U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1123

Part of Journal of Research of the National Bureau of Standards, Volume 21, August 1938

SEPARATION, BY DISTILLATION WITH ACETIC ACID, OF THE AROMATIC HYDROCARBONS FROM THE FRACTION OF A MIDCONTINENT PETROLEUM BOILING BETWEEN 154° AND 162° C.[1]

By Frank W. Rose, Jr.[2] and Joseph D. White [2a]

ABSTRACT

A method is presented for the separation, by distillation with an azeotropic agent, acetic acid, of narrow-boiling petroleum fractions into concentrates containing (1) a mixture of paraffins and naphthenes and (2) the aromatic hydrocarbons. This procedure simplifies the subsequent task of separating the individual components and is applicable to petroleum fractions boiling in the range 130° to 175° C. Data are given on the behavior of synthetic mixtures of *n*-nonane and isopropylbenzene with acetic acid. Except for about 10 percent of intermediate material, the separation of these mixtures in a 30-plate glass column is roughly quantitative.

The systematic distillation, with acetic acid, of the fraction of an Oklahoma petroleum boiling normally between 154° and 162° C resulted in a paraffin-naphthene mixture and an aromatic concentrate. Traces of aromatic hydrocarbons were removed from the paraffin-naphthene mixture by adsorption on silica gel. Redistillation of the aromatic concentrate with acetic acid removed all but the aromatic hydrocarbons. By proper recycling of the intermediate fractions, only about 1 percent of the entire fraction remained not allocated to the concentrates. Distillation of the paraffin-naphthene mixture as oil at 215 mm Hg showed (1) paraffinic constituents boiling near 157° C and (2) napthenic constituents boiling near 161° C. On distillation of the aromatic concentrate, the major portion of the distillate had a boiling range of 158.5° to 164.5° C, about 5° higher than that of the material from which it came. Apparently this material contains *n*-propylbenzene and the methylethylbenzenes as well as higher boiling trimethylbenzenes.

CONTENTS

Page
I. Introduction 168
II. Previous methods of separating aromatic hydrocarbons as a class 168
  1. Chemical methods 168
  2. Physical methods 169
III. Acetic acid as an azeotropic agent 169
  1. Behavior with synthetic mixtures 169
  2. Behavior with petroleum fractions 172
    (*a*) Distillation fraction 172
    (*b*) Aromatic concentrates 174
IV. Experimental procedure 175
  1. Distillation 175
  2. Treatment of the paraffin-naphthene mixture 176
  3. Treatment of intermediate fractions 177
  4. Treatment of the aromatic concentrates 177

---

[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.

[2] Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

[2a] Formerly Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

Page
V. Results 178
1. Original material 178
2. Paraffin-naphthene mixture 179
3. Aromatic constituents 183
VI. Conclusions 183
VII. References 184

I. INTRODUCTION

The systematic examination of the gasoline fraction of a crude petroleum may be considerably simplified if, after distillation has produced cuts boiling over moderately narrow ranges, such fractions are then separated into several concentrates containing different classes of hydrocarbons.[3,4] The concentrates can then be redistilled and subsequently treated in a manner appropriate to the individual constituents.[5,6]

The following report describes azeotropic distillation with acetic acid as a method for the separation of aromatic hydrocarbons from the paraffinic and naphthenic hydrocarbons. It is shown that the various members of each class (within a narrow-boiling range) manifest approximately the same behavior towards the reagent.

II. PREVIOUS METHODS OF SEPARATING AROMATIC HYDROCARBONS AS A CLASS

1. CHEMICAL METHODS

Early in the investigation of petroleum, the reactivity of aromatic hydrocarbons led to the use of chemical methods for their detection and estimation. The first investigators of petroleum employed either nitration or sulfonation, customarily treating a petroleum distillate having a narrow-boiling range with an acid or mixture of acids [7] [3, 4]. However, nitration is limited to those instances in which the procedure yields either a single product or a mixture of products that can be identified and analyzed (as by freezing point [5]). The presence of isomeric parent hydrocarbons in the original fraction, or the lack of a definite end product in the nitration, obviously increases the difficulties of analysis. Hence the method is most feasibly applied to benzene and toluene. Nitration possesses several disadvantages: (1) the original aromatic hydrocarbon cannot be easily recovered; (2) the nitrating mixture may destroy labile constituents; (3) dehydrogenation (by oxidation) of the polysubstituted cyclohexanes can occur with such a mixture;[8] and (4) the last traces of acid are removed with difficulty from the unattacked oil. If dehydrogenation occurs, not only are some components possibly lost but the presence of others may be falsely indicated. The effect of residual traces of

---

[3] Throughout this paper, the mixture of paraffinic and naphthenic hydrocarbons of a particular boiling range, remaining after the removal of all aromatic constituents, is referred to as the paraffin-naphthene mixture.

[4] This separation is feasible either before or after the removal of the normal paraffins by crystallization.

[5] Figures in brackets indicate the literature references at the end of this paper.

[6] The problem of the separation of petroleum into its constituent hydrocarbons has been discussed in a more general aspect by Washburn [1] and more recently by Rossini [2].

[7] In this report no attempt will be made to give details of the various processes discussed, nor will references be given to an extensive literature. However, when such methods have been used by this project, appropriate references will be made.

[8] V. Baeyer [6] has shown that on treatment with nitric-sulfuric acid mixtures some of the hydrogenated aromatic hydrocarbons yield nitro compounds of the corresponding aromatic hydrocarbon. The authors have obtained, by this method, trinitromesitylene from 1, 3, 5-trimethylcyclohexane [7].

acid is noticed on redistillation, where they seem to have a catalytic effect on the cracking of the oil in the still pot.

The process of sulfonation is somewhat analogous to that of nitration and has many of the same disadvantages, although it can be used in many instances to separate isomeric aromatic hydrocarbons.[9] The resulting sulfonic acids may be converted to the barium salts or the sulfonamides, with subsequent identification, or may be hydrolyzed with recovery of the parent aromatic hydrocarbon. As some benzenoid hydrocarbons do not readily react with sulfuric acid, care must be taken to insure their complete removal from the paraffin-naphthene mixture. Further, the action of sulfuric acid may alter the positions of the side chains of the higher aromatic hydrocarbons (Jacobsen reaction).

Another method for the detection of aromatic hydrocarbons is the formation of aromatic acids by oxidation of the side chains. An objection to this method is that the only information to be gained is the relative positions of the side chains, leaving indeterminate the length and structure.

2. PHYSICAL METHODS

Extraction is one of the physical methods which can be used for the separation of the aromatic hydrocarbons as a group. Many solvents which have been used for this purpose, include liquid sulfur dioxide [8, 9, 15], liquid sulfur dioxide and petroleum ether [9, 16], aniline [4], and many others. However, both the miscible aromatic phase and the immiscible paraffin-naphthene mixture will be contaminated by mutual solution unless an apparatus is used which has reflux and a large number of theoretical plates [17, 18, 19].

Selective adsorption can be utilized to remove aromatic hydrocarbons. The aromatic hydrocarbons can be quantitatively removed from the paraffinic and naphthenic consituents by adsorption on silica gel [20, 28], but its limited capacity renders the method impractical for aromatic concentrations above 7 to 8 percent.

