U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP824

Part of Journal of Research of the National Bureau of Standards, Volume 15, September 1935

PRESENT STATUS OF THE ISOLATION AND IDENTIFICATION OF THE VOLATILE HYDROCARBONS IN A MIDCONTINENT PETROLEUM [1]

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ABSTRACT

The work to date of the American Petroleum Institute's Research Project 6 on the fraction of a midcontinent petroleum boiling normally between 55 and 180° C is summarized. In the fraction, 55 to 145°, estimates have been made of the percentage contents of the 22 hydrocarbons actually isolated, the 6 hydrocarbons detected and in process of separation, and the 19 hydrocarbons whose presence in significant amounts is suspected. These quantities have been represented graphically in relation to the curves showing the distribution with temperature of the volume and the refractive index of the distillate. The composition of the large volumes of material which distilled in narrow temperature ranges before and after the removal of certain hydrocarbons is discussed.

It is probable that the foregoing 47 hydrocarbons will account for practically all of the material in this fraction. On this assumption the relative amounts of paraffin, naphthene, and aromatic hydrocarbons in the fraction are estimated to stand in the ratio of 6:3:1.

CONTENTS

I. INTRODUCTION

The work carried on at the National Bureau of Standards by the American Petroleum Institute Research Project 6 on the chemical constitution of petroleum, has reached the stage where it is profitable to survey the results obtained to date on the naphtha fraction of a midcontinent petroleum.

The study of the composition of petroleum is important, aside from its purely scientific interest, because of the rapidly increasing use of

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

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petroleum as a source of chemical raw materials. The importance is increased by the desire of the petroleum industry for information by which its more familiar products, gasoline and lubricating oil, may be intelligently improved.

In the present work [3] the analysis has been made as rigorous as possible by isolating hydrocarbons of sufficient purity to identify them by comparison of their physical properties with those of known hydrocarbons [1.2] [4] It has also been possible to estimate the rela-

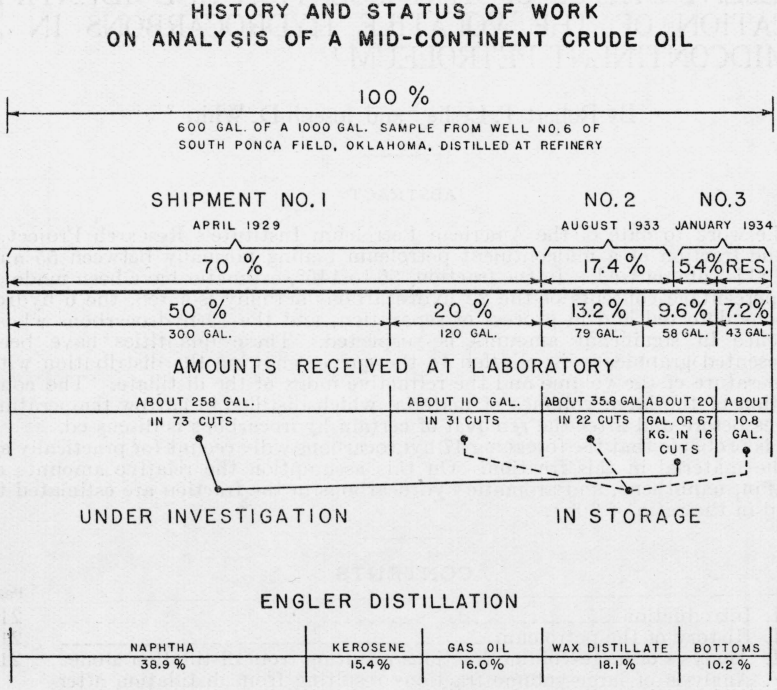

FIGURE 1.—*History and status of work on analysis of a midcontinent petroleum.*

Divisions showing percentages are drawn to scale on base line.

tive amounts of these hydrocarbons in the naphtha fraction as well as in the crude oil.

This paper surveys the results obtained so far on all the fractions of a midcontinent petroleum normally boiling between 55 and 145° C, and lists the constituents found in the fraction boiling between 145 and 180° C.

II. HISTORY OF THE PETROLEUM

In order to make the results of the work as complete as possible, a history of the petroleum from the well to the laboratory of the National Bureau of Standards has been kept. The essential details of volumes, percentages, and dates are shown graphically in figure 1. The original

[3] This investigation was begun in 1926 and was directed by E. W. Washburn until the time of his death in 1934. The work is being continued under the direction of F. D. Rossini. Individual contributions to the work have been reported at intervals in current scientific journals, and references to a number of these appear in this paper.

[4] Numbers in brackets refer to references at the end of paper.

3,800 liters (1,000 gallons) was supplied by the Marland Oil Co., from its well no. 6 in the South Ponca Field of Oklahoma, care being taken to avoid contamination with oils from other wells. It was shipped to the Sun Oil Co. for fractionation into quantities which could be handled in the laboratory. The assay distillation supplied by the Marland Oil Co. is shown at the bottom of the figure as an aid in identifying the laboratory fractions with their commercial classification. About 2,270 liters (600 gallons) of this material was carefully distilled in a small commercial still, and the lower-boiling fractions, representing about 70 percent of the crude oil, were sent to the laboratory in 1929 in approximately 12-liter fractions. The residue

