The Effect of Time and Depth of Burial on the Naphtha and Gas Oil Content of Crude Oil

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Several geochemists have postulated that thermal cracking of organic material at low temperature over long periods of time results in the formation of the lower-boiling fractions of crude oil. Thus Hunt (1962) showed that ancient sediments did contain low-boiling hydrocarbons, whereas all previous work on recent sediments failed to indicate their presence. Biederman (1965) used the gas chromatographic data by Martin et al. (1963) to show that there is an increase in the content of individual low-boiling hydrocarbons of crude oil in the following order: young, shallow oils; young, deep oils; old, shallow oils; and old, deep oils. Silverman (1962) has proposed mechanisms whereby lighter portions of complex molecules are split off as a function of time and temperature. The latter is of course related to depth of burial. Finally Phillipi (1965) has provided an excellent treatise on the effect of time and depth on the mechanism of petroleum generation.

Recently the Bureau of Mines has placed the data from over 7,000 crude oil analyses on IBM cards, and it seemed that a study of these on the basis of geologic age and depth of burial might provide additional evidence for the general theories underlying the presentations of the authors cited above and of others who agree with this theory. The author acknowledges the capable assistance of Mrs. Wileen Crossman in the preparation and distribution of the IBM cards.

The cards were sorted to show both the naphtha content and the gas-oil content by geologic periods. The naphtha is the material distilled to a temperature of 200 C, fractions 1-7 inclusive, in the Bureau of Mines routine crude oil analysis, a typical example of which is shown in Table I. The gas oil is the material distilled between 200 C at atmospheric [illegible]

TABLE 1

[illegible]

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 65044

IDENTIFICATION

Midland Farms field — Texas
Ellenburger, Cambro-Ordovician — Andrews County
12,635 - 12,655 feet

GENERAL CHARACTERISTICS

Gravity, specific, 0.763 Gravity, ° API, 54.0 Pour point, ° F., below 5
Sulfur, percent, 0.06 Color, green
Viscosity, Saybolt Universal at 100° F. 34 sec. Nitrogen, percent, 0.010

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 747 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	5.3	5.3	0.632	92.4					
2	167	4.6	9.9	.657	83.9	1.3	1.37900	133.9		
3	212	6.0	15.9	.692	73.0	8.0	1.38902	127.4		
4	257	6.8	22.7	.716	66.1	10	1.40129	129.9		
5	302	7.2	29.9	.734	61.3	11	1.41147	133.0		
6	347	6.7	36.6	.750	57.2	12	1.41954	131.2		
7	392	6.8	43.4	.762	54.2	12	1.42547	129.8		
8	437	7.1	50.5	.776	50.8	13	1.43238	131.1		
9	482	6.8	57.3	.789	47.8	13	1.43888	131.6		
10	527	6.4	63.7	.800	45.4	14	1.44496	132.0		
STAGE 2—Distillation continued at 40 mm. Hg										
11	392	5.0	68.7	0.824	40.2	21	1.45335	136.6	40	30
12	437	6.1	74.8	.830	39.0	20	1.45761	132.3	44	40
13	482	4.4	79.2	.838	37.4	21	1.46390	141.8	52	50
14	527	3.4	82.6	.856	33.8	26	1.47032	138.3	66	60
15	572	3.4	86.0	.864	32.3	27	1.47705	133.7	100	75
Residuum		7.7	93.7	.901	25.5					

Carbon residue, Conradson: Residuum, 0.8 percent; crude, 0.07 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	15.9	0.662	82.3	
Total gasoline and naphtha	43.4	0.712	67.3	
Kerosine distillate	20.3	.788	48.1	
Gas oil	12.0	.828	39.4	
Nonviscous lubricating distillate	8.6	.836-.864	37.8-32.3	50-100
Medium lubricating distillate	1.7	.864-.868	32.3-31.5	100-200
Viscous lubricating distillate	–	–	–	Above 200
Residuum	7.7	.901	25.5	
Distillation loss	6.3			

pressure (fraction 8) and 225 C at 40 mm mercury pressure (fraction 12) inclusive. The geologic periods used were as follows:

Paleozoic rocks

Cambro-Ordovician and Ordovician
Siluro-Devonian
Mississippian
Pennsylvanian
Permian

Post-Paleozoic rocks

Triassic
Jurassic
Cretaceous
Tertiary.