A very promising process for the separation of aromatic hydrocarbons from a petroleum distillate is distillation with an added component. By the formation of binary azeotropic mixtures, the original ratio of the various classes may be materially altered in the vapor phase, and separation becomes possible. This general procedure has been used to separate hydrocarbons by addition of methyl alcohol [21, 22], ethyl alcohol [22], *tert*-butyl alcohol [26], and acetic acid [23, 24].

III. ACETIC ACID AS AN AZEOTROPIC AGENT

1. BEHAVIOR WITH SYNTHETIC MIXTURES

Acetic acid as an azeotropic agent to separate paraffinic and naphthenic hydrocarbons has been used by Schicktanz [23], who pointed out that it fulfills the requirements of an azeotropic agent in that it does not react with, nor polymerize, the hydrocarbons, is easily and quantitatively removable from the hydrocarbons (by washing with water), and is inexpensive and readily available. Although having a

---

[9] See White and Rose [8] (xylenes), Mair and Schicktanz [9] (trimethylbenzenes), Smith and coworkers [10, 11, 12] (tri- and tetramethylbenzenes), Clarke and Taylor [13] (xylenes), Armstrong and Miller [14] (general).

low-boiling point (118.1° C), it forms azeotropes with petroleum hydrocarbons over a considerable range and may be used successfully with hydrocarbons boiling from 130° to 175° C [25].

During a separation of the paraffinic and naphthenic constituents occurring in a fraction of petroleum normally boiling between 135° and 140° C, the authors found that the last fractions of certain distillations of paraffin-naphthene mixtures with acetic acid had abnormally high refractive indices (see [24], p. 946, footnote 7). Investigation indicated the presence of aromatic hydrocarbons thought to have been completely removed previously by extraction with liquid sulfur dioxide, followed by treatment with concentrated sulfuric acid.

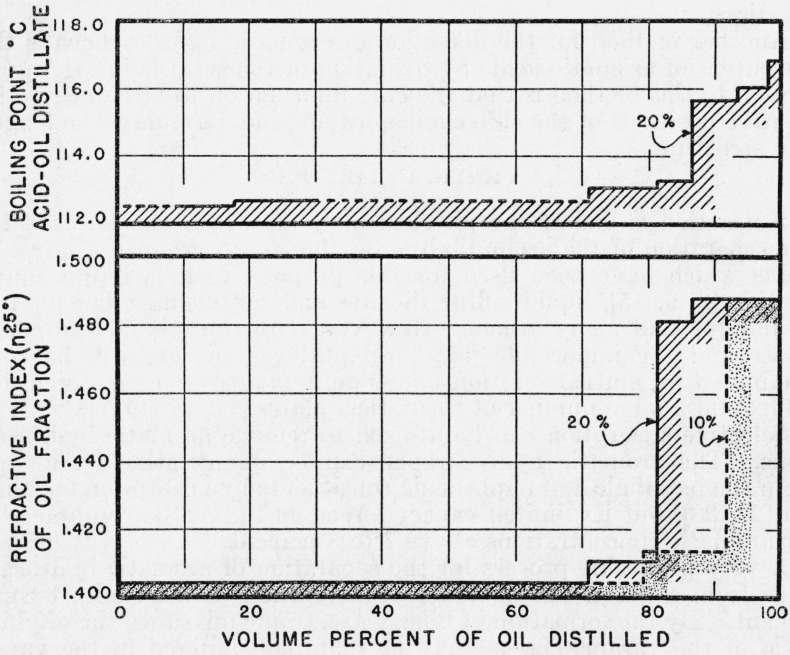

FIGURE 1.—*Data from the distillation of synthetic mixtures of n-nonane and isopropylbenzene (concentration indicated) with acetic acid.*

The scale of ordinates gives, for the upper graph, the boiling points in degrees centigrade at 760 mm Hg of the acid-oil distillates; for the lower graph, the refractive indices of the oil fractions after separation from the acid. The scale of abscissas gives the volume percentage of oil distilled on the basis of recovery.

The complete removal of these last traces of aromatic hydrocarbons by this procedure suggested a general application of the method to the separation of aromatic hydrocarbons from paraffin-naphthene mixtures. Accordingly, a synthetic system was investigated, using *n*-nonane (previously isolated from this petroleum and designated as Lot II [27] boiling point 150.5° C) and synthetic isopropylbenzene (from Eastman Kodak Co., boiling point 152.5° C). These compounds were not of the highest purity (about 95 percent) but were pure enough to be regarded as substantially single components. The first mixture investigated contained 10 percent of isopropylbenzene and 90 percent of *n*-nonane. A charge of 500 ml of this mixture was distilled with 1,700 ml of glacial acetic acid (commercial grade). The results are given in table 1 and figure 1.

TABLE 1.—*Results of the distillation of a synthetic mixture of n-nonane (90 percent) and isopropylbenzene (10 percent) with acetic acid*

Fraction number	Volume		Total oil	Refractive index	Total percentage distilled [b]
	Distillate [a]	Oil			
	ml	*ml*	*ml*	n_D^{25}	
1	102	31	31	1.4043	6.4
2	108	(38) [c]	69		14.3
3	104	37	106	1.4039	22.0
4	126	(44)	150		31.1
5	109	39	189	1.4038	39.2
6	106	(37)	226		46.9
7	115	35	261	1.4038	54.2
8	108	(38)	299		62.0
9	132	48	347	1.4042	72.0
10	96	(34)	381		79.1
11	184	62	443	1.4138	92.0
12	128	21	464	1.4874	96.3
13	110	16	480	1.4885	99.6
14	110	2	482	1.4877	100.0
15	108	No oil [d]			
16	122	do. [d]			
17	106	do. [d]			
18	68	do.			
Residue	120	do.			

[a] Acid and oil.
[b] On basis of recovery.
[c] Figures in parentheses are estimated.
[d] Emulsion formed on dilution (1:1) with water.

In the lower portion of figure 1, the curve marked 10 percent shows the data plotted as volume percentage of oil distilled (on the basis of recovery) against refractive index.[10] Fractions 1, 3, 5, 7, and 9 had slight differences in refractive index (table 1, column 5) which were caused by traces of naphthenic material in the *n*-nonane. Fractions 2, 4, 6, 8, and 10 were washed with water as a single unit and had a refractive index of 1.4038. Thus, approximately 85 percent of the *n*-nonane was recovered, free of aromatics. The loss of 18 ml (4 percent) may be ascribed to handling and to the slight solubility of the aromatic hydrocarbons in the acetic acid-water phase formed on dilution. (A method for minimizing the latter loss is described in the systematic procedure. See section IV.)

To determine the effect of concentration, a charge (375 ml) containing 20 percent of isopropylbenzene was distilled with an excess of acetic acid. The results are given in table 2 and figure 1 (curve marked 20 percent). The percentage of the *n*-nonane (free of aromatics) recovered, and the amount of intermediate material, was relatively the same as in the previous distillation. The size of the intermediate cut might have been less in both cases had the distillation fractions been smaller. The boiling points of the fractions of this distillation are shown graphically in the upper portion of figure 1. The rise of boiling point at the end of the distillation indicates a fractionation of the acetic acid-isopropylbenzene azeotrope and pure acetic acid. The boiling point curve is similar to that for refractive index, and hence is indicative of the relative concentrations of the two components.