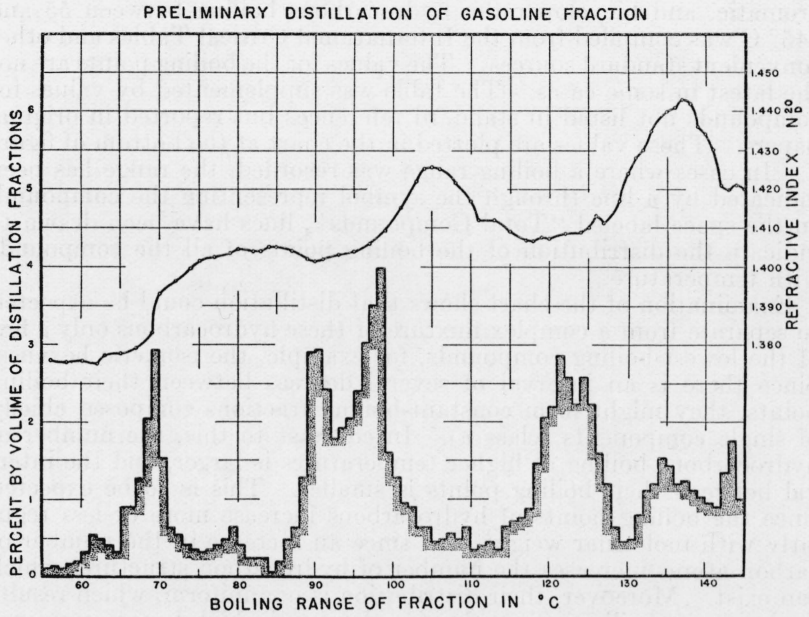

FIGURE 2.—*Preliminary distillation of the fraction of petroleum boiling between 55 and 145° C.*

The graph at the bottom of the figure shows the distribution of the volume with respect to boiling range. Volumes are indicated on the scale at the left. The curve at top of figure shows the refractive indices of distillation fractions boiling at 1 degree.

was divided into two approximately equal parts, one of which was carefully fractionated at reduced pressures and shipped to the laboratory at later dates.

Consecutive cuts of the lower-boiling fractions were redistilled in an atmosphere of carbon dioxide until the boiling point reached 240° C. The material redistilled represented approximately 50 percent of the original 2,270 liters. The distillate was carefully refractionated in laboratory stills [3] until considerable separation of material had occurred and further separation became slow.

Figure 2 shows the volumes and refractive indices of the fractions boiling between 55 and 145° C at the end of the preliminary distillation. Most of this graph was constructed from data appearing in previous papers [4, 5, 6, 7, 8, 9]. The remainder of the graph was con-

structed from data taken from unpublished notes. About 315 liters boiled within this region. Although this volume is about 14 percent of the 2,270 liters, it represents, by reason of losses, a considerably larger percentage of the crude oil. The distillate was distributed chiefly in 4 temperature ranges: 10 percent in the range 65 to 70° C, 30 percent in the range 90 to 100° C, 25 percent in the range 115 to 130° C, and 15 percent in the range 130 to 145° C.

III. ANALYSIS OF LARGE-VOLUME FRACTIONS RESULTING FROM DISTILLATION ALONE

A table of boiling points of paraffin, naphthene (monocycloparaffin), aromatic, and bicycloparaffin hydrocarbons boiling between 55 and 145° C was compiled from the International Critical Tables and other convenient standard sources. The values for the boiling points are not the latest in some cases. The table was supplemented by values for compounds not listed in standard references but reported in original papers. These values are plotted in the chart at the bottom of figure 3. In cases where a boiling range was recorded, the range has been indicated by a line through the symbol representing the compound. In the space labeled "Total Compounds", lines have been drawn to indicate the distribution of the boiling points of all the compounds with temperature.

Examination of the chart shows that distillation could be expected to separate from a complex mixture of these hydrocarbons only a few of the lowest-boiling compounds, for example, the isomeric hexanes. Since there is an interval of several degrees between their boiling points, they might form constant-boiling fractions composed chiefly of single components (class a). In contrast to this, the number of hydrocarbons boiling at higher temperatures is larger, and the interval between their boiling points is smaller. This is to be expected since the boiling points of hydrocarbons increase more or less regularly with molecular weight, and since an increase in the number of carbon atoms increases the number of hydrocarbon structures which can exist. Moreover, their distribution is nonuniform, which results in clusters of boiling points the complexity of which becomes greater with rising temperature. Distillation of a mixture of hydrocarbons boiling at the same temperature or in close proximity yields a fraction which is constant-boiling or substantially so. Such a fraction will be classed as that of the true solution type (class b). Constant-boiling fractions of this type can be separated completely only by the aid of other processes of fractionation in addition to distillation. The difficulty of separating a mixture by distillation alone is also complicated by the existence of a third class of constant-boiling fractions known as azeotropic mixtures (class c) which have minimum or maximum boiling point. These cannot be separated by simple distillation alone.

The analysis of petroleum may be less difficult than that of a mixture of all the possible hydrocarbons because it may contain fewer compounds in appreciable quantities; nevertheless it presents similar problems. It follows, therefore, that complete separation into component hydrocarbons of the large-volume fractions which result from the distillation of petroleum must be accomplished in stages in which certain of the hydrocarbons are removed by the application of special methods adapted to the particular fraction at hand. These large-