In Figure 1 panels A and B represent the distribution of the naphtha content in 5-percent intervals for 2,704 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 the post-Paleozoic oils do not attain well-defined distribution curves; that the Tertiary oils show slightly saw-toothed distribution averaging about 11% in the range from 15 to 45% naphtha; that Cretaceous and Jurassic oils show maximums in the 30- to 35-percent range, with continuing contributions above this range; that the Triassic oils are erratic, presumably because of the small number. The Paleozoic oils in Panel B all form well-defined distribution curves with maximums at 35-40% of the naphtha. There appears to be a tendency for the oils from the older rocks to give more symmetrical groups, with less concentration in the low-naphtha-content area.

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

Oils from Paleozoic rocks (Permian, Pennsylvanian, Mississippian, Siluro-Devonian, Ordovician and Cambro-Ordovician)

1. Produced from rocks 2,000 ft or less
2. Produced from rocks 10,000 ft or more

Oils from post-Paleozoic rocks (Tertiary, Cretaceous, Jurassic, and Triassic)

1. Produced from rocks 2,000 ft or less
2. Produced from rocks 10,000 ft or more.

The data for the Paleozoic oils are shown in Figure 2 and for post-Paleozoic oils in Figure 3. In panel A of Figure 2 the oils from 2,000 ft or less do not as a group form the more normal distribution histogram shown in panel B. However, there are maximums that shift to the right with increase in age. Thus the Permian oils have a maximum at the 20- to 25-percent range; the Pennsylvanian oils also have a maximum at this same range, but are skewed toward the high-content side. The Mississippian oils have a definite maximum in the 30- to 35-percent range (see below), and the Siluro-Devonian oils have a maximum in the 30- to 35-percent range and are also skewed toward the high side. The few Ordovician oils, discounting those in the 0- to 5-percent range, (see below) are mostly in the 20- to 30- and 30- to 35-percent ranges. In contrast the oils from 10,000 ft or more shown in panel B show a definite maximum at the 40- to 45-percent range, and a distribution pattern only a little skewed to the low-content side. It is of interest geologically that the high peak for

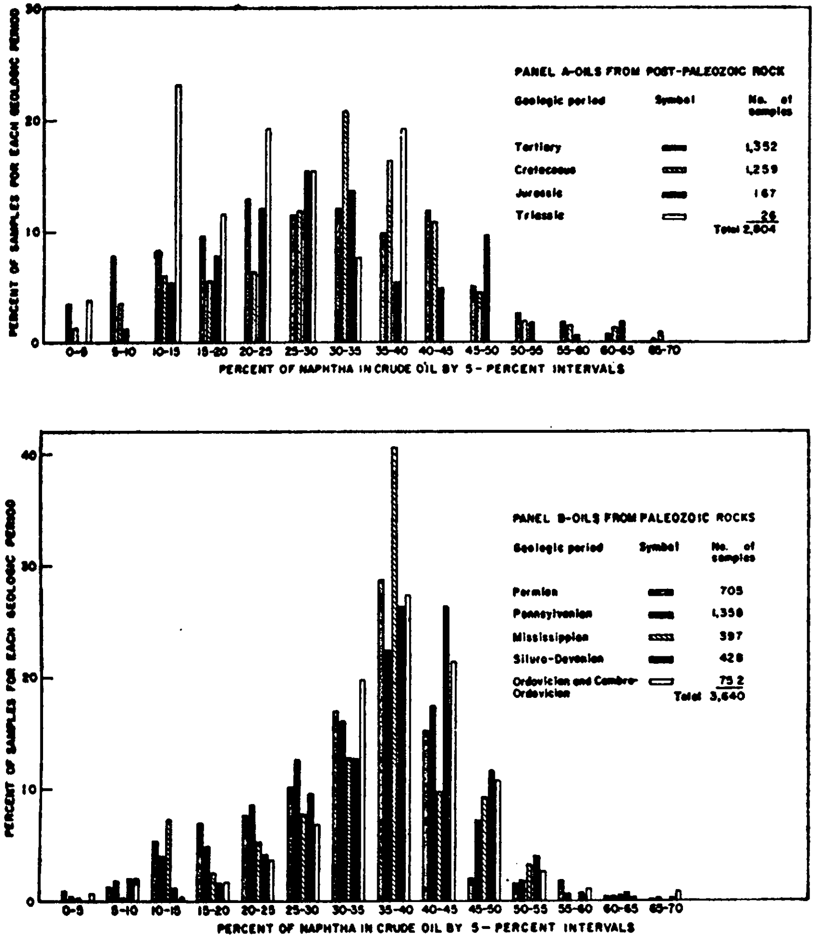

FIGURE 1.-Distribution of Naphtha Content of Crude Oil by Geological Period.

