

REVIEW OF THE LITERATURE ON THE CONSTRUCTION,
TESTING, AND OPERATION OF LABORATORY FRACTIONATING COLUMNS
AND
SUPERFRACTIONATION STUDIES

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SUPERFRACTIONATION STUDIES

By

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REVIEW OF THE LITERATURE ON THE
CONSTRUCTION, TESTING, AND OPERATION OF
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By
C. C. WARD

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REVIEW OF THE LITERATURE ON THE CONSTRUCTION, TESTING, AND OPERATION OF LABORATORY FRACTIONATING COLUMNS¹

BY C. C. WARD²

INTRODUCTION

Fractional distillation is one of the most important laboratory tools in the field of petroleum research. Two methods of distillation are used. "Continuous" distillation employs a continuous feed of constant composition and permits the simultaneous removal of several fractions from different sections of the column. Each fraction is different from the others but in itself has a fairly constant composition. "Batch" distillation uses only an initial charge and provides a progressive series of fractions, each having a different composition. The latter method usually is more satisfactory for analytical fractionation, and the considerations in the present paper apply principally to batch distillation.

The many articles that record the more recent developments in laboratory fractionating equipment are widely scattered, and a convenient compilation of the data has not been published. The Bureau of Mines has published several reports dealing with the fractionation of petroleum (*1, 16, 17, 18, 23, 33, 67, 71, 81*),³ but these reports apply largely to commercial applications and to continuous distillation. It is the purpose of the present paper to cover the construction, testing, and operation of laboratory fractionating columns as recorded in the literature. A study of this literature has shown that special distillation problems require many types of fractionating equipment. However, for most laboratory studies of petroleum, equipment in which the following requirements are fulfilled will provide satisfactory fractionation:

1. A corrosion-resistant, evenly heated stillpot of proper size for the charge being distilled.
2. An adiabatic column so equipped that efficient contacting between vapor and reflux is attained.
3. A total condenser with a very small hold-up and a variable reflux proportioning device.
4. Adequate control of the operating variables to attain maximum efficiency.

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One phase of petroleum research being carried on by the Bureau of Mines in cooperation with the State of Oklahoma at the Bartlesville Petroleum Experiment Station concerns the laboratory frac-

¹ Work on manuscript completed December 1938.

² Junior chemical engineer, Bureau of Mines, Bartlesville, Okla.

³ Italicized numbers in parentheses refer to citations in the bibliography at the end of this report. Page references represent those in the citation and not in this technical paper.

tionation of petroleum, and this paper, a review of the literature on this subject, was compiled and published under this cooperative agreement.

It was prepared under the general supervision of R. A. Cattell, chief engineer of the Petroleum and Natural Gas Division, Bureau of Mines, Washington, D. C.; N. A. C. Smith, supervising engineer, and Ludwig Schmidt, senior petroleum engineer, Petroleum Experiment Station, Bureau of Mines, Bartlesville, Okla.; and under the direct supervision of H. M. Smith, petroleum chemist, Petroleum Experiment Station, Bureau of Mines, Bartlesville, Okla.

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SCOPE OF REPORT

This report, which presents and discusses the material cited in 86 references, is divided into four parts—(1) general consideration of fractionating unit design and operation; (2) evaluation of columns, giving examples showing how the number of theoretical plates can be determined by either graphical or analytical methods and giving vapor-liquid equilibria data for some common binary test mixtures; (3) discussion and tabulation of details of the construction, operation, and evaluation of various fractionating units; (4) conclusions as to the principal factors to be considered when designing an efficient fractionating unit.

GENERAL CONSIDERATIONS

The principles underlying the design and operation of batch fractionating units are presented in this report without detailed reference to the physical and thermodynamic laws on which they are based. The original references, especially Badger and McCabe (2) or Walker, Lewis, McAdams, and Gilliland (83), should be consulted if the reader wishes to study this underlying theory.

DEFINITIONS

The following terms are used in this paper:

Binary test mixture.—A two-component liquid mixture that may be used to determine the separating efficiency of a column.

Bubble cap.—An inverted cup with a notched or slotted periphery to disperse the vapor in small bubbles beneath the surface of the liquid on the bubble plate.

Bubble plate.—A horizontal plate equipped with one or more bubble caps and with passages for ascending vapor and descending liquid.

Dephlegmator.—A partial condenser.

Diameter of the column.—The inside diameter, unless otherwise stated.

"Fractionation."—The term commonly applied to rectification.

Fractionating assembly.—The fractionating column and all its accessories.

Free space.—The void space in the packed section of the column.

Height of rectifying section.—Height of the packed or bubble-plate section, unless otherwise stated.

H. E. T. P.—The height equivalent to a theoretical plate.

Hold-up.—The operating hold-up is the volume of vapor and liquid in the column under operating conditions. The static hold-up is the volume of liquid normally retained in the column after operation has ceased.

Packing.—Particles of inert material placed in the rectifying section of the column to increase the vapor and liquid contacting surfaces.

Partial condenser.—An apparatus in which a portion of the vapor is condensed and returned to the column as reflux while the uncondensed portion is separately liquefied and recovered as product.

Partial reflux.—A process in which a portion of the condensate is returned to the column as reflux and the rest is withdrawn as product.

Perfect plate.—A plate that effects complete equilibrium between vapor and liquid.

Plate efficiency.—The degree with which an actual plate approaches the equilibrium effected by a perfect plate.

Pressure drop.—The decrease in pressure between any two points in the fractionating assembly (unless otherwise stated, between the pot and the head).

Rectification.—A distillation carried out in such a way that condensate is brought into contact with the rising vapors, thus causing an exchange of heat and materials, whereby the vapors are enriched in the more volatile component.

Rectifying section.—That height of the distillation column occupied by packing, bubble plates, or other rectifying devices.

Reflux.—Condensate that is returned to the column and flows countercurrent to the vapor stream.

Reflux ratio.—Ratio of condensate returned to the column to that withdrawn as product.

Stillhead.—The portion of the fractionating unit above the rectifying section, usually consisting of one or more condensers and a reflux proportionating device.

Stillpot.—The container in which the charge is vaporized.

Theoretical plate.—A column section that will effect equilibrium between vapor and liquid.

Total condenser.—A device in which all the vapors are liquefied.

Total reflux.—The process in which all the condensate is returned to the column and no product is withdrawn.

