SEPARATION OF HYDROCARBONS BY AZEOTROPIC DISTILLATION [1]*

By Beveridge J. Mair,[2] Augustus R. Glasgow, Jr.,[2] and Frederick D. Rossini

ABSTRACT

The following topics are discussed: the principles involved in azeotropic distillation; the substances that form azeotropic mixtures with hydrocarbons; the separation of hydrocarbons by azeotropic distillation, including aromatics from naphthenes and paraffins, naphthenes from paraffins, aromatic hydrocarbons having different numbers and kinds of rings, naphthene hydrocarbons having different numbers of naphthene rings, olefin hydrocarbons, and isomeric hydrocarbons; the differences in the change of boiling point with pressure for the different types of hydrocarbons; and the benefits of distillation at reduced pressure prior to azeotropic distillation at the normal operating pressure. A general procedure is outlined for separating a given (gasoline or kerosene) fraction of petroleum by means of distillation alone in its several variations (at the normal distilling pressure, at reduced pressure, and with an azeotrope-forming substance). A list is given of the hydrocarbons which are known to be separable in a substantially "pure" state by distillation alone from petroleum or its products.

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I. INTRODUCTION

In the work of the American Petroleum Institute Research Project 6 on the chemical constitution of petroleum, the separation of pure hydrocarbon compounds is accomplished by the appropriate inter-

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locking of the fractionating processes of distillation, crystallization, extraction, and adsorption. Each of these processes has one or more variations: distillation may be performed at the fixed "normal" operating pressure,[3] or by alternate distillation at the normal and at reduced pressure, or by distillation with an azeotrope-forming substance; crystallization may be performed by simple refrigeration of the mixture of hydrocarbons followed by equilibrium melting with centrifuging, or by refrigeration of the mixture dissolved in an appropriate solvent followed by equilibrium melting with centrifuging; extraction may be performed with different solvents and at different temperatures; and adsorption may be performed with different adsorbents. Of the foregoing processes, distillation at a fixed pressure produces fractionation substantially according to size of molecules or molecular weight; whereas fractionation substantially according to type of molecule is produced by distillation at alternating different pressures, by distillation with an azeotrope-forming substance, by extraction, and by adsorption.

Although the most effective and complete results usually are obtained by utilizing all four processes of fractionation and their appropriate variations, it frequently may happen that distillation alone, in its several variations, may suffice to bring about a substantially complete separation of given hydrocarbons or of groups of isomeric hydrocarbons. When it is possible to use distillation alone, the laboratory or plant has the advantage of being able to utilize distillation apparatus or equipment that is already available and that has been developed to a high degree of efficiency for operations on both small and large scales.

In this paper are presented a discussion of azeotropic distillation and of substances that form azeotropic mixtures with hydrocarbons, a description of the separation of various kinds of hydrocarbons by azeotropic distillation, a discussion of the benefits of prior distillation at reduced pressure, an outline of a general procedure for separating a given gasoline or kerosene fraction of petroleum by using only distillation in its several variations, and a list of hydrocarbons known to be separable by distillation alone.

II. PRINCIPLES INVOLVED IN AZEOTROPIC DISTILLATION

In the ideal liquid solution, the partial vapor pressure, p_i, of a given component, i, is equal to the mole fraction, N_i, of component i multiplied by the vapor pressure, p_i°, of component i in the pure state at the given temperature:

$$p_i = N_i p_i^{\circ}. \tag{1}$$

The total vapor pressure, P, is the sum of the several partial vapor pressures:

$$P = \Sigma p_i. \tag{2}$$

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[3] As used in this paper, "normal" pressure refers not to atmospheric pressure but to that pressure at which the distillation of material of a given boiling range normally is performed, and reduced pressure refers to a pressure below that which is normal for the given material. In this laboratory, for example, normal pressure is 770 mm Hg for material boiling up to about 130° C at atmospheric pressure, 217 mm Hg for material boiling from about 130° to 200° C at atmospheric pressure, and 56.8 mm for material boiling from about 200° C to 260° C at atmospheric pressure. For hydrocarbons of the gasoline and kerosene ranges, the lowering of the boiling point between 770 and 217 mm and between 217 and 56.8 mm is 40° to 45° C.

For an ideal solution of two components, A and B, the partial vapor pressures are:

$$p_A = N_A p_A^\circ \tag{3}$$
$$p_B = N_B p_B^\circ = (1 - N_A) p_B^\circ \tag{4}$$

and the total vapor pressure is:

$$P = p_A + p_B = p_B^\circ + N_A (p_A^\circ - p_B^\circ). \tag{5}$$

The relations given by eq 3, 4, and 5, each of which is linear with the mole fraction, are shown graphically in part I of figure 1.

The laws of the ideal solution, as expressed by the foregoing equations, imply that, in the ideal solution of two components A and B, the interaction between the unlike molecules is the same as that between the like molecules.

In many real binary solutions, it is found that the interaction between the unlike molecules is not sigificantly different from the interaction between the like molecules, and the resulting partial and total vapor pressures are subtantially in accord with the relations holding for the ideal solution. Two such real binary solutions that are substantially ideal are the solution of ethylene bromide (1,2-dibromoethane) and propylene bromide (1,2-dibromopropane), the vapor pressures of which [1] [4] are illustrated in part II of figure 1, and the solution of n-heptane and methylcyclohexane, the vapor pressures of which [2, 3] are illustrated in part III of figure 1. In each of these cases, the respective components are very similar in molecular character.

Deviations from the laws of the ideal solution will occur when the interaction between unlike molecules is substantially different from that between like molecules. In the absence of other disturbing influences, such as the formation of hydrogen bonds, one property that may be used, within appropriate limits, to predict whether two given components may form a nearly ideal solution is that of the dipole moment of the molecules, which measures their polarity. Excluding components that form hydrogen bonds, substances of like polarity will be expected to form solutions in which the departures from ideality are not large. As summarized by Hildebrand [4]: "The total intermolecular field (in solutions of nonelectrolytes) includes contributions from the following effects: The potential between permanent electric dipoles; the potential between a permanent dipole and the temporary dipole it may induce in another molecule; the potential of actual chemical or electron pair bonds that may be formed; the potential due to the interaction always occurring between electron systems, regardless of the presence or absence of the foregoing effects . . . It is becoming evident, again, that the term 'association,' under which we have lumped all departures from normal behavior, must be subdivided into association arising from the interaction of dipoles and that due to the formation of definite chemical bonds. Of these [latter], perhaps the most interesting are the hydrogen bonds, or 'bridges' between oxygen, nitrogen, or fluorine atoms [which is] a species of chemical interaction. Substances containing hydroxyl [such as water and the alcohols], carboxyl [such as the ketones and aldehydes], or amino groups [such as aniline and other amines] show a type of association markedly

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

different from that of most other dipoles, such as those due to halogens." (For a detailed discussion of real solutions and their departures from ideality, see references [4, 5, 6, 7, 8, 9, 10].)

MOLE FRACTION OF COMPONENT A IN THE LIQUID PHASE
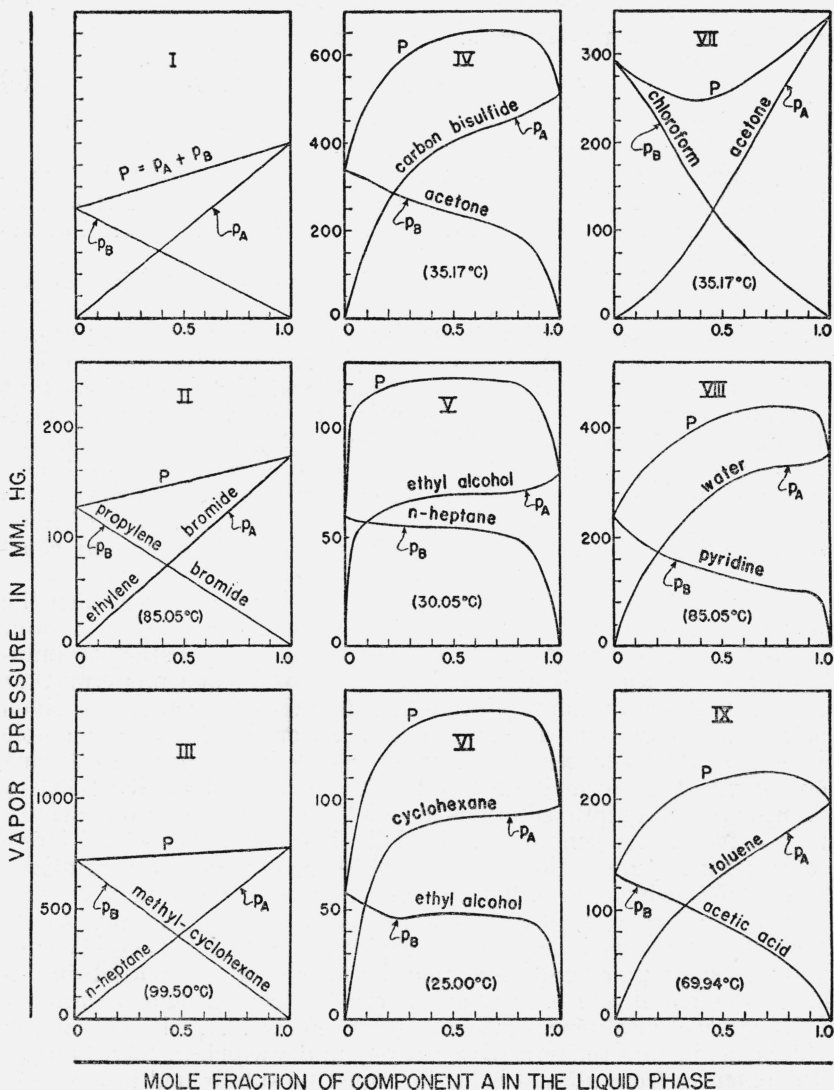
FIGURE 1.—*Partial and total vapor pressures of the ideal and of eight real binary solutions.*

The scale of ordinates gives the vapor pressure in mm Hg, and the scale of abscissas gives the mole fraction of the component that is the more volatile in the pure state. The data are from the following sources II, IV, VII, VIII, and IX, from Zawidsky [1]; III from Beatty and Calingaert [2] and Willingham and Rossini [3]; V from Ferguson, Freed, and Morris [11]; VI from Washburn and Handorf [12].