the Mississippian oils (panel A) at 30-35% 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 separate Illinois county. The Ordovician oils with 0-5% naphtha (panel A) are from the Arbuckle Limestone in Montgomery and Labette counties in Kansas, and three separate counties in Oklahoma. It seems probable that these oils have been subject to "weathering" of some form. The geology of these Kansas oils is discussed by Neumann et al. (1947).

In panel A of Figure 3 the data for oils from 2,000 ft or less are presented. The large percentage of those oils having naphtha contents of 15% or below is marked. In contrast the data for oils from 10,000 ft or more shown in panel B show a distribution pattern with a maximum in the 30- to 35-percent range (excluding two Cretaceous oils that are essentially condensates). Although the distribution is still somewhat

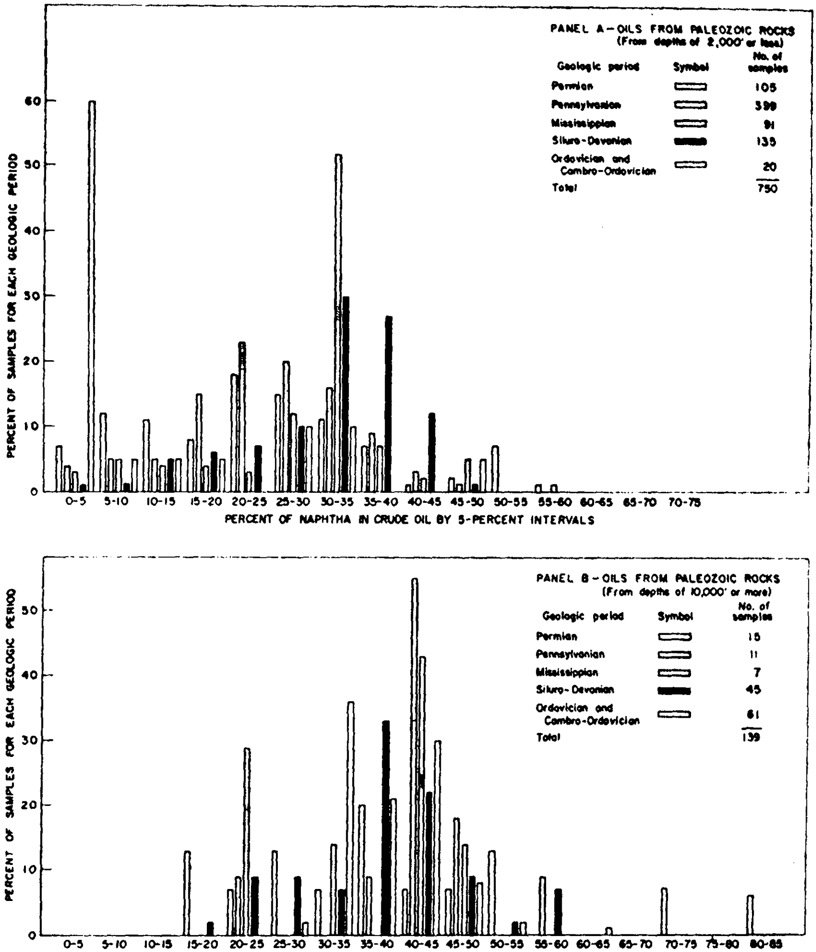

FIGURE 2.– Distribution of Naphtha Content of Crude Oil According to Depth of Burial in Paleozoic Rocks.

weighted in the low-content side of the maximum, the approach to a normal distribution curve is very apparent.