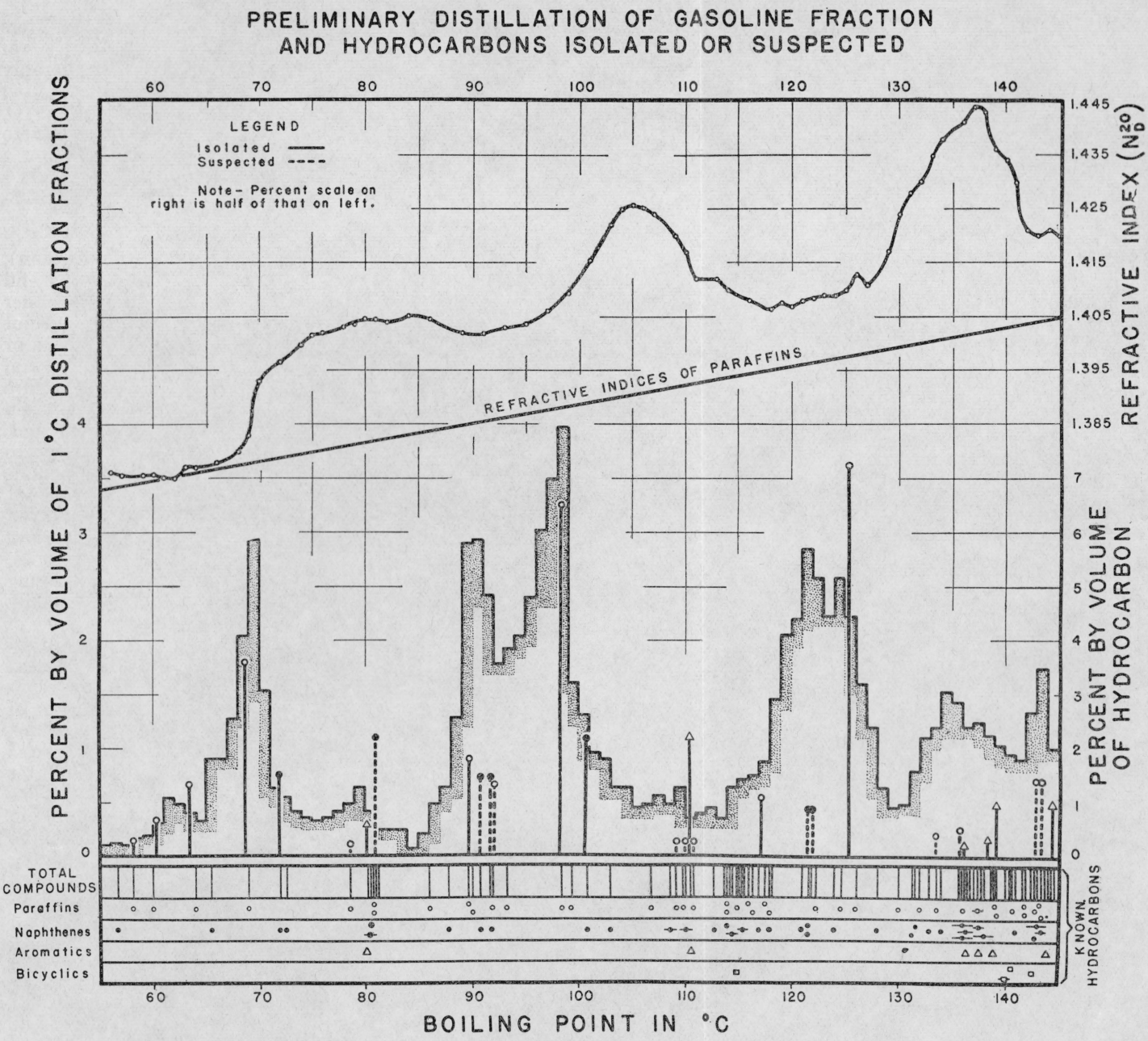

FIGURE 3.—*Composite graph of preliminary distillation, amounts of hydrocarbons removed or indicated, and distribution of boiling points of known hydrocarbons.*

The chart at the bottom of the figure gives the boiling points of known hydrocarbons, the different symbols representing the various classes. In the space entitled "Total Compounds", the lines show the distribution of all the boiling points.

Above the chart is shown the distillation graph with its volume scale to the left. The perpendicular lines, with their scale to the right, indicate the amounts of hydrocarbons isolated from or suspected in the distillate. (See legend in the figure.)

The curve at the top of the figure shows the refractive-indices of distillation fractions boiling at 1 degree intervals. The diagonal line below the refractive-index curve represents the mean values of the refractive indices of the paraffin hydrocarbons.

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volume fractions distil in narrow temperature ranges because they are composed of single constant-boiling fractions or a group of adjoining constant-boiling fractions. After the isolation of the predominant compounds, subsequent distillations usually cause the distribution of the remaining hydrocarbons in a new set of relatively large-volume fractions from which other compounds can be isolated.

The first set of these fractions encountered in the petroleum distilling between 55 and 145° C is shown by the distillation curve above the chart in figure 3. The refractive indices of the fractions are indicated by the upper curve in the same figure. The diagonal line drawn just below the refractive-index curve represents the mean value of the refractive indices of the paraffin hydrocarbons and will be called the paraffin base-line. The mean refractive indices of naphthenic and aromatic hydrocarbons would lie in the neighborhood of 1.420 and 1.500, respectively. The values for the individual compounds are somewhat irregular, however, and show no definite trend with relation to boiling points. The tendency of the refractive indices of the petroleum fractions is parallel to the paraffin base-line. This is probably caused by the preponderance of paraffin hydrocarbons in the material.

The solid perpendicular lines in the figure represent hydrocarbons which could be readily isolated from the first set of distillation fractions. Those capped by open circles are paraffinic, those by solid disks are naphthenic, and those by triangles are aromatic. They have been placed at temperatures corresponding to the boiling points of the purest samples isolated. In some instances they fail to coincide with the boiling points reported in the literature, but the identity of the isolated compounds has been proved by the similarity of other properties. The dotted lines are those hydrocarbons which could be isolated or definitely suspected only after the removal of the more prominent constituents, and whose presence accounted in part for changes in the refractive-index curve or for slight accumulations of volume. These lines have been placed at their reported boiling points, except where it was necessary to separate slightly lines representing compounds boiling at identical temperatures. The heights of the solid lines show the estimated percentages of those hydrocarbons which were isolated, while the heights of the dotted lines represent the quantity of the suspected or detected hydrocarbons. The latter quantities are estimated on the basis of refractive index and volume of the distillate at a later stage in the analysis when the presence of the hydrocarbons became evident.

Table 1 summarizes the nature of the large-volume fractions which appear in figure 3. It is seen that one of these, boiling between 58 and 65° C, is composed of a group of constant-boiling fractions of the single-component type. Five others chiefly contain virtually constant-boiling fractions of the true-solution type. The remaining three contain azeotropic mixtures which are attributable to the presence of benzene, toluene, and the xylenes, respectively. The bulk of these aromatic constituents was found in those mixtures which boiled at considerably lower temperatures than the boiling points of the pure hydrocarbons [4, 10]. The abrupt rises in the refractive-index curve over the paraffin base-line correspond chiefly to the presence of aromatic compounds.

