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HYDROCARBONS IN THE GASOLINE FRACTION OF SEVEN REPRESENTATIVE CRUDES, INCLUDING ALL THE DISTILLATE TO 102° C AND THE AROMATICS TO 160° C[1, 2]

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ABSTRACT

This paper is the second report of an investigation on the analysis of the gasoline fraction of representative crude petroleums by the API Research Project 6 at the National Bureau of Standards. The samples for analysis were selected so as to cover the largest possible range in composition; included one high in aromatics, one high in isoparaffins, one high in normal paraffins, and one high in naphthenes (cycloparaffins); and came from the following fields: Ponca, Okla.; East Texas; Bradford, Pa.; Greendale-Kawkawlin, Mich.; Winkler, Tex.; Midway, Calif.; Conroe, Tex. The fractionating processes of adsorption and distillation were used in the analysis.

Data are given on the amounts of the individual hydrocarbons (paraffins and naphthenes, 40° to 102° C, and aromatics to 160° C) in the gasoline fraction of the seven naphthas. A number of conclusions have been drawn from the data.

CONTENTS

[1] This investigation is part of the work of Research Project 6 of the American Petroleum Institute, from whose research fund financial assistance has been received.

[2] Presented on November 10, 1943, before the Division of Refining of the American Petroleum Institute at its annual meeting in Chicago, Ill.

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I. INTRODUCTION

A year ago the API Research Project 6 reported a description of a method for analyzing the gasoline fraction of petroleum, with preliminary results on East Texas and Oklahoma crudes [1].* This was the first report on an investigation of the hydrocarbons in the gasoline fraction of a number of representative crudes, selected so as to cover the largest possible range in composition.

The present paper is the second report on this investigation and gives the results obtained on the hydrocarbons in the gasoline fraction of seven different naphthas, covering the paraffins and naphthenes to 102° C and the aromatics to 160° C. Subsequent reports will deal with the paraffin and naphthene hydrocarbons above 102° C and the aromatics above 160° C.[4]

II. NAPHTHAS INVESTIGATED

The Advisory Committee [5] for the API Research Project 6 drew up the following specifications for the naphthas to be investigated:

The gasoline fraction should be the straight-run cut, preferably from large-scale operation or at least obtained by fractionation comparable to refinery fractionation. The 90-percent point should be near 350° F (177° C). The material should be washed with caustic to remove hydrogen sulfide. The sample should contain its full proportion of hexanes but should preferably be debutanized. Each contributor should provide 15 gallons of the product, of which 5 gallons should be sent to Project 6 at the National Bureau of Standards and 10 gallons should be retained in safe storage by the supplier.

The seven naphthas selected by the Advisory Committee for investigation are shown in table 1, which gives the field from which the crude was produced, the general type of the naphtha, and the company supplying the sample. As may be seen from the table, the naphthas include two which are classed as intermediate, one high in paraffins, one high in normal paraffins, one high in isoparaffins, one high in naphthenes, and one high in aromatics. The intermediate naphtha labeled Ponca, Okla. is from the original Midcontinent petroleum that was under investigation by the API Research Project 6 for many years and from which a total of 69 pure hydrocarbons have been isolated from the gas, gasoline, and kerosine fractions [2].

TABLE 1.—*Source and general type of the naphthas investigated*

Field	Type	Supplier
Ponca, Okla	Intermediate	Continental Oil Co.
East Texas	do	Standard Oil Development Co.
Bradford, Pa	High in paraffins	Quaker State Oil Refining Co.
Greendale-Kawkawlin, Mich	High in normal paraffins	Pure Oil Co.
Winkler, Tex	High in isoparaffins	Standard Oil Co. (Indiana).
Midway, Calif	High in naphthenes	Standard Oil Co. of California.
Conroe, Tex	High in aromatics	Humble Oil & Refining Co.

*Figures in brackets indicate the literature references at the end of this paper.

[4] For reports of previous investigations on hydrocarbons in straight-run gasolines, the reader is referred a number of papers published by Fenske and associates from the Petroleum Refining Laboratory of the Pennsylvania State College [6, 7, 8, 9, 10].

[5] J. Bennett Hill, Sun Oil Co., chairman; Wm. J. Sweeney, Standard Oil Development Co., Seymour W. Ferris, The Atlantic Refining Co.; Albert E. Miller, Technical Advisory Committee, Petroleum Industry War Council.

III. GENERAL DESCRIPTION OF THE METHOD

As previously reported [1], the method of analysis consists essentially in applying the fractionating processes of adsorption and distillation to the naphtha fraction. The process of adsorption is used to separate a given sample of a gasoline fraction into two portions, one containing all the paraffin and naphthene hydrocarbons and the other containing all the aromatic hydrocarbons, together with the nonhydrocarbon components. From the latter portion, the small amount of nonhydrocarbon components (principally sulfur compounds) are separated by further adsorption to give a clean aromatic portion. Then the paraffin-naphthene portion and the clean aromatic portion are separately subjected to an analytical distillation at a high reflux ratio in columns of high efficiency and low holdup.

It is well known that a mixture of aromatic hydrocarbons with paraffins and naphthenes constitutes a nonideal mixture, and that the distillation of such a mixture yields quite unsatisfactory results, primarily because aromatic hydrocarbons in mixtures with paraffins and naphthenes have much greater partial pressures at a given temperature and concentration than are called for by the ideal solution laws, and hence always concentrate in the distillate at temperatures appreciably below their normal boiling points. On the other hand, a mixture of paraffins and naphthenes (cycloparaffins) is substantially ideal, and likewise a mixture of aromatic hydrocarbons is substantially ideal. The separate distillation of these two mixtures yields results which are quite satisfactory. This is a great advantage of the present method of analysis.

The separation of the naphtha into a paraffin-naphthene portion and an aromatic portion by the process of adsorption requires only 1 or 2 days, depending upon the quantity of aromatics to be separated. On the other hand, as previously reported [1], the analytical distillation of the two separate portions may be made to require as little as 2 or 3 days or as much as 2 or 3 months, depending on the extent to which the resolution by distillation is to be carried.

IV. PROCEDURE OF THE PRESENT INVESTIGATION

The procedure followed in the analysis of the seven naphthas is given hereinafter.

1. DETERMINATION OF THE AMOUNTS OF AROMATIC AND SULFUR COMPOUNDS

The sulfur content of the naphthas as received was determined by the ASTM lamp method under the supervision of R. C. Hardy in the Lubrication and Liquid Fuels Section of this Bureau.

The amount of sulfur compounds, in percentage by volume, was calculated from the percentage by weight of sulfur, using the factor 3.7. This factor was obtained by assuming that each sulfur compound has one atom of sulfur per molecule, that the average molecular weight of the sulfur compounds is 130, and that the average density of the sulfur compounds is 0.83.

The aromatic content of each naphtha as received was determined by the method of analysis by adsorption [1, 3] recently developed by the API Research Project 6 at this Bureau.

2. SEPARATION OF THE NAPHTHA INTO A PARAFFIN-NAPHTHENE PORTION AND AN AROMATIC PORTION

The process of adsorption used in the present investigation to separate and recover the aromatic hydrocarbons from the paraffins and naphthenes is discussed in the first report [1, 4]. The quantity of sample was selected so as to produce not less than about 500 ml of a clean aromatic portion nor less than about 3,500 ml of a paraffin-naphthene portion.

3. ANALYTICAL DISTILLATIONS

The analytical distillations of the seven aromatic portions and the seven paraffin-naphthene portions were performed at a high reflux ratio in columns of high separating efficiency and low holdup [1]. Fractions were collected in amounts ranging from about 6 to 7½ ml, thus producing about 550 fractions from each paraffin-naphthene portion and nearly 100 fractions from each aromatic portion, or a total of about 650 fractions from each naphtha and about 4,500 fractions from all seven naphthas. From each distillation, which was performed as previously reported [1] at a controlled pressure of 770 mm Hg, a record was obtained giving the boiling point as a function of the volume of distillate.

4. EXAMINATION OF THE FRACTIONS OF DISTILLATE

For each fraction of distillate, measurement was made of the refractive index, n_d, at 25° C. From these data, a plot was made giving the refractive index of the distillate as a function of its volume. Over the range from about 75° to 95° C, several successive fractions were combined for measurement of the density. The latter data with the refractive index yielded a plot of refractivity intercept, $n-d/2$, as a function of volume, for the range 75° to 95° C.

5. DETERMINATION OF THE INDIVIDUAL PARAFFINS AND NAPHTHENES

The individual paraffin and naphthene hydrocarbons in the range 40° to 102° C. were determined as follows:

Cyclopentane, 2,2-dimethylbutane.—The sum of these two components was determined from the boiling point-volume plot, and the relative amounts of the two components from the refractive index-volume plot. Combination of these data gave values for the two components individually.

2,3-Dimethylbutane, 2-methylpentane, 3-methylpentane, n-hexane, methylcyclopentane.—Each of these components was determined individually, using both the boiling point-volume and the refractive-index–volume plots.