---

[10] All refractive indices in this report are for n_D^{25}.

TABLE 2.—*Results of the distillation of a synthetic mixture of n-nonane (80 percent) and isopropylbenzene (20 percent) with acetic acid*

Fraction number	Volume		Total oil	Refractive index	Total percentage distilled [b]	"Azeotropic" boiling point [c]
	Distillate [a]	Oil				
	ml	*ml*	*ml*	n_D^{25}		*°C*
1	108	30	30	1.4040	8.2	
2	107	34	64	1.4038	17.5	112.5
3	108	43	107	1.4037	29.2	112.7
4	120	43	150	1.4036	40.9	
5	107	39	189	1.4036	51.6	
6	105	37	226	1.4036	62.0	
7	102	33	259	1.4039	71.0	
8	100	38	297	1.4107	81.3	113.1
9	102	18	315	1,4817	86.0	113.3
10	175	29	344	1.4884	93.9	115.7
11	110	18	362	1.4884	97.8	116.1
12	102	4	366	1.4884	100.0	116.9
13	102	No oil [d]				117.5
14	98	do.[d]				117.8
Residue	358	do.[d]				117.9

[a] Acid and oil.
[b] On basis of recovery.
[c] Relative only.
[d] Formed emulsion on dilution (1:1) with water.

2. BEHAVIOR WITH PETROLEUM FRACTIONS

(a) DISTILLATION FRACTION

A criterion of any process for the separation of a petroleum into its various classes of hydrocarbons is that all members of a class behave similarly. Schicktanz [25] has shown that, for hydrocarbons having approximately the same boiling point at 760 mm Hg, the boiling points of the corresponding azeotropes with acetic acid fall in the order paraffin <naphthene <aromatic hydrocarbon, and that class distinctions can be validly made. In a closely fractionated cut of petroleum, the components will have substantially the same boiling points and their azeotropes may be expected to follow the order predicated, and to yield results comparable to those found for the binary mixtures.[11]

To test this hypothesis, a fraction from the systematic distillation of the gasoline fraction of a midcontinent petroleum (the source and treatment of which are described in section IV, 1) boiling between 110.5° and 111.0° C at 215 mm Hg, or approximately 154° C at 760 mm Hg, was distilled with acetic acid. The results are given in table 3 and figure 2. The gradual rise in the refractive index curve (fig. 2) to the 90-percent point shows a slow separation of the paraffinic and naphthenic constituents, while the sharp break indicates a fairly complete separation of the aromatic hydrocarbons. The high refractive index of the last 8 percent indicates that it is chiefly aromatic and that no considerable portion of paraffinic or naphthenic material is present. Nitration of a sample of the original material (n_D^{25} 1.4314) yielded an unattacked oil, which, after distillation from sodium, had a refractive index of 1.4254. The change in refractive index would

---

[11] A fraction which has a wide boiling range may include a naphthene whose boiling point at 760 mm Hg is so much higher than that of some aromatic hydrocarbon present that there may be an overlapping of the boiling points of the corresponding azeotropes with a resultant lack of separation.

indicate a concentration of about 9 percent of aromatic hydrocarbons and agrees with the data from the acetic acid distillation.

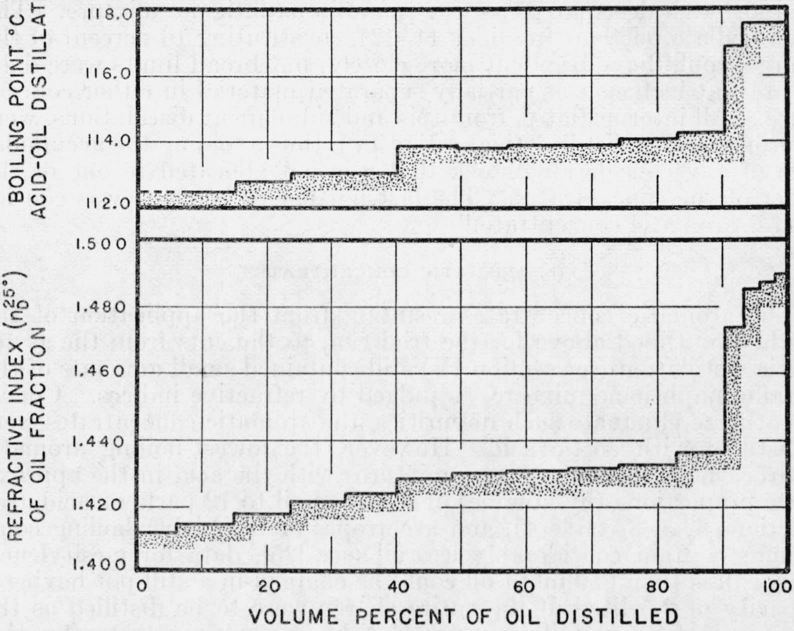

FIGURE 2.—*Data from the distillation of a petroleum fraction boiling between 110.5° and 111.0° C at 215 mm* Hg *(154° C at 760 mm* Hg*) with acetic acid.*

The scale of ordinates gives, for the upper graph, the boiling points in degrees centigrade at 760 mm Hg of the acid-oil distillates; for the lower graph, the refractive indices of the oil fractions after separation from the acid. The scale of abscissas gives the volume percentage of oil distilled on the basis of recovery.

TABLE 3.—*Results of the distillation of a petroleum fraction (bp 110.5° to 111.0° C at 215 mm* Hg*) with acetic acid*

Fraction number	Volume		Total oil	Refractive index	Total percentage distilled [b]	"Azeotropic" boiling point [c]
	Distillate [a]	Oil				
	ml	*ml*	*ml*	n_D^{25}		°*C*
1	102	25	25	1.4119	6.2	
2	102	36	61	1.4142	15.1	112.5
3	100	35	96	1.4172	23.8	112.8
4	104	35	131	1.4212	32.4	113.1
5	96	31	162	1.4239	40.2	113.1
6	101	34	196	1.4281	48.5	113.9
7	110	35	231	1.4301	57.3	113.8
8	117	38	269	1.4308	66.7	113.9
9	102	32	301	1.4319	74.5	113.9
10	110	34	335	1.4328	83.0	114.1
11	100	30	365	1.4363	90.5	114.3
12	109	12	377	1.4738	93.4	116.9
13	100	10	387	1.4853	95.9	117.6
14	106	9	396	1.4874	98.1	117.6
15	110	7	403	1.4906	99.8	
16	100	1	404	1.4909	100.0	
17	54	Trace		1.4901		
Residue		No oil				

[a] Acid and oil. [b] On basis of recovery. [c] Relative only.

Filtration of the combined fractions 1 to 10 through silica gel gave no significant separation, and showed that the oil was free of aromatic hydrocarbons. This portion, comprising 83 percent of the original charge, was designated as the paraffin-naphthene mixture. The intermediate portion (fractions 11, 12), constituting 10 percent of the charge, could have been cut more closely, but broad limits were fixed to prevent inclusion of partially separated material in either concentrate. All intermediates, from this and subsequent distillations, were appropriately redistilled (see section IV), thus avoiding the accumulation of any considerable stock that was not allocated to one or the other of the concentrates. The last portion (7 percent) was considered "aromatic concentrate."