With regard to vapor pressures (which, at the pressures considered here, are substantially equal to the respective fugacities and, therefore, are a true measure of the escaping tendency of the components

from the given solutions), departures of real solutions from the ideal behavior are manifested as an increase or decrease in the partial vapor pressures from what would be their ideal values for the given concentrations, and as a corresponding increase or decrease in the total vapor pressure.

In figure 1, part IV gives the partial and the total vapor pressures for the binary solution of acetone and carbon disulfide [1] and part VII gives the same data for the binary solution of acetone and chloroform [1]. It is interesting to note that acetone forms with carbon disulfide a mixture having a total vapor pressure that is greater than that of carbon disulfide alone, which is the more volatile pure component, and hence there results a minimum-boiling azeotropic mixture. On the other hand, acetone forms with chloroform a mixture having a total vapor pressure that is less than that of the less volatile pure component, which in this solution is chloroform, and there results a maximum-boiling azeotropic mixture.

Part VIII of figure 1 gives the vapor-pressure relations for the binary solution of water and pyridine [1], which system exhibits marked deviations from ideality and yields a mixture having a total vapor pressure greater than that of the more volatile pure component, and there results a minimum-boiling azeotropic mixture. In figure 1, parts V, VI, and IX show the partial and total vapor pressures for three binary systems, in which one component is respectively a paraffin, a naphthene, and an aromatic hydrocarbon: part V, n-heptane and ethyl alcohol [11]; part VI, cyclohexane and ethyl alcohol [12]; part IX, toluene and acetic acid [1]. In each of these systems, there occurs a mixture having a total vapor pressure greater than that of the more volatile pure component, which results in a minimum-boiling azeotropic mixture. For these systems, the departures from ideality are exceedingly large and yield in each case an azeotropic mixture having a boiling point considerably below that of the lower-boiling component.
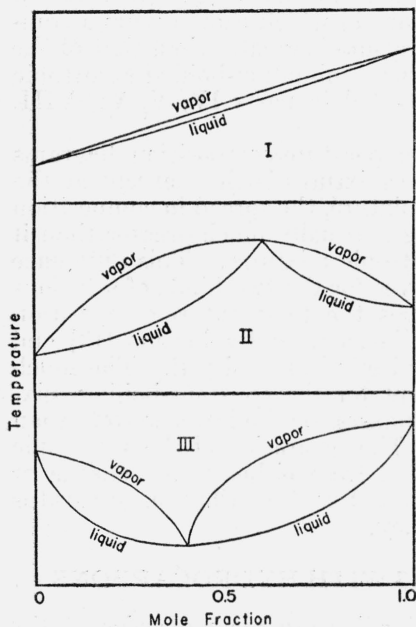
FIGURE 2.—*General temperature-composition diagrams for the liquid and vapor phases of the three types of binary solutions in which the components are completely soluble in one another.*

The scale of ordinates gives the temperature, and the scale of abscissas gives the mole fraction of that component which is the less volatile in the pure state. Part I represents ideal and other solutions in which the boiling point is, for all concentrations, always intermediate between the boiling points of the two pure components. Part II represents solutions in which there occurs a concentration for which the total vapor pressure is less than that of the less volatile pure component, forming a maximum-boiling azeotropic mixture. Part III represents solutions in which there occurs a concentration for which the total vapor pressure is greater than that of the more volatile pure component, forming a minimum-boiling azeotropic mixture.

For binary solutions in which the two components are completely miscible in the liquid phase, there are three possible kinds of temperature-composition diagrams (including both the liquid and vapor

phases), as illustrated in figure 2. Part I of figure 2 is illustrative of all ideal or other solutions in which the total vapor pressure is never less than that of the less volatile pure component nor greater than that of the more volatile pure component. That is to say, for this class of solutions, the boiling point of the liquid phase is for every concentration always intermediate between the boiling points of the two pure components. The binary systems illustrated in parts I, II, and III of figure 1 fall in this class. Part II of figure 2 is illustrative of those solutions in which there occurs a composition for which the total vapor pressure is less than that of the less volatile pure component, yielding a maximum-boiling mixture. The binary system illustrated in part VII of figure 1 falls in this class. Part III of figure 2 is illustrative of those solutions in which there occurs a composition for which the total vapor pressure is greater than that of the more volatile pure component, yielding a minimum-boiling azeotropic mixture. The binary systems illustrated in parts IV, V, VI, VIII, and IX of figure 1 fall in this class.

One characteristic feature of the temperature-composition diagrams for those systems forming azeotropic mixtures is that, except at the composition of the constant-boiling mixture, the spread in composition between the liquid and vapor phases is usually much greater than it is in systems that do not form azeotropic mixtures. This difference in the shapes of the liquid-vapor curves for the two kinds of solutions is illustrated in figure 3, which gives the temperature-composition diagrams for the binary system of benzene and n-hexane [13] and for the binary system of benzene and ethyl alcohol [14]. The much greater spread in composition (except for the constant-boiling mixture) between the liquid and vapor phases for the latter system than for the former is readily apparent. The separation of the azeotropic mixture of benzene and ethyl alcohol from either pure benzene or pure ethyl alcohol may be accomplished with distillation apparatus of relatively small separating efficiency.

III. AZEOTROPIC MIXTURES WITH HYDROCARBONS

With some exceptions, nearly all polar organic molecules of the proper volatility form, with hydrocarbons of the paraffinic, naphthenic, aromatic, and olefinic classes, mixtures that have a total vapor pressure greater than that of the more volatile pure component, yielding minimum-boiling azeotropic mixtures. The organic compounds that form azeotropic mixtures with these hydrocarbons include those containing hydroxyl, carboxyl, cyanide, amino, nitro, and other structural groups that tend to produce polarity in organic molecules.[5] For a substantially complete list of the data that have been pub-

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[5] All of the binary azeotropic mixtures in which one component is a hydrocarbon that have come to the attention of the authors are minimum-boiling with the exception of one system, that of pentachloroethane and 1,3,5-trimethylbenzene, which is a maximum-boiling one. It is likely that pentachloroethane will form maximum-boiling azeotropic mixtures with other hydrocarbons. Pentachloroethane differs from most of the other substances that form azeotropic mixtures with hydrocarbons (for which data are available) in that the polarity of the molecules in the latter class is produced by introducing an —OH, or C=O, or —CN, or similar group, into a molecule that is otherwise hydrocarbon; whereas the polarity of the penta-chloroethane molecule is produced by introducing a C—H bond into a molecule that otherwise is all composed of C—Cl bonds. Hexachloroethane is substantially nonpolar.
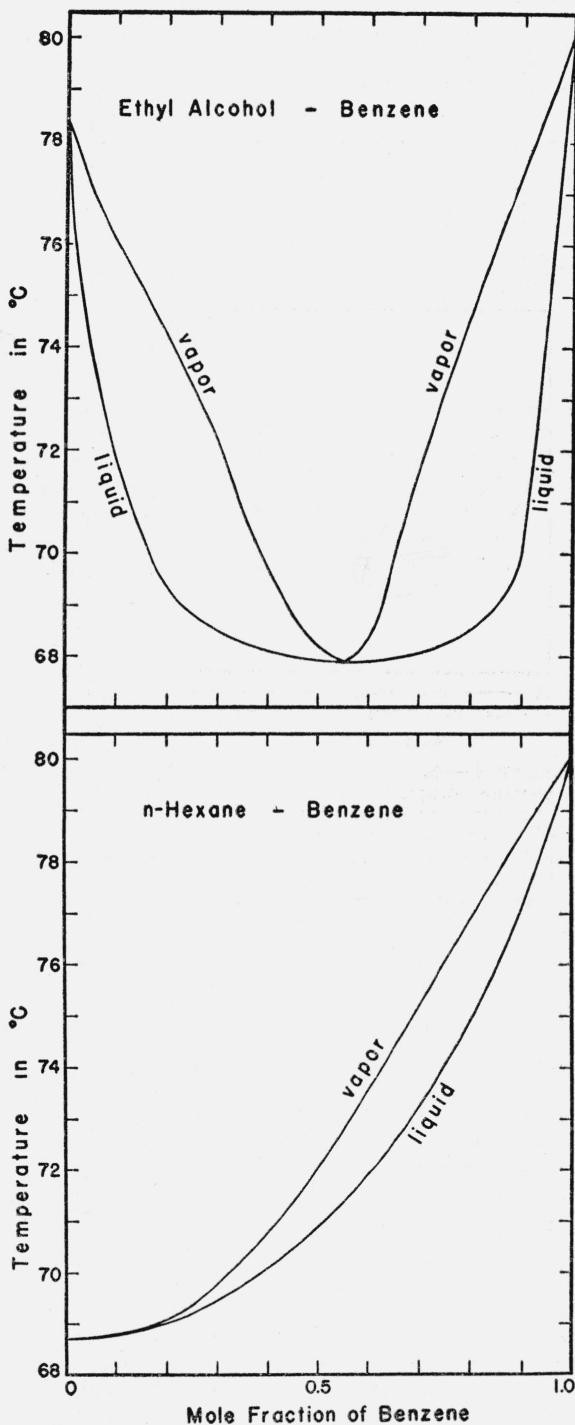
FIGURE 3. — *Temperature-composition diagrams for both the liquid and vapor phases for the binary solutions of ethyl alcohol and benzene and of n-hexane and benzene at a pressure of 1 atmosphere.*

The scale of ordinates gives the temperature in degrees centigrade, and the scale of abscissas gives the mole fraction of benzene. The diagram for the system of ethyl alcohol and benzene was constructed from the data of Fritzweiler and Dietrich [14] and that for the system of n-hexane and benzene was constructed from the data of Tongberg and Johnston [13].