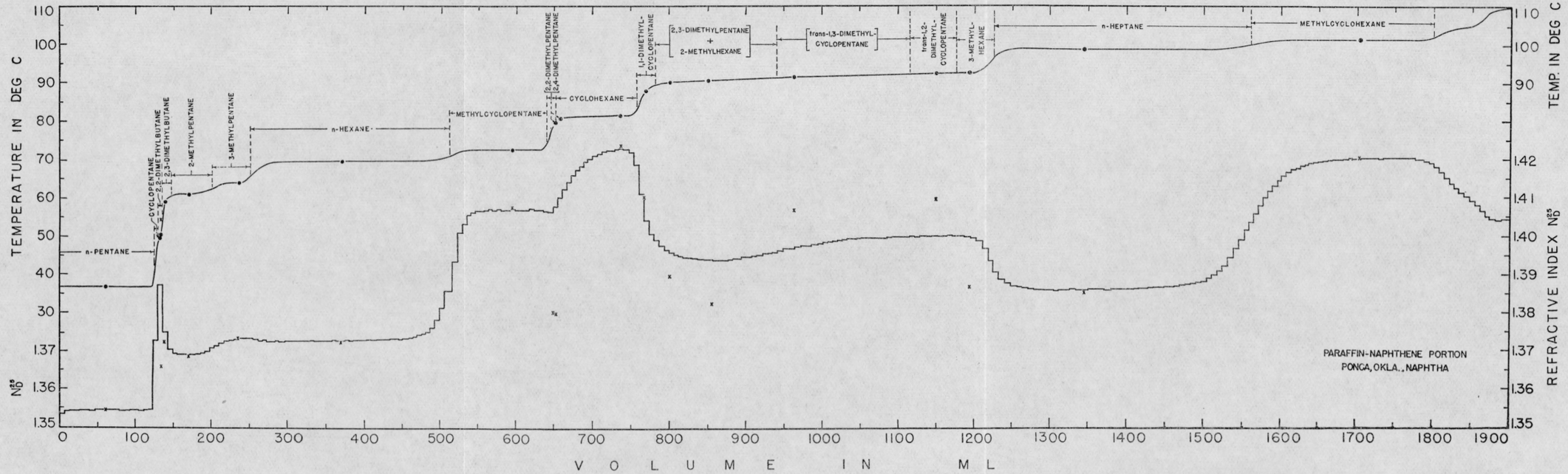

FIGURE 1.—*Plot of the boiling point and refractive index as a function of volume for the distillate, to 102° C, from the analytical distillation of the paraffin-naphthene portion of the Ponca, Okla. naphtha.*

The scale of ordinates on the left gives the boiling point at 770 mm Hg in degrees centigrade and that on the right the refractive index, n_D, at 25° C. The scale of abscissas gives the volume of distillate in milliliters. The solid circles and crosses give the boiling points and refractive indices, respectively, of the indicated pure components.

See figure 1 for explanations of curves and symbols.

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2,2-Dimethylpentane plus 2,4-dimethylpentane, cyclohexane.—The sum of these three components was determined from the boiling-point–volume plot. The relative amount of the paraffins to the naphthene was determined from the refractivity-intercept–volume and refractive-index–volume plots. These two lots of data yielded the amount of cyclohexane and the sum of the two dimethylpentanes.

1,1-Dimethylcyclopentane, 2,3-dimethylpentane plus 2-methylhexane, trans-1,3-dimethylcyclopentane, trans-1,2-dimethylcyclopentane, 3-methylhexane.—The sum of these six components was determined from the boiling-point–volume plot. The relative amounts of the three paraffins and the three naphthenes was determined from the refractivity-intercept–volume plot. The amount of 1,1-dimethylcyclopentane was estimated from the boiling-point–volume plot. The sum of the first four components and the sum of the last two components were estimated from the boiling-point–volume and refractivity-intercept–volume plots. The relative amounts of trans-1,2-dimethylcyclopentane and 3-methylhexane were estimated from the refractive-index–volume and refractivity-intercept–volume plots. These five lots of data serve to solve for the individual amounts of four hydrocarbons and the sum of two hydrocarbons, as indicated.

n-Heptane, methylcyclohexane.—Each of these components was determined individually from the boiling-point–volume and refractive-index–volume plots.

6. DETERMINATION OF THE INDIVIDUAL AROMATIC COMPONENTS

The individual aromatic components to 160° C were determined as follows:

Benzene, toluene.—Each of these components was determined individually from the boiling-point–volume plot.

Ethylbenzene, p-xylene, m-xylene, o-xylene.—The sum of the four C_8 aromatics was determined from the boiling-point–volume plot. The amount of *o*-xylene was determined from the boiling-point–volume plot. The fractions containing all the ethylbenzene and *p*-xylene were combined, including the material from 111° to 150° C, and the amounts of ethylbenzene and of *p*-xylene in this mixture were determined[6] individually by the method of measurement of freezing points recently developed by the API Research Project 6 at this Bureau [5]. The amount of *m*-xylene was obtained by difference.

Isopropylbenzene, n-propylbenzene.—Each of these components was determined individually from the boiling-point–volume plot.[7]

[6] These determinations were made by A. J. Streiff, Research Fellow on the API Research Project 6 at this Bureau.

[7] The other C_9 aromatics normally boil above 160° C and will be discussed in a later report.

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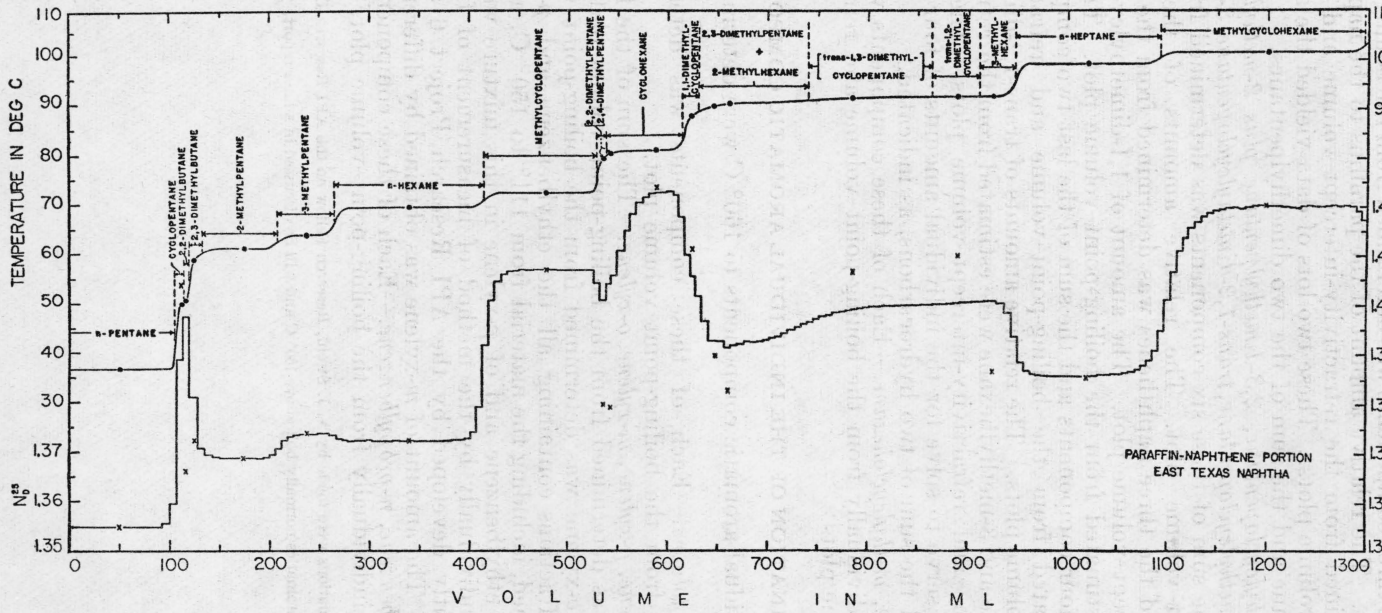

FIGURE 2.—*Plot of the boiling point and refractive index as a function of volume for the distillate, to 102° C, from the analytical distillation of the paraffin-naphthene portion of the East Texas naphtha.*