TABLE 1.—*Analysis of large-volume fractions of figure 3*

Approx. boiling range	Chief class of constant-boiling fraction present [1]	Nature of constituents	Names of chief constituents	Methods of separation or detection
°C				
58 to 65 [2]	a	Paraffinic	2,3-Dimethylbutane	Distillation.
			2-Methylpentane	Do.
			3-Methylpentane	Do.
65 to 71	c	Paraffinic	*n*-Hexane	Distillation with methyl and ethyl alcohol, nitration followed by crystallization.
		Naphthenic	Methylcyclopentane	
		Aromatic	Benzene	
76 to 81	b	Paraffinic	2,2-Dimethylpentane	Nitration followed by crystallization.
		Naphthenic	Cyclohexane	
		Aromatic	Benzene	
85 to 92	b	Paraffinic	2-Methylhexane	Crystallization with solvent.
			3-Methylhexane	
		Naphthenic	1,2-Dimethylcyclopentane	Suspected from refractive-index curve.
			1,3-Dimethylcyclopentane	
95 to 101	c	Paraffinic	*n*-Heptane	Nitration followed by distillation and crystallization.
		Naphthenic	Methylcyclohexane	
		Aromatic	Toluene	
107 to 110	b	Paraffinic	2,5-Dimethylhexane	Suspected from volume of distillate and refractive-index curve; toluene separated by nitration.
			2,4-Dimethylhexane	
			2,2,3-Trimethylpentane	
		Aromatic	Toluene	
115 to 127	b	Paraffinic	*n*-Octane	Crystallization with and without solvent.
			2-Methylheptane	
		Naphthenic	*m*-Dimethylcyclohexane	
			p-Dimethylcyclohexane	
131 to 140	c	Paraffinic	2,5-Dimethylheptane	Paraffins suspected from volume of distillate and refractive-index curve.
			2,4-Dimethylheptane	
		Aromatic	*o*-, *m*-, and *p*-Xylenes	Aromatics isolated by extraction and sulfonation.
			Ethylbenzene	
142 to 144	b	Paraffinic	2-Methyloctane	Paraffins suspected from refractive-index curve; aromatics isolated by extraction and distillation.
			3-Methyloctane	
		Aromatic	*o*-Xylene	

[1] a indicates a substantially pure substance; b, an ideal solution of 2 or more hydrocarbons having nearly identical boiling points; c, an azeotropic (minimum or maximum boiling) mixture.
[2] Resolved into 3 fractions by further distillation.

The hydrocarbons which have been separated from this first set of distillation fractions are as follows:

(1) The normal paraffins; hexane, heptane, octane.

(2) The 2-methyl derivatives of these normal paraffins.

(3) Two other isomers of hexane; 2,3-dimethylbutane and 3-methylpentane.

(4) Methylcyclopentane and methylcyclohexane.

(5) All the possible aromatic hydrocarbons; benzene, toluene, ethylbenzene and the three xylenes.

As indicated by their refractive indices, 6 of the distillation fractions contained hydrocarbons in addition to those isolated.