Vaporization rate.—The amount of vapor evolved in the stillpot per unit time.

Vapor velocity.—The forward rate of flow of material in the column.

OPERATING PRINCIPLES

SIMPLE DISTILLATION

When a mixture of two miscible liquids is heated, the vapors evolved usually will be richer in the lower-boiling component than was the original mixture. If these vapors are removed and condensed, the condensate will contain a larger proportion of the lower-boiling component and the remaining liquid more of the higher-boiling material. This operation, simple distillation, is suitable only for the crude separation of materials with widely divergent boiling points.

PARTIAL CONDENSATION

When the vapor evolved from a two-component mixture is cooled slightly, it is partly condensed, and the resulting condensate is relatively rich in the higher-boiling component. The remaining vapor, thus relatively richer in the lower-boiling material, can then be condensed and removed as product. Many simple unlagged laboratory columns operate through a combination of simple distillation and partial condensation, the vapors being partly condensed on the cool walls of the column.

RECTIFICATION

Rectification, the most efficient fractionation principle, is used where a high degree of separation is required. In this process all the vapor is condensed after it leaves the column, and a portion of the condensate is returned to the top of the column as "reflux." Reflux flowing down the column is brought into contact with the ascending vapors and exchanges of heat and material take place. Part of the less volatile component in the vapor is condensed through abstraction of heat by the reflux. The heat absorbed by the reflux causes vaporization of its more volatile component, thereby enriching the vapor. The efficiency with which these thermal reactions occur depends largely upon the degree with which the column approaches adiabatic operation.

FRACTIONATING UNIT

STILLPOT

The stillpot contains the charge that it may acquire the heat necessary for vaporization, provides space for separating the vapor from the liquid, and holds the liquid that remains after distillation. It should be of corrosion-resistant material and of suitable size and shape for the charge being distilled.

COLUMN

Usually, a fractionating column is a cylindrical shell containing a device, or devices, to cause (1) intimate contact between the rising vapors and descending reflux and (2) separation of entrained liquid droplets (fog) from the rising vapor. These devices usually are (1) perforated plates, (2) bubble-cap plates, or (3) rings, chain, helices, or similar "packing." Several centrifugal columns (37, 41, 65) also have been developed, but few data as to their application to petroleum research are available.

Perforated plate column.—The simplest plate column consists of a vertical series of horizontal plates, usually equally spaced, in an upright cylinder. Reflux liquid collects on each plate, and vapors rising through the perforations prevent it from returning to the plate below except through an overflow tube on each plate provided to maintain a constant depth of liquid. When the pressure created by the vapor velocity is too low to overcome the static head of the liquid on the plate, the liquid will drop through the perforations, whereas too high a velocity will lift the liquid off the plate and decrease the intimacy of contact. Since the vapor velocity must conform to these relatively narrow limits, the operating range of perforated plate columns is somewhat restricted. In large-diameter columns, especially, the plates must be level or the vapor will pass through the perforations in the higher side and the liquid through those in the lower side without suitable contact.

Bubble-cap plate column.—The bubble-cap plate column contains a vertical series of horizontal plates, usually equally spaced throughout the length of the column. Each plate is equipped with an overflow tube to maintain a constant liquid level and provide passage for reflux liquid down the column. The lower end of each of these tubes is closed by a liquid seal on the plate below. One or more vapor tubes

on each plate provide a passage for vapor up the column. Over each of these tubes is a bubble cap of larger diameter to deflect the vapor beneath the surface of the liquid before passing to the plate above. Bubble caps are of various designs. A common type clears the plate by a small distance, and the periphery is either notched or slotted to increase the area of contact and to deliver the vapor from the plate below in the form of small bubbles beneath the surface of the liquid.

Packed column.—A packed column is a cylindrical shell filled at random with small pieces of inert solid material. Vapor and liquid are contacted largely on the surfaces of the packing material. Packed columns are simple and economical to construct and with suitable packing they have a small liquid hold-up and low pressure drop and compare favorably with other types of columns in effectiveness of separation per unit of length. Packed columns are especially adapted to vacuum distillation because of the low pressure drop. Channeling of the vapors and incomplete wetting of the packing are disadvantages of this type of column. However, if the ratio of column diameter to diameter of the individual packing units is greater than 8 to 1 (β) and the ratio of column height to column diameter is greater than 15 to 1 (*58, p. 1195*), the tendency to channel will be slight.

Insulation.—A rectifying column is most efficient when it is adiabatic throughout its length. That is, there should be no lateral heat flow in or from the column, and the quantity of heat extracted by the condenser, or condensers, at the top of the column in liquefying the vapors should equal the latent heat of the vapors entering the base of the column. This can be attained most nearly by combining efficient insulation with an auxiliary source of heat to counterbalance that lost to the surrounding atmosphere.

Packing.—The ideal packing offers uniformly distributed interstices, a large surface for contact, and enough free space for a desirable throughput. Too large packing has a small area for contact. On the other hand, too small packing allows insufficient throughput. Many refractory materials and metals have been used to fabricate packing of a large number of shapes and sizes.

Hold-up.—The volume of the hold-up in a packed column depends principally upon the packing. Small liquid and vapor hold-up is a factor that too often is neglected in column design. When the hold-up is small, more efficient fractionation results, as the effective fractionating surfaces are being used to rectify material having a relatively narrow composition gradient.

STILLHEAD

The vapors from the column pass to the stillhead, which includes that portion of the fractionating device above the column. It usually consists of a condenser and a reflux proportioning device. Generally the stillhead performs two operations—condensing the product and providing reflux for the column. If, however, the stillhead includes a partial condenser, it may perform a third operation—aiding the column in fractionation. As pointed out previously, partial condensation enriches the vapors with light material; but the usual condenser is a very poor device for this purpose, adds to the difficulty of control,

and necessitates a second condenser for the distillate. Therefore, the general tendency is to use a total condenser that liquefies all the vapors, returns a part to the column as reflux, and delivers the rest to the product line. The amount of liquid hold-up should be given careful consideration in the design of a total condenser. A large hold-up in the condenser results in partial reblending of the separated components and consequently some loss in fractionation.

OPERATING VARIABLES

REFLUX RATIO

The ideal fractionation process requires a column of infinite height, in which the ascending vapors and descending reflux are contacted so intimately that equilibrium between the two phases is reached at every point. That is, there will be an infinite number of differential changes in composition. This ideal process is impossible, of course, and the practical column has only a limited number of sections, each of which must effect a large change in composition. To effect these large changes, it is necessary to use a greater amount of reflux than that theoretically required in an ideal column.