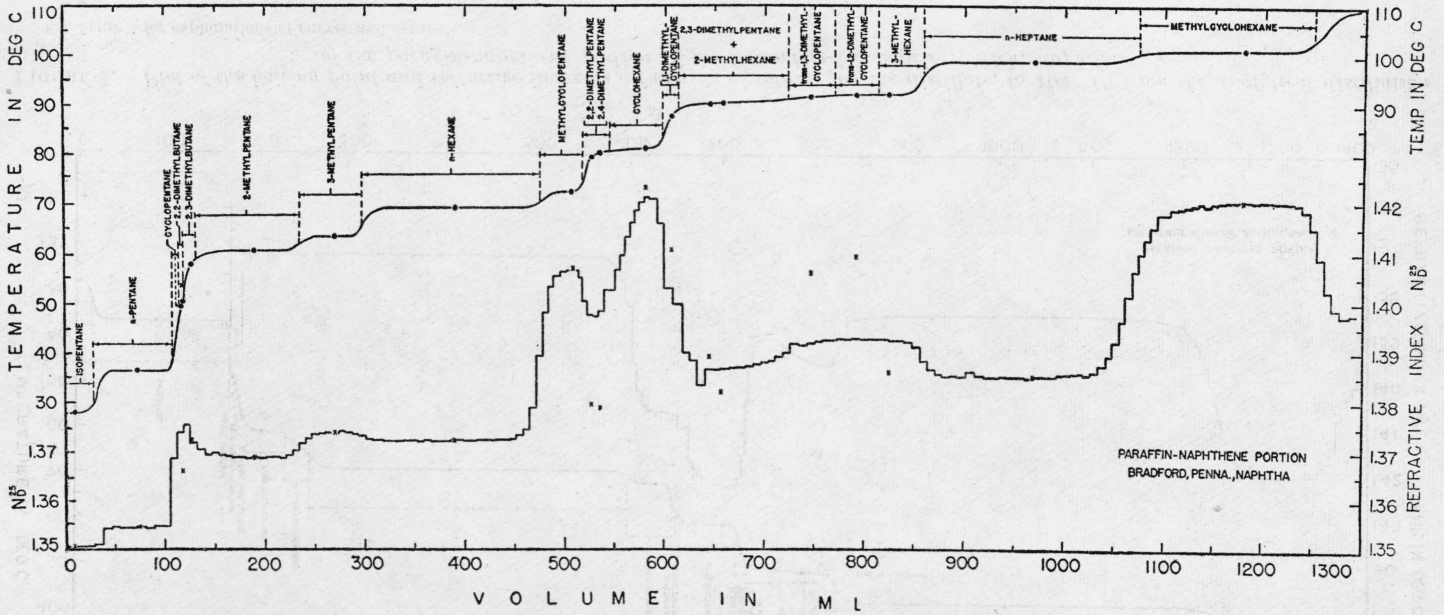

FIGURE 3.—*Plot of the boiling point and refractive index as a function of volume for the distillate, to 102° C, from the analytical distillation of the paraffin-naphthene portion of the Bradford, Pa. naphtha.*

See figure 1 for explanations of curves and symbols.

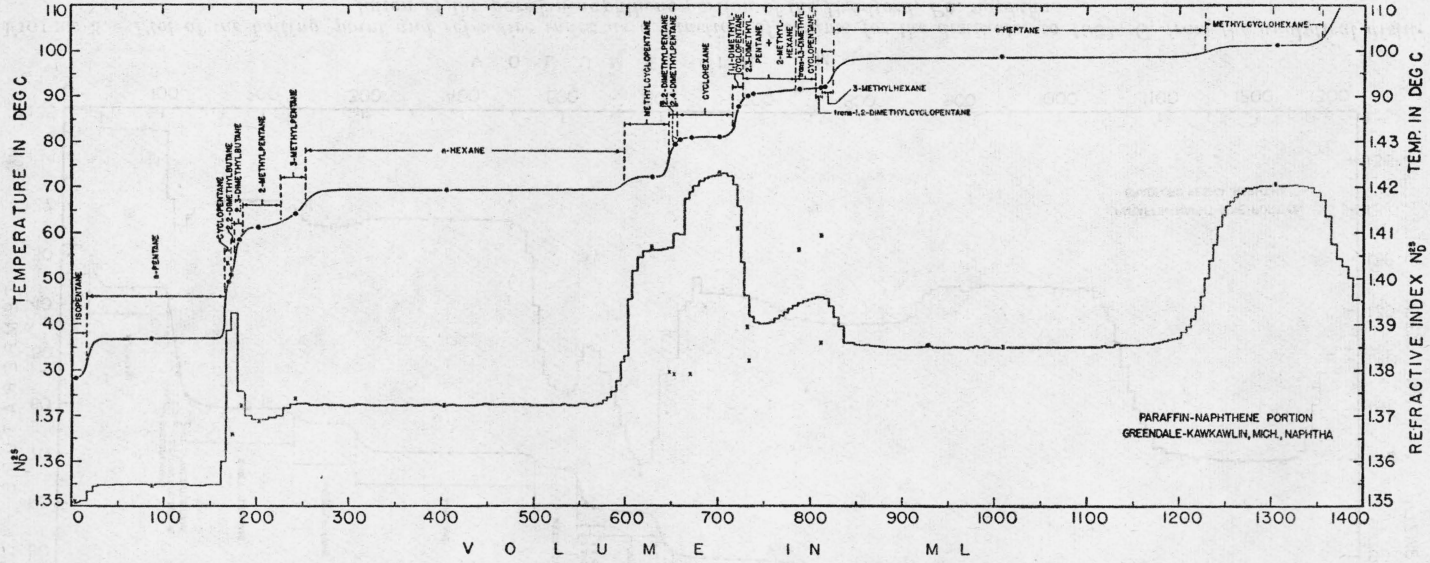

FIGURE 4.—*Plot of the boiling point and refractive index as a function of volume for the distillate, to 102° C, from the analytical distillation of the paraffin-naphthene portion of the Greendale-Kawkawlin, Mich. naphtha.*

See figure 1 for explanations of curves and symbols.

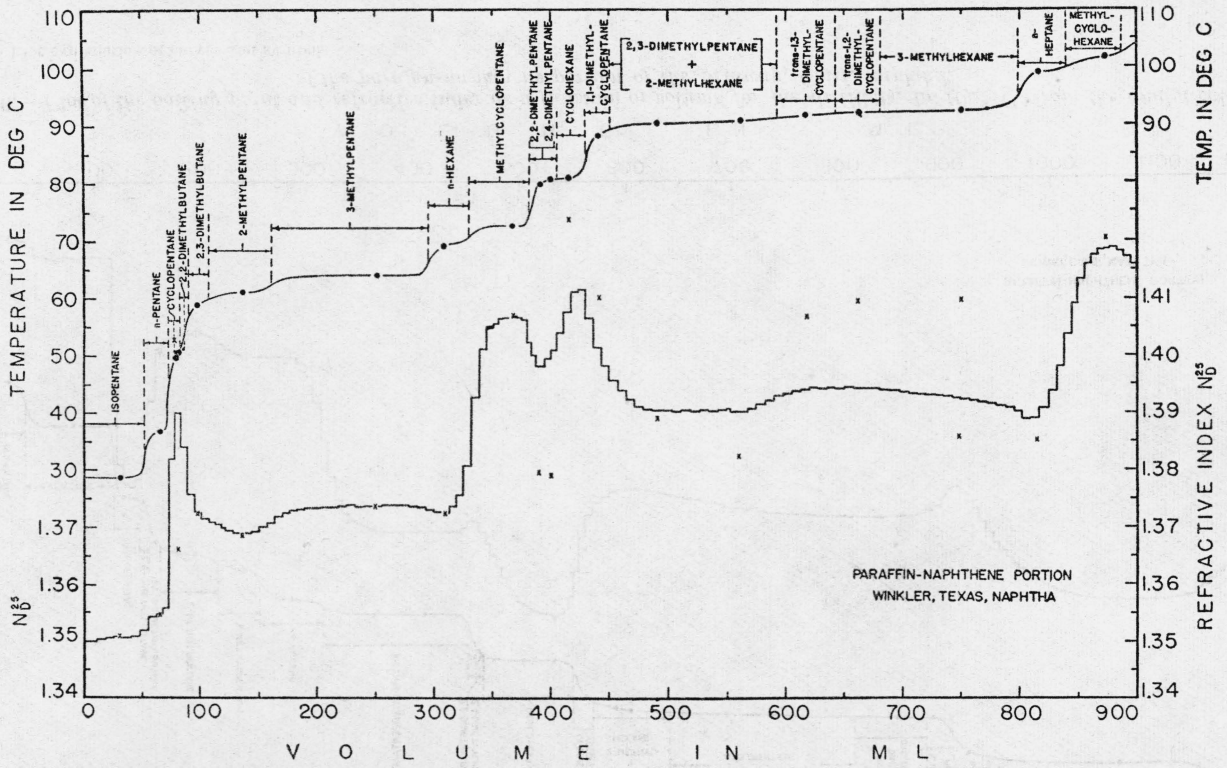

FIGURE 5.—*Plot of the boiling point and refractive index as a function of volume for the distillate, to 102° C, from the analytical distillation of the paraffin-naphthene portion of the Winkler Tex. naphtha.*

See figure 1 for explanations of curves and symbols.