A distribution analysis similar to that made for the naphthas was carried out for the gas oils, and the data are shown in Figure 4 for the effect of age. The results are the converse of those for the naphthas, as should be expected if there is a long time effect of age resulting in the thermal cracking of gas oils. Panel A shows the distribution for the oils from post-Paleozoic rocks. The peak is in the 25- to 30- percent range, but the significant part is the weighting on the high-content side of the maximum, especially noticeable for Tertiary oils. Panel B show-

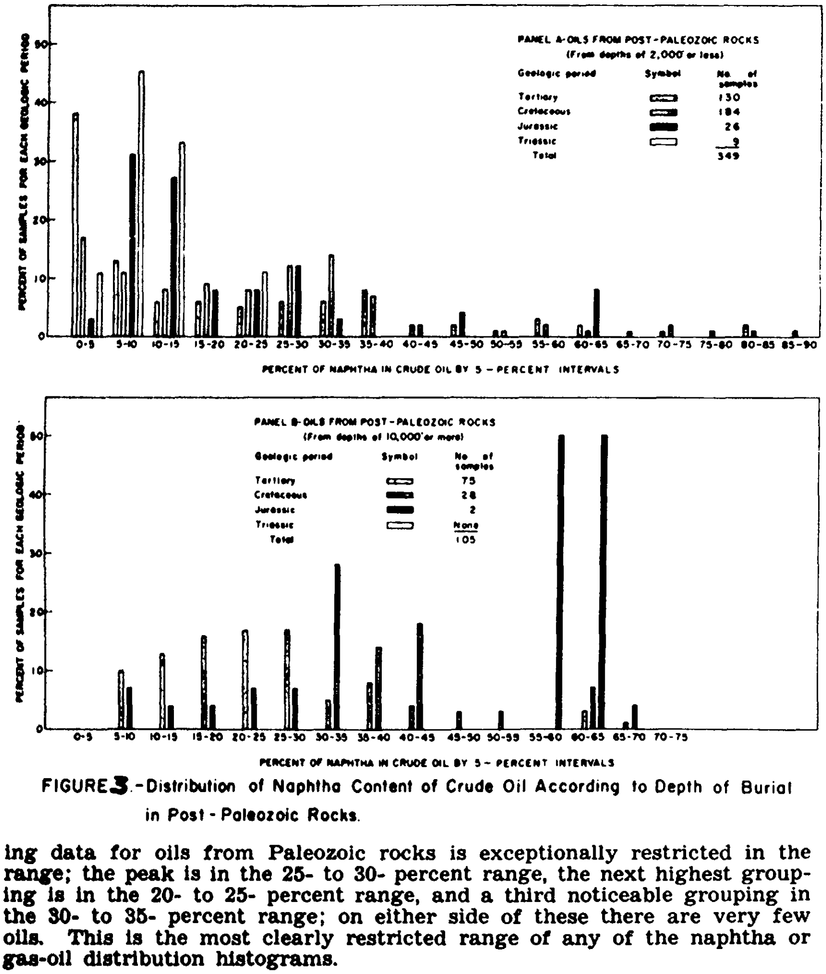

FIGURE 3.-Distribution of Naphtha Content of Crude Oil According to Depth of Burial in Post-Paleozoic Rocks.

ing data for oils from Paleozoic rocks is exceptionally restricted in the range; the peak is in the 25- to 30- percent range, the next highest grouping is in the 20- to 25- percent range, and a third noticeable grouping in the 30- to 35- percent range; 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 5 and 6 the same data are used to show the effects of depth of burial as was done for the naphtha content. The distribution graph in panel A of Figure 5 for post-Paleozoic oils from 2,000 ft or less has a significantly greater proportion of samples in the percentage ranges above the maximum at 25-30% as compared to similar data for oils from 10,000 ft or more in panel B. The effect of depth of burial for Paleozoic oils shown in Figure 6 is not clear. In fact there appears to be somewhat of a reversal in that the oils from 10,000 ft or more, panel B, are weighted slightly in the high side. The high for the Ordovician oils at the 30- to 35- percent range is due exclusively to Ellenburger oils of the Permian Basin in West Texas and New Mexico. The similarity in the histograms in panels A and B may indicate that, regardless of depth of burial, Paleozoic oils are old enough to have closely approached an equilibrium condition. The author believes that the data presented in Figures 1 through 6 make a strong case for investigators, such as Phillipi, Bieder-