Ethyl Alcohol — Benzene

n-Hexane — Benzene

Mole Fraction of Benzene

lished on azeotropic mixtures having a hydrocarbon as one component, the reader is referred to the publications of Lecat [23, 24, 25, 26].

On the basis of the existing data on the azeotropic mixtures of hydrocarbons of the various types, together with the experimental data presented in section IV of this paper, the following conclusion may be drawn: For the five binary minimum-boiling azeotropic mixtures formed between a given azeotrope-forming substance and a paraffin, naphthene, monoolefin, diolefin, and aromatic hydrocarbon, respectively, with the five hydrocarbons having the same boiling point, the departure of the partial and total vapor pressures from ideality will be greatest for the paraffin azeotrope and least for the aromatic azeotrope, with the others intermediate and usually in the order given. In terms of the difference in boiling point between the lower-boiling pure component and the minimum-boiling azeotropic mixture, the lowering is greatest for the paraffin azeotrope and least for the aromatic azeotrope, with the others intermediate and usually in the order given. For a given azeotrope-forming substance and the three hydrocarbons, paraffin, naphthene, and aromatic, all boiling at the same temperature, the foregoing relations are illustrated schematically in figure 4.

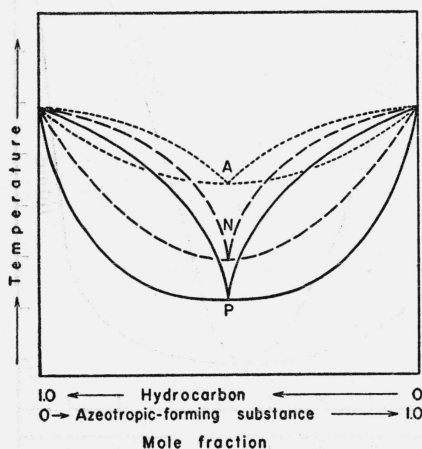1.0 ◄——— Hydrocarbon ◄——— 0
0 ──► Azeotropic-forming substance ———► 1.0

Mole fraction

FIGURE 4.—*Schematic temperature-composition diagrams for both the liquid and vapor phases for binary solutions of a given azeotrope-forming substance with an aromatic hydrocarbon, a naphthene hydrocarbon, and a paraffin hydrocarbon, respectively, all having the same boiling point in the pure state at a given pressure.*

The scale of ordinates gives the temperature, and the scale of abscissae gives the mole fraction. These diagrams illustrate the differences to be expected in the boiling points of the binary azeotropic mixtures formed between a given azeotrope-forming substance and hydrocarbons of the aromatic, naphthene, and paraffin classes, all of the same normal boiling point. The compositions of such azeotropic mixtures will usually be somewhat but not greatly different. (In this diagram, the compositions of the azeotropic mixtures are given the same value for convenience in illustration.)

Figure 5 illustrates how, with a given azeotrope-forming substance, ethyl alcohol, the boiling point and the composition of the azeotropic mixture changes with the boiling point of the members of a given homologous series of hydrocarbons. Data are given for isopentane, n-pentane, n-hexane, n-heptane, and n-octane of the paraffins, for cyclohexane and methylcyclohexane of the naphthenes, for 3-methylbutene-1 and 2-methylbutene-2 of the monoolefins for 2-methylbutadiene-1,3 and hexadiene-1,5 for the diolefins, and for benzene and toluene of the aromatics [24]. When the boiling point of the hydrocarbon is considerably below that of the azeotrope-forming substance, the composition of the azeotrope mixture will be high in the given hydrocarbon, as shown for the two pentanes and the two pentenes. As the boiling point of the hydrocarbon increases, the boiling point of the azeotropic mixture, always below that of the hydrocarbon, moves toward the boiling point of the pure azeotrope-forming substance, and the composition of the azeotropic mixture likewise becomes leaner in hydrocarbon, with both the boiling point and the composition approaching those of the pure azeotrope-forming substance as a limit. Since this is the general behavior of

such systems, the dashed line, giving the loci of the points representing the boiling point and composition of the binary azeotropic mixtures of ethyl alcohol with the paraffin hydrocarbons listed, can be used to estimate the boiling point and composition of binary azeotropic

FIGURE 5.—*Plot of the values of the boiling point and composition of the binary azeotropic mixtures formed between ethyl alcohol and five paraffin hydrocarbons, two naphthene hydrocarbons, two monoolefin hydrocarbons, two diolefin hydrocarbons, and two aromatic hydrocarbons, respectively, together with the boiling points of the pure components.*

The scale of ordinates gives the temperature in degrees centigrade, and the scale of abscissas gives the mole fractions of ethyl alcohol in the respective azeotropic mixtures. The straight lines are drawn to join the boiling point and composition of the azeotropic mixture with the boiling point of the corresponding hydrocarbon in the pure state. The curved dashed line gives the loci of the points representing the boiling points and compositions of the binary azeotropic mixtures of ethyl alcohol with isopentane, *n*-hexane, *n*-heptane, and *n*-octane. The data are from Lecat [24]. (See text for discussion).

mixtures of ethyl alcohol with other paraffin hydrocarbons of known boiling point for which no data on azeotropic mixtures exist. It will be noted that the points for the other hydrocarbons fall above the line for the paraffin hydrocarbons approximately in the order naphthene, monoolefin, diolefin, and aromatic. It appears that, with a given

azeotrope-forming substance, all hydrocarbons of about the same boiling point will form azeotropic mixtures having roughly the same composition in terms of mole fractions of the azeotrope-forming substance, and that the boiling points of these same azeotropic mixtures usually will decrease in the order aromatic, diolefin, monoolefin, naphthene, and paraffin. The same general relations hold for the hydrocarbons with other azeotrope-forming substances, for which diagrams similar to figure 5 may also be prepared.

Figure 6 illustrates how with a given hydrocarbon, benzene, the boiling point and composition of the azeotropic mixture changes with

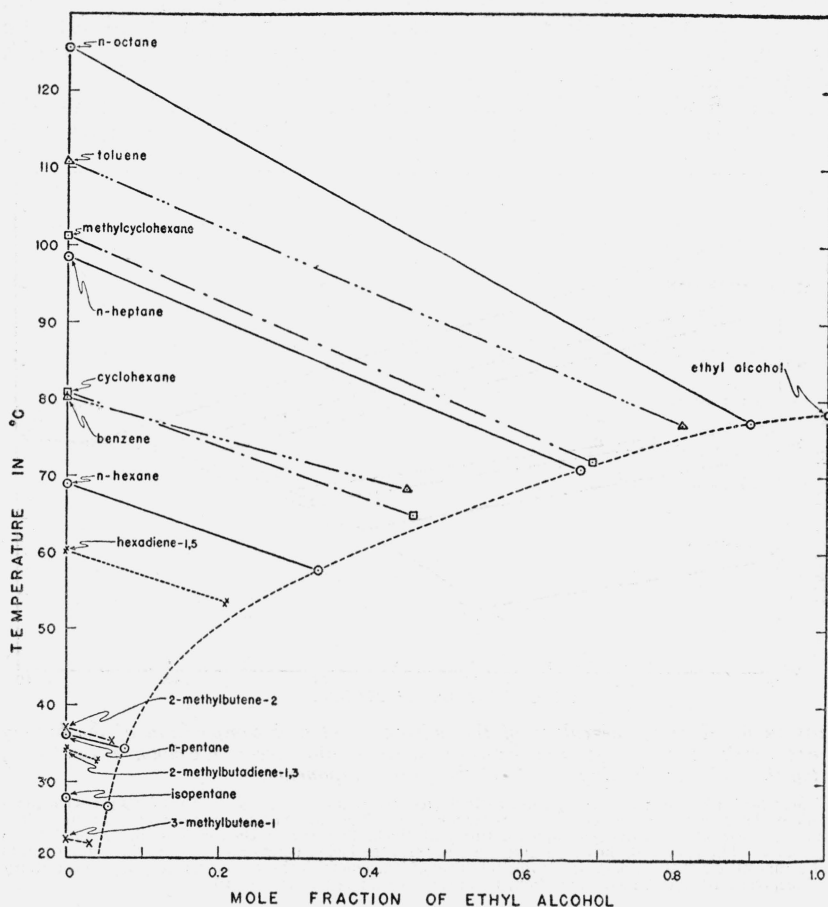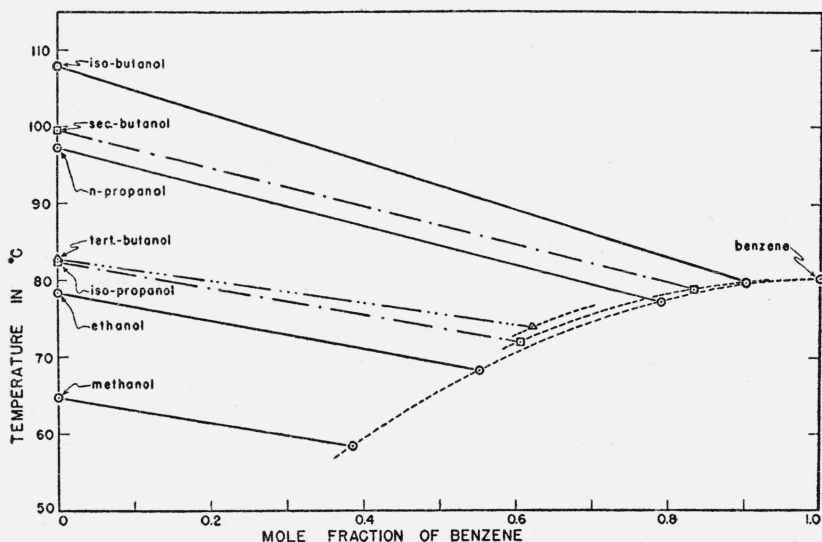FIGURE 6.—*Plot of the values of the boiling point and composition of the binary azeotropic mixtures formed between benzene and seven alcohols, respectively, together with the boiling points of the pure components.*