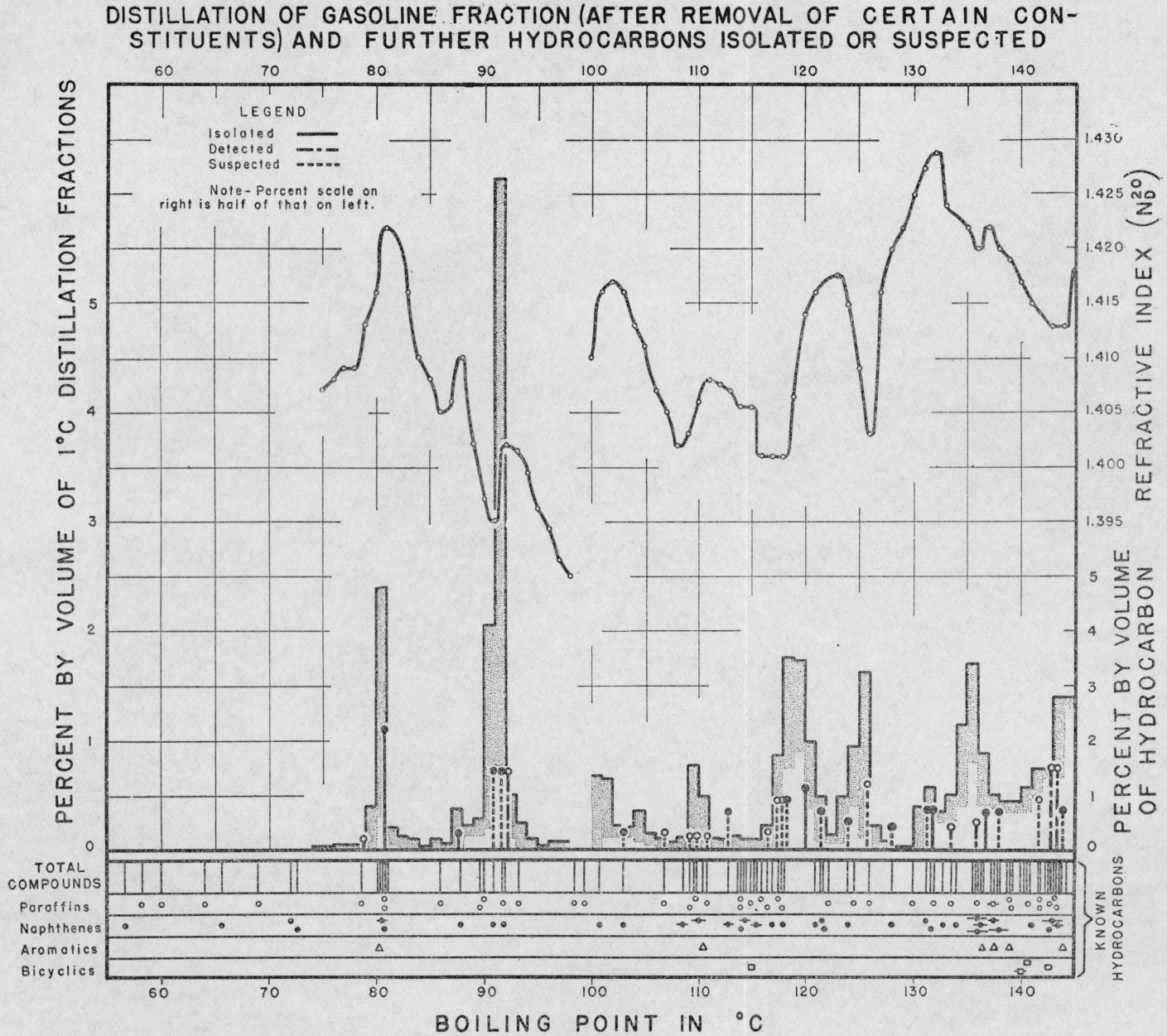

FIGURE 4.—*Composite of distillation after removal of certain constituents, amounts of hydrocarbons removed or indicated, and distribution of the boiling points of known hydrocarbons.*

[The representation of data is similar to that in figure 3.]

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IV. ANALYSIS OF LARGE-VOLUME FRACTIONS RESULTING FROM DISTILLATIONS AFTER REMOVAL OF CERTAIN HYDROCARBONS BY SPECIAL METHODS

After the removal of the hydrocarbons from the first set of distillation fractions, the remaining material was repeatedly redistilled until a new set of fractions, shown in figure 4, was obtained.[5] The same conventions of representation have been observed as in figure 3 except that some constituents not yet isolated, whose presence has been strongly suspected from additional data, are classed as detected and are indicated by broken lines. It will be observed that some of the volume peaks of figure 3 have disappeared while others have become more prominent and new ones have appeared. The changes

TABLE 2.—*Analysis of large-volume fractions of figure 4*

Approx. boiling range	Chief class of constant boiling fraction present [1]	Nature of constituents	Names of chief constituents	Method of separation or detection
°C				
79 to 81	b	Naphthenic Paraffinic	Cyclohexane 2,2-Dimethylpentane	Crystallization.
87 to 89	a	Naphthenic	1,1-Dimethylcyclopentane	Do.
90 to 92	b	Naphthenic Paraffinic	1,2-Dimethylcyclopentane 1,3-Dimethylcyclopentane 3-Methylhexane	Suspected from refractive index curve; 3-methylhexane detected by refractive index and chlorosulfonic acid treatment.
103 to 106	b	Naphthenic Paraffinic	Ethylcyclopentane 2,2,3,3-Tetramethylbutane	Suspected from volume of distillate and refractive-index curve.
109 to 111	b	Naphthenic Paraffinic	1,2,4-Trimethylcyclopentane. 2,5-Dimethylhexane 2,4-Dimethylhexane 2,2,3-Trimethylpentane	Do.
117 to 122	b	Paraffinic Naphthenic	3,4-Dimethylhexane 4-Methylheptane 3-Methylheptane Cycloheptane *m*-Dimethylcyclohexane *p*-Dimethylcyclohexane	Crystallization with solvent or suspected from volume of distillate and refractive-index curve.
123 to 127	b	Paraffinic Naphthenic	(*n*-Octane) 2,2,5-Trimethylhexane 1-Methyl-2-ethylcyclopentane. *o*-Dimethylcyclohexane	Suspected from volume of distillate and refractive index.
130 to 132	b	Naphthenic	Ethylcyclohexane *n*-Propylcyclopentane	Crystallization with solvent; the cyclopentane suspected from refractive index and behavior on freezing.
134 to 137	b	Paraffinic Naphthenic	2,4-Dimethylheptane 2,5-Dimethylheptane Nonanaphthene 1, 3, 5-Trimethylcyclohexane.	Nonanaphthene isolated by crystallization; others detected after subsequent fractionation.
140 to 145	b	Paraffinic Naphthenic	2-Methyloctane 3-Methyloctane 4-Methyloctane 1, 2, 4-Trimethylcyclohexane.	Detected from volume of distillate, refractive-index curve, and subsequent fractionation.

[1] a, indicates a substantially pure substance; b, an ideal solution of 2 or more hydrocarbons having nearly identical boiling points; c, an azeotropic (minimum or maximum boiling) mixture.

[5] Portions of this graph have been published in earlier papers [5, 6, 11, 12].

in slope in certain portions of the refractive-index curve have also become more marked because of the closer fractionation which could be obtained on the now less complex mixture. In the absence of aromatics these changes in refractive index become significant in predicting the presence of naphthenes and paraffins. The amounts of these predicted hydrocarbons were calculated by dividing the volume of the distillate boiling in a given temperature range between the naphthenes and paraffins in the ratio indicated by its refractive index.

Table 2 summarizes the results of a study of the large-volume fractions appearing in figure 4. Below 75° C the material has been completely identified and between 98 and 100° C all the material has been attributed to *n*-heptane and methylcyclohexane (7). Any other constituents in these boiling ranges were in such small quantities that their detection was considered impracticable. It will be observed that after the removal of the aromatic constituents, no pronounced tendency to form azeotropic mixtures was detected. All the large-volume fractions, except that at 87 to 89° C, have been explained by the presence of true solutions of hydrocarbons whose boiling points lie close together. This single exception was probably of the same type [6], in which other constituents were present in quantities too small to be detected.

V. STUDY OF THE COMPOSITION OF THE FRACTION BOILING BETWEEN 55 AND 145° C

Figure 5 is a chart of all the hydrocarbons obtained in the two stages of fractional distillation and special treatments to which the material was subjected. Tables 3, 4, and 5 list these hydrocarbons, with their estimated amounts, in their respective classes (paraffin, naphthene, and aromatic). An attempt has been made to estimate the quantities of the hydrocarbons present as percentages of the total volume, but the losses which have occurred prevent close estimates. The percentages can be compared among themselves, assuming that the content of each constituent has been estimated with the same degree of accuracy. When the entire fraction has been worked out, it will be possible to adjust the values of percentage content to represent more nearly the actual amounts. Meanwhile the figures are reported unadjusted so that they will remain consistent with the values of percentages already published. Table 3 shows that of the paraffin constituents, which account for about 33 percent of the total volume, the 3 normal ones form about 17 percent, 10 monomethyl derivatives 12 percent, 7 dimethyl derivatives 2.3 percent, and other types 1.7 percent. Similarly table 4 shows that 9 cyclopentanes form about 7.5 percent, 8 cyclohexanes 8.5 percent, and cycloheptane 1.0 percent. Table 5 shows that benzene constitutes 0.6 percent, while its monomethyl derivative (toluene) amounts to 2.2 percent, and the ethyl and dimethyl derivatives to 2.5 percent.

