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SEPARATION OF CONSTANT-BOILING MIXTURES OF NAPHTHENE AND PARAFFIN HYDROCARBONS BY DISTILLATION WITH ACETIC ACID.[1]

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ABSTRACT

Constant-boiling fractions of gasoline normally boiling in the temperature range 130 to 174° C, and consisting of naphthene and paraffin hydrocarbons, have been successfully separated by distilling with acetic acid. The azeotropic mixtures formed by the hydrocarbons and the acid aid in separately concentrating the paraffin and naphthene groups, which, although never absolutely pure, can be separated further by other physical methods.

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I. INTRODUCTION

It is very difficult and sometimes impossible to obtain pure hydrocarbons from gasoline by fractional distillation alone. This is especially true of gasoline consisting of varying amounts of the two types of hydrocarbons, naphthenes, and paraffins, which are distributed throughout the boiling range. This is caused in part by the tendency of the different types of hydrocarbon molecules present to form azeotropic mixtures, and in part by the fact that the boiling points of the different substances are so close together that separation by distillation is impractical.

Although the various homologous series of hydrocarbons belong to the class of substances known as molecularly nonassociated,[3] their mixtures deviate considerably from the laws of ideal solutions. This is shown by the work of previous investigators [4, 5] who have studied the simple binary mixture of benzene and *n*-hexane, which cannot be

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[3] K. Von Auwers, Z. phys. Chem. **30**, 300 (1899).

[4] J. H. Bruun and M. M. Hicks-Brunn, BS J. Research **5**, 933 (1930). RP239.

[5] C. O. Tongberg and F. Johnston, Ind. Eng. Chem. **25**, 733 (1933).

separated quantitatively by systematic fractional distillation alone. Such systems, which deviate considerably from Raoult's law of solutions, may be successfully separated by distillation if a third component[6] is added. Under these conditions, the equilibrium is altered by the formation of new azeotropic mixtures. The effectiveness of such a separation will depend, however, upon the difference in molecular structure of the various hydrocarbons in question,[7] and the characteristics of the third component. It is essential, also, that the added component shall not react with, or polymerize, the hydrocarbons, and shall be readily and quantitatively removable from the hydrocarbons after the separation has been effected.

Glacial acetic acid, which is highly molecularly associated,[8] has been found in this laboratory to be very effective as a third component in the separation of constant-boiling fractions of gasoline consisting of naphthene and paraffin hydrocarbons. Although acetic acid is a low-boiling liquid (118.1° C), it tends to form azeotropes with hydrocarbons boiling over a considerable temperature range, and can be used successfully for the separation of the constant-boiling fractions of gasoline normally boiling in the range 130 to 174° C. It is also inexpensive, does not attack or decompose the hydrocarbons in question, and is readily removed quantitatively from the hydro-carbons by washing with water.

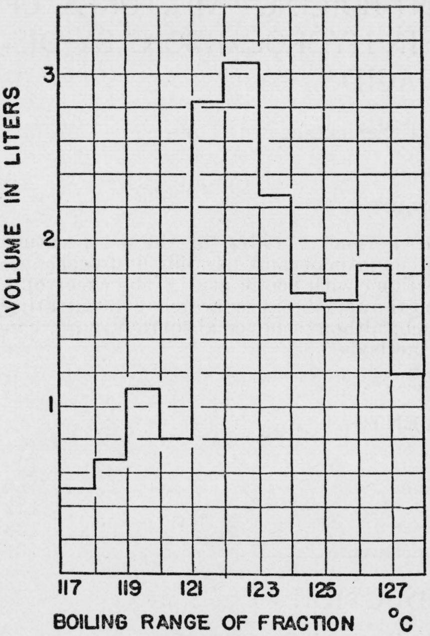

FIGURE 1.—*Distribution of the petroleum distillate by volume with respect to boiling range at 215-*mm *pressure*