(b) AROMATIC CONCENTRATES

The aromatic concentrates resulting from the application of the method, outlined above for the trial run, to the cuts from the systematic distillation (see section IV) still contained small amounts of the paraffin-naphthene mixture, as judged by refractive indices. Consequently, to eliminate such impurities, the aromatic concentrates were redistilled with acetic acid. However, the lowest-boiling aromatic hydrocarbons form azeotropic mixtures with the acid in the approximate proportions (by volume) of 1 part of oil to 12 parts of acid (see fractions 4, 5, 6, table 4), and azeotropes of the higher-boiling compounds contain considerably less oil (see [25], data for mesitylene). Hence, less than 250 ml of oil could be charged in a still pot having a capacity of 2.5 liters if the entire charge were to be distilled as the azeotropic mixture. Treatment of 5 liters of concentrates by this method would be tedious and would involve heavy losses in handling because of the solubility of the aromatic hydrocarbons in the dilute acetic acid solutions necessarily formed on separating the oil. Hence the volume of acid used was purposely limited to little more than that required to completely remove the nonaromatic portion. Various concentrations of acid were tried with the following results: (1) 1 acid:2 oil [12]—had apparently an inadequate quantity of acid since the refractive index of the last possible distillate [13] was below that for aromatic hydrocarbons; (2) 3 acid:1 oil—gave very poor separation, (this was satisfactory for the untreated petroleum distillate); and (3) 1 acid:1 oil, or 2 acid:1 oil—gave satisfactory results. The data of a typical distillation are given in table 4. The charge consisted of 1,600 ml of acetic acid and 800 ml of the aromatic concentrate removed from distillation cuts whose original boiling range was 117° to 118° C (215 mm Hg). Fraction 7 and the residue were assumed to contain only aromatic hydrocarbons. The head fractions were appropriately combined with similar fractions from other distillations of aromatic concentrates and again distilled with acetic acid, to yield results analogous to those listed in tables 3 and 4.

This method can also be used in the separation of aromatic hydrocarbons from concentrates obtained by other means. The authors have used distillation with acetic acid to separate an "isopropylbenzene" fraction from a concentrate (30 to 50 percent aromatic) obtained by adsorption on silica gel [28].

---

[12] All ratios are expressed in terms of volume.

[13] As soon as the last of the azeotropic mixture leaves the still pot, ebullition ceases because the boiling point of the remaining oil is about 45° C higher (about 162° C at 760 mm Hg).

TABLE 4.—*Results of the distillation of an aromatic concentrate with acetic acid*

Fraction number	Volume		Total oil	Refractive index	Total percentage distilled [b]	"Azeotropic" boiling-point [c]
	Distillate [a]	Oil				
	ml	*ml*	*ml*	n_D^{25}		*°C*
1	114	24	24	1.4399	3.1	116.1
2	110	14	38	1.4581	5.1	117.5
3	125	9	47	1.4779	6.1	117.8
4	110	7	54	1.4818	7.0	117.9
5	110	8	62	1.4848	8.0	118.0
6	124	8	70	1.4880	9.1	118.1
7	88	5	75	1.4900	9.7	118.1
Residue	-----------	698	773	1,4971	100.0	-----------

[a] Acid and oil.
[b] On basis of recovery.
[c] Relative only.

IV. EXPERIMENTAL PROCEDURE

1. DISTILLATION

The source and preliminary treatment of the fraction from the midcontinent (Oklahoma) petroleum used in this investigation have been described elsewhere [28]. After six distillations through glass columns (three at 760 mm Hg followed by three at 215 mm Hg), a 24-liter fraction was obtained which boiled in the range 110. 5° to 118° C at 215 mm Hg (154° to 162° C at atmospheric pressure). A Pyrex glass bubble-cap column having 30 plates (medium size) [29], and operated at a reflux ratio of 10:1 and a rate of 1 ml/min, was used in both the oil and acid distillations.

A routine charge for the acid distillation consisted of 1,500 to 1,700 ml of acetic acid and 500 ml of oil. However, the half-degree cuts from the last systematic distillation as oil were not mixed; instead, smaller quantities of oil with the same proportion of acid were charged when necessary. The distillate was taken off in fractions of approximately 100 ml, and the boiling point of each fraction determined with an externally heated modified Cottrell boiling-point apparatus, designed by S. T. Schicktanz. The distillation was continued for only a few cuts of 100 ml after the break in the boiling point curve had occurred (see figs. 1 and 2). After the still had cooled, the column was cleared of liquid insofar as possible by a gentle application of vacuum to the still pot. Then about 300 ml of acetic acid was added at the top of the column. This procedure left the column filled only with the acid and insured the return of any aromatic material in the column to the still pot. The column was again cleared of liquid as far as possible and the oil and the remainder of the acid for the next charge were added to the still pot. Heat was then applied and, after several hours of total reflux, the distillation was continued. The residue, including any material sucked down from the column, was removed at the end of every fifth charge or when the final charge of material from any half-degree cut had been reached.

A variation in the usual technique was introduced advantageously whenever the still was empty and clean; e. g., at the start of a systematic distillation or when a single distillation was to be made. At the start of a distillation, the water in commercial glacial acetic acid causes difficulty in the operation of the still by clogging stopcocks and capillaries (as in reflux regulators) as well as by forming a ternary azeotrope with the acid and oil, which interferes with the normal progress of separation. The acid may be dehydrated by charging the still with an excess of acetic acid and distilling off the additional acid before introducing the oil. The first distillate contains the water, leaving the acid in the still anhydrous. The oil can be charged when the still has cooled.

On completion of a distillation, the distillate was divided into three portions on the basis of boiling point: (1) the paraffin-naphthene mixture, (2) the intermediate fractions, and (3) the aromatic concentrate. As pointed out in section III, 1, the boiling point is a measure of the aromatic content, after due consideration has been given to the influence of naphthenes. On this basis, the fractions adjacent to the abrupt change in boiling point are intermediate in composition. Thus the division was made by locating the break and allotting the fractions immediately above and below it to "intermediates," while all of the distillate boiling below the intermediate portion became "paraffin-naphthene mixture" and that above, "aromatic concentrate."

2. TREATMENT OF THE PARAFFIN-NAPHTHENE MIXTURE

The fractions from the acid distillation designated as paraffin-naphthene mixture were combined, diluted with four times their volume of water, the emulsion was allowed to stand until clear, and the oil separated. The oil was then washed several times with water and finally with a saturated solution of sodium bicarbonate. All similar material from each half-degree cut (as of the previous systematic distillation as oil) was combined and filtered through silica gel to remove water and any traces of acetic acid or aromatic material. The filtration through the silica gel was carefully watched and any later portions of a fraction which showed a rise in refractive index were refiltered. Steam distillation of the gel was employed to insure quantitative recovery of the material adsorbed by the gel.

Generally, the material adsorbed by the gel was only 0.01 higher in refractive index than the filtrate, which indicated only traces of aromatic material. Occasionally, however, the refractive index of the adsorbed portion was sufficiently high (1.450) to show the presence of some aromatic constituents. On completion of the treatment with silica gel, the aromatic portion of the adsorbed material from the entire range, 110.5° to 118° C, was separated by a distillation with acetic acid.