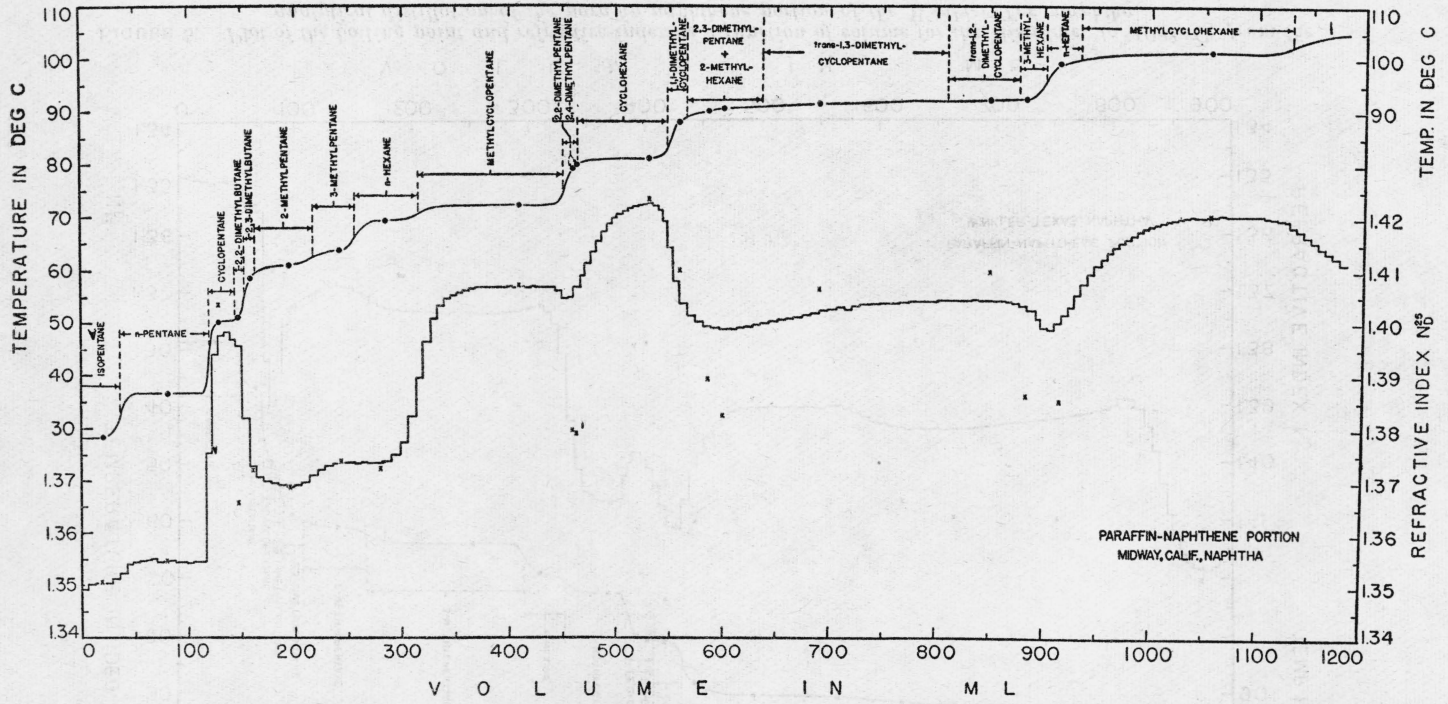

FIGURE 6.—*Plot of the boiling point and refractive index as a function of volume for the distillate, to 102° C, from the analytical distillation of the paraffin-naphthene portion of the Midway, Calif. naphtha.*

See figure 1 for explanation of curves and symbols.

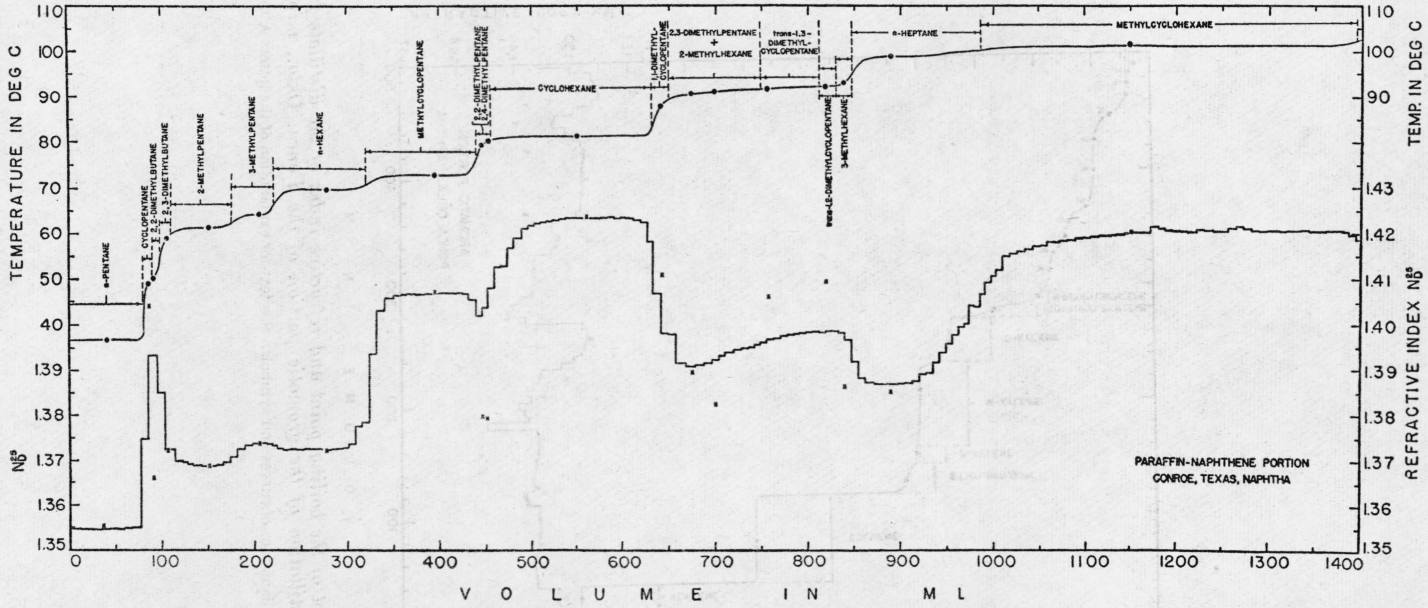

FIGURE 7.—*Plot of the boiling point and refractive index as a function of volume for the distillate, to 102° C, from the analytical distillation of the paraffin-naphthene portion of the Conroe, Tex. naphtha.*

See figure 1 for explanations of curves and symbols.

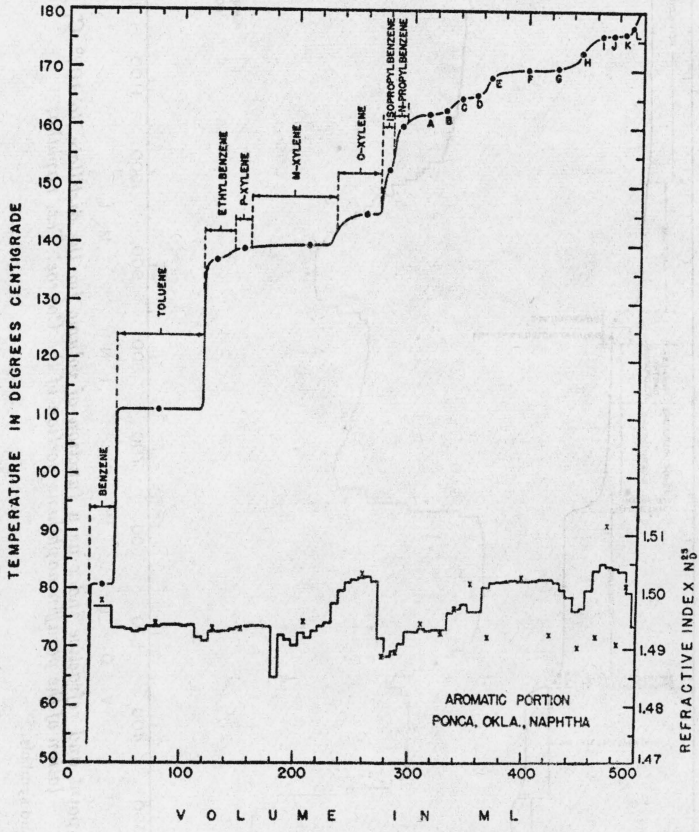

FIGURE 8.—*Plot of the boiling point and refractive index of the distillate from the analytical distillation of the aromatic portion of the Ponca, Okla., naphtha.*

See figure 1 for explanations of curves and symbols. See text for explanation of the letters A to L.

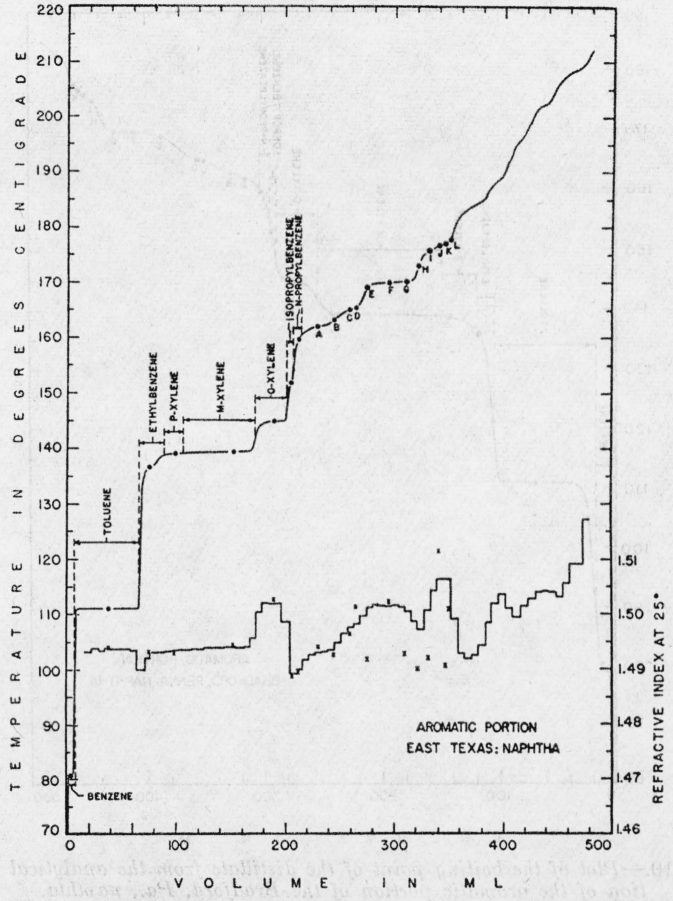

FIGURE 9.—*Plot of the boiling point and refractive index of the distillate from the analytical distillation of the aromatic portion of the East Texas naphtha.*

See figure 1 for explanations of curves and symbols. See text for explanation of the letters A to L.

