprenoid hydrocarbons in petroleum, oil shale and ancient rocks and their meaning in the history of the world.

Summary

Figure 53 shows the major sources of isoalkanes that have been suggested in relation to the size of the molecule. All sources except the amino acids are lipids.

Cycloalkane Sources

Naphthenes are possibly the most important general type of hydrocarbon component in crude oil, but there is little in the literature except unproved theories as to their origin. There is general agreement that their original source material is lipids including primarily terpenes and their oxygenated derivatives such as alcohols, ketones, and aldehydes, and unsaturated fatty acids and waxes.

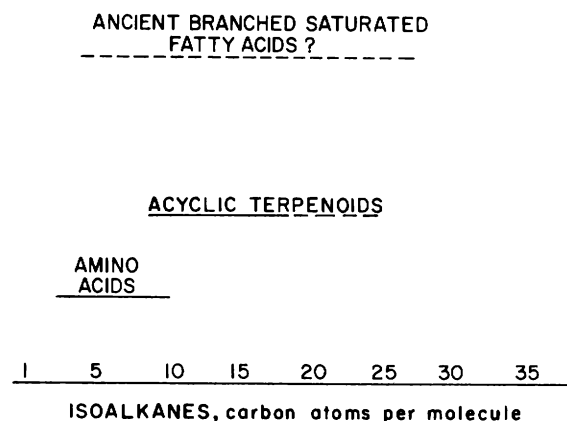


FIGURE 53.—Sources of Isoalkanes.

Unsaturated Fatty Acids

Brook (29) in 1952 suggested catalytic cyclizations of dienes in the presence of an acid catalyst through a carbonium ion mechanism. The major source of most dienes would be the unsaturated fatty acids. These are prevalent in both terrestrial and marine organisms. Both Brooks and Breger (26) believe that the Diels-Alder reaction between an acyclic diene and a second component having an ethylenic linkage flanked by one or more activating groups such as carbonyl or carboxyl is possible and probable. This reaction again requires unsaturated compounds most easily found in the unsaturated fatty acids.

Terpenoids

Possibly a more promising source is the terpenoids, including the hydrocarbon terpenes and their simple oxygenated derivatives such as alcohols and ketones. This theory is put forth by Mair (130). A glance at the terpenoid section of Robinson's book (157) on the

organic constituents of higher plants present many structures that could reasonably be transformed into petroleum naphthenes. Figure 54, which shows terpenoid pathways, is taken from Robinson, and while the mechanisms are not known, for the most part the end products are. The possibilities for conversion to monocycloparaffins and polycycloparaffins can be seen. It is obvious that much research is needed in this area.

Summary

Figure 55 shows the major source of cycloalkanes that have been suggested according to molecular weight. All are lipids.

Aromatic Sources

More attention has been paid to possible precursors for aromatics, probably because they offer better analytical possibilities than the naphthenes. However, the proposed source materials are the same: Unsaturated fatty acids, terpenoids, steroids. The chief addition

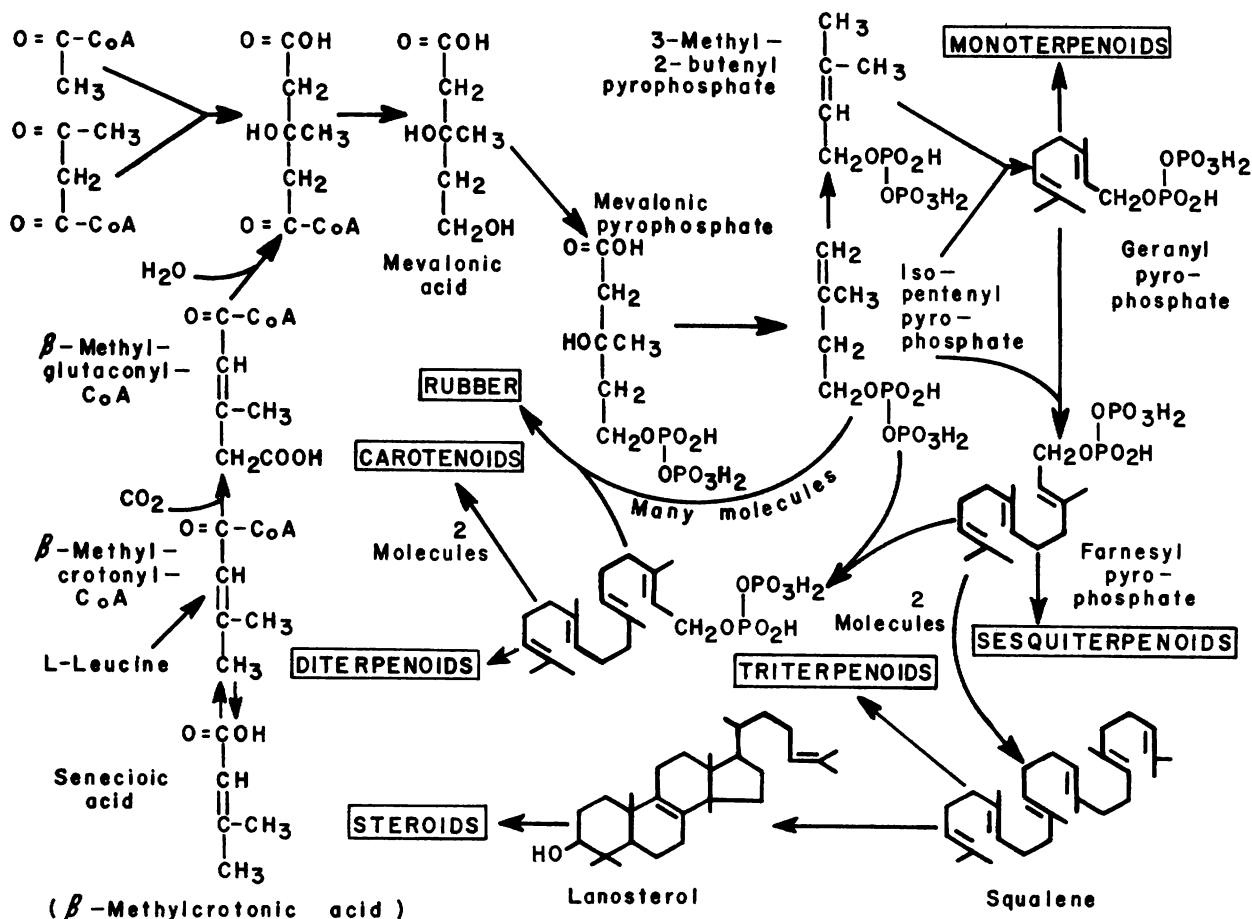


FIGURE 54.—Terpenoid and Steroid Pathways. (From Robinson (157), by permission.)

ACYCLIC AND
MONOCYCLIC
MONOTERPENOIDS

MONOCYCLIC
AND BICYCLIC
SESQUI TERPENOIDS

CYCLIC DI-
TERPENOIDS

POLYCYCLIC
TRITERPENOIDS

UNSATURATED FATTY ACIDS (ACYCLIC DIENES) PLUS
MONOOLEFINS (DIELS-ALDER REACTION)

UNSATURATED FATTY ACIDS
(CYCLIZATION)

WAXES

1 5 10 15 20 25 30 35 40

CYCLOALKANES, carbon atoms per molecule

FIGURE 55.—Sources of Cycloalkanes.

is that of carotenoids and polyhydroxyquinone-type pigments.

Unsaturated Fatty Acids

Breger (26) believes that the Diels-Alder reaction involving unsaturated fatty acids can be the precursor of both naphthenes and aromatics, depending upon subsequent hydrogenation or dehydrogenation reactions.

C₁₈, C₂₀, C₂₂ unsaturated fatty acids with three to six double bonds are suggested by Erdman (67) as a good source of both benzene and naphthalene hydrocarbons.

Terpenoids

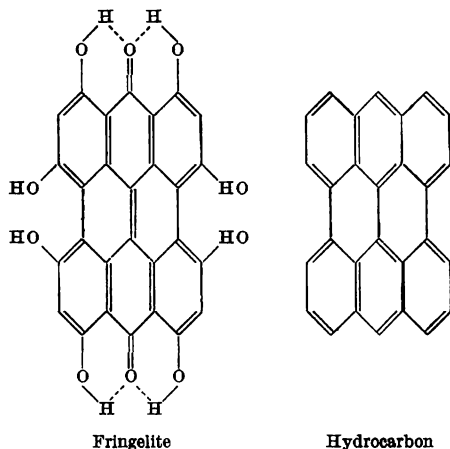
Mair (130) again reverts to terpenoids as source material: Acyclic and monocyclic terpenes for benzenes, diterpenoids for naphthalene, some steroids for phenanthrenes. He believes that the terpenes offer the most prolific source of methyl groups for both naphthenes and aromatics. Erdman also feels that the terpenes offer good possibilities for the low-molecular-weight aromatics.

Carotenoids, and particularly β -carotene, have been shown by Mulik and Erdman (142), Mader (128), and Day and Erdman (54) to yield toluene, *o*-, *m*-, and *p*-xylene, 2,6-dimethylnaphthalene, and ionene (1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene). Sediments containing carotene give these same products on heating, and in addition benzene and vinylbenzene; however, these latter two are not derived from the lipid carotenoid fraction. Schwendinger and Erdman (160) have shown the presence of useful quantities of carotenoids in recent sediments; the same researchers have also shown that sterols (161) are present. Douglas and Mair (61) have presented data showing that elemental sulfur will react with sterols such as cholesterol to give benzene and alkyl derivatives of naphthalene and phenanthrene and with farnesol to yield 1,6-dimethyl-4-isopropylnaphthalene as one product. The reactions have not been tried under geological conditions.

Polyhydroxyquinone Pigments

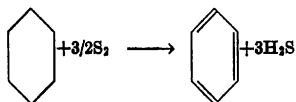
Blumer (20-21) and Thomas and Blumer

(174) in a series of painstaking researches have shown that polyhydroxyquinone pigments (fringelites) can accumulate in marine fossils and are slowly reduced to polycyclic hydrocarbons. Below is given an example of a precursor fringelite and a derived hydrocarbon:



Finally, Barghoorn and Tyler (10) by pyrolysis of Precambrian Gunflint chert have produced *n*-alkanes, isoalkanes, cyclohexane, benzene, toluene, xylene, and isopropylbenzene. These aromatics may be the results of pyrolysis, but 400° C is not usually a high enough temperature to produce aromatics. The conclusion is that these were present in the minute pores of the rocks. Presumably they resulted from some ancient biochemical action.

Dehydrogenation.—The discussion of the origin of aromatics would not be complete without discussing the possible dehydrogenation of cycloalkanes to aromatics by the action of sulfur. The generalized reaction



is thermodynamically feasible, as the plot of the gibbs energy of reaction versus temperature in figure 56 shows. The values are all negative, even at well below ordinary ambient temperatures. Whether such reactions can or do occur in crude oil is questionable because crude oils are known that undoubtedly contain simple cyclohexanes but yet have appreciable amounts of dissolved elemental sulfur, and this seems to be contrary to the above thermodynamic conclusion. Perhaps the reaction will proceed only under certain environmental conditions that provide catalytic activity.

Summary

Figure 57 shows the major sources of aromatics that have been suggested according to molecular weight, and all are lipids.

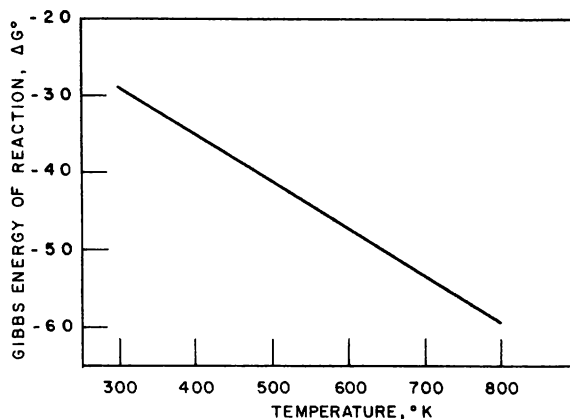
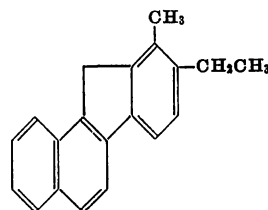
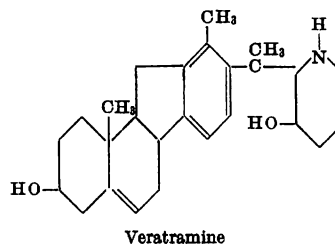


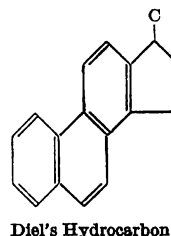
FIGURE 56.—Reaction of Cyclohexane With Sulfur To Form Benzene.