An approximate estimate of the aromatic material recovered led to the conclusion that the paraffin-naphthene mixture had contained, on the average, 1 percent of aromatic hydrocarbons after the acetic acid distillation. It is believed that most of this aromatic impurity could have been eliminated by better grouping of the fractions in the systematic distillation.

The paraffin-naphthene mixture, after filtration through silica gel, was distilled as oil (without an added component) at 215 mm Hg under the conditions given above. The results are discussed in section V.

3. TREATMENT OF INTERMEDIATE FRACTIONS

The fractions, designated above as intermediate, were not separated from the acetic acid but were redistilled, the separation being comparable to that attained in the original acetic acid distillation. The procedure was identical with that followed in handling the original fractions. Whenever possible, the charges consisted of intermediates from the same half-degree cut (as of the previous distillation as oil). However, where it was necessary to mix intermediates from different half-degree cuts, the results were similar. The paraffin-naphthene mixture obtained from the redistillation of the intermediates was treated with silica gel and appropriately blended into the bulk of the paraffin-naphthene mixture during distillation as oil at 215 mm Hg.

An additional amount of paraffin-naphthene mixture was obtained from: (1) the distillation with acetic acid of the material adsorbed by silica gel and (2) the purification of the aromatic concentrate (see below). These fractions were combined, treated with silica gel, distilled as oil at 215 mm Hg and blended according to boiling point with the bulk of the paraffin-naphthene mixture during the systematic distillation as oil at 215 mm Hg. By this method, less than 150 ml of intermediates was left from the entire range.

4. TREATMENT OF THE AROMATIC CONCENTRATES

In the discussion (see section IV, 1) of the manner in which the acetic acid distillate was apportioned, all material boiling above the "intermediate" was considered aromatic material. Moreover, since only a few fractions were distilled after the intermediate fraction, the major portion of the aromatic material remained in the still pot. Since the residues were not removed after each distillation, aromatic hydrocarbons accumulated in the still pot. This was desirable because it avoided extensive washing of the aromatic concentrate, with attendant losses. The losses occurring in the separation of the oil from the acetic acid by dilution with water are due, in part, to the solubility of the aromatic hydrocarbons in the dilute acetic acid, as well as to the formation of very stable emulsions. It was found, however, that one simple distillation of the separated aqueous phase concentrated the aromatic hydrocarbons which were dispersed, as well as dissolved, in the dilute acetic acid. The first few milliliters of the distillate consist of a ternary azeotrope, oil-acetic acid-water, which on condensation and cooling separates into two layers. Hence all the dilute acetic acid from the separation of the aromatic concentrate was so treated. The 200 ml of oil recovered was combined with the bulk of the aromatic concentrate. The desirability of this procedure lies in its economy not only of material but also of time, since long delays in allowing the emulsions to clear are avoided.[14]

In section III,2(b), in which the purification of aromatic concentrates is discussed, it is shown that other classes of hydrocarbons can be removed from the aromatic concentrate by a redistillation with acetic acid. Consequently, the entire aromatic concentrate was so treated to remove the last of the paraffin-naphthene mixture. Precautions were observed against mixing over too great a boiling range.[15]

---

[14] The solubility of the paraffin-naphthene mixture in dilute acetic acid is negligible and does not warrant a similar treatment.

[15] Reasons for care in blending are given in footnote 11.

The aromatic concentrate, now freed of other hydrocarbons, was filtered through silica gel to remove gums, acetic acid, water, and odorous material. The filtrate was then systematically distilled as oil at 215 mm Hg in columns packed with 240 cm of locket chain (60 to 70 theoretical plates) at a rate of less than 0.5 ml per minute and a reflux ratio of 30:1. The results are given in section V, 3.

V. RESULTS

1. ORIGINAL MATERIAL

The volumes and refractive indices of the 0.5° C cuts of gasoline distillate used in this investigation and described in section IV,1, are given in columns 2 and 3, respectively, of table 5, while the boiling points at 760 mm Hg are given in column 4. In figure 3, the relations of volume and refractive index to boiling range are illustrated by the graphs marked "original." The refractive index curve is almost entirely above 1.435. This is an excellent indication (for this region) of the presence of aromatic hydrocarbons.

TABLE 5.—*Results of the systematic separation by azeotropic distillation of the petroleum distillate boiling normally between 154° and 162° C*

Original oil				Paraffin-naphthene mixture				Aromatic concentrate
Boiling range of fraction (215 mm Hg)	Volume	Ref. index	Boiling point [a] (760 mm Hg)	Volume [b]	Ref. index [b]	Ref. index [c]	Boiling point [a] (760 mm Hg)	Volume [b]
°*C*	*ml*	n_D^{25}	°*C*	*ml*	n_D^{25}	n_D^{25}	°*C*	*ml*
110.5 to 111.0	460	1.4314	----------	418	1.4260	1.4254	----------	42
111.0 to 111.5	1,020	1.4329	154.7	865	1.4262	1.4261	154.4	155
111.5 to 112.0	520	1.4343	155.2	487	1.4281	----------	155.1	33
112.0 to 112.5	1,200	1.4354	155.7	1,062	1.4282	1.4274	155.6	138
112.5 to 113.0	1,272	1.4364	156.3	992	1.4268	----------	155.8	280
113.0 to 113.5	1,885	1.4372	156.7	1,564	1.4264	1.4258	156.4	321
113.5 to 114.0	1,264	1.4378	157.2	1,005	1.4261	----------	156.8	260
114.0 to 114.5	1,502	1.4383	157.6	1,155	1.4250	1.4233	157.5	346
114.5 to 115.0	1,458	1.4385	158.1	1,192	1.4241	----------	158.2	263
115.0 to 115.5	1,130	1.4387	158.6	880	1.4217	1.4199	159.0	250
115.5 to 116.0	3,073	1.4365	159.3	2,323	1.4204	1.4176	159.5	750
116.0 to 116.5	2,470	1.4340	159.9	1,836	1.4193	1.4168	160.1	624
116.5 to 117.0	3,010	1.4332	160.5	2,300	1.4189	----------	160.0	710
117.0 to 117.5	1,987	1.4341	161.2	1,435	1.4193	1.4174	160.8	552
117.5 to 118.0	2,182	1.4355	161.9	1,752	1.4218	----------	----------	430

[a] Relative only.
[b] Composite from weighted values of bulk and intermediate (see text).
[c] From nitration tests.

Before distillation with acetic acid, the concentration of aromatic constituents was investigated by nitration tests on small samples of the original distillate. The refractive indices of the unattacked oil (after distillation from sodium) are given in table 5, column 7. All cuts tested gave three layers with the nitrating acid.

From the difference in the refractive indices of the original and the unattacked oils, the concentrations of aromatic hydrocarbons in the various cuts may be estimated. However, any destruction of naphthenic material present would lead to an abnormally low refractive index of the unattacked oil and consequent positive errors in the estimates of the concentration of the aromatic hydrocarbons.