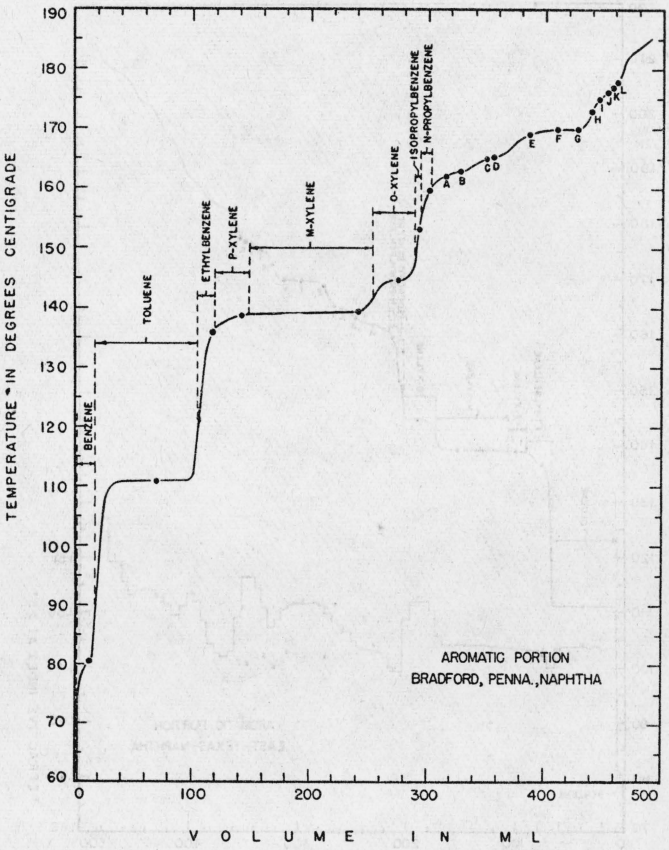

FIGURE 10.—*Plot of the boiling point of the distillate from the analytical distillation of the aromatic portion of the Bradford, Pa., napthta.*

The scale of ordinates gives the boiling point at 770 mm Hg in degrees centigrade. The scale of abscissas gives the volume of distillate in ml. The solid circles give the boiling points of the indicated pure components. See text for explanation of letters A to L.

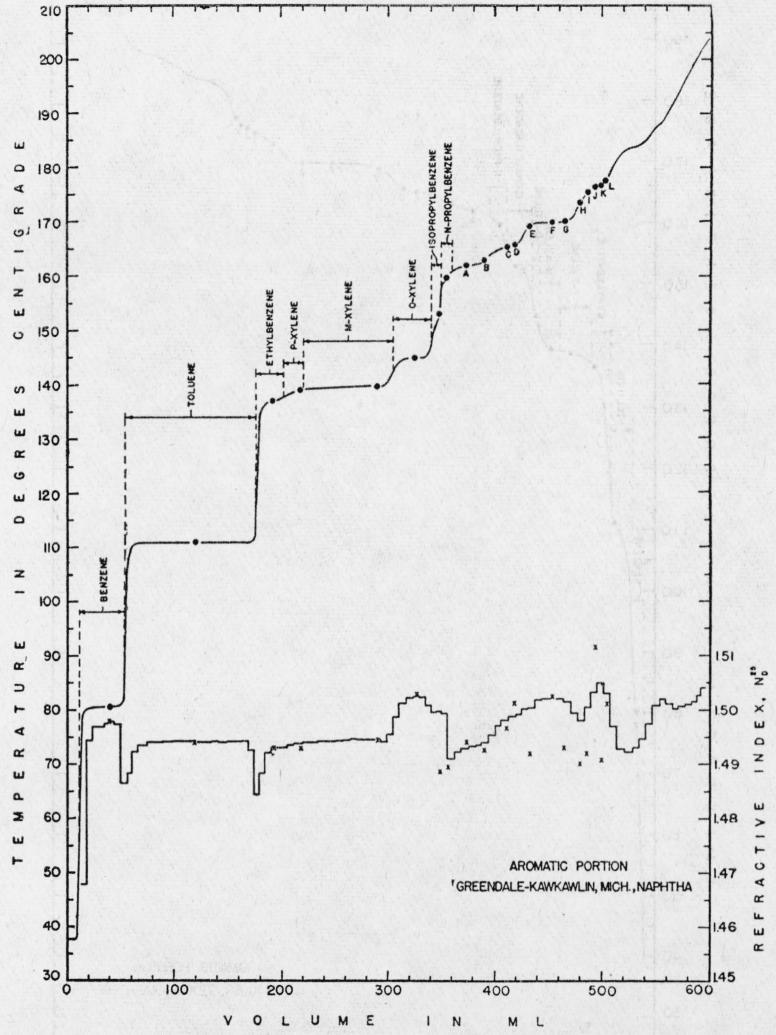

FIGURE 11.—*Plot of the boiling point and refractive index of the distillate from the analytical distillation of the aromatic portion of the Greendale-Kawkawlin, Mich. naphtha.*

See figure 1 for explanations of curves and symbols. See text for explanations of the letters A to L

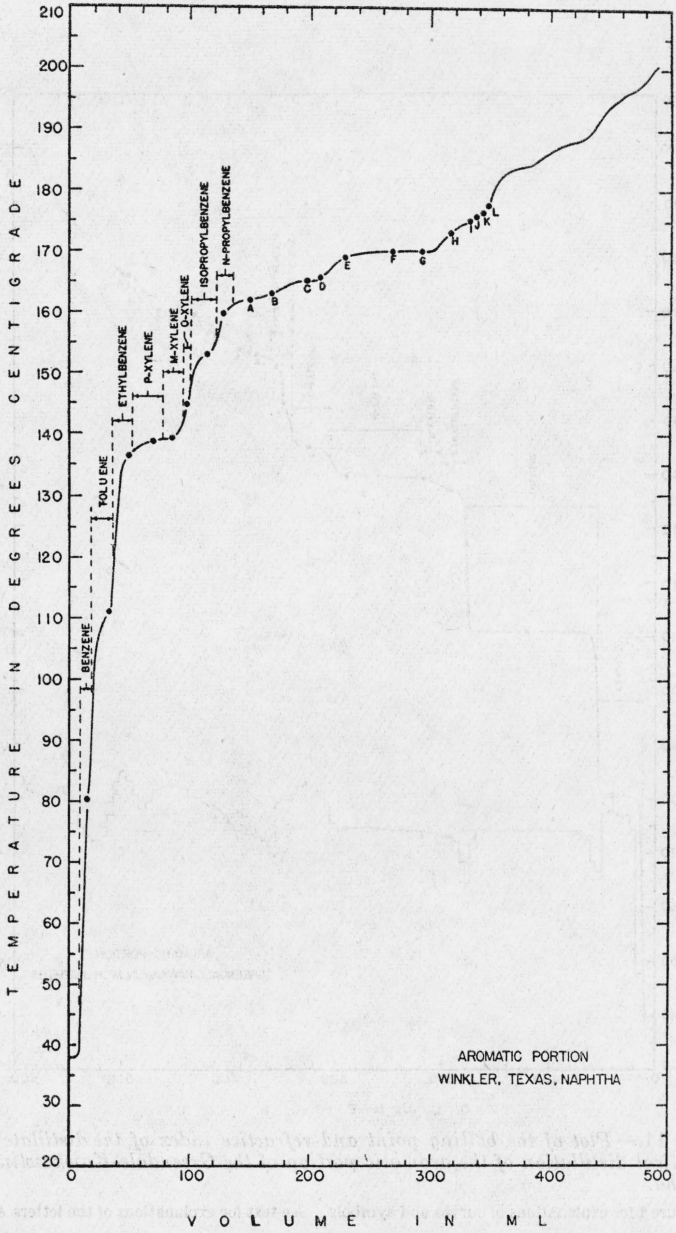

FIGURE 12.—*Plot of the boiling point of the distillate from the analytical distillation of the aromatic portion of the Winkler, Tex. naphtha.*

See figure 10 for explanations of curves and symbols. See text for explanations of the letters A to L.