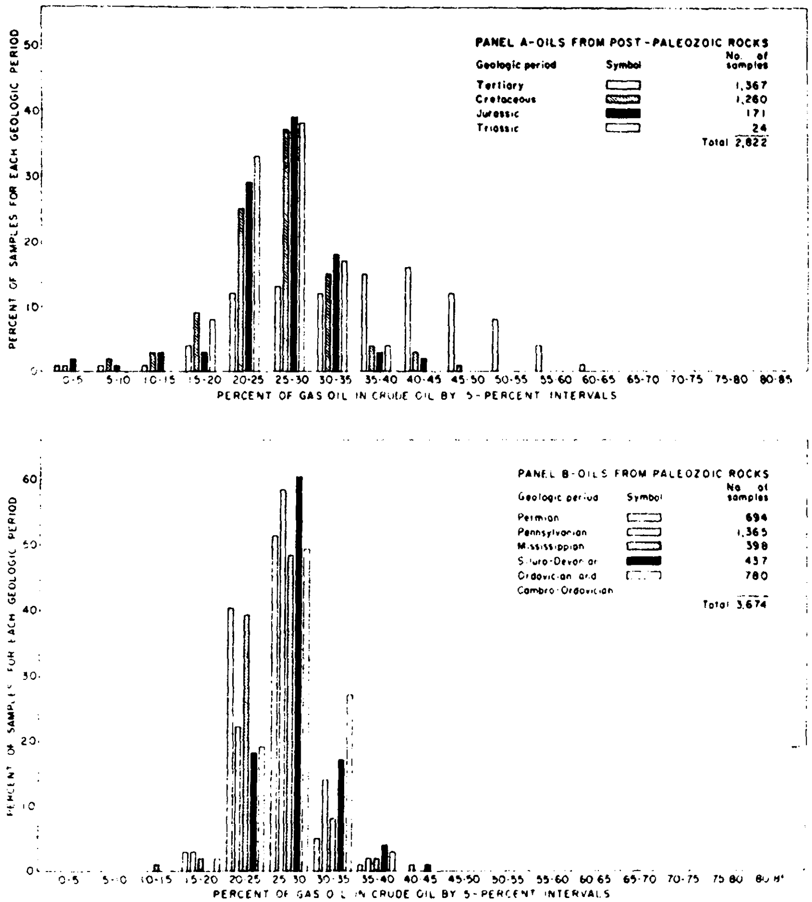

FIGURE 4.—Distribution of Gas Oil Content of Crude Oil by Geologic Period

man, Silverman and Hunt, who espouse the theory that the effects of time and depth of burial on organic matter are responsible for the lighter portion of petroleum.

A few hundred crude oil analyses of recent years have included specific dispersion data that made it possible to calculate the aromatic content of the naphtha, fractions 1-7 inclusive, boiling to 200 C. Therefore a distribution analysis of 283 oils was made on the same geologic basis as used previously, and separating the aromatic content into the following percentage ranges: 0-5, 6-10, 11-15, 16-20, over 20. It has been the author's belief for some time that the maximum aromatic content of crude oil naphthas is about 10% except for certain of the Permian oils of West Texas and the younger oils such as those of the Tertiary period. The histogram in Figure 7 bears this out along with the following points:

1. All the young Tertiary oils contain aromatics, and the percentage is fairly evenly divided over the entire range to >20%.