Cycloalkanoaromatic Sources

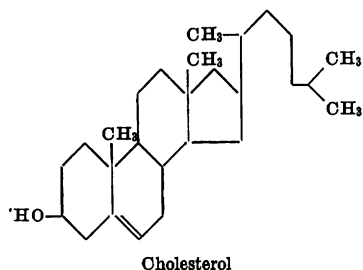
With knowledge of source material for cycloalkanes and aromatics so little advanced, it is not surprising that there is not much known regarding the cycloalkanoaromatics. Probably the best source on the basis of present knowledge is again the steroids. Mair gives an example of an alkaloid veratramine, as a possible source of a benzofluorene.



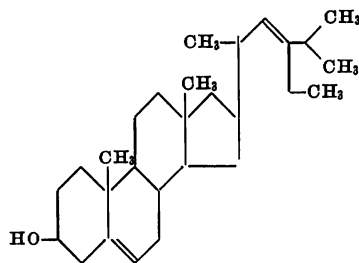
Another example would be Diel's hydrocarbon recently isolated from petroleum (132) which is very similar in structure to cholesterol.



3-Methyl-1,2-cyclopentanophenanthrene



Cholesterol



Stigmasterol

Cyclopentanophenanthrenes have been found in petroleum and their structures suggest steroids such as stigmasterol or cholesterol as the original source material for these compounds essentially by a process of dehydrogenation. It is probably of significance that while reactions such as this release hydrogen the formation of alkanes from both saturated and unsaturated fatty acids demands a source of hydrogen. Thus through the wide range of possible reactions the requirements can be met.

Carruthers and Watkins (36) recently reported identification of 1,2,3,4-tetrahydro-2,2,9-trimethylpicene from a high-boiling U.S. petroleum distillate. They postulate that it may have been formed from triterpenes or isoprenoids by stepwise cyclization and dehydrogenation.

Very recently (82-83) optically active pentacyclic triterpenoids have been isolated from Nigerian crude oil, and one of these hydrocarbons, gammacerane, has also been identified in Green River, Colorado, oil shale bitumen.

ACYCLIC AND MONOCYCLIC MONOTERPENOIDS

MONOCYCLIC AND BICYCLIC SESQUITERPENOID

CYCLIC DITERPENOID

POLYCYCLIC TRITERPENOID

POLYHYDROXY QUINONES

CAROTENOIDS

UNSATURATED FATTY ACIDS

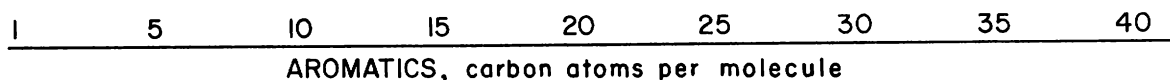


FIGURE 57.—Sources of Aromatics.

The presence in petroleum and oil shale of these pentacyclic triterpenes is further evidence for the biologic origin of petroleum and oil shale, as these compounds are abundantly distributed in terrestrial plants, and alcohol derivatives are found in widely distributed protozoa. The authors suggest that the evidence indicates a part of the Nigerian crude oil may have had terrestrial origin. Other evidence that all crude oils are not of marine origin is accumulating.

The tetrahydronaphthalenes or tetralins are fairly prevalent in crude oil. In fact this particular bicyclic configuration, whether it be in the tetrahydro state, completely hydrogenated to decalin, or completely dehydrogenated to naphthalene, seems to be one of the dominant structures in crude oil. Even though only a few of each type have been found thus far, those that have been found are usually present in considerable quantity (129). It seems probable that the reactions suggested for cycloalkanes and aromatics can also yield tetrahydronaphthalenes, as it is only a matter of the degree of hydrogenation.

PRECURSORS FOR SULFUR COMPOUNDS

The origin of sulfur compounds in petroleum is obscure. As with hydrocarbons, there are two general theories: (1) That the sulfur compounds are either directly or indirectly derived from the original source material. This may occur by simple preservation of certain sulfur compounds found in living matter, for example alkylthiols in radish and onion roots, cyclic sulfides in plants of the *Compositae* family, thiophene derivatives in the roots of *chrysanthamum vulgare*. The plants involved here are all classed as higher plants (157); there seems to be little information as to the sulfur content and even less as to the actual sulfur compounds in the lower orders of both plants and animals such as algae and plankton.

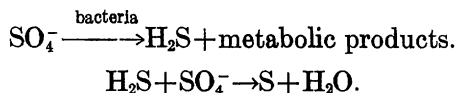
The indirect source of sulfur from the original source material considers that complex sulfur-containing compounds break down to yield sulfur compounds found in petroleum. Robinson (157) for example shows that dimethyl- β -propiothelin found in marine algae decomposes as follows:



Even more indirectly such compounds as certain amino acids like L-cysteine $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{COOH}$ or L-methionine $\text{CH}_3\text{S}(\text{CH}_2)\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ can be completely decomposed

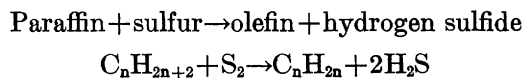
to yield sulfur or hydrogen sulfide that then may react with the hydrocarbons or hydrocarbon precursors present to yield the simple sulfur compounds found in petroleum. Henniker (80) discusses this theory as advanced by Deflandre (57) and reaches the conclusion that it is untenable. However, Henniker is concerned primarily with the formation of thiophenes, and appears to assume a pyrolytic action on sulfur-containing bituminous matter that has been formed by the action of the sulfur or hydrogen sulfide on carbonaceous matter. The possible formation of alkylthiols or sulfides utilizing this source of sulfur is not mentioned.

The second general theory is based on the bacterial reduction of SO_4^- ions in the presence of hydrocarbons as food, by micro-organisms such as *vibrio desulfuricans* to yield hydrogen sulfide. That this action occurs has been demonstrated many times. Feeley and Kulp (70) propose that this reaction, followed by the interaction of SO_4^- and H_2S to yield elemental sulfur, are the mechanisms whereby sulfur accumulations in salt domes are formed. Schematically without showing balanced equations, the following sequence of events can be postulated:



These reactions provide both hydrogen sulfide and sulfur that may combine in a number of different ways with hydrocarbons or other compounds to yield sulfur compounds. The writer believes that although there undoubtedly are sulfur compounds in petroleum that are directly or indirectly related to the source material, the major portion of the sulfur compounds have originated by reaction of hydrocarbons or heterocompounds with hydrogen sulfide or sulfur generated from the sulfate ion by bacterial action. The data given below show that such reactions are thermodynamically feasible. The source of the data used in the thermodynamical calculations are as follows: Hydrocarbons (2); hydrogen sulfide (69); alkylthiols and sulfides (162); pyrrolidine (126); tetrahydrofuran (28); thiacyclopentane (88); ammonia (91); water (90); thiophene (89).

Reaction (a)

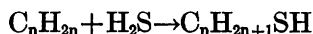


This reaction has been used for years as a laboratory means of producing hydrogen sulfide, using paraffin wax as the hydrocarbon. The relationships of the gibbs energy of reaction

and temperature are shown on figure 58 for C_2H_6 , C_4H_{10} , C_6H_{12} , C_8H_{18} , $C_{20}H_{42}$ and cyclohexane. The slope of these curves is negative, as for the splitting reactions of paraffin discussed previously. This reaction may be a source of hydrogen sulfide if geological conditions, especially temperature, are favorable, but is probably not a predominant source of hydrogen sulfide in crude oil.

Reaction (b)

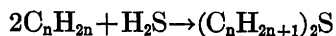
Olefin + hydrogen sulfide → alkanethiol



The data for the reaction of an olefin with hydrogen sulfide to yield an alkanethiol are shown on figure 59 for C_2H_4 , C_4H_8 , C_6H_{12} and cyclohexane. These reaction curves all have a positive slope and negative gibbs energy values at temperatures consonant with geochemical limitations. The reactions to form branched chain thiols have similar thermodynamic characteristics.

Reaction (c)

Olefin + hydrogen sulfide → alkyl sulfide



The data for the reaction of olefin with hydrogen sulfide is shown in figure 60 for C_2H_4 and

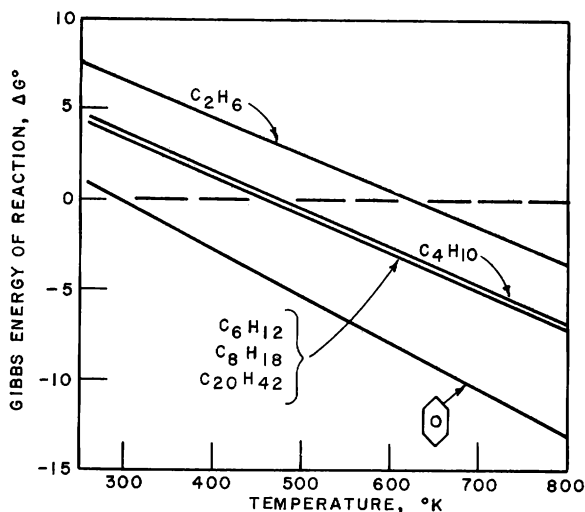


FIGURE 58.—Reaction of *n*-Alkanes and Cyclohexane To Form Olefins and Hydrogen Sulfide.

C_4H_8 . The curve shown for the ethylene reaction is slightly displaced from the 1-butene curve but both have a positive slope and large negative gibbs energy value at the lower temperature. There is little to choose between the reaction to give thiols and sulfides, the tem-

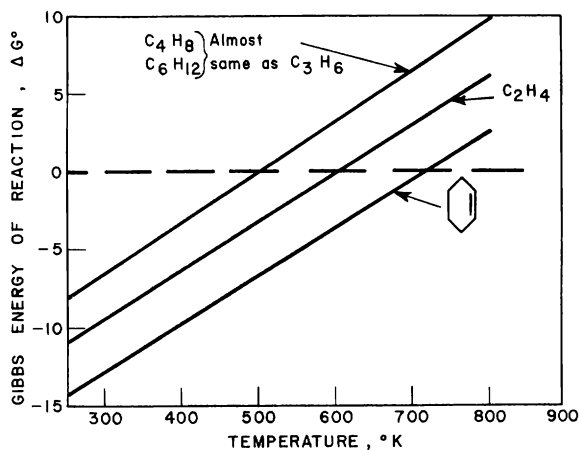


FIGURE 59.—Reaction of *n*-Olefins With Hydrogen Sulfide To Form Thiols.

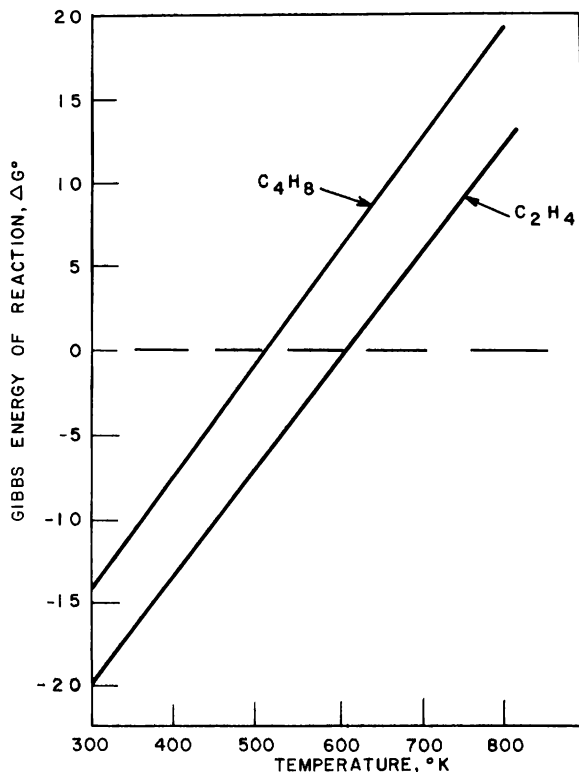


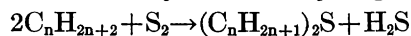
FIGURE 60.—Reaction of *n*-Olefins With Hydrogen Sulfide To Form Sulfides.

perature where $\Delta G^\circ = 0$ is $500^\circ K$ for butane to thiol, and $505^\circ K$ for the formation of sulfide.