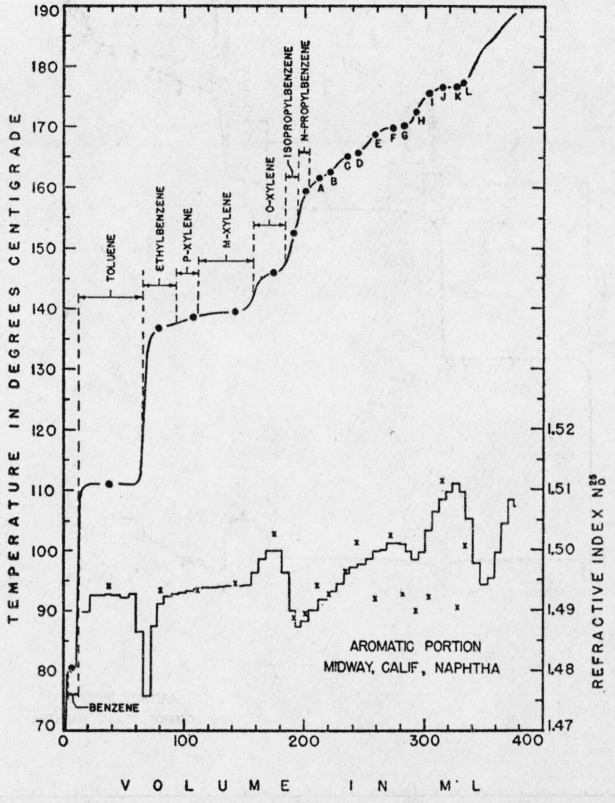

FIGURE 13.—*Plot of the boiling point and refractive index of the distillate from the analytical distillation of the aromatic portion of the Midway, Calif. naphtha.*

See figure 1 for explanations of curves and symbols. See text for explanations of the letters A to L.

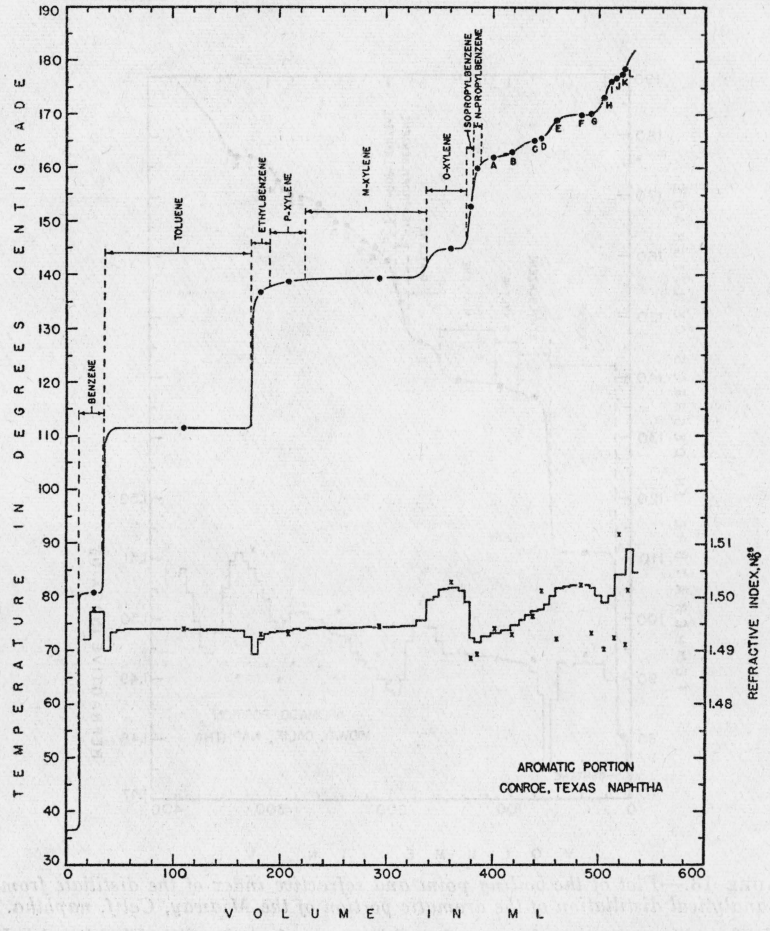

FIGURE 14.—*Plot of the boiling point and refractive index of the distillate from the analytical distillation of the aromatic portion of the Conroe, Tex. naphtha.*

See figure 1 for explanations of curves and symbols. See text for explanations of the letters A to L.

V. ANALYTICAL DATA ON THE SEVEN NAPHTHAS

The analytical data obtained [8] on the seven naphthas are given in figures 1 to 14 and tables 2 to 5.

Table 2 gives the amounts of the aromatic and sulfur compounds in the naphthas as received.

Figures 1 to 7 give, respectively, for the paraffin-naphthene portion of each of the seven naphthas to 102° C, plots of the boiling point and the refractive index of the distillate as a function of its volume. Figures 8 to 14 give, respectively, for the aromatic portion of each of the seven naphthas plots of the boiling point and (except for the Bradford, Pa., and Winkler, Tex., naphthas) the refractive index of the distillate as a function of its volume.

TABLE 2.—*Aromatic and sulfur content of the naphthas as received*

Naphtha	Sulfur content	Sulfur compounds content	Aromatic hydrocarbons content
	% (*by wt*)	% (*by volume*)	% (*by volume*)
Ponca, Okla.	0.017	0.06 ±.03	9.8±.2
East Texas	.033	.12 ±.04	10.4±.2
Bradford, Pa.	.012	.04 ±.02	8.3±.3
Greendale-Kawkawlin, Mich.	.014	.05 ±.02	7.2±.2
Winkler, Tex.	.159	.59 ±.10	4.9±.2
Midway, Calif.	.045	.17 ±.05	8.0±.2
Conroe, Tex.	.002	.007±.005	27.6±.5

TABLE 3.—*Amounts of the individual hydrocarbons in the paraffin-naphthene portion, 40° to 102° C, of the seven naphthas*

Component	Boiling point at 1 atm.	Ponca, Okla.	East Texas	Bradford, Pa.	Greendale-Kawkawlin, Mich.	Winkler, Tex.	Midway, Calif.	Conroe, Tex.	Estimated uncertainty of individual determination
		Percentage, by volume, of the paraffin-naphthene portion, 40° to 102° C							
	° C								±
Cyclopentane	49.26	0.40	0.74	0.57	0.62	1.16	2.39	0.76	0.12
2,2-Dimethylbutane	49.74	.33	.44	.40	.13	0.92	0.81	.61	.12
2,3-Dimethylbutane	57.99	.66	1.09	1.14	.76	2.08	.98	.99	.12
2-Methylpentane	60.27	3.27	6.30	9.10	3.45	6.61	5.50	4.94	.12
3-Methylpentane	63.28	3.03	4.79	5.41	2.27	16.53	3.73	3.42	.12
n-Hexane	68.74	15.79	12.59	15.61	29.06	4.47	6.14	7.59	.10
Methylcyclopentane	71.81	7.60	9.49	3.65	4.04	6.12	13.02	9.11	.10
2,2-Dimethylpentane	79.20	0.83	2.38	2.29	0.76	3.25	1.47	1.29	.20
2,4-Dimethylpentane	80.51								
Cyclohexane	80.74	6.23	4.80	4.75	5.14	2.57	8.10	13.29	.15
(2,2,3-Trimethylbutane)	80.88	------	------	------	------	------	------	------	------
(3,3-Dimethylpentane)	86.06	------	------	------	------	------	------	------	------
1,1-Dimethylcyclopentane	87.5	1.42	1.43	1.41	0.93	2.45	1.87	1.37	.40
2, 3-Dimethylpentane	89.79	9.46	9.23	9.76	4.86	17.67	7.01	7.60	.50
2-Methylhexane	90.05								
trans-1,3-Dimethylcyclopentane	90.8	10.41	10.23	4.00	1.76	6.08	17.05	4.77	.60
trans-1,2-Dimethylcyclopentane	91.9	3.56	4.11	3.76	0.63	4.69	6.66	1.25	.50
3-Methylhexane	91.95	2.87	3.05	4.03	.93	14.55	1.96	1.43	.50
(3-Ethylpentane)	93.47	------	------	------	------	------	------	------	------
(*cis*-1,3-Dimethylcyclopentane)	(?)	------	------	------	------	------	------	------	------
n-Heptane	98.43	19.92	12.13	18.82	34.04	5.02	3.85	10.63	.12
(2,2,4-Trimethylpentane)	99.24	------	------	------	------	------	------	------	------
(*cis*-1,2-Dimethylcyclopentane)	99.3	------	------	------	------	------	------	------	------
Methylcyclohexane	100.93	14.22	17.20	15.30	10.61	5.82	19.46	30.95	.20
Total	------	100.00	100.00	100.00	100.00	100.00	100.00	100.00	------

[8] Eileen D. Mitchell, Laboratory Assistant on the API Project 6 at this Bureau, assisted in measuring refractive indices and preparing the illustrations for this report.