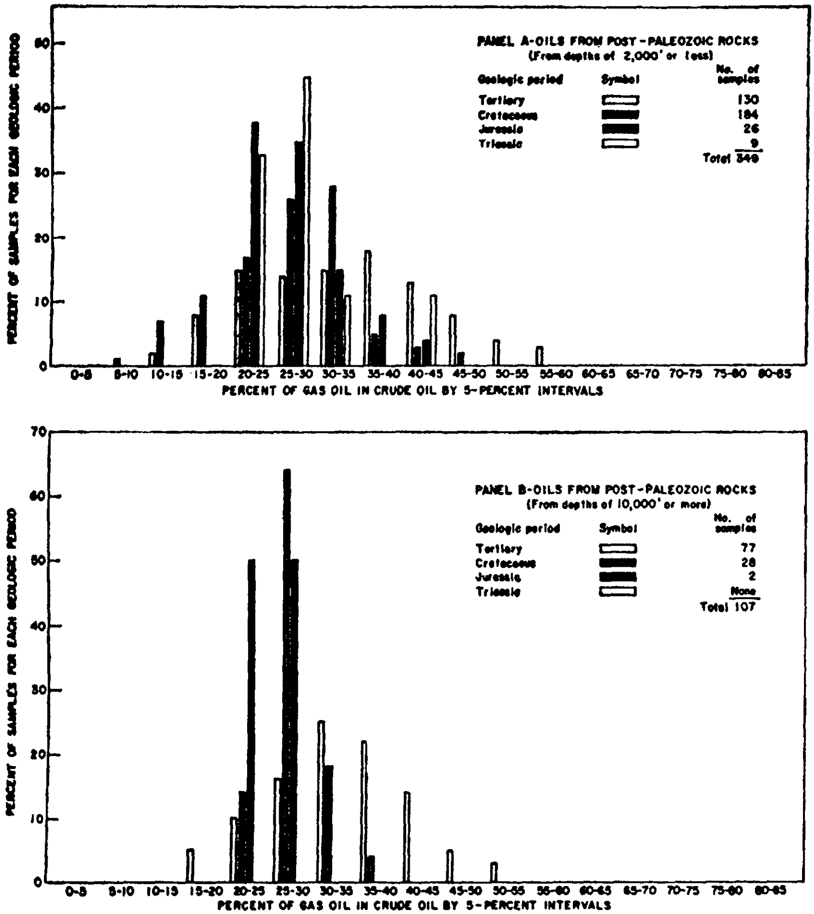

FIGURE 5.- Distribution of Gas Oil Content of Crude Oil According to Depth of Burial in Post-Paleozoic Rocks.