II. DESCRIPTION OF THE FRACTION OF GASOLINE

The gasoline fraction, consisting essentially of naphthene and paraffin hydrocarbons, was obtained by removing the aromatic hydrocarbons from a carefully fractionated portion of petroleum, boiling between 118 and 130° C at 215-mm pressure,[9] which corresponds to 162 to 174° C at 760 mm. The bulk of the aromatic hydrocarbons was removed first by extraction with liquid sulphur dioxide[10] at −35° C. The hydrocarbons immiscible with sulphur dioxide were subsequently treated with concentrated sulphuric acid for 22 hours at room temperature to remove all the remaining aromatic substances. The

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[6] J. H. Bruun and M. M. Hicks-Brunn, BS J. Research **5**, 933 (1930). RP239.

[7] S. T. Schicktanz, *Azeotropism as exhibited by three classes of hydrocarbons, aromatic, naphthene, and paraffin, with acetic and propionic acids* (to be published in J. Research NBS).

[8] T. M. Fenton and W. E. Gardner, J. Chem. Soc. **1930**, 694.

[9] B. J. Mair and S. T. Schicktanz, BS J. Research **11**, 665 (1933) RP614.

[10] R. T. Leslie, BS J. Research **8**, 591 (1932) RP439.

remaining unsulphonated oil layer, consisting essentially of naphthene and paraffin hydrocarbons, was washed repeatedly with sodium carbonate and then with water in order to remove all traces of sulphuric acid or sulphonated products. This mixture of hydrocarbons was then subjected to a systematic distillation at 215-mm pressure in a column packed with locket-chain.[11]

Little separation was produced by the third systematic distillation. In table 1 are shown the results of a third systematic distillation of one of the portions of oil, which consisted of a number of fractions from the second distillation combined according to boiling point and refractive index. The spread of the boiling points and refractive indices of the distilled fractions is almost identical with the spread of the boiling points and refractive indices of the fractions used to make up the original charge. The total amount of material of the original isodecane fraction was apparently so well distributed over its temperature range by the third systematic distillation that further fractionation by straight distillation of the oil appeared to be impractical. The distribution by volume of the isodecane fraction with respect to boiling-point range is shown in figure 1.

TABLE 1.—*Separation obtained during the third systematic fractionation of the gasoline*

Fraction	Percentage of charge distilled	Boiling point at 215 mm Hg	Refractive index n_D^{25}
Original		122 to 123	1.4221 to 1.4268
1	4.07	122.2	1.4259
2	3.82	122.3	1.4249
3	3.62	122.3	1.4249
4	3.82	122.4	1.4249
5	3.95	122.4	1.4252
6	3.36	122.4	1.4253
7	3.36	122.3	1.4248
8	3.69	122.3	1.4246
9	3.36	122.3	1.4246
10	4.26	122.3	1.4234
11	2.13	122.3	1.4239
12	3.56	122.3	1.4245
13	4.07	122.4	1.4238
14	3.17	122.4	1.4234
15	3.36	122.4	1.4236
16	3.88	122.4	1.4234
17	3.62	122.4	1.4230
18	3.36	122.6	1.4228
19	3.24	122.7	1.4229
20	3.24	122.7	1.4226
21	3.82	122.7	1.4230
22	3.24	122.9	1.4225
23	3.69	123.0	1.4226
24	3.88	123.0	1.4214
25	3.43	123.2	1.4214
26	3.88	123.2	1.4213
27	3.43	123.3	1.4212
28	3.62	123.4	1.4213

According to the refractive indices, each 1.0° C fraction, throughout the distillation range, consisted of a mixture of varying amounts of naphthene and paraffin hydrocarbons, with no indication of the separation of a pure hydrocarbon.

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[11] S. T. Schicktanz, BS J. Research **11**, 89 (1933) RP579.