Reaction (d)

Paraffin + sulfur →

alkyl sulfide + hydrogen sulfide



Whereas the reaction curve of sulfur with paraffins to form olefin and hydrogen sulfide

had a negative slope, the reaction curve to form alkyl sulfides and hydrogen sulfides has a positive slope with favorable gibbs energy values. This appears to be a possible reaction. The data for ethane and *n*-hexane are shown in figure 61. There is very little difference between the two curves.

Reaction (e)

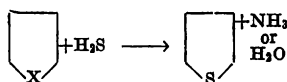
Paraffin + sulfur → alkanethiol + hydrogen sulfide



Similarly the reaction of a paraffin with sulfur to form alkylthiols also gives a curve with a positive slope (figure 62), for ethane and *n*-hexane, although it is a low value giving a curve that is rather flat. Of the two reactions of paraffins with sulfur to yield alkyl sulfides or alkylthiols, the temperatures for $\Delta G^\circ = 0$ are alkyl sulfide, 555° K, and alkanethiol, 550° K. Thus there is little difference at equilibrium. However, the sulfide curve is steep and has lower free energy values at the lower temperatures.

Reaction (f)

Nitrogen or oxygen heterocyclic + hydrogen sulfide → cyclic sulfide + ammonia or water



X = NH or O

The conversion of heterocyclics such as pyrrolidine and tetrahydrofuran to thiacyclopentane.

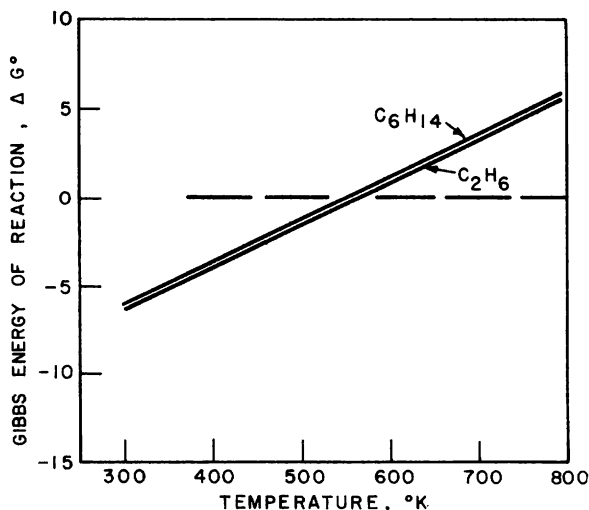


FIGURE 61.—Reaction of *n*-Alkanes With Sulfur To Form Sulfides.

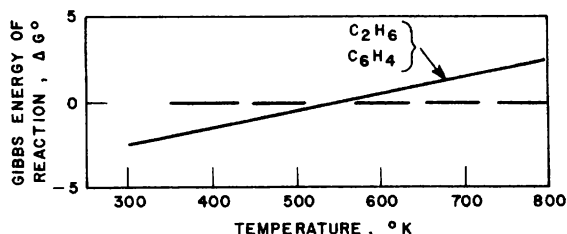
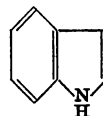
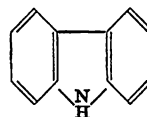


FIGURE 62.—Reaction of *n*-Alkanes With Sulfur To Form Thiols.

tane was suggested several years ago by Birch (15). This still seems to be an attractive proposal and the thermodynamic data shown in figure 63 bear this out. The pyrrolidine curve is very flat and has a slightly positive slope; the tetrahydrofuran curve is slightly steeper, but has a negative slope. Both reactions have large negative ΔG° values. However, thus far neither pyrrolidine or tetrahydrofuran have been found in petroleum. This same reaction should apply to indole



and carbazole



and these compounds have both been found in petroleum. Also the products of the reactions of these compounds with hydrogen sulfide

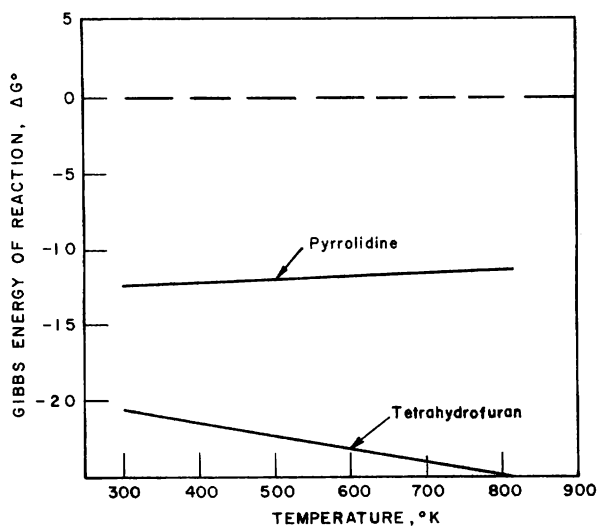
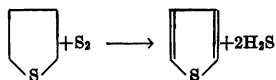


FIGURE 63.—Reaction of Pyrrolidine and Tetrahydrofuran With Hydrogen Sulfide To Form Thiacyclopentane.

would be benzothiophene and dibenzothiophene, both of which are present in appreciable quantities in many crude oils, and probably present in smaller quantities in all oils.

Reaction (g)

Cyclic sulfide + sulfur → thiophene + hydrogen sulfide



The curve for this reaction, figure 64, has a negative slope and decidedly negative values for ΔG° at geologically acceptable temperatures as shown for thiacyclopentane.

The types of reactions suggested above could account for most of the sulfur compounds found in petroleum as given in table 33. The formation of thiophenic compounds by pyrolytic means is not tenable with geologic concepts of temperature, while the routes suggested above meet these requirements. It is possible that if and when sulfur isotope ratios for $\text{S}_{32}/\text{S}_{34}$ are available for sulfur compounds separated from a crude oil that some clue as to possible origin will be found. This writer's views may be summarized as follows:

1. The organic debris from which it is believed crude oil is formed contribute but little to the sulfur compounds found in petroleum, either directly or by preservation or indirectly by generating hydrogen sulfide or elemental sulfur.

2. Most of the sulfur compounds originate by reaction of hydrocarbons or heterocyclic oxygen or nitrogen compounds with hydrogen sulfide or elemental sulfur.

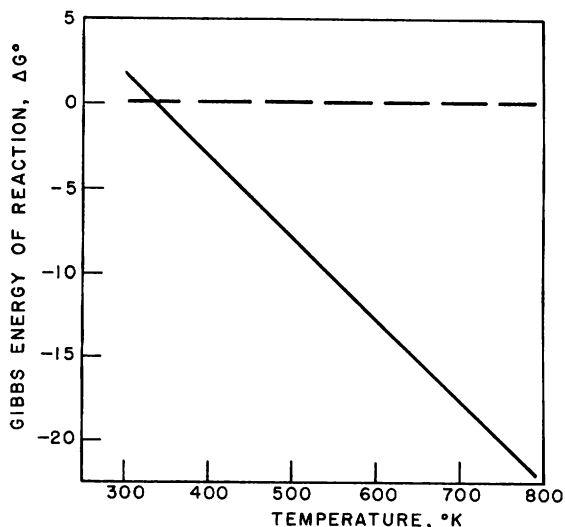


FIGURE 64.—Reaction of Thiacyclopentane With Sulfur To Form Thiophene.

3. The type reactions included in paragraph 2 seem to be thermodynamically feasible.

4. Most of the hydrogen sulfide and sulfur are the result of microbial reduction of the sulfate ion in the water associated with the organic material.

PRECURSORS FOR NITROGEN COMPOUNDS

The previous section indicated that it was the writer's view that most sulfur compounds in petroleum were the result of secondary reactions and not directly derived from the original organic deposits. In contrast the evidence seems to indicate, to this writer, that nitrogen compounds are derived from the organic debris. There are several reasons for this belief: There is no independent source of nitrogen as there is for sulfur; elemental nitrogen is not reactive as is sulfur; ammonia does not appear to be a likely reactant under geological conditions; proteins are common in organic matter, but are easily subject to bacterial degradation to yield nitrogen or ammonia, which would escape; if the nitrogen or ammonia were to be used synthesis would be required; Lochte (38) points out that high nitrogen content (above 0.2 percent) is very rare in petroleum. Alkaloidal plants are not common, yet protein is found practically everywhere; he also states that alkaloidal plant source beds would probably be found in the case of young petroleum. High nitrogen content is not usually found in old oils; most of the nitrogen compounds thus far found in petroleum are heterocyclic and there is every reason to believe that this will be true for those yet to be discovered. These lines of reasoning lead to the theory that most of the nitrogen compounds are derived from nitrogen heterocyclics found in nature or from more complex compounds that degrade to the heterocyclics that are found. The major types of nitrogen compounds identified up to now in petroleum (table 34) are pyridines, quinolines, and carbazoles with indication of indoles and more complex molecules such as indolocarbazoles. Nitrogen heterocyclics are fairly common in nature, particularly as parts of more complex molecules such as the alkaloids. This has led Lochte (38) to propose that most of the nitrogen compounds found in petroleum result from the degradation of alkaloids. Degens (58) ⁹ provides a good discussion of the subject; the following is a quote from his book:

A number of natural products are related to (1) pyrrole (hemoglobin, chlorophyll, vitamin B₁₂); (2) indole (tryptophan, some alkaloids; strychnine, indigo); (3) purine (adenine, guanine, some al-

⁹ Work cited in footnote 6.

kaloids; caffeine); (4) pyrimidine (thymine, cytosine, uracil, thiamine); (5) pyridine, quinoline, and isoquinoline (vitamin B₆, some alkaloids; nicotine, quinine, morphine); (6) pyran (some plant pigments: flavons, anthocyanins); (7) pteridine (vitamin B₁₀).

The resemblance between nitrogen compounds found in petroleum and possible precursors is shown in figure 65. Although porphyrins have been found in many crude oils, pyrroles have yet to be reported. Dunning (62) and Degens (68) give good discussions of the porphyrin question as it relates to petroleum.

Most of the evidence now at hand points

to the nitrogen compounds in petroleum as having been formed from naturally occurring nitrogenous compounds of the alkaloid type. Much remains to be done in obtaining better definitions of the nitrogen compound types in crude oil and in studies of the organic matter in sediments for nitrogen compounds.