The term "reflux ratio," which expresses the quantity of reflux used, has unfortunately acquired several different meanings, all of which are used in the literature. It has been used to express the ratio of quantity of reflux to quantity of product, quantity of vapor to quantity of product, and quantity of reflux to quantity of vapor with the quantities expressed in units of weight, volume, or heat. In terms of the first definition, reflux ratio may range from zero to infinity, in the second definition from unity to infinity, and in the third from zero to unity. The most common definition of reflux ratio is quantity of reflux to quantity of product, and it is used throughout this paper.

VAPOR VELOCITY

A high vapor velocity is desirable from the standpoint of product recovery, but an excessive vapor velocity lowers the degree of fractionation. Entrainment, or the mechanical carrying of small droplets of liquid by the vapor, is the limiting factor for vapor velocity in plate columns. If the velocity becomes so great that entrainment continues from plate to plate, fractionation decreases. In packed columns the limiting vapor velocity is that at which flooding occurs. In either type of column a greater vapor velocity results in greater back pressure, which is important in some instances.

DISTILLATION RATE

Distillation rate is a function of the vapor velocity and the reflux ratio. A high vapor velocity increases the distillation rate but decreases the period of contact between vapor and reflux liquid. A high reflux ratio decreases the distillation rate but increases the degree of fractionation.

EVALUATION OF FRACTIONATING COLUMNS

A number of methods have been used to evaluate the many fractionating columns that have been described in the literature. A common procedure is to distill a known mixture and determine the temperature-volume curve. However, the distillation temperature, as given by a thermometer or thermocouple, is not reliable under ordinary conditions because it is affected by such factors as superheating of the vapors, drafts in the room, variations in distillation rate, and changes in atmospheric pressure. Further, according to Bruun and Schickltanz (11, p. 872), tests based on the temperature-volume curve are of little value, especially if the boiling points of the components are close together, because comparatively small differences in boiling points may correspond to large differences in composition.

NUMBER OF THEORETICAL PLATES AND H. E. T. P.

A more satisfactory test for evaluating a fractionating column is to determine the equivalent number of theoretical plates or the number of theoretically perfect plates necessary to make the same separation as the column, assuming identical operating conditions. To make this determination, a binary mixture is distilled until the column operation is stabilized and samples of the distillate and of the liquid in the stillpot are withdrawn and analyzed by suitable means. From data thus obtained, the equivalent number of theoretical plates necessary to make this separation can be calculated, as explained later in this section.

The number of theoretical plates in a specific column indicates the separation that can be made with that column but is not satisfactory for comparing columns of different lengths. Thus, tests of two columns of unequal length may indicate that the longer has more theoretical plates and will give better over-all separation but that it does not provide as efficient separation per unit length. For this reason, comparisons of columns usually are based on the height of a column section that will effect equilibrium between vapor and liquid. This height, which is that required to make a separation equivalent to the separation made by one perfect plate, or height of an equivalent theoretical plate, is commonly designated as the H. E. T. P., as suggested by Peters (59). Mathematically, the H. E. T. P. is the quotient of the length of the packed or bubble-plate section divided by the number of theoretical plates in that section.

The H. E. T. P. is a useful criterion for rating columns according to the efficiency of separation but, unfortunately, it does not take into account the rate of distillation and the thermal efficiency. However, the efficiency of separation, as measured by H. E. T. P., is the most essential requirement in most laboratory columns. Volume of product per unit time, as measured by rate of distillation, may or may not be of major importance, depending upon the type of work being carried out. In most laboratory columns, especially those used in research work, the thermal efficiency or amount of heat required per gram of product is of minor importance.

When testing plate columns, the efficiency of separation is often expressed by "plate efficiency" rather than by the H. E. T. P. Plate

efficiency is the number of theoretical plates divided by the number of actual plates, times 100.

Columns can be tested with either total or partial reflux. Many columns are rated according to determinations made under total reflux, as all results thus obtained are comparable and intercomparisons between columns are possible. Although a column tested with total reflux will indicate a larger number of theoretical plates than the same column tested with partial reflux, the determination of the number of theoretical plates is less difficult with total reflux and the calculations are simpler. Furthermore, a column that is equivalent to a large number of theoretical plates with total reflux probably will make effective separation under operating conditions. However, to determine more closely the separation that may be expected under operating conditions, the column should be tested with the same reflux ratio and boiling rate that will be used in actual operation.

METHODS AND THEIR APPLICATION

In 1925 McCabe and Thiele (48) and Murphree (53) published graphic methods for determining the number of plates in a column in which continuous distillation was used. The same methods may be used, however, for batch distillation, if the column is operating with infinite reflux, or for partial reflux, if the volume of material in the stillpot is large compared to that in the column. In this latter case the results represent conditions only at the particular instant when the still liquid is sampled. Graphic methods are satisfactory for a column having about 30 or less theoretical plates, but with a greater number of plates these methods become less accurate and more tedious to use.

When the number of plates in a column of more than about 30 plates is determined, an algebraic method is more satisfactory. Several algebraic methods (13, 20, 26, 44, 54, 75, 80) have been published, but in the writer's opinion the equations proposed by Fenske (26) and by Dodge and Huffman (20) seem the most practical. They have been used without alteration in the hypothetical examples given below. It must be remembered, however, that the equations can be used only if the test mixture is ideal, that is, if it obeys Raoult's law, which states that the partial pressure of any component is equal to the product of the vapor pressure of the pure component and its mol fraction in solution.

The method of taking and analyzing samples and the subsequent calculations necessary for determining the number of theoretical plates are explained in the following illustrative examples. To facilitate comparisons, the same nomenclature is used in all the examples, the same compositions for the still liquid and distillate samples are used in the problem with total reflux and the problem with partial reflux, and each problem is solved by both graphic and algebraic methods.