III. METHOD

Each of the 1° fractions could be separated further by distillation upon the addition of acetic acid (glacial) to the oil. An excess of acid was used at all times in order to have pure acetic acid remaining in the still pot after all the hydrocarbons had been removed. This made it possible to distill the oil at temperatures below the boiling point of acetic acid (118.1° C), thereby decreasing the possibility of changing the composition of the oil by cracking or polymerization. This required approximately a 4:1 ratio of acid to oil, since the azeotropes formed by the hydrocarbons of the oil fraction having a boiling point of 123° C at 215-mm pressure contained between 70 and 77 percent of acid.

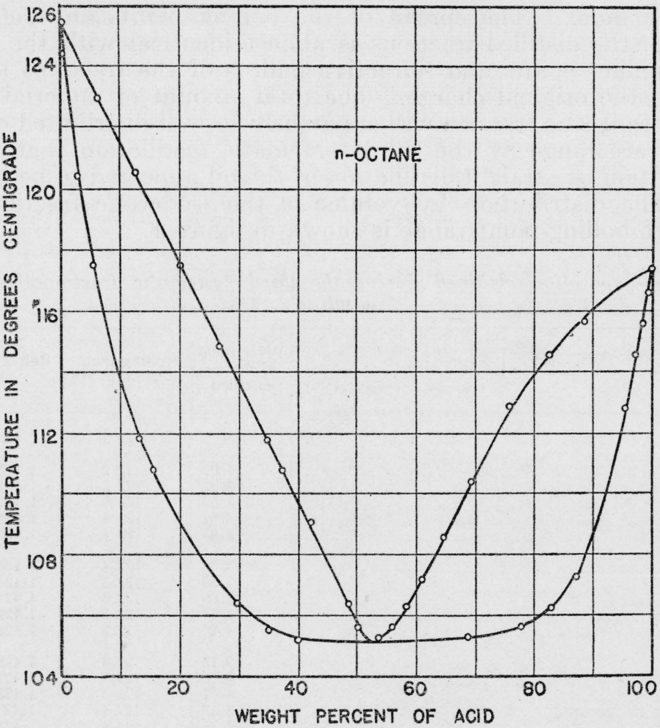

Figure 2.—*Composition-temperature diagram for the vapor and liquid phases for the binary mixture of n-octane and acetic acid.*

Because of this procedure only that part of the system which consisted of the azeotropes and acetic acid was made use of in the distillation. This is illustrated in figure 2, which shows the composition-temperature diagram of both the vapor and liquid phases for the binary system of *n*-octane and acetic acid. The minimum boiling point of this binary system is 105.1° C at 760-mm pressure and consists of 52.5 percent by weight of acid and 47.5 percent of hydrocarbon. The boiling point and the percentage of acid in the azeotrope increase as the number of carbon atoms in the hydrocarbon molecule is increased. For example, a gasoline fraction boiling at 132° C at 760-mm pressure formed an azeotrope consisting of approximately 56 percent by weight of acid.

The azeotropic mixtures of acid and hydrocarbons were distilled into 100-ml fractions at a rate of approximately 1 ml per minute at atmospheric pressure. The separation of the hydrocarbons occurring during the distillation was followed by determining the refractive index of the oil in every second or every fifth fraction. The acetic acid was removed from the oil of each fraction by washing three times with water in a separatory funnel before determining the refractive index. Although the acid distillations afforded an effective separation of the two classes of hydrocarbons in the constant-boiling fractions of gasoline, it was necessary to subject the intermediate cuts to several successive acid distillations in order to concentrate the bulk of the paraffins and naphthenes into separate fractions, leaving only a small amount of material which was intermediate in composition. Because of the corrosive action of the acetic acid, it was not possible to use the chain-packed columns and, consequently, all the separations were made in an all-glass 30-bubble-cap column.[12]

IV. RESULTS

In table 2 are given the results of a distillation, which is characteristic of all the distillations carried out. The first portion of distillate invariably separated into two layers, presumably because of the water in the acetic acid. In many instances, the hydrocarbons recovered from this first fraction had a high refractive index, indicating inefficiency of separation caused by the formation of a complex azeotropic system consisting of acid, water, and hydrocarbons. The remaining fractions obtained during these distillations were homogeneous at room temperature, and the refractive index, beginning low, gradually increased.