The scale of ordinates gives the temperature in degrees centigrade, and the scale of abscissas gives the mole fractions of benzene in the respective azeotropic mixtures. The straight lines are drawn to join the boiling point and composition of the azeotropic mixture with the boiling point of the corresponding alcohol in the pure state. The curved dashed lines give, respectively, the loci of points representing the boiling points and compositions of the binary azeotropic mixtures of benzene with the primary, secondary, and tertiary alcohols, respectively. The data are from Lecat [24]. (See text for discussion.)

the boiling point and structure of a homologous series of azeotrope-forming substances, the alcohols. Data are given for azeotropic mixtures of benzene with methyl alcohol, ethyl alcohol, *n*-propanol, *iso*-propanol, *iso*-butanol, *sec*-butanol, and *tert*-butanol [24]. For benzene with the primary alcohols, increase in the boiling point of the alcohols produces an increase in the boiling point of the azeotropic mixture and a shift in composition toward higher content of hydrocarbon. In the limit of high-boiling alcohols, the boiling point and composition of the azeotropic mixture will approach those of pure benzene as a limit. It is also interesting to note the effect of the structure of the alcohol on the location of the line representing the boiling point and composition of the azeotropic mixtures. The lowest dashed line represents azeotropic mixtures of benzene with the primary alcohols, the next higher dashed line represents the secondary

alcohols, and the highest dashed line is drawn (on the basis of one point for the *tert*-butanol) to represent the tertiary alcohols. The departure from ideality is seen to be greatest for the primary alcohols, and least for the tertiary alcohols. Similar diagrams may be prepared for other hydrocarbons and other homologous series of azeotrope-forming substances.

IV. SEPARATION OF HYDROCARBONS BY AZEOTROPIC DISTILLATION

1. GENERAL DISCUSSION

In the work of the API Research Project 6 on the separation of hydrocarbons by azeotropic distillation in the laboratory, it is usually required of an azeotrope-forming substance that it

(a) have a boiling point near (not more than 30° or 40° C away from) the boiling range of the hydrocarbons to be separated;

(b) be completely soluble in water and preferentially less soluble in the hydrocarbon at room temperature, in order that the removal of the azeotrope-forming substance from the hydrocarbon with which it is associated in the azeotropic distillate may be accomplished easily by extraction with water;

(c) be completely soluble in the hydrocarbon at the distillation temperature, and for some degrees below this, in order that two phases shall not form in the condenser and reflux regulator and thus cause difficulty in the operation of the latter, and, where packed instead of bubble-cap columns are used, in order that the liquid phase in the rectifying section shall be entirely homogeneous, thus avoiding the possibility of irregular segregation of two liquid phases in the packed section;

(d) be readily obtainable in a sufficiently pure state at reasonable cost; and

(e) be nonreactive with hydrocarbons or with the material of the still.

Among the large number of substances that are available for use in the azeotropic distillation of hydrocarbons, those that have been used in this laboratory include the following compounds, which alone boil approximately at the temperatures given:

Compound	Boiling point at 1 atm
	° C
Methyl alcohol [15, 16]_____	66
Ethyl alcohol [15]_____	78
Methyl cyanide [6]_____	82
Acetic acid [17, 18, 19]_____	118
Ethylene glycol monomethyl ether [6]_____	125
Ethylene glycol monoethyl ether [6]_____	135
Ethylene glycol monomethyl ether acetate [6]_____	144
Ethylene glycol monobutyl ether [20] [6]_____	171
Diethylene glycol monomethyl ether [21] [6]_____	194

[6] See figures 7, 8, and 9 of this paper.

In preparing for the separation of the hydrocarbons occurring in any given fraction of petroleum, it is necessary to have the mixture of hydrocarbons well separated by a systematic and efficient distillation into a series of substantially constant-boiling fractions, prior to the azeotropic distillation. This is necessary in order to avoid having any paraffins mixed with lower-boiling naphthenes and, in turn, any paraffins and naphthenes mixed with lower-boiling aromatics, which kind of mixing will tend to nullify the separation normally attainable by the azeotropic distillation of mixtures of hydrocarbons of the same boiling point.

In connection with the selection of a suitable azeotrope-forming substance, there must be considered, in addition to the requirements already mentioned, the volume of hydrocarbon material that is to be distilled in one charge and the relation of this volume to the capacity and hold-up of the distillation column. If the available narrow-boiling charge is relatively small in volume, then it is best to select an azeotrope-forming substance boiling 30° to 40° C below the hydro-carbon material, in order that the concentration of hydrocarbon in the azeotropic distillate may be small.

For most of the work in this laboratory, it has been found desirable to use an azeotrope-forming substance whose boiling point is 0° to 30° C below that of the hydrocarbon material to be separated. The composition of the azeotropic distillate usually will range from about 0.2 to 0.6 mole fraction of hydrocarbon. As can be seen from figures 5 and 6, the use of a higher-boiling or lower-boiling azeotrope-forming substance will result in an azeotropic distillate having, respectively, a higher or lower concentration of hydrocarbon. Unless there is some restriction as to the volume of the still pot in reference to the volume of hydrocarbon to be charged, and unless there is some limitation as to the time available for the distillation of a given lot of material, it is usually best to use an amount of azeotrope-forming substance in excess of the amount required to carry all of the hydrocarbon material out of the distillation column as azeotropic distillate.

In the following parts 2 to 5 of this section are presented the results of azeotropic distillations each performed as a single batch distillation in a column having a separating efficiency equivalent to from 90 to 100 theoretical plates. Ten of the eleven sets of data are new.

2. SEPARATION OF AROMATICS FROM NAPHTHENES AND PARAFFINS

Figure 7 illustrates the results obtained in separating aromatic hydrocarbons from naphthenes and paraffins by azeotropic distillation, the separation being indicated by the change in refractive index of the hydrocarbon portion of each fraction of distillate with the amount of hydrocarbon recovered.

Part I of figure 7 shows the separation obtained in the azeotropic distillation, with methyl cyanide (boiling point 82° C), of a mixture of toluene (boiling point 110.6° C) with a substantially constant-boiling (110.0° to 110.5° C) fraction of petroleum containing paraffin hydrocarbons with some naphthenes. The separation of toluene from these paraffin and naphthene hydrocarbons having substantially the same boiling point is almost quantitative.

FIGURE 7.—*Diagrams illustrating the separation of aromatic hydrocarbons from naphthenes and paraffins by azeotropic distillation.*

The scale of ordinates gives the refractive index of the hydrocarbon recovered from the azeotropic distillate, and the scale of abscissas gives the percentage of the hydrocarbon recovered. The distillations were performed in a Bruun [36] glass bubble-cap column, of 138 rectifying units, equipped with a special pot, head, and jacket assembly [3], with a reflux ratio of 40 or 50 to 1, a rate of removal of distillate of 20 to 25 ml per hour, and a total time of distillation of about 100 hours.

Part I shows the results of the azeotropic distillation, with methyl cyanide at atmospheric pressure, of a mixture of toluene (boiling point 110.6° C) with a narrow-boiling (110.0° to 110.5° C) mixture of paraffins and naphthenes. The azeotropic distillate contained about 20 percent by volume of aromatics and about 25 percent of paraffins and naphthenes, with the latter two forming a two-phase mixture with methyl cyanide at the distillation temperature.

Part II shows the results of the azeotropic distillation, with ethylene glycol monobutyl ether at 770 mm Hg, of the mixture of aromatic, naphthene, and paraffin hydrocarbons naturally occurring in a narrow-boiling (166° to 169° C) fraction of Midcontinent petroleum. The azeotropic distillate contained about 60 percent by volume of hydrocarbon, increasing from aromatic to naphthene to paraffin.

Part II of figure 7 shows the separation obtained in the azeotropic distillation, with ethylene glycol monobutyl ether (boiling point 171° C), of a narrow-boiling (166° to 169° C) fraction of petroleum containing aromatic, naphthene, and paraffin hydrocarbons [20]. There is noted here the almost complete separation of the aromatic hydrocarbons from the naphthenes and paraffins, and also a partial separation of the paraffins from the naphthenes.

Bruun and Hicks-Bruun [15] have described the use of methyl and ethyl alcohols in the separation of that fraction of petroleum normally boiling between 54° and 75° C, which contained the four higher-boiling hexanes, cyclohexane, methylcyclopentane, and benzene.

Rose and White [19] have described in detail the separation of the aromatic hydrocarbons from narrow-boiling fractions of petroleum of the range 154° to 162° C by azeotropic distillation with acetic acid (boiling point 118° C).

Tongberg and Johnston [13] have described the separation of benzene from n-hexane by azeotropic distillation with tert-butanol.

3. SEPARATION OF NAPHTHENES FROM PARAFFINS

Figure 8 illustrates the results obtained in separating naphthene hydrocarbons from paraffin hydrocarbons by azeotropic distillation.

Part I of figure 8 shows the separation obtained in the azeotropic distillation, with methyl alcohol (boiling point 66° C), of a substantially constant-boiling (92° C) fraction of paraffin and naphthene hydrocarbons [16].