NUMBER OF THEORETICAL PLATES WITH TOTAL REFLUX

Data.—A mixture of *n*-heptane and methylcyclohexane was refluxed in column A for several hours to assure equilibrium conditions. Approximately 1-ml. samples of the reflux liquid and still liquid were

withdrawn as nearly simultaneously as possible. The sample of reflux liquid was obtained by drawing liquid very slowly from the product line, so that approximately equilibrium conditions were maintained. The sample of still liquid was withdrawn from a tube extending into the boiling liquid in the still. Both sampling lines had been cleaned previously to avoid stagnant liquid being withdrawn with the sample. Analysis of the samples by refractive index showed the refractive index of the distillate to be 1.3989 and that of the still liquid 1.4077. A refractive index-composition curve plotted from the data in table 2 (p. 14) shows these values to correspond to 0.65 and 0.40 mol fraction of *n*-heptane in the distillate and still liquid, respectively. The following nomenclature is used:

x_{f_1} = 0.40, mol fraction of *n*-heptane in the still;

x_{f_2} = 0.60, mol fraction of methylcyclohexane in the still;

x_{e_1} = 0.65, mol fraction of *n*-heptane in the distillate;

x_{e_2} = 0.35, mol fraction of methylcyclohexane in the distillate;

R = reflux ratio (ratio of reflux to product);

α = 1.07, relative volatility of *n*-heptane and methylcyclohexane (ratio of their vapor pressures), value determined by Beatty and Calingaert (5);

$n+1$ = total number of theoretical plates, including the still;

n = number of theoretical plates in the column.

Problem.—Using the graphic method of McCabe-Thiele (48), determine the number of theoretical plates in column *A* when operating under total reflux.

Solution.—1. Using the data in table 2, plot the vapor-liquid equilibrium curve (I in fig. 1) and draw the equal composition or 45° line (II).

2. Erect vertical lines at points corresponding to the compositions of the still liquid (x_{f_1} = 0.40) and the reflux (x_{e_1} = 0.65).

3. Starting at $x = x_{e_1}$ on the diagonal, draw a series of rectangular steps between the equilibrium curve and the 45° line until the point $x = x_{f_1}$ is passed.

The total number of steps (15.15) is $n+1$, the total number of plates in the column and still. Therefore, $n = 14.15$, the number of plates in the column only.

Data.—*n*-Heptane and methylcyclohexane form an ideal mixture; therefore, the same problem can be solved by algebraic methods.

Problem.—Using Dodge and Huffman's (20) equation, determine the number of theoretical plates in column *A* when operating with total reflux.

Solution:

$$\begin{aligned} n+1 &= \frac{2.303}{\alpha-1} \left(\log \frac{x_{e_1}}{x_{f_1}} + \alpha \log \frac{1-x_{f_1}}{1-x_{e_1}} \right) \text{ (Dodge-Huffman),} \\ &= \frac{2.303}{1.07-1} \left(\log \frac{0.65}{0.40} + 1.07 \log \frac{1-0.40}{1-0.65} \right), \\ &= 15.17, \\ n &= 14.17 \text{ plates.} \end{aligned}$$

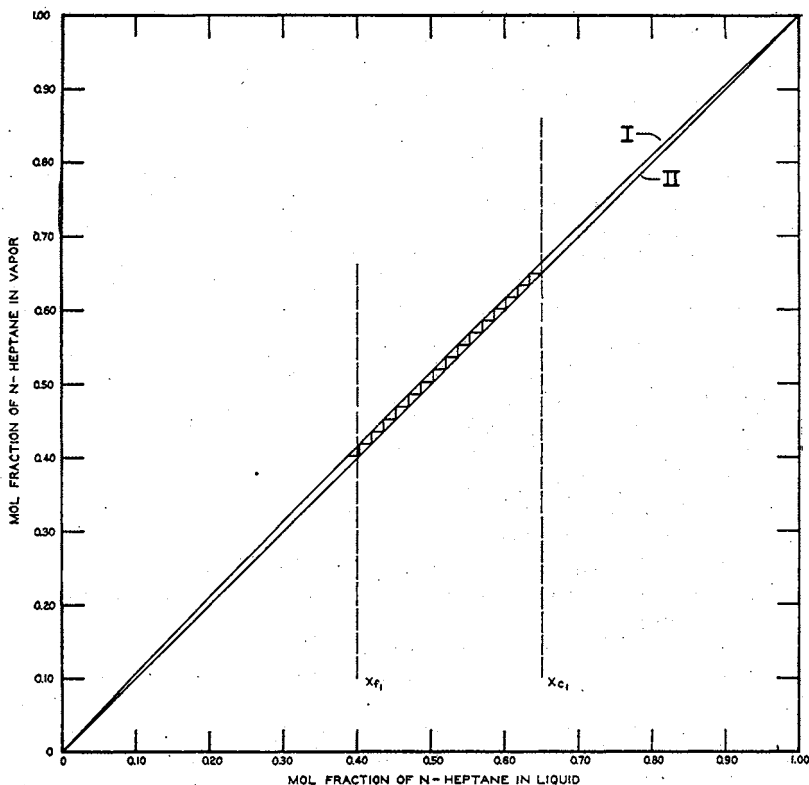


FIGURE 1.—McCabe-Thiele diagram with total reflux.

Problem.—Using the equation proposed by Fenske (26), calculate the number of theoretical plates in column A, when operating with total reflux.

Solution:

$$\frac{x_{c1}}{x_{c2}} = (\alpha)^{n+1} \frac{x_{f1}}{x_{f2}} \text{ (Fenske),}$$

$$\frac{0.65}{0.35} = (1.07)^{n+1} \frac{0.40}{0.60},$$

$$(1.07)^{n+1} = 2.786,$$

$$n+1 = 15.15,$$

$$n = 14.15 \text{ plates.}$$

(NOTE.—This equation can also be used in the form $n+1 = 34.0 \log \frac{x_{c1}/x_{c2}}{x_{f1}/x_{f2}}$, where 34.0 represents $\frac{1}{\log \alpha}$).

H. E. T. P. WITH TOTAL REFLUX

Data.—The packed section of column A is 45 cm. long. Determination of the number of theoretical plates by the graphic method,

by Dodge and Huffman's equation, and by Fenske's equation resulted in 14.15, 14.17, and 14.15 plates, respectively.

Problem.—What is the H. E. T. P. when the number of plates determined by each of the above methods is used?