PRECURSORS FOR OXYGEN COMPOUNDS

The source of the fatty acids found in petroleum seems to be a direct preservation of

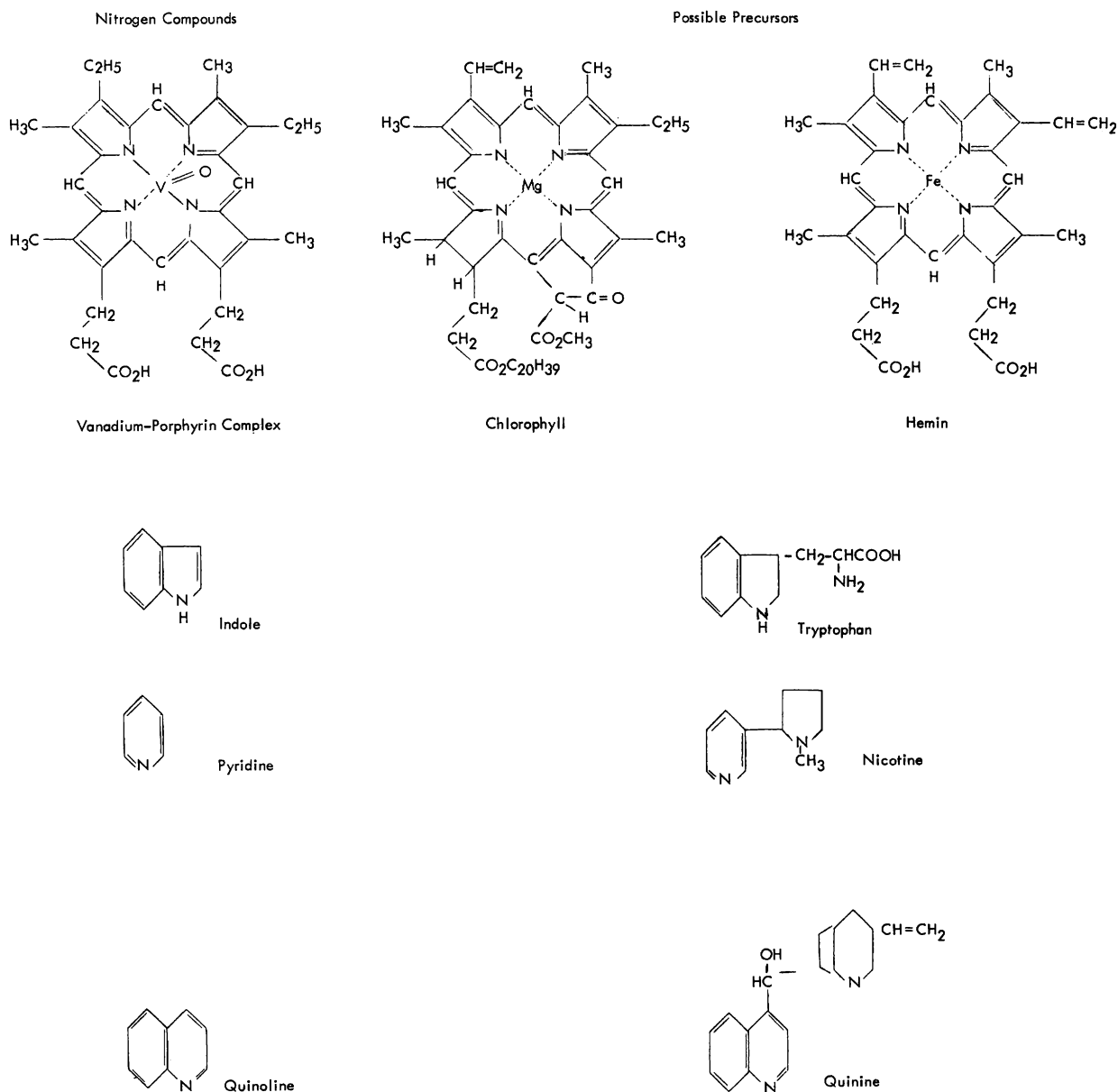


FIGURE 65.—Some Possible Precursors of Nitrogen Compounds.

organic acids found in nature. The discussion given previously regarding fatty acids as sources of alkanes also indicated their widespread occurrence in nature and availability as a source for petroleum fatty acids.

In contrast the origin of the naphthenic acids is very obscure. They do not appear to be the result of oxidation of petroleum, for when crude oil is oxidized by air the acids resulting are not like the naphthenic acids found in crude oil. One acid (2,2,6-trimethylcarboxylic acid), isolated from both Signal Hill and San Joaquin Valley, Calif., crude oils, is of interest. Dunning (62, p. 411)¹⁰ states:

The occurrence of this acid is at least philosophically interesting because examination of the structural formula of β -carotene shows that the end groups are of the 2,2,6-trimethylcyclohexane structure and would require only hydrogenation of a double bond and oxidation of the carotene chain to form this acid. This particular acid is listed only as an example, and it would be extremely

difficult to establish the validity of this relationship. However, an examination of the structural components of the common natural pigments reveals that this could possibly account for many of the complex minor constituents of petroleum.

Much work remains to be done before the origin of the naphthenic acids becomes clear.

The phenols found in crude oil presumably originate from such natural products as lignins and tannic substances which are abundant in nature. Ketones can theoretically be prepared from acids by pyrolysis of the meta salts of the fatty acids, but neither the formation of the salt nor the temperature of pyrolysis conforms to geological limitations. There are no suggestions as to a possible source for the fluorenones which have been identified in crude oil. About all that has been said is that little is known about the oxygen compounds in crude oil and their origin.

¹⁰ Reprinted by permission of Pergamon Press, Inc., Long Island, N.Y.

THE FUTURE COULD BE EXCITING AND FRUITFUL

In two recent publications (94, 167) the author has suggested research problems that deserve attention in the field of petroleum composition. These problems are not suggested because their solution will immediately solve some industry problem; rather they are the suggestions of a scientist to fulfill an abiding curiosity as to what constitutes petroleum and how it originated. Some of the earlier suggestions plus some additional ideas are presented here with the hope they will eventually meet receptive response.

It seems evident that the written and graphic portrayal of our current knowledge of the quantitative and qualitative composition of petroleum presented in this report will have only scratched the surface compared with the data that will be available in the years ahead. Admittedly the current picture, considered as a whole, is complex and will tend to increase in complexity; nevertheless there are signs of underlying simplifications if only parts of the picture are considered. For example, Forziati and coworkers (73) in 1944 and Smith and Rall (170) in 1953 showed that there appeared to be linear relationships between certain normal paraffins, such as hexane and heptane. Utilizing recent GLC data, this paper points out that there is evidence for such a simplifying relationship, but within limits. The difficulty now is to determine the character of and reason for the limits. More extensive compositional and geological studies of crude oils that fall outside of limits that fit most oils should be fruitful. It is this author's opinion that, when enough good quantitative data are

available together with environmental data for the crude oil source, simplifying relationships will be found that will resolve much of the complexity that now seems dominant.

The data presented in this report show very clearly that there has been only one carefully planned and executed research on the overall composition of petroleum. This is the work of API RP 6 (129) and it relates only to a single crude oil and covers essentially only hydrocarbons. The other data available are fragments, and as the reader must realize by now, are extremely difficult to put together to make even a partially complete picture. The situation regarding sulfur compounds is almost analogous, except that there have been both the API RP 48 and the BP laboratories providing data on two different oil types. Only the nitrogen compounds through the kerosine and light gas oil distillates have been systematically studied; and there has been no carefully organized study of oxygen compounds.

1. There should be studies analogous to API RP 6 conducted on several crude oils of diverse compositional characteristics. Starts have been made but most of them end at C₇ or C₈. With today's methods of separation and analysis, work equivalent to that of API RP 6 could be greatly shortened. Further, the research should emphasize quantitative as well as qualitative data. The complete picture should include not only hydrocarbons, but sulfur, nitrogen, and oxygen compounds as well. It would be especially advantageous if hydrocarbons and heteroatomic compounds could be determined on the same crude oils. It is not

suggested that this research be carried out for individual compounds in the higher boiling part of crude oil, but, in keeping with the subject of this paper, be restricted to the naphtha and gas oil portion of the oil. However, the heavier parts could well be the object of research such as is planned for new API RP 60 to determine the types of classes of compounds in heavy oils.

2. Clearly, hydrocarbon studies of the gas oil need concerted attention now. The data presented show plainly that, with a few exceptions, research on hydrocarbon composition has stopped at the end of the gasoline boiling range. Research on higher boiling material must include development of new or improved separation techniques, analytical procedures, and identification methods. Great attention must be paid to obtaining quantitative data. Correlated studies of a series of crude oils of different characteristics should be part of the plan. Synthesis of hydrocarbons and determination of their properties for use in identification problems must go hand-in-hand with or preferably ahead of the other research. Finally, model systems should be established, keeping in mind crude oil environmental conditions, to provide explanations for the presence of certain compounds or types of compounds as well as possible correlative relationships. The recent work on the generation of hydrocarbons from fatty acids by Jurg and Eisma (95) is an excellent example.

3. Research on sulfur compounds needs to be expanded to include more crude oils and to encompass the high-molecular-weight compounds. Our knowledge of the more volatile compounds is good for one crude oil and fair for two or three others. Much more ample coverage is needed on a quantitative basis for the entire range of distillate portions for a series of crude oils having apparently different sulfur types, such as those from Wasson, Tex., and Wilmington, Calif. Although a few high-boiling sulfur compounds have been made, more are needed for identifying type and individual compound, although much progress on type identification can be achieved with relatively few pure compounds. The study of reactive systems that could lead to the elucidation of the origin of sulfur compounds under geologic conditions is an important adjunct of the separation and identification problem. Reaction of elemental sulfur with hydrocarbons or heterogeneous compounds and the possible dehydrogenation of naphthenes by elemental sulfur should be studied. The recent report by Douglas and Mair (61) is a start in the right direction. The reaction of hydrogen sulfide with heterogeneous compounds and the place of pyrite in the sulfur-petroleum picture also need elucidation. As a corollary to this there should be

increased attention to the overall sulfur content of terrestrial and marine organic matter and to the types of compounds present in such material.

4. Research on nitrogen compounds in petroleum is currently receiving much attention, and a considerable increase in data should be forthcoming within the next few years. However, here, as for the other research proposals, greater diversification is needed along with special attention to quantitative data. The separation of some of the naturally occurring alkaloids and possibly some amino acids, for example, and a study of their reactions under geologic conditions would be a most useful supplement to the separation and identification researches. The recent report on distribution of benzocarbazoles by Snyder (172) seems significant.

5. Oxygen compounds have received little attention—some of the oxygen compounds discovered have been byproducts of other research—yet the work of Jurg and Eisma (95) indicates the importance of looking for traces of the possible precursors of the paraffin hydrocarbons in crude oil, and of greatly extending this model type of research in several directions. Two very recent contributions in this regard are the identification of saturated fatty acids in oil shale (110) and of isoprenoid acids in a California petroleum (37).

6. Statistical relationships of quantities of naphtha and gas oils to geologic age, environment and depth is a promising study. This would be a refinement and extension of the data discussed under "Naphtha." Much more complete correlation with stratigraphy and geological conditions such as outcropping and lithology could yield most interesting results.

7. Isoprenoids appear to be a universal constituent of crude oils. If this is true, and it still needs to be established, then they could be of value in geochemistry. For example they could be useful in tracing migration. These compounds should be mobile and have little tendency to be adsorbed on the rocks. Thus they should continue to be present in approximately the same ratios to each other during the course of a postulated migration. Also further studies may indicate significant differences in the quantities present depending on stratigraphy and lithology of the reservoir rocks.

8. The availability of good quantitative data will enable better assessments to be made of the relationships between hydrocarbons and hydrocarbon classes, such as the relative amounts of isomers, differences in hydrocarbon ratios, possible significance of certain hydrocarbons, such as 1,2,4-trimethylbenzene and relationships of these data with geologic environment.

9. Although the present trend is to discourage research on the separation and identification of individual hydrocarbons, the writer believes this is entirely wrong from a scientific viewpoint, and even from a long-range industrial outlook. The great advances that can come from the identification of individual compounds are well exemplified by the identification of thiophene and its homologues, the benzo-

thiophenes and dibenzothiophenes, the quinolines, the isoprenoid hydrocarbons, the recently discovered triterpanes, the isoprenoic acids, and many others. These are the keys that keep unlocking doors to new, interesting, and valuable pathways. Let us not lose sight of the real frontiers of petroleum chemistry as it concerns the composition of petroleum.

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¹¹ Titles enclosed in parentheses are translations from the language in which the item was originally published.