Part II of figure 8 shows the separation obtained in the azeotropic distillation, with ethylene glycol monomethyl ether acetate (boiling point 144° C), of a narrow-boiling (157° to 158° C) fraction of petroleum containing paraffins and naphthenes.

Part III of figure 8 shows the separation obtained in the azeotropic distillation, also with ethylene glycol monomethyl ether acetate (boiling point 143° C) of a narrow-boiling (177° to 178° C) fraction of petroleum containing paraffins and naphthenes.

Part IV of figure 8 shows the separation obtained in the azeotropic distillation, with ethylene glycol monobutyl ether (boiling point 171° C), of a narrow-boiling (167° to 168° C) fraction of petroleum containing paraffins and naphthenes [20].

Part V of figure 8 shows the separation obtained in the azeotropic distillation, with diethylene glycol monomethyl ether (boiling point 193° C), of a narrow-boiling (200° to 201° C) fraction of petroleum containing paraffins and naphthenes [21].

Schicktanz [17] has described in detail the separation of naphthenes from paraffins in a narrow-boiling (165° to 166° C) fraction of petroleum by azeotropic distillation with acetic acid (boiling point 118° C).

Figure 9 illustrates the results obtained in the distillation of the same narrow-boiling (157° to 158° C) mixture of paraffins and naphthenes with three different azeotrope-forming substances. The results shown by the dotted line were obtained with ethylene glycol monomethyl ether acetate (boiling point 144° C), those shown by the dashed line were obtained with ethylene glycol monoethyl ether (boiling point 135° C), and those shown by the solid line were obtained with ethylene glycol monomethyl ether (boiling point 125° C). The experiment with ethylene glycol monomethyl ether gave the best separation.
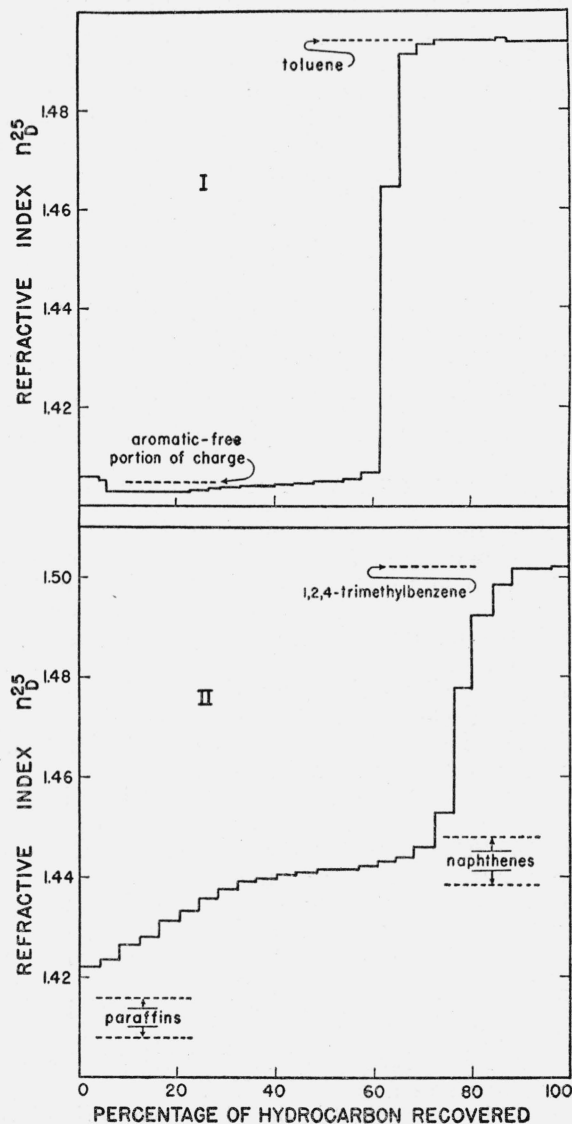
FIGURE 8.—*Diagrams
illustrating the separa-
tion of naphthene hydro-
carbons from paraffins
by azeotropic distilla-
tion.*

The scale of ordinates gives the
refractive index of the hydrocar-
bon recovered from the azeo-
tropic distillate and the scale of
abscissas gives the percentage of
the hydrocarbon recovered. The
distillations were performed in
the following columns: Part I in
a helix-packed column, with
rectifying section $\frac{5}{8} \times 100$ in.,
equivalent to about 90 theoret-
ical plates; parts II and V, in
helix-packed columns with recti-
fying sections 1×110 in. equiv-
alent to about 100 theoretical
plates [3]; parts III and IV in
the Bruun bubble-cap column
described under figure 7. The
rate of removal of distillate was
from 12 to 20 ml/hour, with a
reflux ratio of 40 or 50 to 1 and a
total time of distillation of about
100 hours.

Part I shows the results of the
azeotropic distillation with
methyl alcohol at atmospheric
pressure, of a narrow-boiling-
(91.4° to 91.8° C) mixture of par-
affins and naphthenes. The
azeotropic distillate contained
about 60 percent by volume of
hydrocarbon.

Part II shows the results of
the azeotropic distillation, with
ethylene glycol monomethyl
ether acetate at 770 mm Hg, of a
narrow-boiling (157° to 158° C)
mixture of paraffins and naph-
thenes. The azeotropic distil-
late contained about 40 percent
by volume of hydrocarbon.

Part III shows the results of
the azeotropic distillation, with
ethylene glycol monomethyl
ether acetate at 770 mm Hg, of a
narrow-boiling (177° to 178° C)
mixture of paraffins and naph-
thenes. The azeotropic distil-
late contained about 20 percent
by volume of hydrocarbon.

Part IV shows the results of
the azeotropic distillation, with
ethylene glycol monobutyl ether
at 770 mm Hg, of a narrow-boil-
ing (167° to 168° C) mixture of
paraffins and naphthenes. The
azeotropic distillate contained
about 70 percent by volume of
hydrocarbon.

Part V shows the results of the
azeotropic distillation, with
diethylene glycol monomethyl
ether at 770 mm Hg, of a narrow-
boiling (200° to 201° C) mixture
of paraffins and naphthenes.
The azeotropic distillate con-
tained about 55 percent by
volume of hydrocarbon.
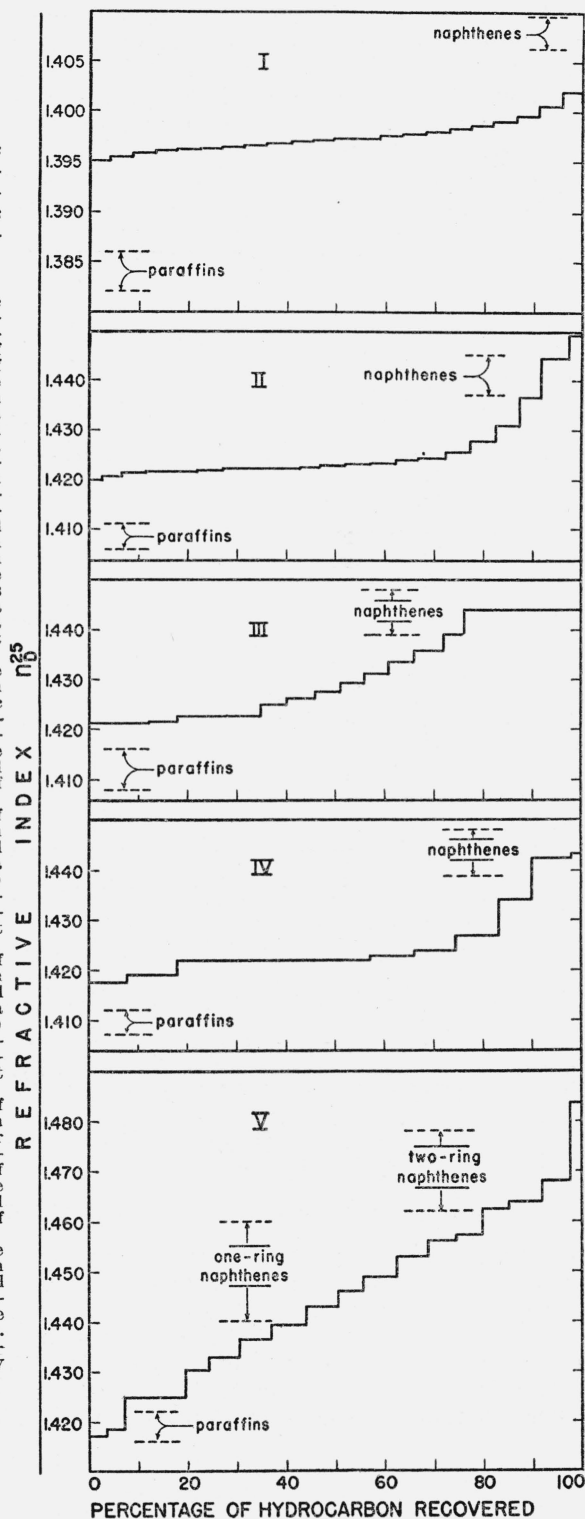
As contrasted with the separation of aromatic hydrocarbons from naphthenes and paraffins, which is a relatively easy fractionation, as shown in figure 7, the separation of naphthenes from paraffins is accomplished with greater difficulty, as indicated by the curves in figures 8 and 9. Whereas the complete separation of nearly all of the aromatic material may be accomplished by one azeotropic distillation in an efficient rectifying column, several such distillations, involving appropriate blending of the partially separated hydro-
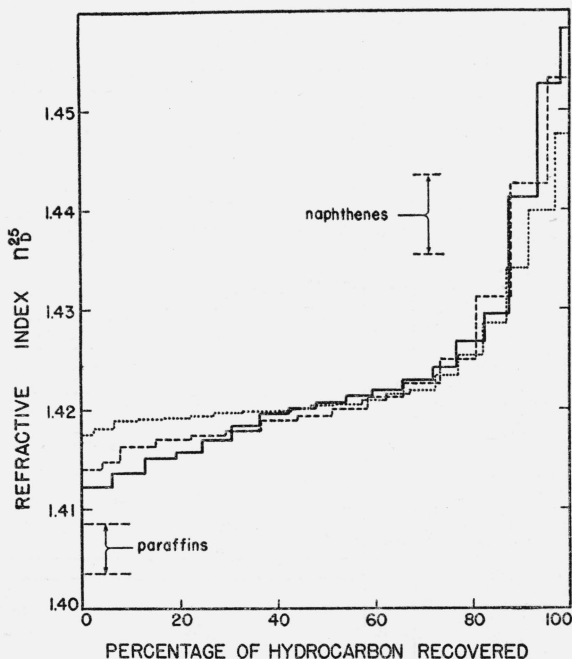
FIGURE 9.—*Diagram illustrating the separation of a given mixture of paraffins and naphthenes with three different azeotrope-forming substances.*