TABLE 4.—*Amounts of the individual aromatic hydrocarbons in the aromatic distillate, to 160° C, for the seven naphthas*

Component	Boiling point at 1 atm	Ponca, Okla.	East Tex.	Bradford, Pa.	Greendale-Kawkawlin, Mich.	Winkler, Tex.	Midway, Calif.	Conroe, Tex.	Estimated uncertainty of individual determination
		Percentage, by volume, of the aromatic portion, to 160° C							
	°C								
Benzene	80.10	8.1	3.3	3.7	12.5	7.1	4.2	6.1	±0.6
Toluene	110.62	27.1	27.4	29.3	35.2	14.2	26.9	36.5	±.5
Ethylbenzene	136.19	9.9	10.7	5.0	7.2	13.0	13.9	4.6	±1.2
p-Xylene	138.35	5.1	7.9	9.7	5.6	19.8	9.2	8.8	±1.2
m-Xylene	139.11	27.1	30.6	35.3	23.9	13.4	22.6	30.2	±2.0
o-Xylene	144.42	14.1	13.9	12.1	10.3	4.8	13.2	10.1	±0.7
*Iso*propylbenzene	152.40	3.8	2.5	1.9	2.6	16.6	5.5	1.6	±.6
n-Propylbenzene	159.22	4.2	3.7	3.0	2.7	11.1	4.5	2.1	±.8
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	

TABLE 5. *Amounts of the individual hydrocarbons (paraffins and naphthenes, 40° to 102° C, and aromatics to 160° C) in the original naphtha (approx.)*

Component	Boiling point at 1 atm	Ponca, Okla.	East Tex.	Bradford, Pa.	Greendale-Kawkawlin, Mich.	Winkler, Tex.	Midway, Calif.	Conroe, Tex.	
		Percentage by volume of the distillate 40° to 180° C							
PARAFFIN AND NAPHTHENE									
	°C								±
Cyclopentane	49.26	0.14	0.28	0.21	0.24	0.30	0.73	0.23	0.05
2,2-Dimethylbutane	49.74	.11	.17	.15	.05	.23	.25	.19	.05
2,3-Dimethylbutane	57.99	.23	.41	.43	.30	.52	.30	.31	.05
2-Methylpentane	60.27	1.12	2.39	3.42	1.34	1.67	1.68	1.53	.05
3-Methylpentane	63.28	1.04	1.82	2.04	0.88	4.18	1.14	1.07	.05
n-Hexane	68.74	5.39	4.78	5.79	11.24	1.13	1.88	2.36	.04
Methylcyclopentane	71.81	2.60	3.61	1.38	1.56	1.55	3.98	2.82	.04
2,2-Dimethylpentane	79.20	0.29	0.91	0.86	0.30	0.83	0.45	0.40	.08
2,4-Dimethylpentane	80.51								
Cyclohexane	80.74	2.13	1.83	1.79	1.99	.61	2.47	4.13	.06
(2,2,3-Trimethylbutane)	80.88								
(3,3-Dimethylpentane)	86.06								
1,1-Dimethylcyclopentane	87.5	0.49	0.55	0.53	0.36	.62	0.57	0.43	.16
2,3-Dimethylpentane	89.79	3.23	3.50	3.67	1.88	4.47	2.14	2.36	.20
2-Methylhexane	90.05								
trans-1,3-Dimethylcyclopentane	90.8	3.55	3.89	1.50	0.68	1.54	5.21	1.48	.25
trans-1,2-Dimethylcyclopentane	91.9	1.22	1.56	1.41	.24	1.19	2.03	0.39	.20
3-Methylhexane	91.95	0.98	1.16	1.51	.36	3.68	0.60	.45	.20
(3-Ethylpentane)	93.47								
(*cis*-1,3-Dimethylcyclopentane)	(?)								
n-Heptane	98.43	6.81	4.61	7.07	13.17	1.27	1.18	3.30	.05
(2,2,4-Trimethylpentane)	99.24								
(*cis*-1,2-Dimethylcyclopentane)	99.3								
Methylcyclohexane	100.93	4.86	6.54	5.75	4.10	1.47	5.95	9.61	.08
AROMATIC									
Benzene	80.10	0.46	0.21	0.19	0.63	0.13	0.20	1.23	0.03
Toluene	110.62	1.53	1.73	1.52	1.77	.26	1.28	7.37	.03
Ethylbenzene	136.19	0.56	0.68	0.26	0.36	.23	0.66	0.93	.06
p-Xylene	138.35	.29	.50	.50	.28	.36	.44	1.78	.06
m-Xylene	139.11	1.53	1.93	1.83	1.20	.24	1.08	6.10	.10
o-Xylene	144.42	0.80	0.88	0.63	0.52	.09	0.63	2.04	.04
Isopropylbenzene	152.40	.21	.16	.10	.13	.30	.26	0.32	.03
n-Propylbenzene	159.22	.24	.23	.16	.14	.20	.21	.42	.04

The letters *A* to *L* in figures 8 to 14 indicate the position, with regard to boiling point, of the 12 possible aromatic hydrocarbons normally boiling between 160° and 180° C, as follows: *A*, 1–methyl-3-ethylbenzene; *B*, 1-methyl-4-ethylbenzene; *C*, 1, 3, 5-trimethylbenzene; *D*, 1-methyl-2-ethylbenzene; *E*, *tert*-Butylbenzene; *F*, 1, 2, 4-trimethylbenzene; *G*, *iso*butylbenzene; *H*, *sec*-butylbenzene; *I*, 1-methyl-3-*iso*propylbenzene; *J*, 1, 2, 3-trimethylbenzene; *K*, 1-methyl-4-*iso*propylbenzene; *L*, 1-methyl-2-*iso*propylbenzene. The analytical data on the aromatics above 160° C are now being studied.

Table 3 gives the amounts of the individual paraffin and naphthene hydrocarbons, 40° to 102° C, in each of the seven naphthas, in terms of the percentage by volume of the paraffin-naphthene portion, 40° to 102° C. The last column gives the estimated uncertainty of an individual determination.

Table 4 gives the amounts of the individual aromatic hydrocarbons to 160° C in each of the seven naphthas, in terms of the percentage by volume of the aromatic portion to 160° C. The last column gives the estimated uncertainty of an individual determination.

Table 5 gives the amounts of the individual hydrocarbons (paraffins and naphthenes, 40° to 102° C, and aromatics to 160° C) expressed in terms of the whole distillate, 40° to 180° C. (This was actually taken as the sum of the volumes of the paraffin-naphthene portion, 40° to 180° C, and of the aromatic portion to 180° C.) The last column gives the estimated uncertainty of an individual determination.

VI. DISCUSSION AND CORRELATION OF THE RESULTS

1. AMOUNTS OF AROMATIC AND SULFUR COMPOUNDS

As seen in table 2, the sulfur content of six of the naphthas is below 0.05 percent by weight, with the seventh naphtha, Winkler, Tex., containing 0.16 percent by weight. The corresponding amounts of sulfur compounds ranges from 0.007 to 0.17 percent by volume for six of the naphthas and is 0.59 percent by volume for the Winkler, Tex. naphtha. For five of the naphthas, the aromatic content ranges from 7.2 to 10.4 percent by volume, whereas the Winkler, Tex. naphtha is 4.9 and the Conroe, Tex. naphtha is 27.6 percent by volume.

2. AMOUNTS OF THE INDIVIDUAL PARAFFIN AND NAPHTHENE HYDROCARBONS, 40° TO 102° C

Table 3 shows that the paraffin-naphthene portions of the seven naphthas contain the same hydrocarbon components, the difference between the several naphthas being in the relative amounts of the components.

There are listed in table 3 the six possible hydrocarbon components (excluding naphthenes other than alkyl cyclopentanes and alkyl cyclohexanes), which were not present in detectable amounts. These include three C_7 *iso*paraffins (2,2,3-trimethylbutane, 3,3-dimethylpentane, and 3-ethylpentane), one C_8 *iso*paraffin (2,2,4-trimethylpentane),[9] and two alkyl cyclopentanes (*cis*-1,3-dimethylcyclopentane and *cis*-1,2-dimethylcyclopentane). To our knowledge, no one of these six hydrocarbons has yet been definitely identified as a component of naturally occurring petroleum.

[9] The other octanes normally boil above 102° C and will be discussed in a later report.

3. RELATIVE AMOUNTS OF PARAFFINS AND NAPHTHENES, AND OF NORMAL PARAFFINS, *ISO*PARAFFINS, ALKYL CYCLOPENTANES, AND ALKYL CYCLOHEXANES

Table 6 gives in the second and third columns the relative amounts of total paraffins and total naphthenes in the paraffin-naphthene portion, 40° to 102° C, for the seven napthas. In the last four columns of table 6 are given the relative amounts of the normal paraffins, *iso*paraffins, alkyl cyclopentanes, and alkyl cyclohexanes, which four classes appear (as will be seen later) to be the ones which are characteristic of the paraffin-naphthene portion of several crudes.

TABLE 6.—*Relative amounts of the total paraffins and total naphthenes, and of normal paraffins, isoparaffins, alkyl cyclopentanes, and alkyl cyclohexanes*

Naphtha	Total paraffins	Total naphthenes	Normal paraffins	*Iso*-paraffins	Alkyl cyclopentanes	Alkyl cyclohexanes
	Percentage, by volume, paraffin-naphthene portion, 40° to 102° C		Percentage, by volume, of the paraffin-naphthene portion, 40° to 102° C			
Ponca, Okla	56.2	43.8	35.7	20.5	23.4	20.4
East Texas	52.0	48.0	24.7	27.3	26.0	22.0
Bradford, Pa	66.6	33.4	34.4	32.2	13.4	20.0
Greendale-Kawkawlin, Mich	76.3	23.7	63.1	13.2	8.0	15.7
Winkler, Tex	71.1	28.9	9.5	61.6	20.5	8.4
Midway, Calif	31.5	68.5	10.0	21.5	41.0	27.5
Conroe, Tex	38.5	61.5	18.2	20.3	17.3	44.2

It is interesting to note the large range in composition covered: Total paraffins, 31 to 76; total naphthenes, 24 to 69; normal paraffins, 9 to 63; *iso*paraffins, 13 to 62; alkyl cyclopentanes, 8 to 41; alkyl cyclohexanes, 16 to 44.