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APPENDIX.—CRUDE OIL ANALYSES

Oil A

Bureau of Mines Bartlesville Laboratory
Sample 61161

IDENTIFICATION

Fasken field
Ellenburger, Cambro-Ordovician
12,604-12,638 feet

Texas
Andrews County

GENERAL CHARACTERISTICS

Gravity, specific, 0.786 Gravity, ° API, 48.5 Four point, ° F., below 5
Sulfur, percent, less than 0.10 Color, green
Viscosity, Saybolt Universal at 100° F., 36 sec. Nitrogen, percent, less than 0.01

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 757 mm. Hg
First drop, 81 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test, ° F.
1.....	122	1.2	1.2							
2.....	167	3.0	4.2	0.665	81.3	5.1	1.37477	125.8		
3.....	212	5.5	9.7	.691	73.3	7.5	1.38844	129.3		
4.....	257	7.6	17.3	.714	66.7	9.4	1.39977	130.7		
5.....	302	6.9	24.2	.732	61.8	10	1.41023	133.1		
6.....	347	8.3	32.5	.747	57.9	11	1.41818	131.4		
7.....	392	7.2	39.7	.760	54.7	11	1.42452	131.7		
8.....	437	7.4	47.1	.774	51.3	12	1.43121	132.7		
9.....	482	7.8	54.9	.785	48.8	12	1.43739	134.3		
10.....	527	8.2	63.1	.800	45.4	14	1.44432	134.4		

Stage 2—Distillation continued at 40 mm. Hg

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test, ° F.
11.....	392	5.2	68.3	0.818	41.5	19	1.45263	134.3	38	30
12.....	437	7.4	75.7	.829	39.2	20	1.45913	139.0	42	35
13.....	482	5.0	80.7	.838	37.4	21	1.46459	143.3	49	50
14.....	527	4.0	84.7	.863	32.5	30	1.47145	142.4	64	65
15.....	572	4.2	88.9	.867	31.7	28			93	80
Residuum		10.0	98.9	.902	24.2					

Carbon residue, Conradson: Residuum, 3.1 percent; crude, 0.4 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	9.7	0.684	75.4	
Total gasoline and naphtha.....	39.7	0.725	63.7	
Kerosene distillate.....	23.4	.787	48.3	
Gas oil.....	15.4	.826	39.8	
Nonviscous lubricating distillate.....	9.4	.839-.868	37.2-31.5	50-100
Medium lubricating distillate.....	1.0	.868-.869	31.5-31.3	100-200
Viscous lubricating distillate.....				Above 200
Residuum.....	10.0	.909	24.2	
Distillation loss.....	1.1			

Oil B

Bureau of Mines Bartlesville Laboratory
Sample 54078

IDENTIFICATION

Bagley field
Siluro, Devonian
10,762-10,960 feet

New Mexico
Lea County

GENERAL CHARACTERISTICS

Gravity, specific, 0.797 Gravity, ° API, 46.0 Four point, ° F., below 5
Sulfur, percent, 0.34 Color, NPA 7
Viscosity, Saybolt Universal at 100° F., 35 sec. Nitrogen, percent, 0.008

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 748 mm. Hg
First drop, 104 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test, ° F.
1.....	122									
2.....	167									
3.....	212	2.8	2.8	0.674	78.4		1.38465	124.7		
4.....	257	5.5	8.3	.708	68.4	6.6	1.39753	121.5		
5.....	302	8.8	17.1	.727	63.1	8.0	1.40694	121.4		
6.....	347	9.6	26.7	.746	58.2	10	1.41667	124.7		
7.....	392	9.7	36.4	.765	53.5	13	1.42596	125.0		
8.....	437	8.7	45.1	.783	49.2	16	1.43449	127.2		
9.....	482	9.9	55.0	.798	45.8	18	1.44264	128.2		
10.....	527	10.5	65.5	.814	42.3	21	1.45101	131.5		

Stage 2—Distillation continued at 40 mm. Hg

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test, ° F.
11.....	392	3.2	68.7	0.831	38.8	25	1.45983	135.8	40	20
12.....	437	6.9	75.6	.837	37.6	24	1.46273	137.8	43	40
13.....	482	6.5	82.1	.844	36.2	24	1.46781	140.1	51	55
14.....	527	5.4	87.5	.855	34.0	26			64	75
15.....	572	4.8	92.3	.867	31.7	28			94	90
Residuum		7.6	99.9	.919	22.5					

Carbon residue, Conradson: Residuum, 2.6 percent; crude, 0.1 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	2.8	0.674	78.4	
Total gasoline and naphtha.....	36.4	0.735	61.0	
Kerosene distillate.....	22.1	.799	45.6	
Gas oil.....	12.6	.836	37.8	
Nonviscous lubricating distillate.....	12.9	.843-.870	36.4-31.1	50-100
Medium lubricating distillate.....	1.3	.870-.873	31.1-30.6	100-200
Viscous lubricating distillate.....				Above 200
Residuum.....	7.6	.919	22.5	
Distillation loss.....	1.1			

OIL C

Bureau of Mines Bartlesville Laboratory
Sample 56102

IDENTIFICATION

Minas field
Miocene (Telisa)Indonesia
Central Sumatra

GENERAL CHARACTERISTICS

Gravity, specific, 0.861 Gravity, ° API, 32.8 Pour point, ° F., 75
Sulfur, percent, 0.10 Color, brownish black
Viscosity, Saybolt Universal at 100° F., 92 sec. Nitrogen, percent, 0.130
130° F., 66 sec.

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 751 mm. HgFirst drop, 84 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122									
2	167	2.3	2.3	0.658	83.6		1.37257	123.6		
3	212	2.3	4.6	.700	70.6	12	1.39106	119.3		
4	257	3.4	8.0	.726	63.4	15	1.40455	123.3		
5	302	3.7	11.7	.745	58.4	17	1.41479	122.1		
6	347	3.4	15.1	.757	55.4	15	1.42371	129.1		
7	392	3.5	18.6	.772	51.8	16	1.43201	129.4		
8	437	3.8	22.4	.790	47.6	15	1.44036	132.2		
9	482	4.8	27.2	.805	44.3	21	1.44880	136.8		
10	527	6.1	33.3	.819	41.3	23	1.45625	143.6		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	3.7	37.0	0.830	39.0	24	1.46246	151.9	39	30
12	437	5.1	42.1	.834	38.2	22	1.46454	150.7	43	50
13	482	5.2	47.3	.842	36.6	23			51	70
14	527	7.9	55.2	.855	34.0	26			65	95
15	572	7.0	62.2	.871	31.0	30			100	15 m. p.
Residuum		37.3	99.5	.952	17.1					

Carbon residue, Conradson: Residuum, 3.7 percent; crude, 1.5 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	4.6	0.679	76.9	
Total gasoline and naphtha	18.6	0.732	61.8	
Kerosine distillate	14.7	.807	43.8	
Gas oil	10.8	.835	38.0	
Nonviscous lubricating distillate	18.1			50-100
Medium lubricating distillate				100-200
Viscous lubricating distillate				Above 200
Residuum	37.3	.952	17.1	
Distillation loss	.5			

OIL D

Bureau of Mines Bartlesville Laboratory
Sample 57056

IDENTIFICATION

Kawkawlin field
Dundee dolomite
2,820-2,905 feetMichigan
Bay County
15N-4E

GENERAL CHARACTERISTICS

Gravity, specific, 0.854 Gravity, ° API, 34.2 Pour point, ° F., below 5
Sulfur, percent, 0.45 Color, greenish black
Viscosity, Saybolt Universal at 100° F., 57 sec. Nitrogen, percent, 0.102
130° F., 51 sec.

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 740 mm. HgFirst drop, 88 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	0.9	0.9	0.672	79.1	-)				
2	167	1.4	2.3	.686	74.8	15)				
3	212	2.7	5.0	.710	67.8	17)	1.38674	124.1		
4	257	3.4	8.4	.732	61.8	18	1.40568	127.9		
5	302	4.4	12.8	.746	58.2	17	1.41376	130.2		
6	347	4.5	17.3	.761	54.4	17	1.42212	132.2		
7	392	6.1	23.4	.778	50.4	19	1.43022	131.9		
8	437	5.6	29.0	.795	46.5	22	1.43955	136.7		
9	482	6.6	35.6	.813	42.6	25	1.44894	140.7		
10	527	7.2	42.8	.825	40.0	26	1.45592	141.0		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	3.9	46.7	0.831	38.0	25	1.46550	151.5	38	20
12	437	6.2	52.9	.847	35.6	28	1.47233	154.6	43	35
13	482	4.6	57.5	.869	31.3	36	1.48547	163.1	52	45
14	527	4.3	61.8	.891	27.3	43	1.49639	178.8	72	55
15	572	5.5	67.3	.907	24.5	47	1.50536	198.3	120	65
Residuum		30.7	98.0	.963	15.4					

Carbon residue, Conradson: Residuum, 10.1 percent; crude, 3.5 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	5.0	0.696	71.8	
Total gasoline and naphtha	23.4	0.745	58.4	
Kerosine distillate	12.4	.812	42.8	
Gas oil	11.4	.845	36.0	
Nonviscous lubricating distillate	8.4	.864	32.3-25.7	50-100
Medium lubricating distillate	4.7	.900	25.7-23.0	100-200
Viscous lubricating distillate				Above 200
Residuum	30.7	.963	15.4	
Distillation loss	2.0			

Oil E

Bureau of Mines Bartlesville Laboratory
Sample 58016

IDENTIFICATION

Bradford field
Upper Devonian

Pennsylvania
McKean County

GENERAL CHARACTERISTICS

Gravity, specific, 0.820 Gravity, ° API, 41.1 Pour point, ° F., below 5
Sulfur, percent, 0.11 Color, green
Viscosity, Saybolt Universal at 100° F., 44 sec. Nitrogen, percent, 0.010

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 753 mm. Hg
First drop, 20 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index n_D at 20° C.	Specific dispersion	S. U. viso. 100° F.	Cloud test, ° F.
1	122									
2	167	2.0	2.0	0.671	79.4	-				
3	212	4.5	6.5	.713	67.0	18)	1.39133	127.6		
4	257	6.9	13.4	.738	60.2	21	1.41120	126.6		
5	302	5.8	19.2	.756	55.7	22	1.42140	136.0		
6	347	5.9	25.1	.770	52.3	22	1.42893	136.9		
7	392	5.6	30.7	.781	49.7	21	1.43482	134.7		
8	437	5.7	36.4	.793	46.9	21	1.44056	134.6		
9	482	5.7	42.1	.805	44.3	21	1.44635	134.0		
10	527	6.7	48.8	.817	41.7	22	1.45097			

STAGE 2—Distillation continued at 40 mm. Hg

11	392	1.9	50.7	0.827	39.6	23	1.46003	-	39	24
12	437	5.1	55.8	.835	38.0	23	1.46241	-	43	40
13	482	5.7	61.5	.843	36.4	23	1.46648	-	52	60
14	527	5.3	66.8	.854	34.2	25	1.47197	-	66	70
15	572	6.6	73.4	.864	32.3	27	-	-	100	80
Residuum		25.0	98.4	.900	25.7					

Carbon residue, Conradson: Residuum, 1.6 percent; crude, 0.3 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	6.5	0.700	70.6	
Total gasoline and naphtha	30.7	0.754	56.2	
Kerosene distillate	18.1	.806	44.1	
Gas oil	8.7	.833	38.4	
Nonviscous lubricating distillate	12.6	.841-.864	36.8-32.3	50-100
Medium lubricating distillate	3.3	.864-.870	32.3-31.1	100-200
Viscous lubricating distillate				Above 200
Residuum	25.0	.900	25.7	
Distillation loss	1.6			

Oil F

Bureau of Mines Bartlesville Laboratory
Sample 58012

IDENTIFICATION

Beaver Lodge field
Mission Canyon, Ordovician
10,495-14,066 feet

North Dakota
Williams County

GENERAL CHARACTERISTICS

Gravity, specific, 0.797 Gravity, ° API, 46.0 Pour point, ° F., below 5
Sulfur, percent, 0.23 Color, green
Viscosity, Saybolt Universal at 100° F., 34 sec. Nitrogen, percent, 0.022