The scale of ordinates gives the refractive index of the hydrocarbon recovered from the azeotropic distillate, and the scale of abscissas gives the percentage of the hydrocarbon recovered. The distillations were performed in the Bruun bubble-cap column described under figure 7, with a rate of removal of distillate of about 15 ml/hour, a reflux ratio of about 50 to 1, and a total time of distillation of about 100 hours.

The dotted line, the dashed line, and the solid line show the results obtained with ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether, and ethylene glycol monomethyl ether, respectively, on the same narrow-boiling (157° to 158° C) mixture of paraffins and naphthenes. The azeotropic distillate contained about 40 percent by volume of hydrocarbon.

carbons, are required to bring about the separation of the naphthenic material from the paraffinic.

4. SEPARATION OF AROMATIC HYDROCARBONS

Figure 10 illustrates the results obtained in separating various kinds of aromatic hydrocarbons from one another.

Part I of figure 10 shows the separation obtained in the azeotropic distillation, with diethylene glycol monomethyl ether at 217 mm Hg, of a narrow-boiling (204° to 206° C at 760 mm Hg) fraction of aromatic hydrocarbons from the kerosene portion of petroleum. There is indicated here the separation of mono,- di-, or tri-alkyl

benzene from 1,2,3,4-tetramethylbenzene, and in turn this latter from tetrahydronaphthalene.   The latter separation results from the fact that one molecule has a benzene ring and the other is the partially
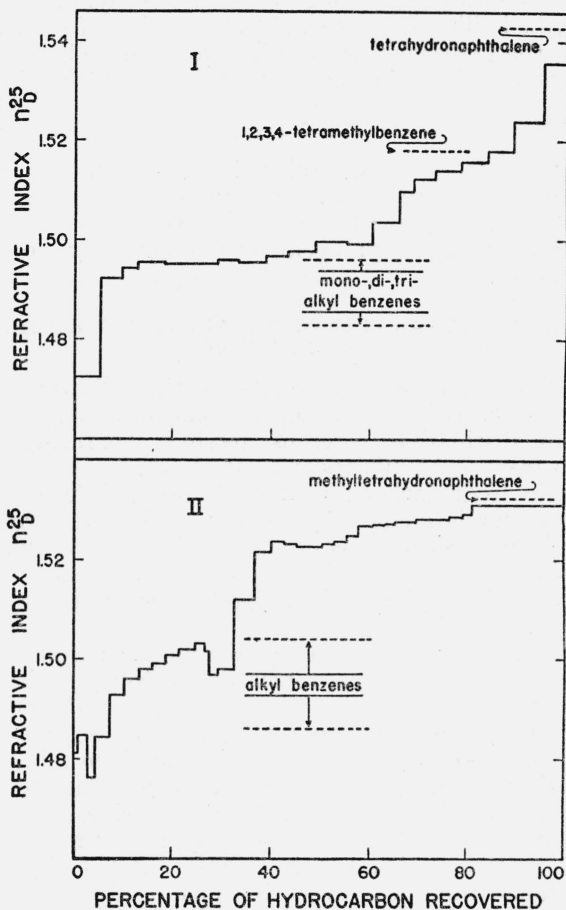
FIGURE 10.—*Diagrams illustrating the separation of different kinds of aromatic hydrocarbons from one another by azeotropic distillation.*

The scale of ordinates gives the refractive index of the hydrocarbon recovered from the azeotropic distillate, and the scale of abscissas gives the percentage of hydrocarbon recovered.   The distillations were performed in columns [3] similar to those for parts II and V under figure 8, at 217 mm Hg, with distillate removed at the rate of 10 to 20 ml/hour, with a reflux ratio of 40 or 50 to 1, and a total time of distillation of about 200 hours.

Part I shows the results of the azeotropic distillation, with diethylene glycol monomethyl ether at 217 mm Hg, of a narrow-boiling (204° to 206° C at 1 atm) mixture of aromatic hydrocarbons separated from the kerosene fraction of petroleum.   The azeotropic distillate contained about 55 percent by volume of hydrocarbon.

Part II shows the results of the azeotropic distillation, with diethylene glycol monomethyl ether at 217 mm Hg, of a narrow-boiling (224° to 225° C at 1 atm) mixture of aromatic hydrocarbons separated from the kerosene fraction of petroleum.   The azeotropic distillate contained about 25 percent by volume of hydrocarbon.

hydrogenated naphthalene composed of one aromatic ring doubly linked to a naphthene ring.   The former separation is interesting in that it occurs between a molecule having a benzene ring with four alkyl radicals and a molecule having a benzene ring with one, two, or

three alkyl radicals, the molecules having about the same boiling point.

Part II of figure 10 shows the separation obtained in the azeotropic distillation, also with diethylene glycol monomethyl ether at 217 mm Hg, of a narrow-boiling (224° to 225° C) fraction of aromatic hydrocarbons from the kerosene portion of petroleum. There is indicated here the separation of alkyl benzenes from methyl tetrahydronaphthalene.

5. SEPARATION OF NAPHTHENE HYDROCARBONS

The separation of one-ring naphthenes fron two-ring naphthenes is indicated in part V of figure 8. Although no actual data are available, it appears that it should be possible to separate a monoalkyl cycloparaffin from a polyalkyl cycloparaffin normally boiling at the same temperature.

6. SUMMARY OF SEPARATIONS OBTAINABLE BY AZEOTROPIC DISTILLATION

From the data that are now available, the following conclusions may be drawn with regard to the separations obtainable by azeotropic distillation in distillation columns having separating efficiencies equivalent to from 50 to 100 theoretical plates:

(a) Aromatic hydrocarbons may be separated from naphthenes and paraffins with relative ease by one appropriate azeotropic distillation in an efficient rectifying column, in mixtures in which the aromatic hydrocarbons normally have boiling points not significantly lower than the boiling points of the naphthenes and paraffins in the given mixtures.

(b) Naphthene hydrocarbons may be separated from paraffins by several distillations with an appropriate azeotrope-forming substance in an efficient rectifying column, in mixtures in which the naphthene hydrocarbons normally have boiling points not significantly lower than the boiling points of the paraffins in the given mixtures.

(c) Aromatic hydrocarbons of different degrees of "aromaticity", resulting from different numbers and kinds of rings, as for example an alkyl benzene, an alkyl tetrahydronaphthalene, and an alkyl naphthalene, may be separated from one another, in mixtures in which the various aromatic hydrocarbons have substantially the same normal boiling points, or in which any differences in boiling point are of the same magnitude and sign as the differences in the boiling points of the corresponding binary azeotropic mixtures. Such separations may require one or more azeotropic distillations in an efficient rectifying column, depending upon the nature of the components of the mixture and its complexity.

(d) Naphthene hydrocarbons having different numbers of naphthene rings in the molecule may be separated from one another, in mixtures in which the various naphthene hydrocarbons have substantially the same normal boiling points, or in which the naphthenes with two rings have boiling points not significantly lower than the boiling points of the naphthenes with one ring. Several azeotropic distillations in an efficient rectifying column usually will be required for the substantially complete separation of such compounds.

The work of this laboratory has not included olefinic hydrocarbons because of their absence from natural petroleum. Nevertheless, on

the basis of the known data on their azeotropic mixtures, by analogy with the paraffins, naphthenes, and aromatics, and considering the work of Matuszak and Frey [34], who devised a procedure for separating the butanes and butenes by azeotropic distillation with sulfur dioxide, the following general conclusions may be drawn with regard to the separations obtainable in azeotropic distillations involving olefinic hydrocarbons in rectifying columns of from 50 to 100 theoretical plates:

(a) Monoolefin hydrocarbons may be separated with relative ease from aromatic hydrocarbons, from paraffin hydrocarbons, and perhaps as easily from diolefin hydrocarbons, but with less ease from naphthene hydrocarbons.

(b) Diolefin hydrocarbons may be separated with relative ease from naphthenes and paraffins, but with less ease from aromatics and monoolefins.

It may be possible to extend the method of azeotropic distillation to the separation of isomers of the same class and subclass of hydrocarbons, by appropriately selecting the azeotrope-forming substance and by using a highly efficient rectifying column. The curve shown in part I of figure 10 indicates that of two alkyl benzenes having about the same boiling point the one with the smaller number of alkyl groups will tend, with a given azeotrope-forming substance, to form a lower-boiling azeotropic mixture than the alkyl benzene with more alkyl groups. Furthermore, it should be possible to improve significantly the separation obtainable in the ordinary distillation in a given rectifying column of two isomers having the same number and kind of groups substituent to the main chain or ring of the molecule and boiling close together, by distilling them with an appropriate azeotrope-forming substance having a boiling point so low that the azeotropic distillate is low in hydrocarbon. Notwithstanding the fact that the difference in the boiling points of the respective azeotropic mixtures may be much less than the difference in the boiling points of the two isomers alone, this procedure may be successful because of the greater spread of the liquid-vapor lines of the temperature-composition diagram for the two azeotropic mixtures (considered as a binary system) than for the binary system of the two isomers alone.