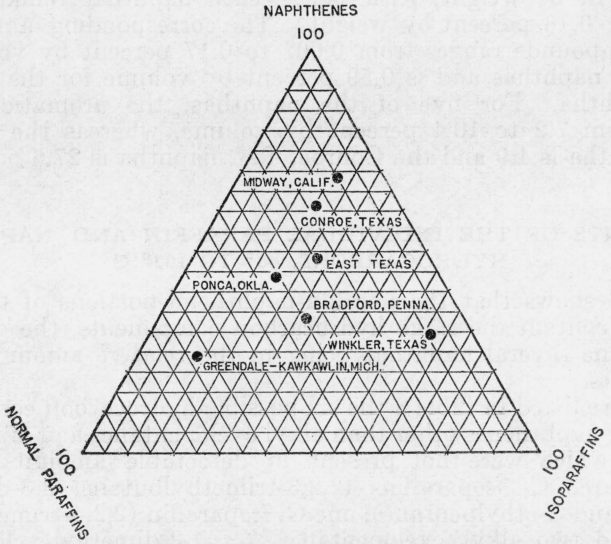

FIGURE 15.—*Triangular plot showing the relation between the content of normal paraffins, isoparaffins, and naphthenes (cycloparaffins), for the distillate, 40° to 102° C, for the seven naphthas.*

A given corner represents 100-percent composition for the component indicated there; the base line opposite the given corner represents zero composition for that component. For example, a point at the normal paraffin corner represents 100-percent-normal paraffins, and a point on the base line opposite (joining the naphthene and *iso*paraffin corners) represents zero normal paraffins.

Figure 15 gives a triangular plot which shows graphically the relative amounts of the normal paraffins, *iso*paraffins, and total naphthenes.

These data indicate the extreme over-all range in composition of the nonaromatic portion of the seven naphthas, and indicate that the Advisory Committee made a good selection of crudes for this investigation.

4. RELATIVE AMOUNTS OF THE COMPONENTS WITHIN GIVEN CLASSES

Table 7 gives, for each of the seven naphthas, the relative amounts of the following individual components and groups of components:

C_6 and C_7 normal paraffins.
C_6 and C_7 *iso*paraffins.
C_6 *iso*paraffins.
Individual C_6 *iso*paraffins.
Individual C_7 *iso*paraffins.
C_5, C_6, and C_7 alkyl cyclopentanes, 40° to 102° C.
Individual alkyl cyclopentanes, 40° to 102° C.
C_6 and C_7 alkyl cyclohexanes.
C_6, C_7, and C_8 aromatic hydrocarbons.
Individual C_8 aromatic hydrocarbons.

For each of these groups, there are given the averages of the relative amounts of the components, together with the ranges covered. It is seen that, within the given classes, the individual hydrocarbons occur in proportions which are of the same order of magnitude for the seven naphthas.

TABLE 7.—*Relative amounts of the components within the various groups*

Group	Components	Boiling point at 1 atm	Ponca, Okla.	East Texas	Bradford, Pa.	Greendale-Kawkawlin, Mich.	Winkler, Tex.	Midway, Calif.	Conroe, Tex.	Range of values	Average value
		°C									
Normal paraffins	*n*-Hexane	68.74	44	51	45	46	47	61	42	42 to 61	48
	n-Heptane	98.43	56	49	55	54	53	39	58	39 to 58	52
	Total		100	100	100	100	100	100	100		100
*Iso*paraffins	C_6		36	46	50	50	43	51	49	35 to 51	47
	C_7		64	54	50	50	57	49	51	49 to 64	53
	Total		100	100	100	100	100	100	100		100
C_6 *iso*paraffins	Dimethylbutanes		14	13	10	14	12	16	16	10 to 16	14
	Methylpentanes		86	87	90	86	88	84	84	84 to 90	86
	Total		100	100	100	100	100	100	100		100
Individual C_6 *iso*paraffins	2, 2-Dimethylbutane	49.74	5	4	3	2	4	7	6	2 to 7	4
	2, 3-Dimethylbutane	57.99	9	9	7	12	8	9	10	7 to 12	9
	2-Methylpentane	60.27	45	50	56	52	25	50	50	25 to 56	47
	3-Methylpentane	63.28	41	37	34	34	63	34	34	34 to 63	40
	Total		100	100	100	100	100	100	100		100
Individual C_7 *iso*paraffins	2, 2-Dimethylpentane	79.20	6	16	14	12	9	14	12	6 to 16	12
	2, 4-Demethylpentane	80.51									
	2, 3-Dimethylpentane	89.79	72	63	61	74	50	67	74	50 to 74	66
	2-Methylhexane	90.05									
	3-Methylhexane	91.95	22	21	25	14	41	19	14	14 to 41	22
	Total		100	100	100	100	100	100	100		100
Alkyl cyclopentanes	C_5		2	3	4	8	6	6	4	2 to 8	5
	C_6		32	36	27	50	30	32	53	27 to 53	37
	C_7		66	61	69	42	64	62	43	41 to 68	58
	Total		100	100	100	100	100	100	100		100

Individual alkyl cyclopentanes	Cyclopentane	49.26	2	3	4	8	6	6	4	2 to 8	5
	Methylcyclopentane	71.81	32	36	27	50	30	32	53	27 to 53	37
	1,1-Dimethylcyclopentane	87.5	6	6	11	12	12	5	8	5 to 12	9
	trans-1,3-Dimethylcyclopentane	90.8	45	39	30	22	29	41	28	22 to 45	33
	trans-1,2-Dimethylcyclopentane	91.9	15	16	28	8	23	16	7	7 to 28	16
	Total		100	100	100	100	100	100	100		100
Individual alkyl cyclohexanes	Cyclohexane	80.74	30	21	24	33	31	29	30	21 to 33	28
	Methylcyclohexane	100.93	70	79	76	67	69	71	70	67 to 79	72
	Total		100	100	100	100	100	100	100		100
Aromatics	C_6		9	4	4	13	10	5	6	4 to 13	7
	C_7		30	29	31	37	20	30	38	20 to 38	31
	C_8		61	67	65	50	70	65	56	50 to 70	62
	Total		100	100	100	100	100	100	100		10
Individual C_8 aromatics	Ethylbenzene	136.19	18	17	9	15	25	24	8	8 to 25	17
	p-Xylene	138.35	9	13	16	12	39	16	16	9 to 39	17
	m-Xylene	139.11	48	48	56	51	26	38	57	26 to 57	46
	o-Xylene	144.42	25	22	19	22	10	22	19	10 to 25	20
	Total		100	100	100	100	100	100	100		100

5. RELATIVE AMOUNTS OF THE ALKYL CYCLOPENTANES AND ALKYL CYCLOHEXANES, 40° TO 102° C

Table 8 gives the relative amounts of the alkyl cyclopentanes and alkyl cyclohexanes, 40° to 102° C. As can be seen, the relative amounts of these two groups of components show little correlation, but rather appear to be characteristic of the crude, just as are the relative amounts of the normal paraffins and isoparaffins.

TABLE 8.—*Relative amounts of the alkyl cyclopentanes and alkyl cyclohexanes in the seven naphthas, 40° to 102° C*

Components	Ponca, Okla.	East Texas	Bradford, Pa.	Greendale-Kawkawlin, Mich.	Winkler, Tex.	Midway, Calif.	Conroe, Tex.
Alkyl cyclopentanes	53	53	34	34	71	60	28
Alkyl cyclohexanes	47	47	66	66	29	40	72
Total	100	100	100	100	100	100	100

1. The gasoline fraction of different crudes may be characterized by specifying the relative amounts of the following five classes of hydrocarbons:[10] Normal paraffins, isoparaffins, alkyl cyclopentanes, alkyl cyclohexanes, and aromatics.

2. The gasoline fractions 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.

4. It appears possible to predict the order of magnitude of the amounts of the individual hydrocarbons, paraffins, and naphthenes, 40° to 102° C, and aromatics to 160° C, in an appropriate fraction of a given naphtha when there are known the relative amounts of the foregoing five classes of hydrocarbons, or alternatively for each class, the amount of one of the main components of that class.

VII. CONCLUSION

On the basis of the data obtained in the present investigation, the following conclusions may be drawn with regard to the composition of the gasoline fraction of different petroleums, to 102° C for paraffins and naphthenes and to 160° C for aromatics. The extent to which these conclusions may be applied to higher-boiling material will be determined by the studies now in progress.

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[10] For the present, bicyclonaphthenes, the first of which is apparently encountered [2] at 147° C, are not considered in this classification.

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