Solution:

$$\begin{aligned} \text{H. E. T. P.} &= \frac{\text{Length of packed section}}{\text{Number of theoretical plates}}, \\ &= \frac{45 \text{ cm.}}{14.15} = 3.18 \text{ cm. (McCabe-Thiele),} \\ &= \frac{45 \text{ cm.}}{14.17} = 3.18 \text{ cm. (Dodge-Huffman),} \\ &= \frac{45 \text{ cm.}}{14.15} = 3.18 \text{ cm. (Fenske).} \end{aligned}$$

PLATE EFFICIENCY WITH TOTAL REFLUX

Data.—Column *A* is a plate column with 20 plates. Determination of the number of theoretical plates by the graphic method, by Dodge and Huffman's equation, and by Fenske's equation resulted in 14.15, 14.17, and 14.15 plates, respectively.

Problem.—What is the plate efficiency when the number of plates determined by each of the above methods is used?

Solution:

$$\begin{aligned} \text{Plate efficiency} &= \frac{\text{Number of theoretical plates}}{\text{Number of actual plates}} \times 100, \\ &= \frac{14.15}{20} \times 100 = 70.8 \text{ percent (McCabe-Thiele),} \\ &= \frac{14.17}{20} \times 100 = 70.9 \text{ percent (Dodge-Huffman),} \\ &= \frac{14.15}{20} \times 100 = 70.8 \text{ percent (Fenske).} \end{aligned}$$

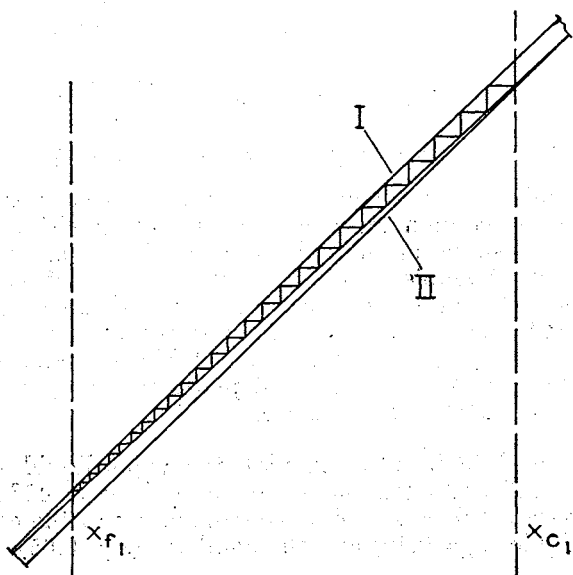
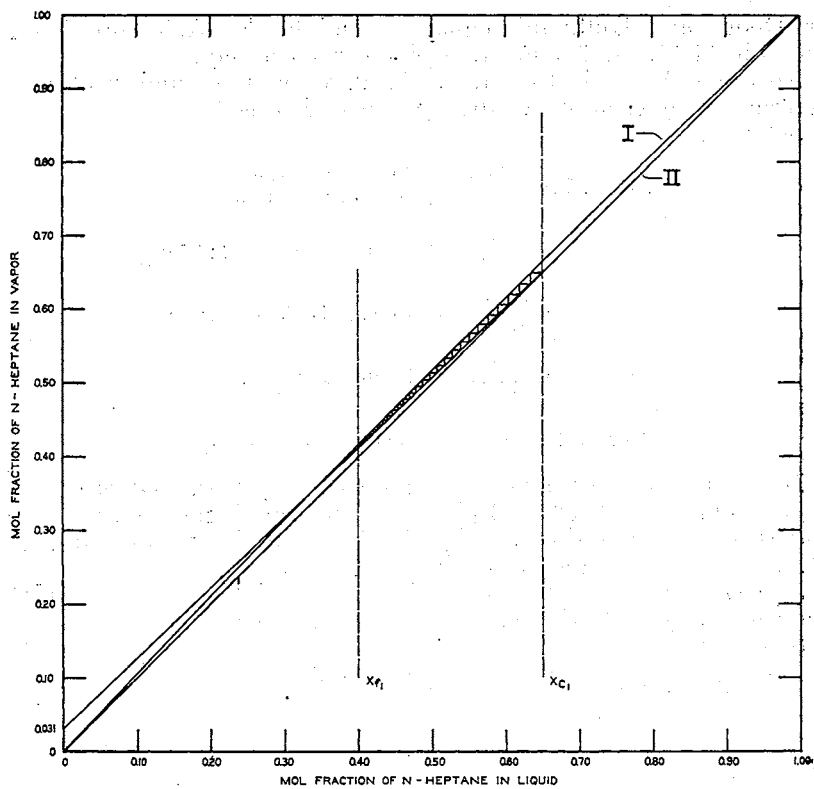
NUMBER OF THEORETICAL PLATES WITH PARTIAL REFLUX

Data.—A mixture of *n*-heptane and methylcyclohexane was distilled in a second column, *B*, which was operating with a reflux ratio of 20 to 1. A sample of the still liquid analyzed 0.40 mol fraction *n*-heptane and a sample of distillate 0.65 mol fraction *n*-heptane. (Note: These samples are of the same composition as those taken from column *A* when it was operating with total reflux.)

Problem.—Using the graphic method of McCabe and Thiele (48), determine the number of theoretical plates necessary to make this separation with a 20 to 1 reflux ratio.

Solution:

1. Using the data in table 2, plot the vapor-liquid equilibrium curve (I in fig. 2) and draw the equal-composition or 45° line (II).
2. Erect vertical lines at points corresponding to the compositions of the still liquid ($x_{r1}=0.40$) and the distillate ($x_{d1}=0.65$).



ENLARGED CENTER PORTION OF MCCABE-
THIELE DIAGRAM.

FIGURE 2.—McCabe-Thiele diagram with partial reflux.

3. Plot the y -intercept $\frac{x_{c_1}}{R+1} = \frac{0.65}{20+1} = 0.0310$ and draw the operating line between this point and the point on the diagonal $x=x_{c_1}$. (Note: The operating line coincides with the 45° line when operating with total reflux.)

4. Starting at $x=x_{c_1}$ on the diagonal, draw a series of rectangular steps between the equilibrium curve and the operating line until the point $x=x_{f_1}$ is passed.

The total number of steps (25.8) is $n+1$, the total number of plates in the column and still. Therefore, $n=24.8$, the number of theoretical plates in the column only.

Problem.—Calculate the equivalent number of theoretical plates by the use of Dodge and Huffman's equation.