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 752 mm. Hg
First drop, 81 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index n_D at 20° C.	Specific dispersion	S. U. viso. 100° F.	Cloud test, ° F.
1	122	6.3	6.3	0.641	89.3	-	1.36213	123.1		
2	167	4.5	10.8	.680	76.6	12	1.38156	125.0		
3	212	8.6	19.4	.722	64.5	22	1.40258	131.2		
4	257	8.9	28.3	.751	56.9	27	1.41803	135.5		
5	302	6.7	35.0	.769	52.5	28	1.42902	147.6		
6	347	6.3	41.3	.783	49.2	28	1.43694	148.2		
7	392	5.3	46.6	.795	46.5	27	1.44257	142.4		
8	437	4.7	51.3	.808	43.6	28	1.44864	143.2		
9	482	5.1	56.4	.822	40.6	29	1.45711	148.2		
10	527	5.6	62.0	.839	37.2	32	1.46701	154.6		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	3.7	65.7	0.852	39.6	35	1.47597	157.4	40	10
12	437	4.8	70.5	.869	31.3	39	1.47988	159.0	46	34
13	482	4.0	74.5	.875	30.2	38	1.48547	-	58	54
14	527	4.4	78.9	.884	28.6	40	1.48968	-	81	70
15	572	4.5	83.4	.893	27.0	41	-	-	145	84
Residuum		12.2	95.6	.932	20.3					

Carbon residue, Conradson: Residuum, 2.7 percent; crude, 0.3 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	19.4	0.686	74.8	
Total gasoline and naphtha	46.6	0.736	60.8	
Kerosene distillate	9.8	.815	42.1	
Gas oil	13.1	.850	35.0	
Nonviscous lubricating distillate	8.6	.871-.886	31.0-28.2	50-100
Medium lubricating distillate	5.3	.886-.897	28.2-24.3	100-200
Viscous lubricating distillate				Above 200
Residuum	12.2	.932	20.3	
Distillation loss	4.4			

Oil G

Bureau of Mines Bartlesville Laboratory
Sample 60050

IDENTIFICATION

Charenton field
Upper Miocene
6,430-6,432 feet

Louisiana
St. Mary Parish

GENERAL CHARACTERISTICS

Gravity, specific, 0.841 Gravity, ° API, 36.8 Pour point, ° F., 15
Sulfur, percent, 0.10 Color, brownish green
Viscosity, Saybolt Universal at 100° F., 42 sec. Nitrogen, percent, 0.02

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 754 mm. Hg
First drop, 149 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API. 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test. ° F.
1.....	122									
2.....	167									
3.....	212	2.2	2.2	0.719	65.3	—	1.40171	141.3		
4.....	257	2.6	4.8	.751	56.9	27	1.41879	139.5		
5.....	302	3.2	8.0	.769	52.5	28	1.42916	142.1		
6.....	347	4.1	12.1	.782	49.5	27	1.43716	145.2		
7.....	392	4.9	17.0	.795	46.5	27	1.44282	144.1		
8.....	437	6.5	23.5	.806	44.1	27	1.44858	141.4		
9.....	482	9.1	32.6	.821	40.9	29	1.45576	145.2		
10.....	527	12.0	44.6	.832	38.6	29	1.46222	147.6		

Stage 2—Distillation continued at 40 mm. Hg

11.....	392	8.2	52.8	0.846	35.8	32	1.46829	149.0	40	20
12.....	437	12.2	65.0	.851	34.8	30	1.46919	145.8	45	40
13.....	482	9.3	74.3	.858	33.4	30	1.47322	—	56	60
14.....	527	7.9	82.2	.869	31.3	32	1.47863	—	76	70
15.....	572	5.4	87.6	.880	29.3	35	—	135	80	
Residuum.....		11.6	99.2	.933	20.2					

Carbon residue, Conradson: Residuum, 4.0 percent; crude, 0.5 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	2.2	0.719	65.3	
Total gasoline and naphtha.....	17.0	0.770	52.3	
Kerosine distillate.....	15.6	.815	42.1	
Gas oil.....	31.4	.843	36.4	
Nonviscous lubricating distillate.....	17.0	.854-.873	34.2-30.6	50-100
Medium lubricating distillate.....	6.6	.873-.884	30.6-28.6	100-200
Viscous lubricating distillate.....	—	—	—	Above 200
Residuum.....	11.6	.933	20.2	
Distillation loss.....	.8			

Oil H

Bureau of Mines Bartlesville Laboratory
Sample 61093

IDENTIFICATION

Gueydan, West field
Hartwell, Upper Miocene
9,612-9,617 feet

Louisiana
Vermilion Parish

GENERAL CHARACTERISTICS

Gravity, specific, 0.829 Gravity, ° API, 39.2 Pour point, ° F., 40
Sulfur, percent, less than 0.10 Color, green
Viscosity, Saybolt Universal at 100° F., 42 sec. Nitrogen, percent, 0.02

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 741 mm. Hg
First drop, 82 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API. 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test. ° F.
1.....	122									
2.....	167	2.8	2.8	0.722	64.5	—	1.40700	138.1		
3.....	212	3.1	5.9	.732	61.8	27	1.41036	145.3		
4.....	257	3.5	9.4	.755	55.9	29	1.42343	146.7		
5.....	302	3.7	13.1	.770	52.3	28	1.43161	155.6		
6.....	347	3.5	16.6	.780	49.9	26	1.43709	151.9		
7.....	392	4.1	20.7	.789	47.8	24	1.44192	148.3		
8.....	437	5.3	26.0	.804	44.5	26	1.44894	150.6		
9.....	482	8.1	34.1	.820	41.1	28	1.45738	151.1		
10.....	527	11.1	45.2	.830	39.0	28	1.46264	151.3		

Stage 2—Distillation continued at 40 mm. Hg

11.....	392	11.6	56.8	0.840	37.0	29	1.46657	147.2	41	30
12.....	437	5.5	62.3	.842	36.6	26	1.46662	141.8	47	50
13.....	482	9.3	71.6	.849	35.2	26	1.46910	137.5	54	65
14.....	527	7.6	79.2	.860	33.0	32	—	72	80	
15.....	572	6.4	85.6	.870	31.1	30	—	115	95	
Residuum.....		10.6	96.2	.917	22.8					

Carbon residue, Conradson: Residuum, 2.6 percent; crude, 0.3 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	5.9	0.727	63.1	
Total gasoline and naphtha.....	20.7	0.761	54.4	
Kerosine distillate.....	13.4	.814	42.3	
Gas oil.....	28.7	.837	37.6	
Nonviscous lubricating distillate.....	17.2	.845-.866	36.0-31.9	50-100
Medium lubricating distillate.....	5.6	.866-.874	31.9-30.4	100-200
Viscous lubricating distillate.....	—	—	—	Above 200
Residuum.....	10.6	.917	22.8	
Distillation loss.....	3.8			

Oil I

Bureau of Mines Bartlesville Laboratory
Sample 57038

IDENTIFICATION

Conroe field
Cockfield, Eocene

Texas
Montgomery County

GENERAL CHARACTERISTICS

Gravity, specific, 0.838 Gravity, ° API, 37.4 Pour point, ° F., 10
Sulfur, percent, less than 0.10 Color, brownish green
Viscosity, Saybolt Universal at 100° F., 36 sec. Nitrogen, percent, 0.027

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 740 mm. Hg
First drop, 79 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	0.7	0.7	0.697	71.5					
2	167	1.6	2.3	.716	66.1	29				
3	212	4.8	7.1	.749	57.4	35	1.40627	134.7		
4	257	8.2	15.3	.778	50.4	40	1.43321	155.8		
5	302	6.6	21.9	.795	46.5	40	1.44532	164.5		
6	347	6.8	28.7	.806	44.1	39	1.45135	161.3		
7	392	5.7	34.4	.813	42.6	36	1.45487	159.0		
8	437	7.1	41.5	.829	39.2	38	1.46297	164.5		
9	482	10.3	51.8	.848	35.4	41	1.47527	173.1		
10	527	11.4	63.2	.861	32.8	43	1.48279	178.6		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	6.0	69.2	0.864	32.3	40	1.48380	170.9	40	25
12	437	7.9	77.1	.867	31.7	38	1.48243	164.8	45	40
13	482	5.8	82.9	.871	31.0	37	1.48466	161.0	55	65
14	527	4.2	87.1	.880	29.3	38			74	80
15	572	4.4	91.5	.887	28.0	38			115	95
Residuum		7.6	99.1	.942	18.7					

Carbon residue, Conradson: Residuum, 4.8 percent; crude, 0.4 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	7.1	0.736	60.8	
Total gasoline and naphtha	34.4	0.784	49.0	
Kerosine distillate		.854	34.2	
Gas oil	42.3			
Nonviscous lubricating distillate	11.1	.869-.885	31.3-28.4	50-100
Medium lubricating distillate	3.7	.885-.891	28.4-27.3	100-200
Viscous lubricating distillate				Above 200
Residuum	7.6	.942	18.7	
Distillation loss	.9			

Oil J

Bureau of Mines Bartlesville Laboratory
Sample 1246

IDENTIFICATION

Miocene formation
820-1,148 feet

Borneo, N.E.I.
Sanga Sanga District

GENERAL CHARACTERISTICS

Gravity, specific, 0.866 Gravity, ° API, 31.9 Pour point, ° F., Below 5
Sulfur, percent, less than 0.1 Color, greenish black
Viscosity, Saybolt Universal at 100° F., 33 sec. Nitrogen, percent,

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 743 mm. Hg
First drop, 117 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122									
2	167	1.5	1.5	0.707	68.6	25				
3	212	5.0	6.5	.755	55.9	38				
4	257	12.9	19.4	.783	49.2	42				
5	302	10.9	30.3	.804	44.5	45				
6	347	7.0	37.3	.816	41.9	44				
7	392	5.7	43.0	.827	39.6	43				
8	437	7.6	50.6	.847	35.6	46				
9	482	9.1	59.7	.878	29.7	56				
10	527	10.5	70.2	.904	25.0	63				

STAGE 2—Distillation continued at 40 mm. Hg

11	392	6.0	76.2	0.923	21.8	68			42	below 5
12	437	4.5	80.7	.933	20.2	69			49	below 5
13	482	4.0	84.7	.954	16.8	76			76	below 5
14	527	3.3	88.0	.965	15.1	78			210	below 5
15	572	3.7	91.7	.971	14.2	78			over 400	below 5
Residuum		8.3	100.0							

Carbon residue, Conradson: Residuum, 8.6 percent; crude, 0.7 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	6.5	0.744	58.7	
Total gasoline and naphtha	37.3	0.790	47.6	
Kerosine distillate		.881	29.1	
Gas oil	41.3			
Nonviscous lubricating distillate	4.8	.934-.956	20.0-16.5	50-100
Medium lubricating distillate	2.8	.956-.964	16.5-15.3	100-200
Viscous lubricating distillate	5.5	.964-.974	15.3-13.8	Above 200
Residuum	8.3	1.002		
Distillation loss				

Oil K

Bureau of Mines Bartlesville Laboratory
Sample 59165

IDENTIFICATION

Main Pass (Block 69) field
Miocene sand
5,550-8,190 feetLouisiana
Plaquemines Parish

GENERAL CHARACTERISTICS

Gravity, specific, 0.873 Gravity, ° API, 30.6 Pour point, ° F., Below 5
Sulfur, percent, 0.25 Color, brownish green
Viscosity, Saybolt Universal at 77° F., 85 sec. Nitrogen, percent, 0.098
100° F., 61 sec.