TABLE 2.—*Acid distillation of a constant-boiling fraction of gasoline n_D^{25} 1.4225 to 1.4238; bp_{215} 122 to 123° C*

Fraction	Volume of fraction, acid plus oil	Refractive index of acid-free oil of specified cuts n_D^{25}	Fraction	Volume of fraction, acid plus oil	Refractive index of acid-free oil of specified cuts n_D^{25}
	ml			ml	
Original	500 oil		11	104	
	1,500 acetic acid		12	104	
1	100	1. 4132	13	104	
2	117		14	101	
3	113		15	102	1. 4251
4	110				
5	109	1. 4142	16	114	
			17	106	
6	105		18	105	
7	119		19	68	1. 4409
8	112				
9	102				
10	111	1. 4174			

In the constant-boiling fractions of gasoline, the paraffin hydrocarbons, which produce the most abnormal solutions with acetic acid, form azeotropic mixtures which are lower-boiling than those formed by the naphthenes. This is clearly shown in column 3 of table 2. The first substance removed from the complex mixture of the originally charged oil by the distillation has a low refractive index which ap-

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[12] J. H. Bruun and S. T. Schicktanz, BS J. Research 7, 851 (1931) RP379.

proaches that of the paraffin hydrocarbons. As the distillation proceeds, the refractive index of the fractions increases and approaches that of the naphthene hydrocarbons.

Although the acid distillation concentrates the paraffin hydrocarbons in the fore part of the distillation and the naphthenes in the latter part, neither group of hydrocarbons can be obtained in a pure state. It appears that the azeotropes formed are not truly simple binary mixtures, but are either ternary mixtures consisting of a large percentage of one type of hydrocarbon, a small amount of the other, and acetic acid, or complex mixtures of binary azeotropes having a constant boiling point. This is substantiated by the ineffective separation produced by redistilling a charge of material of low refractive index. In table 3 are given the results of such a distillation. Very little separation occurred, as is seen by the large volume of material of constant refractive index occurring during the fore part of the distillation.

TABLE 3.—*Redistillation of material of low refractive index*

Fraction	Volume of fraction, acid and oil	Refractive index of acid-free oil n_D^{25}	Fraction	Volume of fraction, acid and oil	Refractive index of acid-free oil n_D^{25}
	ml			ml	
Original material		1.4160 to 1.4210	11	101	
			12	106	
1	93	1.4172	13	104	
2	101		14	114	
3	106		15	96	1.4172
4	100				
5	108	1.4172	16	102	
			17	113	
6	102		18	141	1.4183
7	107		19	106	
8	124		20	110	1.4267
9	110				
10	114	1.4172	21	104	

V. FURTHER SEPARATION OF ACETIC ACID CONCENTRATES

The material with a constant refractive index, which can not be separated further by acid distillation, can be further resolved by subjecting the oil, free from acid, to a simple fractional distillation. In table 4 are shown the results obtained by distilling such a concentrate at 215-mm pressure. The paraffins concentrated apparently in the latter part of the distillation, as is evidenced by the fractions of low refractive index, shown in column 4 of the table. The material in the fore part of the distillation, with an index higher than that of the starting material, can be further separated by an acid distillation.

The curves in figure 3 summarize the relative effectiveness of the various types of distillation. Curve 1 shows the separation occurring during the third systematic distillation of the oil, at 215-mm pressure, using an efficient locket chain packed column. Curve 3 shows the separation obtained during the first acid distillation of a narrow-boiling fraction of gasoline. Curve 2 shows the ineffectiveness of the acid treatment when dealing with a previously distilled paraffin concentrate and curve 4 shows the separation obtained by distilling an acid-free paraffin concentrate at 215-mm pressure.