In cases requiring the purification of a small quantity of a compound in a rectifying column having a capacity and hold-up much too large for the straight distillation of the given quantity of material, azeotropic distillation may be utilized for the purification. In this case, an azeotrope-forming substance can be selected which has a boiling point sufficiently below that of the given material that the azeotropic distillate may have any required low value of concentration of the given compound, and all of the latter then may be put through the still as distillate by using an excess of the azeotrope-forming substance. This method of purification will fail when the impurity is such that there is no significant difference in boiling point between its azeotropic mixture and that of the compound proper. However, in case a ternary azeotrope is formed between the compound, the impurity, and the azeotrope-forming substance, the impurity may be removed at the expense of losing a corresponding amount of the compound proper [28]. [7]

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[7] For a discussion of the use of azeotropic distillation in producing water-free ethyl alcohol and "pure" dioxane on a commercial scale, see [29, 30, 31, 32, 33].

V. DISTILLATION AT REDUCED PRESSURE

1. CHANGE OF BOILING POINT WITH PRESSURE FOR DIFFERENT TYPES OF HYDROCARBONS

It is usually possible to separate a mixture of hydrocarbons of different types but of the same "normal" boiling point by distillation at a pressure reduced below, or elevated above, the "normal" operating pressure [22, 37], because of the fact that in general the different types of hydrocarbons show significantly different changes of the boiling point with pressure.

Figure 11 illustrates the changes of boiling point with pressure shown by several different types of hydrocarbons, referred to the
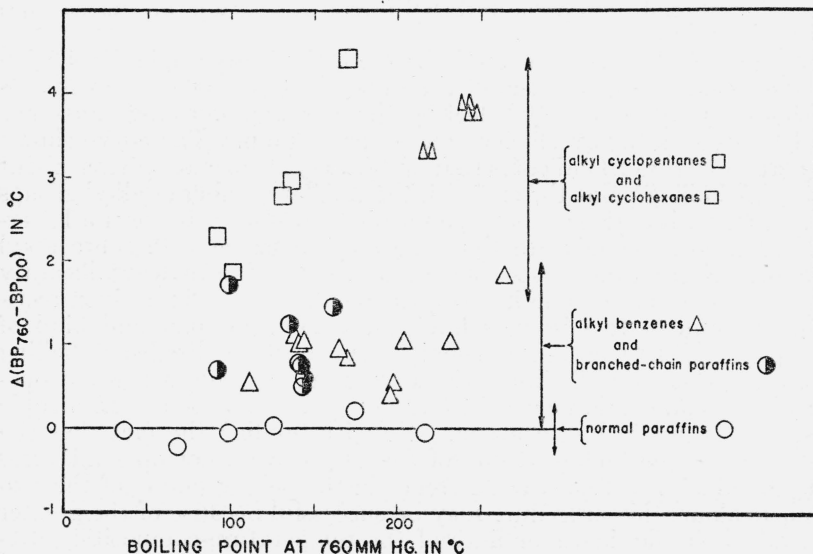

FIGURE 11.—*Difference in the change of boiling point with pressure for several types of hydrocarbons.*

The scale of abscissas gives the value of the boiling point of the given hydrocarbon at 760 mm Hg in °C. The scale of ordinates gives in °C the value of $\Delta (BP_{760}-BP_{100}) = (BP_{760}-BP_{100}) - (44.8+t8-t^2/25,000)$. Here $BP_{760}-BP_{100}$ is the decrease in the boiling point of a given hydrocarbon as the pressure is reduced from 760 to 100 mm Hg; t is BP_{760}, the boiling point of the given hydrocarbon at 760 mm Hg; $44.8+t8-t^2/25,000$ represents the value of $BP_{760}-BP_{100}$ for a hypothetical normal paraffin hydrocarbon having the same boiling point as the given hydrocarbon at 760 mm Hg; $\Delta (BP_{760}-BP_{100})$ is, therefore, the excess lowering of the boiling point of the given hydrocarbon over that of a hypothetical normal paraffin of the same boiling point at 760 mm Hg, as the pressure is reduced from 760 to 100 mm Hg. The various types of hydrocarbons are represented by the following symbols: ◯, normal paraffins; ◐, branched-chain paraffins; ☐, naphthenes; △, alkyl benzenes; △△, naphthalene and methylnaphthalenes. The data were obtained from [3, 16, 20, 22, 28, 35, 38, 39, 40, 41]. See section V for discussion.

values for the normal paraffins as zero. For the normal paraffins with 5, 6, 7, 8, 10, and 12 carbon atoms per molecule, for 8 branched-chain paraffins, for 5 naphthene hydrocarbons, for 11 alkyl benzenes, and for naphthalene and the two methylnaphthalenes, there are plotted in figure 11 values of the quantity

$$\Delta (BP_{760}-BP_{100}) = (BP_{760}-BP_{100}) - (44.8+t/8-t^2/25,000).$$

Here t is BP_{760}, the boiling point of the given hydrocarbon at 760 mm Hg, $BP_{760}-BP_{100}$ is the lowering in boiling point of the given hydro-

carbon corresponding to a change in pressure from 760 to 100 mm Hg, and the quantity $44.8 + t/8 - t^2/25,000$ represents the value of the same property for a hypothetical normal paraffin having the same value of BP_{760}. The equation giving values of $BP_{760} - BP_{100}$ for the normal paraffins was deduced from the data on n-pentane, n-hexane, n-heptane, n-octane, n-decane, and n-dodecane, and represents the existing data within 0.2° C, as can be seen from the values plotted for these normal paraffins. The quantity $\Delta(BP_{760} - BP_{100})$ represents, for a change in pressure from 760 to 100 mm Hg, the excess lowering of the boiling point of the given hydrocarbon over that of a hypothetical normal paraffin hydrocarbon having the same boiling point at 760 mm Hg.

On the basis of the data presented in figure 11, the following conclusions are drawn with regard to the value of $BP_{760} - BP_{100}$ for the branched-chain paraffins, the alkyl benzenes, the alkyl cyclopentanes and alkyl cyclohexanes, and naphthalene and its two methyl derivatives, referred to the values for the normal paraffins of the same boiling point at 760 mm Hg:

(a) For the branched-chain paraffins, the values of $BP_{760} - BP_{100}$ are greater than those for the corresponding normal paraffins by amounts ranging from near zero to about 2° C, with the values for the less highly branched paraffins apparently being smaller than those for the more highly branched paraffins.

(b) For the alkyl benzenes, the values of $BP_{760} - BP_{100}$ are greater than those for the corresponding normal paraffins by amounts ranging from near zero to about 2° C, which range is substantially the same as that for the branched-chain paraffins.

(c) For the alkyl cyclopentanes and alkyl cyclohexanes, the values of $BP_{760} - BP_{100}$ are greater than those for the corresponding normal paraffins by amounts which appear to range from near 1½° to about 4½° C.

(d) For naphthalene and its two methyl derivatives, the values of $BP_{780} - BP_{100}$ are greater than those for the corresponding normal paraffins by amounts lying within the range 3° to 4° C.

On the basis of the foregoing relations, it is evident that a distillation at reduced pressure prior to the azeotropic distillation at the "normal" pressure will enhance the separation obtainable in a mixture of paraffin hydrocarbons with alkyl cyclopentanes or alkyl cyclohexanes and in a mixture of alkyl benzenes with alkyl naphthalenes, but not in a mixture of alkyl benzenes with alkyl cyclopentanes or alkyl cyclohexanes.

2. BENEFITS OF DISTILLATION AT REDUCED PRESSURE PRIOR TO AZEOTROPIC DISTILLATION

It has been previously indicated (in section IV) that it is necessary to have the mixture of hydrocarbons well separated by an efficient regular distillation prior to the azeotropic distillation, in order to avoid having a mixing of the hydrocarbons of various types in a direction that will tend to nullify the separation obtainable by the azeotropic distillation. By the same line of reasoning, any preliminary fractionation that will produce a displacement of the hydrocarbons in the same direction as that to be produced by the azeotropic distillation will enhance the separation obtainable in the latter process.

Since distillation at reduced pressure serves to displace normally higher-boiling naphthenes into fractions containing normally lower-boiling paraffins, it follows that, where possible and practical, any mixture of naphthene and paraffin hydrocarbons should be distilled efficiently at a reduced pressure prior to the azeotropic distillation of the mixture at the "normal" distilling pressure. A similar procedure will enhance the separation of alkyl benzenes from naphthalene and alkyl naphthalenes.

The displacement with decrease in pressure of the boiling points of the aromatic hydrocarbons with respect to those of naphthene hydrocarbons is actually such that, if this mixture is distilled at reduced pressure prior to the azeotropic distillation at "normal" pressure, there results a small decrease in the separation obtainable by the azeotropic distillation; but this reversal is unimportant, because the separation of aromatics from naphthenes by azeotropic distillation is already extremely good. Furthermore, in the distillation of a mixture of hydrocarbons of the same boiling point but of different types, the aromatic hydrocarbons tend to be displaced with reference to the paraffins and naphthenes into lower-boiling fractions, because for the aromatics the ratio of vapor pressure to mole fraction is greater than it is for the naphthenes and paraffins in the same mixture.

In the separation of naphthenes from paraffins, which is in general the most difficult separation encountered in the fractionation of petroleum, the benefits obtainable from the distillation at reduced pressure prior to the azeotropic distillation are important and should be taken advantage of whenever possible.