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

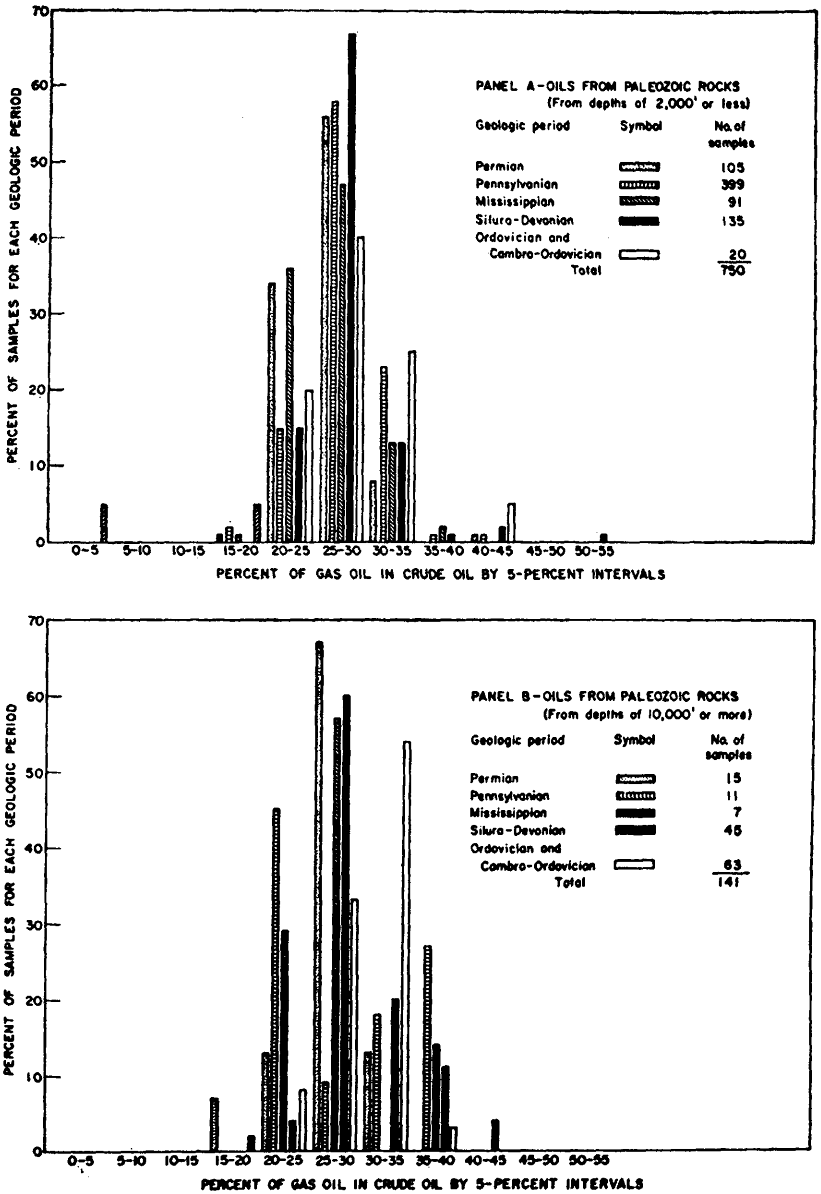

FIGURE 6 —Distribution of Gas Oil Content of Crude Oil According to Depth of Burial in Paleozoic Rocks.

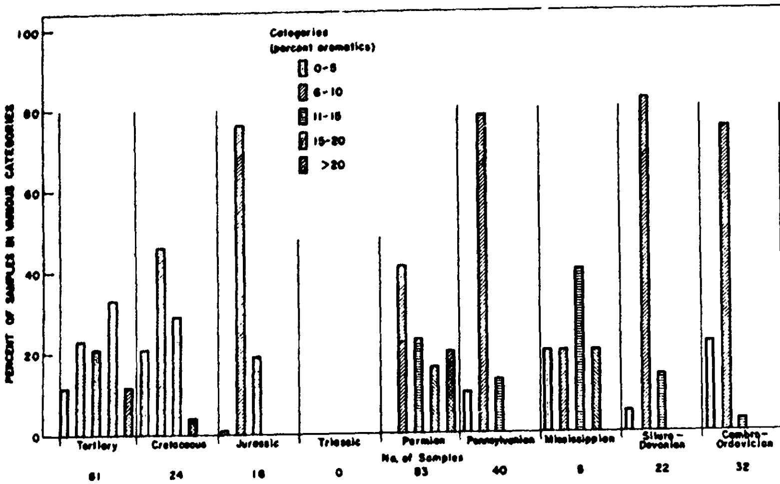

FIGURE 7. - Distribution of Aromatic Content of Naphtha by Geologic Period.

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 are unique in being the only oils of a period older than Tertiary that have a high content of aromatics in their naphthas.
3. It appears that the normal expected aromatic content of a naphtha is 5 to 10%, with the two exceptions noted.

Before sound conclusions regarding the aromatics can be reached there are several studies that 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 a combination of these? Finally, a plausible mechanism is needed to account for the high-aromatic, high-sulfur Permian oils.

This 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.

LITERATURE CITED

Biederman, E. W., Jr. 1965. Crude oil composition—a clue to migration. World Oil. December:78-82.

Hunt, J. M., 1962. *Geochemical Data on Organic Matter in Sediments. Scientific Sessions for Petroleum Production.* Vol. II. Lect. 3d Int. Sci. Conf. Geochem., Microbiol., Petrol. Chem. Part I, Geochem. Microbiol. Budapest, Hungary. 394-419.

Martin, R. L., J. C. Winters and J. A. Williams. 1963. *Composition of Crude Oil by Gas Chromatography and Geological Significance of Hydrocarbon Distribution.* Sixth World Petrol. Cong. Sect. 5 (Pap. 13): 231-260.

Neumann, L. M., N. W. Bass, R. L. Ginter, S. F. Mauney, T. F. Newman, C. Ryniker and H. M. Smith. 1947. Relationship of crude oils and stratigraphy in parts of Oklahoma and Kansas. Bull. AAPG. 31:109.

Phillipi, G. T., 1965. On the depth, time and mechanism of petroleum generation. Geochem. Cosmochim. Acta. 29:1021-1049.

Silverman, S. R. 1962. Carbon isotope geochemistry of petroleum and other natural organic materials. Scientific Sessions for Petroleum Production. Vol. II. Lectures at Third International Scientific Conference for Geochemistry, Microbiology, and Petroleum Chemistry Part I, Geochemistry and Microbiology, Budapest, Hungary. 328-341.