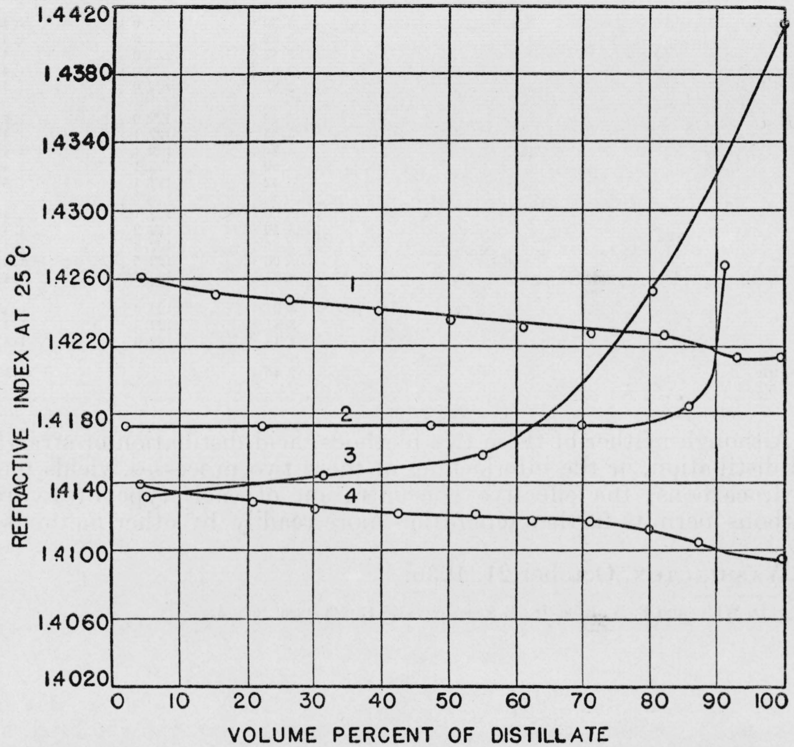

FIGURE 3.—*Separation obtained in the various distillations: (1) Oil distillation at 215-*mm *pressure; (2) acetic acid redistillation of a low refractive index concentrate; (3) acetic acid distillation of a constant-boiling fraction of gasoline; (4) oil distillation at 215-*mm *pressure of a paraffin fraction previously concentrated by acetic acid distillation.*

TABLE 4.—*Distillation at a pressure of 215* mm Hg *of the concentrate of low refractive index from acetic acid distillation*

Fraction	Percentage of charge distilled	Boiling point at 215 mm Hg	Refractive index n_D^{25}
Original			1.4114 to 1.4120
1	4.14	121.4	1.4138
2	4.91	121.8	1.4138
3	3.99	121.8	1.4129
4	3.99	121.9	1.4128
5	4.14	121.9	1.4128
6	3.39	121.9	1.4126
7	3.32	122.0	1.4125
8	2.32	122.0	1.4124
9	2.65	122.0	1.4123
10	2.82	122.0	1.4123
11	3.49	122.0	1.4123
12	3.65	122.1	1.4121
13	3.81	122.1	1.4120
14	3.99	122.1	1.4120
15	3.32	122.1	1.4121
16	5.00	122.1	1.4119
17	3.49	122.2	1.4117
18	3.65	122.3	1.4117
19	5.00	122.5	1.4117
20	4.31	122.6	1.4116
21	4.31	122.6	1.4113
22	3.81	122.6	1.4109
23	4.14	122.6	1.4104
Residue	12.46		1.4095

Although neither of these two methods, acid distillation or straight oil distillation, or the interlocking of these two processes, yields pure hydrocarbons, the effective concentration of each type of hydrocarbons permits further separation more readily by other methods.[13]

WASHINGTON, October 21, 1936.

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[13] J. D. White and F. W. Rose, Jr., J. Research NBS **17**, 943 (1936) RP955.