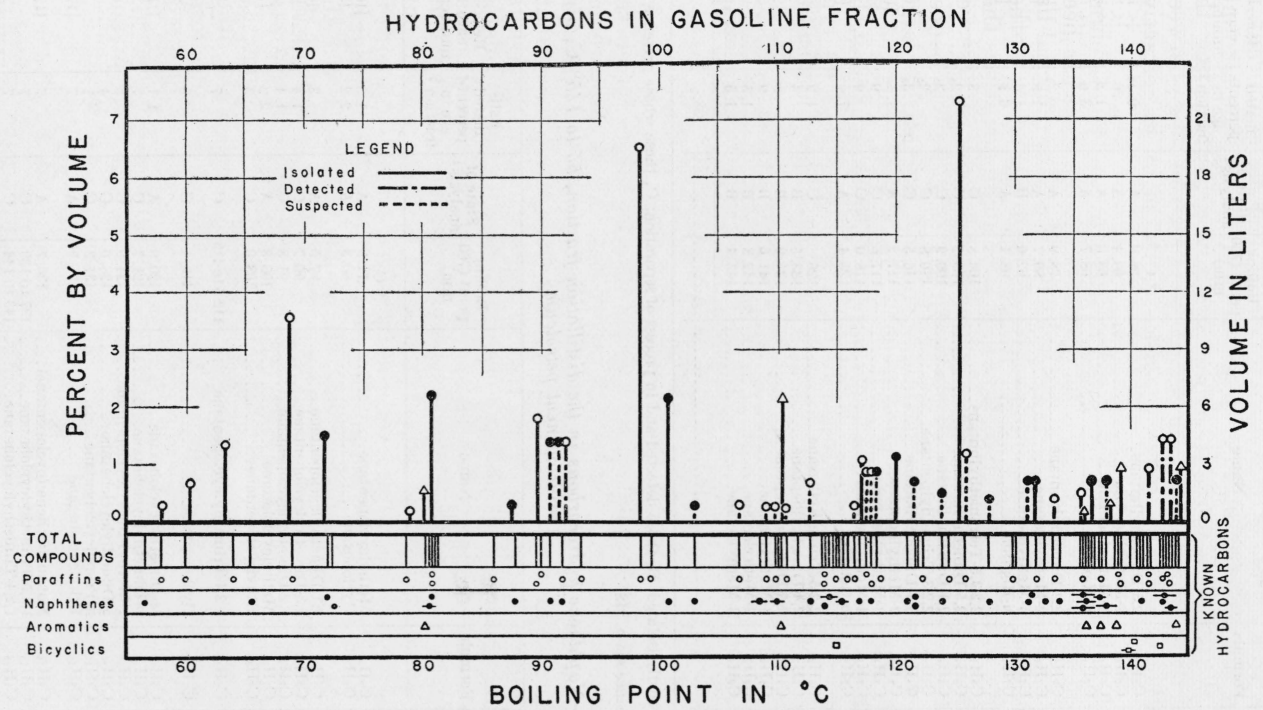

FIGURE 5.—*Composite graph of all the hydrocarbons isolated from or suspected in the fraction of petroleum boiling between 55 and 145° C after the two stages of distillation shown in figures 3 and 4.*

[The representation of data is similar to that in figures 3 and 4.]

TABLE 3.—*Paraffin hydrocarbons in the distillation fraction, 55 to 145° C, of a midcontinent petroleum*

No.	Formula	Name	Boiling point (760 mm)	State of analysis [1]	Estimated percentage in fraction [2]	Reference number
			°C			
1	C_6H_{14}	2,3-Dimethylbutane	58.0	A	0.3	[4, 13]
2	C_6H_{14}	2-Methylpentane	60.4	A	.6	[4, 13]
3	C_6H_{14}	3-Methylpentane	63.3	A	1.3	[4, 13]
4	C_6H_{14}	*n*-Hexane	68.7	A	3.6	[4, 13]
5	C_7H_{16}	2,2-Dimethylpentane	78.9	A	.2	[14]
6	C_7H_{16}	2-Methylhexane	89.7	A	1.8	[6]
7	C_7H_{16}	3-Methylhexane	92.0	B	1.4	
8	C_7H_{16}	*n*-Heptane	98.4	A	6.5	[7]
9	C_8H_{18}	2,2,3,3-Tetramethylbutane	106.8	C	.3	
10	C_8H_{18}	2,5-Dimethylhexane	109.2	C	.2	
11	C_8H_{18}	2,4-Dimethylhexane	109.9	C	.2	
12	C_8H_{18}	2,2,3-Trimethylpentane	110.8	C	.2	
13	C_8H_{18}	3,4-Dimethylhexane	116.5	C	.3	
14	C_8H_{18}	2-Methylheptane	117.2	A	1.1	[15]
15	C_8H_{18}	3-Methylheptane	117.6	C	.9	
16	C_8H_{18}	4-Methylheptane	118.0	C	.9	
17	C_8H_{18}	*n*-Octane	125.4	A	7.3	[8]
18	C_9H_{20}	2,2,5-Trimethylhexane	126	C	1.2	
19	C_9H_{20}	2,4-Dimethylheptane	133.5	B	.4	
20	C_9H_{20}	2,5-Dimethylheptane	135.9	B	.5	
21	C_9H_{20}	4-Methyloctane	141.6	B	.9	
22	C_9H_{20}	2-Methyloctane	142.8	B	1.5	
23	C_9H_{20}	3-Methyloctane	143.4	B	1.5	
Total					33.3	

[1] A, those actually isolated; B, those detected and in process of separation; C, those whose presence is suspected.
[2] For significance see p. 218.