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 742 mm. Hg
First drop, 91 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	0.1	0.1	0.657	83.9					
2	167	.9	1.0	.667	80.6	6.1	1.37306	124.9		
3	212	1.6	2.6	.717	65.9	20	1.39523	125.8		
4	257	2.8	5.4	.744	58.7	24	1.41289	130.1		
5	302	3.1	8.5	.767	53.0	27	1.42616	137.1		
6	347	3.5	12.0	.790	47.6	31	1.43739	138.3		
7	392	4.0	16.0	.805	44.3	32	1.44602	139.8		
8	437	4.6	20.6	.820	41.1	33	1.45313	141.3		
9	482	5.7	26.3	.834	38.2	35	1.46032	144.5		
10	527	8.5	34.8	.843	36.4	34	1.46814	147.2		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	5.5	40.3	0.858	33.4	37	1.47605	152.9	41	14
12	437	8.0	48.3	.864	32.3	37	1.47906	151.2	47	24
13	482	7.6	55.9	.879	29.5	40	1.48527	152.9	60	36
14	527	6.3	62.2	.891	27.3	43	1.49147	-	89	54
15	572	7.4	69.6	.901	25.6	45	1.49691	-	165	70
Residuum		29.6	99.2	.953	17.0					

Carbon residue, Conradson: Residuum, 6.2 percent; crude, 2.0 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	2.6	0.697	71.5	
Total gasoline and naphtha	16.0	0.766	53.2	
Kerosene distillate	4.6	.820	41.1	
Gas oil	25.4	.849	35.2	
Nonviscous lubricating distillate	11.4	.867-.888	31.7-27.9	50-100
Medium lubricating distillate	12.2	.888-.906	27.9-24.7	100-200
Viscous lubricating distillate				Above 200
Residuum	29.6	.953	17.0	
Distillation loss	.8			

Oil L

Bureau of Mines Bartlesville Laboratory
Sample 55129

IDENTIFICATION

Coolinga (Nose) field
Eocene
8,000 feetCalifornia
Fresno County

GENERAL CHARACTERISTICS

Gravity, specific, 0.874 Gravity, ° API, 30.4 Pour point, ° F., 25
Sulfur, percent, 0.33 Color, brownish black
Viscosity, Saybolt Universal at 100° F., 140 sec. Nitrogen, percent, 0.260
130° F., 50 sec.

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 745 mm. Hg
First drop, 84 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	1.0	1.0	0.658	83.6	-				
2	167	1.3	2.3	.687	74.5	16				
3	212	4.0	6.3	.732	61.8	27				
4	257	5.2	11.5	.760	54.7	31	1.42247	136.0		
5	302	4.5	16.0	.780	49.9	33	1.43349	144.1		
6	347	4.2	20.2	.796	46.3	34	1.44234	144.3		
7	392	3.6	23.8	.811	43.0	35	1.45028	138.9		
8	437	4.7	28.5	.827	39.6	37	1.45951	147.1		
9	482	6.2	34.7	.842	36.6	39	1.46950	161.3		
10	527	7.1	41.8	.856	33.8	41	1.47844	163.3		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	4.1	45.9	0.870	31.1	43	1.48370	146.5	41	10
12	437	6.1	52.0	.875	30.2	42	1.48748	166.6	46	30
13	482	6.7	58.7	.890	27.5	46	1.49448	-	64	55
14	527	6.0	64.7	.898	26.1	46	1.50253	-	92	70
15	572	6.6	71.3	.915	23.1	51	-	-	185	90
Residuum		27.7	99.0	.980	12.9					

Carbon residue, Conradson: Residuum, 9.4 percent; crude, 4.2 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	4.4	0.677	77.5	
Total gasoline and naphtha	22.6	0.756	55.7	
Kerosene distillate				
Gas oil	23.7	.854	34.2	
Nonviscous lubricating distillate	8.8	.890-.912	27.5-23.7	50-100
Medium lubricating distillate	6.0	.912-.920	23.7-22.3	100-200
Viscous lubricating distillate	4.5	.920-.925	22.3-21.5	Above 200
Residuum	33.5	.966	15.0	
Distillation loss	1.0			

OIL M

Bureau of Mines Bartlesville Laboratory
Sample 57036

IDENTIFICATION

Hastings (1) field

Texas
Brazoria County

GENERAL CHARACTERISTICS

Gravity, specific, 0.867 Gravity, ° API, 31.7 Pour point, ° F., below 5
Sulfur, percent, 0.21 Color, dark green
Viscosity, Saybolt Universal at 100° F., 47 sec. Nitrogen, percent, 0.083

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 738 mm. Hg
First drop, 84 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	0.7	0.7	0.652	85.5	-				
2	167	1.3	2.0	.682	76.0	13				
3	212	3.3	5.3	.735	61.0	28	1.39544	125.2		
4	257	3.4	8.7	.761	54.4	32	1.41940	130.0		
5	302	3.1	11.8	.783	49.2	35	1.43144	127.5		
6	347	4.3	16.1	.805	44.5	38	1.44415	131.5		
7	392	5.0	21.1	.823	40.4	41	1.45432	140.4		
8	437	5.5	26.6	.837	37.6	42	1.46139	147.8		
9	482	9.0	35.6	.850	35.0	42	1.46861	162.6		
10	527	11.7	47.3	.866	31.9	45	1.47816	153.2		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	8.1	55.4	0.874	30.4	45	1.48354	147.4	43	Below 5
12	437	6.8	62.2	.883	28.8	46	1.48527	145.2	52	Below 5
13	482	5.7	67.9	.892	27.1	46	1.49095	158.6	75	Below 5
14	527	5.4	73.3	.907	24.5	50	1.49610	166.9	130	10
15	572	6.9	80.2	.917	22.8	52	1.50065	-	330	25
Residuum		19.6	99.8	.944	18.4					

Carbon residue, Conradson: Residuum, 4.2 percent; crude, 0.7 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	5.3	0.711	67.5	
Total gasoline and naphtha	21.1	0.775	51.1	
Kerosine distillate				
Gas oil	36.2	.860	33.0	
Nonviscous lubricating distillate	10.4	.881-.899	29.1-25.9	50-100
Medium lubricating distillate	5.1	.899-.911	25.9-23.8	100-200
Viscous lubricating distillate	7.4	.911-.923	23.8-21.8	Above 200
Residuum	19.6	.944	18.4	
Distillation loss	.2			

OIL N

Bureau of Mines Bartlesville Laboratory
Sample 64066

IDENTIFICATION

South Pass (Block 27) field
"M2" Miocene
6.344 feet

Louisiana
Plaquemines Parish

GENERAL CHARACTERISTICS

Gravity, specific, 0.910 Gravity, ° API, 24.0 Pour point, ° F., below 5
Sulfur, percent, 0.35 Color, brownish green
Viscosity, Saybolt Universal at 100° F., 160 sec. Nitrogen, percent, 0.103
130° F., 87 sec.

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 744 mm. Hg
First drop, 289 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122									
2	167									
3	212									
4	257									
5	302									
6	347	1.3	1.3	0.777	50.6		1.42854	113.1		
7	392	1.8	3.1	.825	40.0	41	1.45009	128.4		
8	437	3.0	6.1	.846	35.8	46	1.46104	131.8		
9	482	5.5	11.6	.858	33.4	46	1.46861	137.5		
10	527	5.7	17.3	.866	31.9	45	1.47444	142.5		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	8.2	25.5	0.882	28.9	49	1.48380	152.3	45	Below 5
12	437	11.2	36.7	.897	26.2	52	1.49229	162.5	54	Below 5
13	482	9.6	46.3	.909	24.2	54	1.50086	-	78	Below 5
14	527	8.7	55.0	.922	22.0	57			145	Below 5
15	572									
Residuum		44.3	99.3	.945	18.2					

Carbon residue, Conradson: Residuum, 3.9 percent; crude, 1.8 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline				
Total gasoline and naphtha	3.1	0.805	44.3	
Kerosine distillate				
Gas oil	23.7	.868	31.4	
Nonviscous lubricating distillate	17.7	.890-.913	27.4-23.4	50-100
Medium lubricating distillate	10.5	.913-.928	23.4-20.9	100-200
Viscous lubricating distillate				Above 200
Residuum	44.3	.945	18.2	
Distillation loss	.7			

1 Distillation discontinued at 518° F
2 Distillation discontinued at 527° F

Oil OS

Bureau of Mines Bartlesville Laboratory
Sample 59179

IDENTIFICATION

Lisbon, West field
Sligo formation (Pettit limestone)
5,300-5,500 feetLouisiana
Claiborne Parish

GENERAL CHARACTERISTICS

Gravity, specific, 0.886 Gravity, ° API, 28.2 Pour point, ° F., 35
Sulfur, percent, 1.33 Color, brownish black
Viscosity, Saybolt Universal at 100° F., 360 sec.
130° F., 184 sec. Nitrogen, percent, 0.122

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 745 mm. Hg
First drop, 131 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API. 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test. ° F.
1.....	122									
2.....	167	1.8	1.8	0.683	75.7		1.38030	123.7		
3.....	212	1.7	3.5	.692	73.0	8.0	1.38993	123.1		
4.....	257	3.6	7.1	.714	66.7	9.4	1.39938	123.8		
5.....	302	5.0	12.1	.730	62.3	9.4	1.40778	123.4		
6.....	347	4.4	16.5	.746	58.2	10	1.41619	125.1		
7.....	392	4.4	20.9	.764	53.7	13	1.42558	126.8		
8.....	437	4.4	25.3	.780	49.9	15	1.43408	126.3		
9.....	482	4.7	30.0	.794	46.7	16	1.44234	133.5		
10.....	527	5.9	35.9	.814	42.3	21	1.45163	135.3		

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	2.9	38.8	0.832	38.6	25	1.46382	144.7	39	14
12.....	437	6.3	45.1	.843	36.4	27	1.46939	149.7	45	24
13.....	482	3.9	49.0	.859	33.2	31	1.47827	158.7	56	54
14.....	527	4.3	53.3	.874	30.4	35	1.48496	160.3	75	70
15.....	572	4.9	58.2	.887	28.0	38		115		90
Residuum.....		40.3	98.5	1.017	7.6					

Carbon residue, Conradson: Residuum, 1.6 percent; crude, 0.7 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	3.5	0.687	74.5	
Total gasoline and naphtha.....	20.9	0.731	62.1	
Kerosine distillate.....	15.0	.798	45.8	
Gas oil.....	8.7	.840	37.0	
Nonviscous lubricating distillate.....	9.4	.851-.881	34.8-29.1	50-100
Medium lubricating distillate.....	4.2	.881-.893	29.1-27.0	100-200
Viscous lubricating distillate.....				Above 200
Residuum.....	40.3	1.017	7.6	
Distillation loss.....	1.5			

Oil P5

Bureau of Mines Bartlesville Laboratory
Sample 59200

IDENTIFICATION

Burgan field

Kuwait, Asia

GENERAL CHARACTERISTICS

Gravity, specific, 0.871 Gravity, ° API, 31.0 Pour point, ° F., Below 5
Sulfur, percent, 2.54 Color, brownish black
Viscosity, Saybolt Universal at 77° F., 91 sec.
100° F., 77 sec. Nitrogen, percent, 0.11

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 743 mm. Hg
First drop, 82 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API. 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test. ° F.
1.....	122	2.4	2.4	0.649	86.5					
2.....	167	2.5	4.9	.658	83.6	1.8	1.37309	120.4		
3.....	212	3.4	8.3	.692	73.0	8.0	1.38671	123.0		
4.....	257	4.8	13.1	.721	64.8	13	1.40366	131.8		
5.....	302	4.1	17.2	.748	57.7	18	1.41759	137.1		
6.....	347	4.6	21.8	.769	52.5	21	1.42857	139.9		
7.....	392	3.6	25.4	.782	49.5	21	1.43691	141.0		
8.....	437	4.2	29.6	.797	46.0	23	1.44285	140.9		
9.....	482	4.5	34.1	.812	42.8	24	1.45066	142.3		
10.....	527	5.8	39.9	.830	39.0	28	1.46118	151.6		

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	3.0	42.9	0.851	34.8	34	1.47420	160.3	40	15
12.....	437	5.1	48.0	.862	32.7	36	1.47988	164.2	45	30
13.....	482	4.6	52.6	.879	29.5	40	1.48691	172.6	57	45
14.....	527	5.2	57.8	.897	26.3	46	1.49861	175.4	85	65
15.....	572	4.9	62.7	.914	23.3	51			165	80
Residuum.....		35.8	98.5	.999	10.1					

Carbon residue, Conradson: Residuum, 11.2 percent; crude, 4.6 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	8.3	0.669	80.0	
Total gasoline and naphtha.....	25.4	0.726	63.4	
Kerosine distillate.....	8.7	.805	44.3	
Gas oil.....	13.5	.846	35.8	
Nonviscous lubricating distillate.....	8.6	.869-.900	31.3-25.7	50-100
Medium lubricating distillate.....	6.3	.900-.921	25.7-22.1	100-200
Viscous lubricating distillate.....	2	.921-.922	22.1-22.0	Above 200
Residuum.....	35.8	.999	10.1	
Distillation loss.....	1.5			