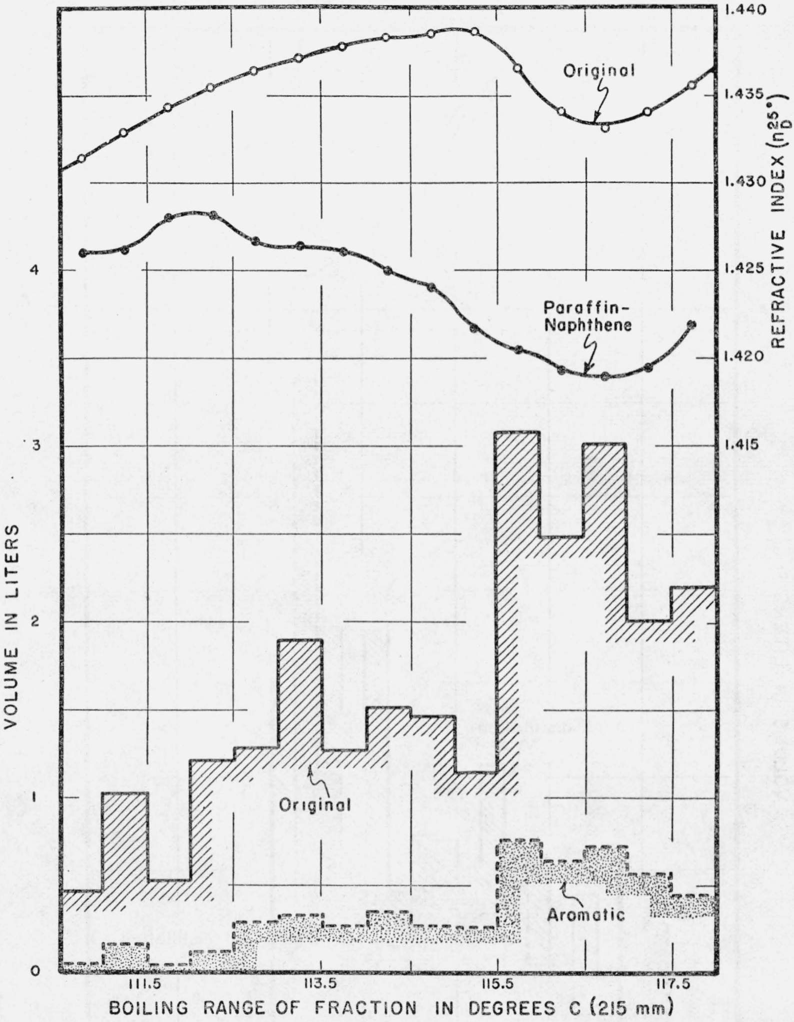

Figure 3.—*Data on the original untreated distillate boiling between 110.5° and 118.0° C at 215 mm* Hg *(154° to 162° C at 760 mm* Hg).

The scale of ordinates at the lower left gives the volume in liters, for each 0.5° C cut, of the original untreated distillate (shaded curve) and the weighted values for the aromatic hydrocarbons therein (stippled curve). The scale of ordinates at the upper right gives the refractive index of the original untreated distillate (circles) and the weighted values for the paraffin-naphthene mixture therein (dots). The scale of abscissas gives the boiling ranges of the fractions (taken in 0.5° C cuts).

2. PARAFFIN-NAPHTHENE MIXTURE

As described in section IV, each 0.5° C cut of the original distillate was separated into an aromatic concentrate and a paraffin-naphthene mixture. Systematic recycling of the intermediates yielded further amounts of these concentrates. By consideration of these minor amounts in relation to the bulk of the concentrates from each 0.5°

cut, weighted values of the volumes and refractive indices of the paraffin-naphthene mixtures as hypothetically existing in each fraction of the original distillate, were derived. These are given in

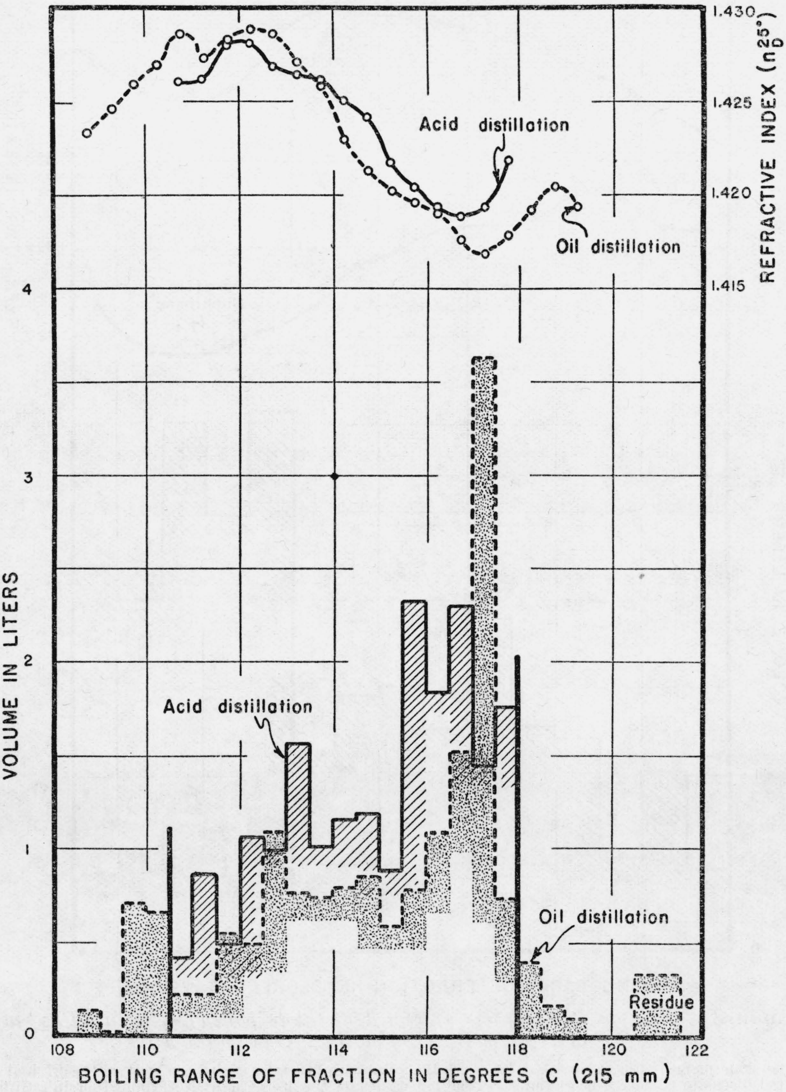

FIGURE 4.—*Data on the paraffin-naphthene mixture originally boiling between 110.5° and 118.0° C at 215 mm* Hg *(154° to 162° C at 760 mm* Hg) *showing (1) the hypothetical occurrence in the untreated distillate (unbroken curves) and (2) the distribution after separation by acetic acid and a subsequent oil distillation (broken curves).*

The scale of ordinates at the lower left gives the volume in liters and that at the upper right gives the refractive index of each 0.5° cut. The scale of abscissas gives the boiling ranges of the fractions (taken in 0.5° cuts).

table 5, columns 5 and 6, respectively. The refractive indices are possibly slightly high, because traces of aromatic constituents later removed by silica gel were present. The data are shown graphically in figure 3. The weighted volume of the paraffin-naphthene mixture is the difference between the volumes of the original distillate (unbroken curve) and the weighted aromatic concentrate (broken curve).