Solution:

$$n+1 = 2.303 \left[\frac{2R+B}{2\sqrt{B^2-4AC}} \left\{ \log \frac{2Ax_{c_1}+B-\sqrt{B^2-4AC}}{2Ax_{f_1}+B-\sqrt{B^2-4AC}} \cdot \frac{2Ax_{f_1}+B+\sqrt{B^2-4AC}}{2Ax_{c_1}+B+\sqrt{B^2-4AC}} \right\} + \frac{1}{2} \log \frac{Ax_{f_1}^2+Bx_{f_1}+C}{Ax_{c_1}^2+Bx_{c_1}+C} \right] \text{ (Dodge-Huffman),}$$

$$A = R(1-\alpha) = 20(1-1.07) = -1.4,$$

$$B = R(\alpha-1) - x_{c_1}(\alpha-1) + \alpha = 20(1.07-1) - 0.65(1.07-1) + 1.07 = 2.4245,$$

$$C = -x_{c_1} = -0.65,$$

$$n+1 = 2.303 \left[\frac{2(20) + 2.4245}{2\sqrt{(2.4245)^2 - 4(-1.4)(-0.65)}} \left\{ \log \frac{2(-1.4)(0.65) + 2.4245}{2(-1.4)(0.40) + 2.4245} \cdot \frac{-\sqrt{(2.4245)^2 - 4(-1.4)(-0.65)}}{-\sqrt{(2.4245)^2 - 4(-1.4)(-0.65)}} \right\} + \frac{1}{2} \log \frac{2(-1.4)(0.40) + 2.4245 + \sqrt{(2.4245)^2 - 4(-1.4)(-0.65)}}{2(-1.4)(0.65) + 2.4245 + \sqrt{(2.4245)^2 - 4(-1.4)(-0.65)}} \right]$$

$$n+1 = 2.303 [14.179 \{ \log 4.653 \cdot 1.333 \} + \frac{1}{2} \log 0.2865],$$

$$n+1 = 25.26,$$

$$n = 24.26 \text{ plates.}$$

LENGTH OF RECTIFYING SECTION

Data.—Assume column B has the same H. E. T. P. as column A . Determination of the number of theoretical plates in column B by the graphic method and by Dodge and Huffman's equation resulted in 24.8 and 24.26 plates, respectively.

Problem.—Calculate the length of the rectifying section of column B , using the number of plates as determined by each of the above methods.

Solution.

Length of the packed section of column $B = \text{H. E. T. P.} \times \text{number of theoretical plates,}$

$$= 3.18 \text{ cm.} \times 24.8 = 78.86 \text{ cm. (McCabe-Thiele),}$$

$$= 3.18 \text{ cm.} \times 24.26 = 77.15 \text{ cm. (Dodge-Huffman).}$$

Table 1 shows that virtually the same results can be obtained by using graphic or analytic solutions. It also shows that to make

the same separation, it is necessary to use a longer column when operating with partial reflux than when total reflux was used. Conversely, in a given column, less separation can be effected with partial reflux than with total reflux. However, the next section will show that experimental evidence is not always in agreement with these theoretical conclusions.

TABLE 1.—Comparison of results obtained by graphic and analytical methods

Method of solving	Reflux ratio	Column A				Column B		
		Number of theoretical plates	H. E. T. P., cm.	Column length, cm.	Plate efficiency, percent	Number of theoretical plates	H. E. T. P., cm.	Column length, cm.
Graphic.....	Infinite...	14.15	3.18	145	70.8			
Do.....	20:1.....					24.8	13.18	78.86
Dodge-Huffman.....	Infinite...	14.17	3.18	145	70.9			
Do.....	20:1.....					24.26	13.18	77.15
Fenske.....	Infinite...	14.15	3.18	145	70.8			

¹ Values assumed in the statement of the problem; other values are calculated.

BINARY TEST LIQUIDS

n-HEPTANE AND METHYLCYCLOHEXANE

n-Heptane (b. p. 98.4° C.) and methylcyclohexane (b. p. 100.8° C.) are an excellent mixture for testing columns used for fractionating petroleum, because both the components are hydrocarbons, their normal boiling points are only 2.4° C. apart, and analysis of the composition by refractive index is easy and accurate.

TABLE 2.—*n*-Heptane and methylcyclohexane

Equilibria data, ¹ mol fraction <i>n</i> -heptane		Analytical data ²	
Liquid	Vapor	Mol fraction <i>n</i> -heptane	Refractive index, 20° C.
0.00	0.0000	0.00	1.4232
.10	.1063	.10	1.4192
.20	.2110	.20	1.4152
.30	.3144	.30	1.4114
.40	.4163	.40	1.4077
.50	.5189	.50	1.4041
.60	.6161	.60	1.4006
.70	.7140	.70	1.3972
.80	.8106	.80	1.3940
.90	.9059	.90	1.3908
1.00	1.0000	1.00	1.3877

¹ Calculated from vapor-pressure relationship given by Beatty and Calingaert (4, 5).

² Values taken from best curve through Bromiley and Quiggle's data (6).

METHYLCYCLOHEXANE AND TOLUENE

Methylcyclohexane (b. p. 100.8° C.) and toluene (b. p. 110.7° C.) form a suitable hydrocarbon mixture for testing columns used in petroleum work because the components are relatively cheap, they can be obtained readily in the pure state, the liquid-vapor phase diagram is known, and the composition can be determined easily by means of refractive index or density. This mixture cannot be used for testing

columns equivalent to more than about 30 theoretical plates and, because it deviates somewhat from an ideal mixture, the number of plates must be determined graphically rather than algebraically.

TABLE 3.—*Methylcyclohexane and toluene*

Equilibria data, ¹ mol fraction methylcyclohexane		Analytical data ¹	
Liquid	Vapor	Mol fraction methylcyclohexane	Refractive index, 20° C.
0.00	0.000	0.00	1.4965
.10	.143	.10	1.4871
.20	.270	.20	1.4782
.30	.378	.30	1.4699
.40	.470	.40	1.4620
.50	.560	.50	1.4544
.60	.650	.60	1.4474
.70	.737	.70	1.4408
.80	.818	.80	1.4345
.90	.906	.90	1.4286
1.00	1.000	1.00	1.4235

¹Data from Quiggle and Fensko (66).

CARBON TETRACHLORIDE AND BENZENE

A carbon tetrachloride (b. p. 76.7° C.) and benzene (b. p. 80.1° C.) mixture is often used to test fractionating columns because it is cheap, the components are readily obtainable in the pure state, and analysis by refractive index or specific gravity is easy and accurate. The disadvantages of the mixture are (a) the composition 91.8 mol percent carbon tetrachloride must be avoided, since a constant boiling mixture is formed; (b) the carbon tetrachloride will react with aluminum packing and will corrode certain other packings if used over a long period of time; (c) it gives somewhat different results than a hydrocarbon mixture (78). However, it is fairly satisfactory for comparing columns or for determining the effect of changing the operating variables.