Oil QS

Bureau of Mines Bartlesville Laboratory
Sample 61016

IDENTIFICATION

Hobbs field
San Andres, Permian
4,144 feet

New Mexico, U.S.A.
Lea County

GENERAL CHARACTERISTICS

Gravity, specific, 0.838 Gravity, ° API, 37.4 Pour point, ° F., below 5
Sulfur, percent, 1.41 Color, greenish black
Viscosity, Saybolt Universal at 100° F., 41 sec. Nitrogen, percent, 0.08

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 741 mm. Hg
First drop, 77 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test, ° F.
1.....	122	4.0	4.0	0.650	86.2					
2.....	167	3.6	7.6	.672	79.1	8.4	1.37663	124.7		
3.....	212	6.1	13.7	.711	67.5	17	1.39610	122.3		
4.....	257	6.2	19.9	.739	60.0	21	1.40946	125.6		
5.....	302	5.7	25.6	.762	54.2	25	1.42354	137.1		
6.....	347	5.3	30.9	.786	48.5	29	1.43663	138.9		
7.....	392	4.6	35.5	.803	44.7	31	1.44648	139.0		
8.....	437	4.5	40.0	.819	41.3	33	1.45476	144.2		
9.....	482	5.4	45.4	.836	37.8	36	1.46385	154.7		
10.....	527	6.0	51.4	.853	34.4	39	1.47410	159.2		

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	4.7	56.1	0.872	30.8	44	1.48560	166.0	43	Below 5
12.....	437	4.3	60.4	.889	27.7	48	1.49315	175.4	53	25
13.....	482	5.3	65.7	.903	25.2	52	1.50197	182.6	77	45
14.....	527	3.7	69.4	.918	22.6	56	1.50764		135	60
15.....	572	7.2	76.6	.925	21.5	56			295	85
Residuum.....		17.9	94.5	.992	11.1					

Carbon residue, Conradson: Residuum, 9.6 percent; crude, 2.0 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	13.7	0.683	75.7	
Total gasoline and naphtha.....	35.5	0.736	60.8	
Kerosine distillate.....	4.5	.819	41.3	
Gas oil.....	17.0	.855	34.0	
Nonviscous lubricating distillate.....	7.9	.884-.909	28.6-24.2	50-100
Medium lubricating distillate.....	4.9	.909-.921	24.2-22.1	100-200
Viscous lubricating distillate.....	6.8	.921-.930	22.1-20.7	Above 200
Residuum.....	17.9	.992	11.1	
Distillation loss.....	5.5			

Oil RS

Bureau of Mines Bartlesville Laboratory
Sample 59054

IDENTIFICATION

Lee Harrison field
Clear Fork, Permian
4,979 feet

Texas
Lubbock County

GENERAL CHARACTERISTICS

Gravity, specific, 0.912 Gravity, ° API, 23.7 Pour point, ° F., 30
Sulfur, percent, 3.23 Color, greenish black
Viscosity, Saybolt Universal at 100° F., 110 sec. Nitrogen, percent, 0.14

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 739 mm. Hg
First drop, 97 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test, ° F.
1.....	122	0.7	0.7	0.658	83.6		1.37334	135.4		
2.....	167	2.3	3.0	.691	73.3	17	1.38799	135.9		
3.....	212	4.3	7.3	.737	60.5	29	1.41117	145.2		
4.....	257	5.2	12.5	.767	53.0	35	1.42859	156.7		
5.....	302	5.4	17.9	.787	48.3	36	1.44036	164.1		
6.....	347	3.9	21.8	.797	46.0	34	1.44560	162.3		
7.....	392	4.3	26.1	.805	44.3	32	1.45000	158.2		
8.....	437	4.1	30.2	.815	42.1	31	1.45724	160.0		
9.....	482	4.1	34.3	.841	36.8	43	1.46756	163.8		
10.....	527	6.5	40.8	.867	31.7	46	1.48167	178.3		

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	3.7	44.5	0.891	27.3	53	1.49902	189.5	42	20
12.....	437	4.6	49.1	.906	24.7	56	1.50545	199.7	48	40
13.....	482	4.5	53.6	.920	22.3	60	1.51399	209.7	64	55
14.....	527	4.6	58.2	.934	20.0	63	1.52282		98	70
15.....	572	5.9	64.1	.944	18.4				195	85
Residuum.....		35.1	99.2	1.039	4.7					

Carbon residue, Conradson: Residuum, 9.0 percent; crude, 3.6 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	7.3	0.715	66.4	
Total gasoline and naphtha.....	26.1	0.767	53.0	
Kerosine distillate.....	4.1	.815	42.1	
Gas oil.....	17.3	.872	30.8	
Nonviscous lubricating distillate.....	8.6	.907-.935	24.5-19.8	50-100
Medium lubricating distillate.....	5.4	.935-.945	19.8-18.2	100-200
Viscous lubricating distillate.....	2.6	.945-.949	18.2-17.6	Above 200
Residuum.....	35.1	1.039	4.7	
Distillation loss.....	.8			

1 Distillation discontinued 568° F

Oil TS

Bureau of Mines Bartlesville Laboratory
Sample 55163

IDENTIFICATION

Richfield field
Kraemer sand, Miocene
4, 100-4,700 feetCalifornia
Orange County
35-9W

GENERAL CHARACTERISTICS

Gravity, specific, 0.918 Gravity, ° API, 22.6 Pour point, ° F., Below 5
Sulfur, percent, 1.86 Color, brownish black
Viscosity, Saybolt Universal at 100° F., 230 sec. Nitrogen, percent, 0.575
130° F., 160 sec.

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 755 mm. Hg
First drop, 136 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test, ° F.
1.....	122									
2.....	167									
3.....	212	3.1	3.1	0.717	65.9	-	1.40138	125.9		
4.....	257	3.9	7.0	.752	56.7	27	1.41476	130.1		
5.....	302	4.3	11.3	.773	51.6	30	1.42628	132.1		
6.....	347	4.1	15.4	.794	46.7	33	1.43753	139.1		
7.....	392	3.5	18.9	.812	42.8	35	1.44793	142.9		
8.....	437	4.1	23.0	.829	39.2	38	1.45687	144.5		
9.....	482	4.7	27.7	.844	36.2	40	1.46745	148.8		
10.....	527	5.9	33.6	.861	32.8	43	1.47566	159.4		

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	3.0	36.6	0.871	31.0	44	1.48314	154.6	41	Below 5
12.....	437	4.7	41.3	.881	22.1	45	1.48971	160.2	48	20
13.....	482	5.0	46.3	.901	25.6	51	1.49876	161.0	66	40
14.....	527	4.9	51.2	.918	22.6	56	1.50733	-	115	55
15.....	572	5.7	56.9	.933	20.2	-	1.51633	-	260	75
Residuum.....		42.9	99.8	1.016	7.8	-				

Carbon residue, Conradson: Residuum, 11.5 percent; crude, 5.8 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	3.1	0.717	65.9	
Total gasoline and naphtha.....	18.9	0.771	52.0	
Kerosene distillate.....	-	-	-	
Gas oil.....	20.7	.858	33.4	
Nonviscous lubricating distillate.....	7.7	.883-.913	28.8-23.5	50-100
Medium lubricating distillate.....	4.6	.913-.927	23.5-21.1	100-200
Viscous lubricating distillate.....	5.0	.927-.941	21.1-18.9	Above 200
Residuum.....	42.2	1.016	7.8	
Distillation loss.....	.2			

1 Distillation discontinued at 558° F

Oil US

Bureau of Mines Bartlesville Laboratory
Sample 54097

IDENTIFICATION

Wilmington field

California
Los Angeles County

GENERAL CHARACTERISTICS

Gravity, specific, 0.937 Gravity, ° API, 19.5 Pour point, ° F., below 5
Sulfur, percent, 1.53 Color, brownish black
Viscosity, Saybolt Universal at 100° F., 470 sec. Nitrogen, percent, 0.662
130° F., 210 sec.

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 742 mm. Hg
First drop, 102 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test, ° F.
1.....	122									
2.....	167	1.1	1.1							
3.....	212	7	1.8	0.737	60.5	-				
4.....	257	2.1	3.2	.756	55.7	29	1.41232	125.6		
5.....	302	2.6	6.5	.774	51.3	30	1.42621	129.5		
6.....	347	2.5	9.0	.797	46.0	34	1.43875	133.2		
7.....	392	2.6	11.6	.819	41.3	39	1.45007	134.4		
8.....	437	3.7	15.3	.838	37.4	42	1.46007	138.4		
9.....	482	4.7	20.0	.855	34.0	45	1.46973	144.3		
10.....	527	6.9	26.9	.874	30.4	49	1.48103	159.3		

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	1.3	28.2	0.890	27.5	53	1.48980	157.8	44	below 5
12.....	437	4.5	32.7	.897	26.3	52	1.49502	161.6	49	do
13.....	482	6.1	38.8	.915	23.1	57	1.50467	166.5	69	do
14.....	527	5.4	44.2	.930	20.7	61			135	do
15.....	572	5.4	49.6	.944	18.4	-			350	do
Residuum.....		49.2	98.8	1.009	8.7	-				

Carbon residue, Conradson: Residuum, 12.8 percent; crude, 7.3 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	1.8	0.737	60.5	
Total gasoline and naphtha.....	11.6	0.780	49.9	
Kerosene distillate.....	-	-	-	
Gas oil.....	19.2	.866	31.9	
Nonviscous lubricating distillate.....	7.7	.898-.922	26.1-22.0	50-100
Medium lubricating distillate.....	4.7	.922-.934	22.0-20.0	100-200
Viscous lubricating distillate.....	6.4	.934-.951	20.0-17.3	Above 200
Residuum.....	49.2	1.009	8.7	
Distillation loss.....	1.2			

Oil VS

Bureau of Mines Bartlesville Laboratory
Sample 31068

IDENTIFICATION

Chusovskii Gorodki field
Upper Carboniferous LimestoneU.S.S.R.
Province of Ural
Russian Platform

GENERAL CHARACTERISTICS

Gravity, specific, 0.939 Gravity, ° API, 19.2 Pour point, ° F., Below 5
Sulfur, percent, 4.87 Color, brownish black
Viscosity, Saybolt Universal at 77° F., 80 sec. Nitrogen, percent, 100° F., 62 sec.

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 741 mm. Hg
First drop, 82° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	2.2	2.2							
2	167	3.3	5.5	10.680	76.6					
3	212	4.4	9.9	.740	59.7	31				
4	257	7.2	17.1	.787	48.3	44				
5	302	8.0	25.1	.817	41.7	51				
6	347	3.3	28.4	.825	40.0	48				
7	392	3.1	31.5	.829	39.2	43				
8	437	2.7	34.2	.858	37.2	42				
9	482	3.6	37.8	.890	33.4	46				
10	527	5.0	42.8		27.5	57				

Stage 2—Distillation continued at 40 mm. Hg

11	892	3.0	45.8	0.936	19.7	74			41	15
12	487	4.7	50.5	.954	16.8	79			47	35
13	482	2.1	52.6	.978	13.2	86			60	55
14	527	4.0	56.6	.990	11.4	90			110	70
15	572	5.5	62.1	1.000	10.0	92			260	85
Residuum.		33.0	95.1							

Carbon residue, Conradson: Residuum, 25.9 percent; crude, 8.5 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	9.9	0.707	68.6	
Total gasoline and naphtha	28.4	0.772	51.8	
Kerosene distillate				
Gas oil	21.0	.886	28.2	
Nonviscous lubricating distillate	7.3	.960-.987	15.9-11.9	50-100
Medium lubricating distillate	3.8	.987-.996	11.9-10.6	100-200
Viscous lubricating distillate	4.6	.996-1.006	10.6-9.2	Above 200
Residuum	33.0	1.106		
Distillation loss	1.9			