As noted in section IV, 2, the paraffin-naphthene mixture was freed of aromatics and systematically distilled as oil at 215 mm Hg. Since the conditions reproduced those of the systematic distillation preceding the separation by acetic acid, no additional efficiency in separation should be manifested in the distillation of the paraffin-naphthene mixture other than that attributed to the existence of a simpler system. It is therefore of interest to contrast the behavior of the paraffin-naphthene mixture during distillation in the presence and absence of the aromatic constituents.

TABLE 6.—*Results of the distillation as oil at 215 mm* Hg *of the separated concentrates*

Boiling range of fraction (215 mm) Hg	Original oil		Paraffin-naphthene mixture			Aromatic concentrate
	Volume	Ref. index	Volume	Ref. index	Boiling point[a] (760 mm Hg)	Volume
°C	*ml*	n_D^{25}	*ml*	n_D^{25}	*°C*	*ml*
<109.0	----------	----------	128	1. 4233	149. 8	----------
109.0 to 109.5	----------	----------	10	1. 4246	----------	----------
109.5 to 110.0	----------	----------	708	1. 4259	153. 9	----------
110.0 to 110.5	----------	----------	659	1. 4270	154. 5	----------
110.5 to 111.0	460	1. 4314	210	1. 4287	155. 6	----------
111.0 to 111.5	1, 020	1. 4329	219	1. 4273	155. 8	----------
111.5 to 112.0	520	1. 4343	540	1. 4284	155. 3	----------
112.0 to 112.5	1, 200	1. 4354	493	1. 4289	155. 9	----------
112.5 to 113.0	1, 272	1. 4364	1, 085	1. 4286	156. 4	----------
113.0 to 113.5	1, 885	1. 4372	760	1. 4271	157. 1	----------
113.5 to 114.0	1, 264	1. 4378	731	1. 4258	157. 4	----------
114.0 to 114.5	1, 502	1. 4383	793	1. 4230	158. 0	----------
114.5 to 115.0	1, 458	1. 4385	849	1. 4213	158. 6	----------
115.0 to 115.5	1, 130	1. 4387	579	1. 4202	159. 0	163
115.5 to 116.0	3, 073	1. 4365	776	1. 4196	159. 2	114
116.0 to 116.5	2, 470	1. 4340	1, 085	1. 4190	159. 9	171
116.5 to 117.0	3, 010	1. 4332	1, 518	1. 4176	160. 3	308
117.0 to 117.5	1, 987	1. 4341	3, 626	1. 4168	160. 8	844
117.5 to 118.0	2, 182	1. 4355	733	1. 4178	----------	678
118.0 to 118.5	----------	----------	392	1. 4191	----------	400
118.5 to 119.0	----------	----------	160	1. 4204	----------	72
119.0 to 119.5	----------	----------	87	1. 4193	----------	254
119.5 to 120.0	----------	----------	----------	----------	----------	146
120.0 to 120.5	----------	----------	----------	----------	----------	329
120.5 to 121.0	----------	----------	----------	----------	----------	232
Unallocated [b]	----------	----------	119	----------	----------	140
Residue	----------	----------	645	1. 4193	----------	568

[a] Relative only.

[b] Material recovered from intermediates of wide boiling range. Intermediate not separated −45 ml.

In figure 4, the solid curves represent the weighted volumes and refractive indices of the paraffin-naphthene mixtures as they hypothetically existed in the original distillate. These curves may be assumed to represent the conditions existing when the vapor-pressure relations of the paraffin-naphthene mixture are modified by the presence of aromatic hydrocarbons. The data on the systematic distillation of the paraffin-naphthene mixture as oil at 215 mm Hg are given in columns 4 and 5 of table 6, and are shown graphically by the broken curves for volume and refractive index in figure 4. These broken curves illustrate the behavior of the paraffin-naphthene mixture in the absence of the aromatic constituents.

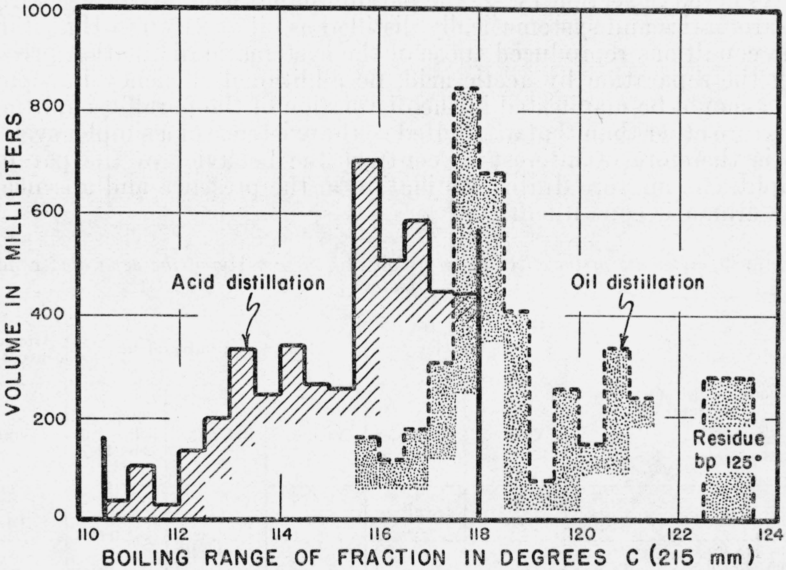

FIGURE 5.—*Data on the aromatic concentrate originally boiling between 110.5° and 118.0° C at 215 mm* Hg *(154° to 162° C at 760 mm* Hg*) showing (1) the hypothetical concentration in the untreated distillate (unbroken curves) and (2) the distribution after separation by acetic acid distillation and a subsequent oil distillation (broken curves).*

The scale of ordinates at the lower left gives the volume in liters and that at the upper right, the refractive index of each 0.5° cut. The scale of abscissas gives the boiling ranges of the fractions (taken in 0.5° cuts).

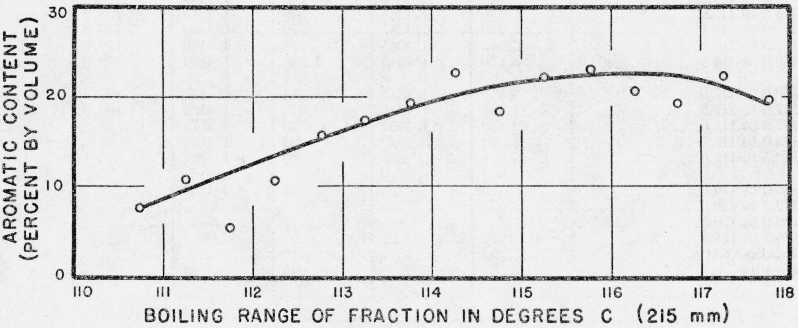

FIGURE 6.—*Data on the concentration of aromatic hydrocarbons in the original untreated distillate boiling between 110.5° and 118.0° C at 215 mm* Hg *(154° to 162° C at 760 mm* Hg*).*

The scale of ordinates gives the aromatic content in percentage by volume. The scale of abscissas gives the boiling ranges of the fractions (taken in 0.5° cuts).