VI. GENERAL PROCEDURE FOR SEPARATING HYDROCARBONS BY DISTILLATION ALONE

The general procedure for separating hydrocarbons from petroleum, by utilizing all of the fractionating processes of distillation, crystallization, extraction, and adsorption, has already been described [27]. It may frequently happen that apparatus for performing extraction and crystallization is not available, or that it is desired to simplify the fractionating procedure, as in connection with the economic requirements of large-scale operation. For such situations, the schematic diagram given in figure 12 illustrates the general procedure that may be followed in separating, by means only of distillation in its several variations, any given fraction of petroleum of the gasoline or kerosene ranges. Figure 12 and its legend are self-explanatory. It will be noticed that in the procedure outlined full advantage is taken of the benefits obtainable by distillation of the mixture of hydrocarbons at reduced pressure prior to their distillation azeotropically at the "normal" pressure.

While the foregoing procedure specifies only the hydrocarbons of the types occurring in petroleum, namely paraffins, naphthenes, and aromatics, appropriate modification of the procedure may be made easily to include the monoolefins and diolefins. For this purpose, there should be kept in mind the general order in which the different types of hydrocarbons arrange themselves with regard to their susceptibility to the process of azeotropic distillation, namely aromatic, diolefin, olefin, naphthene, and paraffin.
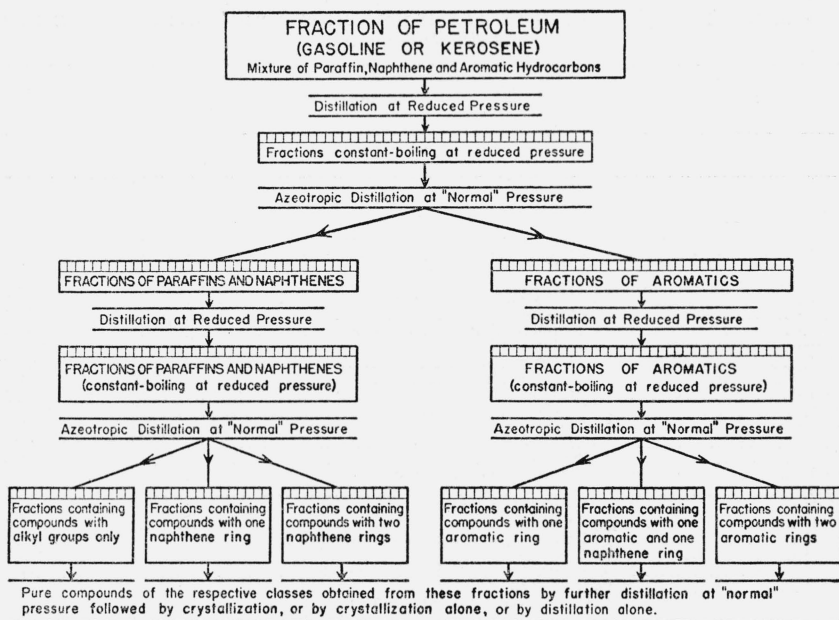
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┌─────────────────────────────────────────────┐
│        FRACTION OF PETROLEUM                  │
│        (GASOLINE OR KEROSENE)                 │
│  Mixture of Paraffin,Naphthene and Aromatic Hydrocarbons │
└─────────────────────────────────────────────┘
                    ↓
        ┌──────────────────────────────┐
        │ Distillation at Reduced Pressure │
        └──────────────────────────────┘
                    ↓
        ┌──────────────────────────────┐
        │ Fractions constant-boiling at reduced pressure │
        └──────────────────────────────┘
                    ↓
        ┌──────────────────────────────┐
        │ Azeotropic Distillation at "Normal" Pressure │
        └──────────────────────────────┘
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FRACTIONS OF PARAFFINS AND NAPHTHENES — Distillation at Reduced Pressure — FRACTIONS OF PARAFFINS AND NAPHTHENES (constant-boiling at reduced pressure) — Azeotropic Distillation at "Normal" Pressure

FRACTIONS OF AROMATICS — Distillation at Reduced Pressure — FRACTIONS OF AROMATICS (constant-boiling at reduced pressure) — Azeotropic Distillation at "Normal" Pressure

| Fractions containing compounds with alkyl groups only | Fractions containing compounds with one naphthene ring | Fractions containing compounds with two naphthene rings | Fractions containing compounds with one aromatic ring | Fractions containing compounds with one aromatic and one naphthene ring | Fractions containing compounds with two aromatic rings |

Pure compounds of the respective classes obtained from these fractions by further distillation at "normal" pressure followed by crystallization, or by crystallization alone, or by distillation alone.

FIGURE 12.—*Schematic diagram illustrating the separation of a fraction (gasoline or kerosene) of petroleum by distillation alone.*

The several variations of distillation employed in this procedure are at "normal" pressure, at reduced pressure, and with an azeotrope-forming substance. (See footnote 3, p. 40, for the meaning of "normal" pressure.)

VII. LIST OF HYDROCARBONS SEPARABLE BY DISTILLATION ALONE

By distillation alone (in its several variations of distillation at "normal" pressure, distillation at reduced pressure, and distillation with an azeotrope-forming substance), it is possible to separate the compounds, or mixtures, listed in table 1 from appropriate crude petroleums or from appropriate products of the refining process. A number of the substances, listed in table 1, are already being produced on a commercial scale from petroleum or petroleum products. These include methane, ethane, propane, isobutane, n-butane, isopentane, n-pentane, 2,2-dimethylbutane, mixed hexanes (54° to 71° C) mixed heptanes (80° to 99° C), mixed octanes (100° to 127° C), ethylene, propylene, mixed butenes, and concentrates of benzene, toluene, and "xylene."

TABLE 1.—*List of hydrocarbons separable from petroleum or petroleum products by distillation alone*

Formula	Name and type	Boiling point at 1 atm
	PARAFFINIC	
		°C
CH_4	Methane	−161.7
C_2H_6	Ethane	−88.6
C_3H_8	Propane	−42.2
C_4H_8	2-Methylpropane (isobutane)	−12.1
C_4H_8	n-Butane	−0.5
C_5H_{12}	2-Methylbutane (isopentane)	27.9
C_5H_{12}	n-Pentane	36.1
C_6H_{14}	2,2-Dimethylbutane (neohexane)	49.8
C_6H_{14}	2,3-Dimethylbutane	58.0
C_6H_{14}	2-Methylpentane	60.3
C_6H_{14}	3-Methylpentane	63.3
C_6H_{14}	n-Hexane	68.7
C_7H_{16}	Mixture of methylhexanes	90 to 92
C_7H_{16}	n-Heptane	98.4
C_8H_{18}	Mixture of methylheptanes	115 to 118
C_8H_{18}	n-Octane	125.6
C_9H_{20}	Mixture of methyloctanes	142 to 145
C_9H_{20}	n-Nonane	150.7
$C_{10}H_{22}$	Mixture of methylnonanes	165 to 168
$C_{10}H_{22}$	n-Decane	174.0
$C_{11}H_{24}$	Mixture of branched-chain undecanes	187 to 191
$C_{11}H_{24}$	n-Undecane	195.8
$C_{12}H_{26}$	Mixture of branched-chain dodecanes	207 to 211
$C_{12}H_{26}$	n-Dodecane	216.3
	Higher-boiling normal paraffins.	
	NAPHTHENIC	
C_5H_{10}	Cyclopentane	49.5
C_6H_{12}	Methylcyclopentane	71.9
C_6H_{12}	Cyclohexane	80.8
C_7H_{14}	Mixture of dimethylcyclopentanes	87.5 to 92
C_7H_{14}	Methylcyclohexane	100.9
C_8H_{16}	Mixture of dimethylcyclohexanes	120 to 124
	Higher-boiling naphthene concentrates.	
	AROMATIC	
C_6H_6	Benzene	80.1
C_7H_8	Toluene	110.6
C_8H_{10}	Ethylbenzene	136.2
C_8H_{10}	Mixture of p-xylene and m-xylene	138 to 140
C_8H_{10}	o-Xylene	144.4
C_9H_{12}	Isopropylbenzene	152.4
C_9H_{12}	n-Propylbenzene	159.5
C_9H_{12}	Mixture of 1-methyl- 3-ethylbenzene and 1 methyl- 4-ethylbenzene.	161 to 162
C_9H_{12}	Mixture of 1-methyl- 2-ethylbenzene and 1,3,5-trimethylbenzene.	164 to 165
C_9H_{12}	1,2,4-Trimethylbenzene	169.2
C_9H_{12}	1,2,3-Trimethylbenzene	176.1
$C_{10}H_{14}$	1,2,3,4-Tetramethylbenzene	204
$C_{10}H_{12}$	Tetrahydronaphthalene	207
$C_{10}H_8$	Naphthalene	218.0
$C_{11}H_{10}$	2-Methylnaphthalene	241.1
$C_{11}H_{10}$	1-Methylnaphthalene	244.8
	OLEFINIC [a]	
C_2H_4	Ethylene	−103.8
C_3H_6	Propylene	−47.7
C_4H_8	2-Methylpropene-1 (isobutene)	−7.0
C_4H_8	Butene-1	−6.4
C_4H_8	trans-Butene-2	1.0
C_4H_8	cis-butene-2	3.6
C_5H_{10}	3-Methylbutene-1	20.1
C_5H_{10}	Mixture of pentene-1 and 2-methylbutene-1	30 to 31
C_5H_{10}	Mixture of cis- and trans-pentene-2	35 to 37
C_5H_{10}	2-Methylbutene-2	38.4

[a] The olefinic hydrocarbons do not occur naturally in petroleum. They are produced mainly as products of the cracking process or by the specific reaction of dehydrogenating the corresponding paraffins.

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