TABLE 4.—*Naphthene hydrocarbons in the distillation fraction, 55 to 145° C, of a midcontinent petroleum*

No.	Formula	Name	Boiling point (760 mm)	State of analysis [1]	Estimated percentage in fraction [2]	Reference number
			°C			
1	C_6H_{12}	Methylcyclopentane	71.8	A	1.5	[16]
2	C_6H_{12}	Cyclohexane	80.8	A	2.2	[5]
3	C_7H_{14}	1,1-Dimethylcyclopentane	87.5	A	.3	[6]
4	C_7H_{14}	1,3-Dimethylcyclopentane	90.7	C	1.4	
5	C_7H_{14}	1,2-Dimethylcyclopentane	91.8	C	1.4	
6	C_7H_{14}	Methylcyclohexane	100.8	A	2.2	[7]
7	C_7H_{14}	Ethylcyclopentane	103.0	C	.3	
8	C_8H_{16}	1,2,4-Trimethylcyclopentane	112.5 to 113	C	.7	
9	C_7H_{14}	Cycloheptane	118.1	C	.9	
10	C_8H_{16}	*m*-Dimethylcyclohexane	120.0	A	1.1	[11]
11	C_8H_{16}	*p*-Dimethylcyclohexane	121.7	C	.7	
12	C_8H_{16}	1-Methyl-2-ethylcyclopentane	124.0	C	.5	
13	C_8H_{16}	*o*-Dimethylcyclohexane	128.0	C	.4	
14	C_8H_{16}	*n*-Propylcyclopentane	131.3	C	.7	
15	C_8H_{16}	Ethylcyclohexane	131.9	A	.7	[17]
16	C_9H_{18}	Nonanaphthene (cyclopentane)	136.7	A	.7	[12]
17	C_9H_{18}	1,3,5-Trimethylcyclohexane	137 to 139	C	.7	
18	C_9H_{18}	1,2,4-Trimethylcyclohexane	143 to 144	C	.7	
Total					17.1	

[1] A, those actually isolated; C, those whose presence is suspected.
[2] For significance see p. 218.

TABLE 5.—*Aromatic hydrocarbons in the distillation fraction, 55 to 145° C, of a midcontinent petroleum*

No.	Formula	Name	Boiling point (760 mm)	State of analysis [1]	Estimated percentage in fraction [2]	Reference numbers
			° C			
1	C_6H_6	Benzene	80.2	A	0.6	[4]
2	C_7H_8	Toluene	110.5	A	2.2	[10]
3	C_8H_{10}	Ethylbenzene	136.1	A	.2$_0$	[18]
4	C_8H_{10}	*p*-Xylene	138.4	A	.3$_0$	[9]
5	C_8H_{10}	*m*-Xylene	139.2	A	1.0	[9]
6	C_8H_{10}	*o*-Xylene	144.4	A	1.0	[9]
Total					5.3	

[1] A, those actually isolated. [2] For significance, see p. 218.

Table 6 summarizes briefly the data shown in figure 5 and tables 3, 4, and 5. Of the 88 known compounds boiling between 55 and 145° C, only 47 have been isolated from or suspected in the petroleum distilling in this temperature range. Although the 47 compounds are shown to account for only 55 percent of the total volume, actually they probably will comprise nearly all the material. This arises from the fact that losses have necessarily occurred in the long process of distillation and in the development of new methods of separation. Thus, while 49 percent of the distillate under investigation boiled between 55 and 100° C, its analysis, which is virtually completed, accounts for only 25.5 percent. A similar situation will probably be found in the analysis of the fraction boiling between 100 and 145° C. On the assumption that the hydrocarbons which have been isolated or suspected account for practically all of the material, it appears from the values in table 6 that the 22 hydrocarbons already isolated account for two-thirds of the entire volume boiling between 55 and 145° C. It may be predicted from the values also given in table 6 that the paraffins, naphthenes, and aromatics are in the ratio of approximately 6:3:1.

TABLE 6.—*Summary of the isolated, detected, and suspected hydrocarbons in the fraction, 55 to 145° C, of a midcontinent petroleum*

Type	Isolated		Detected or suspected		Total		Known hydrocarbons reported boiling in the range 55 to 145° C
	No.	Estimated percentage in fraction [2]	No.	Estimated percentage in fraction [2]	No.	Estimated percentage in fraction [2]	
Paraffins	9	23.0	14	10.0	23	33.0	41
Naphthenes [1]	7	8.5	11	8.5	18	17.0	37
Aromatics	6	5.3	------	----------	6	5.3	6
Bicycloparaffins	------	----------	------	----------	------	----------	4
Total	22	37	25	18	47	55	88

[1] Monocycloparaffins.
[2] These values have been rounded to 2 figures. For significance, see p. 218.

VI. REPORT OF PROGRESS ON THE ANALYSIS OF THE PETROLEUM DISTILLATE BOILING BETWEEN 145 AND 180° C

Some work has been done on the fraction boiling between 145 and 180° C, but the ratio of the number of compounds isolated to the number known to boil in this range is smaller than that in the fraction boiling between 55 and 145° C. The information available concerning the 145 liters comprising this fraction will therefore be considered only briefly in this paper.

On distilling the material, a number of large-volume fractions resulted. Three of the more predominant ones boiled near 150, 160, and 170° C, respectively. The fraction boiling between 148 and 152° C contained 31 liters, a large portion of which was isolated as *n*-nonane [19]. The material boiling between 168 and 173° C (33.5 liters) contained *n*-decane [20] in amount nearly equal to that of *n*-nonane. Together these 2 normal paraffin hydrocarbons comprise about 28 percent of the total volume distilling between 145 and 180° C. From the material boiling near 160° C, mesitylene [21], and from the fraction, 168 to 173° C, pseudocumene and hemimellitene [21] have been isolated. Together they constitute another 4 percent of the total distillate. The presence of a number of other aromatic hydrocarbons is evident, especially the propylbenzenes and the ethyltoluenes in the material boiling between 150 and 160° C, and perhaps some of the butylbenzenes or methylpropylbenzenes in the material boiling from 170 to 180° C. It appears that a greater proportion of aromatic material will be found in the fraction 145 to 180° C, than in that boiling between 55 and 145° C. In addition to the normal paraffin and aromatic constituents the fraction contains isomeric decanes and napththenes.