The curves of figure 4 show that better resolution of the system (paraffin-naphthene mixture) was attained after removal of the aromatic hydrocarbons. The existence of fewer components should, of course, tend to yield sharper separation. The improved resolution is evidenced by the greater range in refractive index and the sharpness of the peak at 117.0° to 117.5° C in the volume-boiling range curve. However, the data form no basis for conclusions concerning the formation of azeotropes. The maxima and minima in the broken curves of figure 4 may be interpreted as indications of a paraffinic component which boils near 117° C at 215 mm Hg (161° C at 760 mm Hg) and of one or more naphthenic constituents which boil near 113° C at 215 mm Hg (157° C at 760 mm Hg).[16]

3. AROMATIC CONSTITUENTS

In the previous section, weighted volumes of the aromatic concentrate separated from each 0.5° C out of the original oil were estimated. These data appear in column 9 of table 5, and graphically as the broken curve for volume in figure 3. The curve is repeated in figure 5 on a larger scale (unbroken curve) and is to be contrasted with the broken curve in figure 5 which represents the relation of boiling point to volume of the same material after distillation as oil at 215 mm Hg, the data for which appear in table 6, column 7. The refractive indices of all fractions except a few initial cuts were greater than 1.490 and varied but little.

Figure 6 [17] shows that the distribution of aromatic hydrocarbons is quite general.

The curves of figure 5 show that the bulk of the aromatic concentrate is found in fractions of the original oil having boiling points considerably lower than the true boiling points of the aromatic hydrocarbons. This result is analogous to those obtained in previous investigations of aromatic hydrocarbons in this petroleum [3, 4, 8].

The shape of the volume-boiling point curve combined with analogies from the behavior of the xylene fraction [8] suggests that the aromatic concentrate contains *n*-propylbenzene, *p*-, *m*-, and *o*-methylethylbenzene, as well as mesitylene. This material is now under investigation.

VI. CONCLUSIONS

The feasibility and advantages of the use of azeotropic agents, in particular acetic acid, have been shown to be valid for the separation of aromatic hydrocarbons from a petroleum distillate. From the degree of resolution obtained, it appears that the relation existing between the concentrations in the liquid and vapor phases is considerably more favorable than usually encountered in a simple distillation without an added component; i. e., the separation factor is high.[18] That is, in the phase diagram for two components where temperature is shown as a function of concentration, the separation of the vapor and liquid lines is large and the concentration is radically altered by the operation of one theoretical plate. If such were not the case, a separation into almost pure paraffin-naphthene mixture and pure aromatic concentrate could not be attained in a still with only about 25 theoretical plates.

---

[16] Tongberg, Fenske, and Sweeney [30] make similar conclusions from the distillation of a number of virgin naphthas.

[17] Percentages attached to cuts having small volumes may be considerably in error.

[18] Swiętoslawski [31] p. 101, states that a mixture of binary azeotropes, on distillation, behaves as though it were composed of individual components which either obey Raoult's law or give only slight deviations therefrom. He also discusses the addition of an "azeotropizer" to a series of chemically related substances.

From the data given in this and previous papers [24, 25, 28], it may be concluded that the method of distillation with acetic acid can also be successfully employed on the xylene fraction (130° to 145° C) and on the trimethylbenzene fraction (162° to 176° C).

The authors take this opportunity to acknowledge the aid of S. T. Schicktanz in the supervision of the distillation, and for his suggestions during the development of the method. They are also grateful for the interest and encouragement of F. D. Rossini, Director of API Research Project 6.

VII. REFERENCES

[1] E. W. Washburn, Ind. Eng. Chem. **22,** 985–988 (1930); **25,** 891 (1933).
[2] F. D. Rossini, Proc. Am. Petroleum Inst. 18 (III) (1937); Oil Gas J. **26,** No. 26, 193 (1937); Refiner Natural Gasoline Mfr. **16,** 545–562 (1937).
[3] J. H. Bruun, R. T. Leslie, and S. T. Schicktanz, BS J. Research **6,** 363–367 (1931) RP280.
[4] J. H. Bruun and M. M. Hicks-Bruun, BS J. Research **6,** 869–879 (1931) RP311.
[5] V. N. Ipatieff and L. Schmerling, J. Am. Chem. Soc. **59,** 1056–1059 (1937).
[6] A. v. Baeyer, Liebigs Ann. Chem. **155,** 275 (1870).
[7] J. D. White and F. W. Rose, Jr., J. Research NBS **13,** 799–810 (1934) RP745.
[8] J. D. White and F. W. Rose, Jr., BS J. Research **9,** 711–719 (1932) RP501.
[9] B. J. Mair and S. T. Schicktanz, BS J. Research **11,** 665–680 (1933) RP614.
[10] L. I. Smith and O. W. Cass, J. Am. Chem. Soc. **54,** 1609 (1932).
[11] L. I. Smith and A. R. Lux, J. Am. Chem. Soc. **51,** 2994 (1929).
[12] L. I. Smith and O. W. Cass, J. Am. Chem. Soc. **54,** 1603 (1932).
[13] H. T. Clarke and E. R. Taylor, J. Am. Chem. Soc. **45,** 830 (1923).
[14] H. E. Armstrong and A. K. Miller, J. Chem. Soc. **45,** 148 (1884).
[15] R. T. Leslie, BS J. Research **8,** 591 (1932) RP439.
[16] J. Tausz and A. Stüber, Z. angew. Chem. **32,** I, 175 (1919).
[17] K. A. Varteressian and M. R. Fenske, Ind. Eng. Chem. **28,** 928 (1936).
[18] M. R. Cannon and M. R. Fenske, Ind. Eng. Chem. **28,** 1035 (1936).
[19] Saal and van Dyck, Proc. World Petroleum Cong. (London) **2,** 352 (1933).
[20] B. J. Mair and J. D. White, J. Research NBS **15,** 51 (1935) RP809.
[21] M. M. Hicks-Bruun and J. H. Bruun, BS J. Research **7,** 799–809 (1931) RP375.
[22] J. H. Bruun and M. M. Hicks-Bruun, BS J. Research **5,** 933–942 (1930) RP239.
[23] S. T. Schicktanz, J. Research NBS **18,** 129 (1937) RP969.
[24] J. D. White and F. W. Rose, Jr. J. Research NBS **17,** 943 (1936) RP955.
[25] S. T. Schicktanz, unpublished.
[26] C. O. Tongberg and F. Johnston, Ind. Eng. Chem. **25,** 733 (1933).
[27] J. D. White and F. W. Rose, Jr., BS J. Research **7,** 907 (1931) RP383.
[28] J. D. White and F. W. Rose, Jr., J. Research NBS **21,** 151 (1938) RP1122.
[29] J. H. Bruun and S. T. Schicktanz BS J. Research **7,** 851 (1931) RP379.
[30] C. O. Tongberg, M. R. Fenske, and W. J. Sweeney, Ind. Eng. Chem. **30,** 166 (1938).
[31] W. Swietoslawski, Ebulliometry (Chemical Publishing Co., New York, N. Y., 1937).

WASHINGTON, April 20, 1938.