TABLE 4.—*Carbon tetrachloride and benzene*

Equilibria data, ¹ mol fraction carbon tetrachloride		Analytical data ¹	
Liquid	Vapor	Mol fraction carbon tetrachloride	Refractive index, 25° C.
0.00	0.000	0.00	1.49794
.10	.122	.10	1.49392
.20	.233	.20	1.48997
.30	.337	.30	1.48589
.40	.437	.40	1.48178
.50	.534	.50	1.47772
.60	.628	.60	1.47369
.70	.720	.70	1.46963
.80	.812	.80	1.46555
.90	.907	.90	1.46142
1.00	1.000	1.00	1.45732

¹Values from curve plotted from Rosanoff and Easley's data (69).

²Values from curve plotted from International Critical Tables (59). Values checked by Rosanoff and Easley's data (69).

BENZENE AND ETHYLENE CHLORIDE

A mixture of benzene (b. p. 80.1° C.) and ethylene chloride (b. p. 83.7° C.) has been used frequently to test columns because it forms an ideal or nearly ideal mixture, the difference in boiling point of the two constituents is small, and the composition can be determined easily by means of a refractive index. Unfortunately, there is some disagreement as to the proper liquid-vapor equilibrium data to use. The author recommends those of Rosanoff and Easley (69) because they check those of Zawidzki (86); and, since the mixture is an ideal one (4, 38), these data can be checked by Raoult's law. A modification of Pahlavouni's (56, 77) data also has been used (32). This gives a larger number of plates than do Rosanoff and Easley's data. Of this modification, Glasgow and Schicktanz (32) say: "While the absolute magnitude of the number of plates may be in error by an appreciable amount, the authors believe that relative to one another, the values are quite reliable." While this mixture is satisfactory for determining the effect of changing the operating variables, it should be used for comparisons of columns only when identical phase diagrams are used. Furthermore, there are likely to be corrosion difficulties if this mixture is used with metal equipment; or, if water is present, there may be hydrolysis of the ethylene chloride, which might affect the results of efficiency tests.

TABLE 5.—Benzene and ethylene chloride

Equilibria data, ¹ mol fraction benzene		Analytical data ²	
Liquid	Vapor	Mol fraction benzene	Refractive index, 25.2° C.
0.00	0.000	0.00	1.44218
.10	.113	.10	1.44750
.20	.222	.20	1.45287
.30	.327	.30	1.45825
.40	.429	.40	1.46366
.50	.527	.50	1.46914
.60	.624	.60	1.47462
.70	.722	.70	1.48020
.80	.818	.80	1.48596
.90	.912	.90	1.49187
1.00	1.000	1.00	1.49779

¹ Values from curve plotted from Rosanoff and Easley's data (69).

² Values from curve plotted from Rosanoff and Easley's data (69). Curve checked by data from International Critical Tables (39, p. 80).

DETAILED CONSIDERATIONS OF MATERIAL TABULATED IN TABLE 6

The headings in the following discussion conform with those in table 6 at the end of this section. Under each heading, the data as given in the table, augmented by untabulated information, are considered, and similarities and differences in construction and operation of the several parts of the column are pointed out. The discussion of each major heading is concluded with a brief statement in which the writer mentions those features that in his opinion seem most advantageous.

STILLPOT

MATERIAL

Small stillpots usually are spherical glass flasks, whereas large stillpots generally are vertical or horizontal metal tanks.

CAPACITY

The size of the charge, its behavior during distillation, and the flooding capacity of the column govern the capacity of the stillpot. It should be large enough to care for thermal expansion and foaming and be of such shape that the evaporating surface of the charge will not be large enough to cause flooding of the column before brisk boiling begins.

SOURCE OF HEAT

Gas, electricity, or a heated bath is used for heating stillpots of laboratory columns. Gas is usually more economical, but, although often used for heating large stillpots, it does not permit close heat regulation and its use should be avoided because of the fire hazard. Electrical heating, which is preferable, may be either external or internal. External units offer a larger, more evenly heated surface, are more simple to construct and use, and are generally preferred. Although control of internal heaters operates with less lag, there is some danger of local overheating and they offer certain mechanical difficulties in construction. In some installations the stillpot is submerged in a heated bath of noninflammable liquid or of lead or nickel shot. This method of heating reduces the fire hazard, but there is a large lag in the response to change in heat input.

The area of heating surface required is a function of the rate of evaporation desired, the temperature difference between the charge and its source of heat, and the physical characteristics of the material of which the kettle is constructed. A large, evenly heated surface is preferable to prevent local overheating and to avoid possible decomposition of the charge.

INSULATION

To avoid local overheating, the temperature difference between the heater and stillpot should be as small as possible and still provide enough heat for vaporization. This temperature difference can be reduced materially by properly insulating the stillpot.

CONCLUSIONS REGARDING STILLPOT

The stillpot should be made of a material that will not corrode under operating conditions and of sufficient capacity to take care of thermal expansion and foaming of the charge. It should be well insulated and preferably heated over a relatively large surface by external electric heating units that can be controlled closely. The stillpot should be provided with connections through which the charge can be introduced and the residue removed, and with a passage through which vapors can enter the column and the reflux return to the still. In small columns one connection may be adequate. If tests for efficiency of separation are to be made, some means should be provided for removing a sample of liquid without interrupting the distillation.

COLUMN

TYPE

Plate columns.—Plate columns are of two general types, perforated and bubble-cap, which for the following discussion can be classed together. A plate column is essentially a series of stills, one above the other. The hot vapors from the plate below supply the heat and the reflux acts as a condensing medium. The efficiency of each plate is determined by comparing the separation effected by it with that made by a theoretical plate. A theoretical plate (2) "fulfills the requirement that the vapor rising from the plate and passing to the plate above is in equilibrium with the liquid leaving the plate and passing to the plate below." Some of the factors that determine the degree in which an actual plate will approach such an ideal plate are:

1. Nature of the mixture being fractionated. Peters (59) found the efficiency lower when high-molecular-weight mixtures are fractionated, and when materials of equal molecular weight are fractionated the efficiency is higher if there is more attraction between similar than between dissimilar molecules.