Table 7 gives a summary of the constituents found so far in this fraction. All together, the 5 compounds listed are shown to comprise about 32 percent of the material boiling between 145 and 180° C. While this fraction no doubt contains other compounds, the complete analysis of the material will result in the isolation of a much smaller number of hydrocarbons than the 80 reported in the literature to boil within this region.

TABLE 7.—*Hydrocarbons isolated from the 145 to 180° C fraction of a midcontinent petroleum*

No.	Formula	Name	Boiling point (760 mm)	Estimated percentage in the fraction	Reference numbers
			°C		
1	C_9H_{20}	*n*-Nonane	150.7	15.5	[19]
2	$C_{10}H_{22}$	*n*-Decane	174.0	12.5	[20]
3	C_9H_{12}	Mesitylene (1, 3, 5-trimethylbenzene)	164.6	.3	[21]
4	C_9H_{12}	Pseudocumene (1, 2, 4-trimethylbenzene)	169.2	3.	[21]
5	C_9H_{12}	Hemimellitene (1, 2, 3-trimethylbenzene)	176.1	.9	[21]
Total				32.2	

TABLE 8.—*Hydrocarbons isolated*

PARAFFINIC

No.	Formula	Hydrocarbon	Estimated amount in crude [1]	Purity of best sample [1 2]	Reference no.
			Percent	*Mole percent*	
1	CH_4	Methane	a	a	
2	C_2H_6	Ethane	a	a	
3	C_3H_8	Propane	a	a	
4	C_4H_{10}	*n*-Butane	a	a	
5	C_5H_{12}	*n*-Pentane	a	a	
6	C_5H_{12}	2-Methylbutane	a	a	
7	C_6H_{14}	*n*-Hexane	0.5	98.3	[4]
8	C_6H_{14}	2, 3-Dimethylbutane		95	[13]
9	C_6H_{14}	2-Methylpentane	.3	95	[13]
10	C_6H_{14}	3-Methylpentane		95	[13]
11	C_7H_{16}	*n*-Heptane	.9	99.9	[7]
12	C_7H_{16}	2, 2-Dimethylpentane	.03	54	[14]
13	C_7H_{16}	2-Methylhexane	.25	99.9	[6]
14	C_7H_{16}	3-Methylhexane	b	b	
15	C_8H_{18}	*n*-Octane	1.0	99.1	[8]
16	C_8H_{18}	2-Methylheptane	.15	97	[15]
17	C_9H_{20}	*n*-Nonane	1.0	99.9	[19]
18	C_9H_{20}	2-Methyloctane	b	b	
19	C_9H_{20}	2, 5-Dimethylheptane	b	b	
20	$C_{10}H_{22}$	*n*-Decane	.8	99.9	[20]

NAPHTHENIC

21	C_5H_{10}	Cyclopentane	a	a	
22	C_6H_{12}	Methylcyclopentane	0.2	98.9	[16]
23	C_6H_{12}	Cyclohexane	.3	99.9	[5]
24	C_7H_{14}	Methylcyclohexane	.3	99.9	[7]
25	C_7H_{14}	1, 1-Dimethylcyclopentane	.04	95	[6]
26	C_8H_{16}	1, 3-Dimethylcyclohexane	.15	98	[11]
27	C_8H_{16}	Ethylcyclohexane	.1	95	[17]
28	C_9H_{20}	Nonanaphthene	.1	99	[12]

AROMATIC

29	C_6H_6	Benzene	0.08	99.8	[4]
30	C_7H_8	Toluene	.3	a	[10]
31	C_8H_{10}	*p*-Xylene	.04	99.9	[9]
32	C_8H_{10}	*o*-Xylene	.12	99	[9]
33	C_8H_{10}	*m*-Xylene	.12	99.9	[9]
34	C_8H_{10}	Ethylbenzene	.03	94	[18]
35	C_9H_{12}	Hemimellitene } trimethylbenzenes	.06	99.9	[21]
36	C_9H_{12}	Pseudocumene } trimethylbenzenes	.2	99.9	[21]
37	C_9H_{12}	Mesitylene } trimethylbenzenes	.02	99.9	[21]

[1] a, not determined; b, determination in progress.
[2] Values calculated from freezing-point data.

VII. CONCLUSION

At the stage of the work reported in this paper, somewhat more than half of the petroleum fraction distilling between 55 and 180° C has been separated into identified contituents. Of the remaining material boiling below 145° C, the greater part has been accounted for by other constituents, the presence of which is suspected from substantial evidence. Considered as a whole the analysis is less speculative and more complete than any similar work previously attempted. Such exact information concerning the individual constituents is not obtainable by the study of the distillation fractions alone but only by the actual isolation of identified compounds. All the hydrocarbons which have been isolated thus far from the petroleum, and upon which this report is based, are given in table 8, together with their estimated purity and percentage content in the crude oil.

In the course of separating the individual hydrocarbons it has been necessary to develop methods which may be utilized on a larger scale for the production of these chemical individuals from petroleum. The analysis has resulted in information which makes it possible to predict the occurrence in similar crude oils of individual hydrocarbons whose presence accounts for the properties of the commercial products of petroleum.

The problem of analyzing the naphtha fraction of petroleum appears at the outset to be one of extreme difficulty. Actually, as more effective methods for the separation are developed and fewer compounds remain to be isolated, the nature of the work becomes less tedious. However, much remains to be done and much additional information will be available when the final report is made.

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WASHINGTON, May 31, 1935.