2. Intimacy of contact between liquid and vapor. This is one of the major factors affecting effectiveness of separation and depends largely on plate and bubble-cap design. It has been determined by a cinematograph (22, p. 109) that the vapor leaves the slot in the bubble cap as a series of bubbles and not, as it appears to the eye, in a continuous stream. Experiments cited by Robinson (68) show that when the bubble emerges from the slot the vapor near the surface of the bubble almost instantaneously reaches equilibrium with the liquid surrounding it, but the vapor in the center of the bubble reaches equilibrium by diffusion only.

3. Length of period of contact between liquid and vapor. When this period is increased, there is greater possibility of effecting equilibrium between the phases. The period of contact can be increased by lowering the vapor velocity (which reduces the throughput) or by increasing the depth of liquid on the plate. The latter practice increases the back pressure and, beyond a certain depth, adds little to the efficiency of the plate, owing to the slow rate of diffusion in the bubble. Experiments performed at the Massachusetts Institute of Technology (68) show that when the spherical bubble rises through the liquid virtually no further reaction will occur during the greater length of its travel than occurred when it emerged from the slot, unless the bubble is distorted, which brings a new portion of the vapor to the surface of the bubble.

4. Plate spacing. Entrainment, which decreases the efficiency of fractionation, is largely affected by the distance between plates. This distance should be such that entrainment is small under practical operating conditions.

5. Reflux ratio and vapor velocity. Plate efficiency is also influenced by the reflux ratio and the vapor velocity. These factors are discussed on pages 25 and 26, respectively.

Few types of plate columns have been designed for fractionation of small volumes. Young and Thomas (85), Dupont (21), and Palkin (57) describe columns having a series of glass trap tubes hung in wire-gauze plates. These plates effect intimate contact between the vapor and liquid, and the trap tubes serve as a passage for reflux down the

column. These columns are easily constructed, can handle a large volume of vapor, and can be operated under vacuum. A perforated plate column using fritted glass disks is described by Schicktzanz (72). The plate efficiency approaches 100 percent, but the back pressure is high, due to the resistance of the small holes to passage of vapors. A "bubbler"-type column designed by Clark and Rahrs (15) consists of a number of staggered glass traps, in each of which the ascending vapors are washed by bubbling through the refluxed liquid. The column is satisfactory for simple separations, but it has a large hold-up, the vapor bubbles emit from one large opening rather than several small ones, and, due to its irregular shape, the column is rather difficult to insulate. Bruun (9, 10) has developed an all-glass bubble-cap column, which has a very low H. E. T. P. As a 100-plate (70 to 72 theoretical plates) column is only 2 meters long, it can be set up in a laboratory of less than average height. There will be no corrosion in the column, due to its all-glass construction; consequently it will retain its efficiency indefinitely. The column plates are nonsiphoning, and if the still is shut down the fractionated portions of the liquid will remain on their respective plates, thus saving several hours necessary to bring the column to equilibrium after a shut-down.

Packed columns.—Some of the advantages and disadvantages of packed columns have been mentioned already. The major variable is the packing, which will be discussed under that heading.

MATERIAL

Glass is normally used for smaller columns because it does not corrode and under certain conditions affords a view of the action in the column. In addition, many types of columns can be constructed or modified by the laboratory worker. Larger columns usually are metal because they are easier to fabricate and are less fragile.

DIAMETER

The obvious advantage of increasing the diameter of fractionating columns is the increased capacity. The capacities of columns are proportional to the squares of their diameters. The hold-up, however, increases in approximately the same ratio, and there is some loss in fractionation.

LENGTH OF THE FRACTIONATING SECTION

Increasing the length of the fractionating section follows the law of diminishing returns; that is, each added increment of length is less effective than the preceding one. Fenske, Tongberg, and Quiggle (29) found this was true, especially in columns of small diameter, which led them to believe it was due partly to channeling in packed columns and partly to some fundamental vapor-liquid equilibrium relationship. However, this should not be construed to indicate that a short column is preferable, as the increase in H. E. T. P. is much smaller than the gain in separation effectiveness due to each added increment of length. Fenske stated (30) and showed graphically (27, p. 1631) that at total reflux the degree of separation increased logarithmically, not linearly, with the number of perfect plates. Since the number of perfect

plates in a given column is a function of its length, for best results the length should be a maximum compatible with operational and constructional requirements.

INSULATION

The relative efficiency of lagged and unlagged columns was determined by Marshall and Sutherland (47), who found, with a properly lagged Hempel column 99 cm. long and provided with maximum reflux, that the effectiveness obtained was 2.4 to 41.5 times as great as that obtained with the same column unlagged and operating at the same distillation rate. The most common methods of insulating a column are with asbestos, magnesia, air jacket, or vacuum jacket. Magnesia and asbestos are easy to apply, are not fragile, do not develop strains, and can be applied to either glass or metal columns. Air jackets allow visibility, protect the column from drafts, and give some insulation owing to the dead air space. Although vacuum jackets provide very efficient insulation, especially if silvered, their use involves mechanical difficulties at high temperatures owing to the difference in temperature of the inner and outer tubes. Podbielniak (62, p. 132) has made vacuum jackets using quartz for the inner tube and pyrex for the outer tube, thus preventing breakage due to thermal expansion. However, the high cost of the tubes has limited their use somewhat. Furthermore, at high temperatures there is an appreciable loss of heat, which cannot be compensated without using an extra heating jacket, thereby losing the advantage of the vacuum jacket.

SOURCE OF HEAT

To compensate for the loss of heat due to radiation, some investigators supply heat to the column. Peters and Baker (60) wrapped resistance wire around the jacket and, in addition, circulated hot air through the jacket. Tongberg, Quiggle, and Fenske (78) used the vapors from the still to jacket a small column and in a longer column wrapped resistance wire in sections, each of which was independently controlled; in the insulation. The heat was so regulated that a thermocouple on the exterior column surface registered the same temperature as did another between the heating element and the column.

CONCLUSIONS REGARDING COLUMN

When selecting a laboratory column for a definite type of fractionation, one should consider the initial cost, the ease of construction, the simplicity of operation, and, most important, the efficiency of the column. The most efficient column is the one that produces the largest volume of the desired product per unit time with the least expenditure of heat. Consideration of these and other factors generally favors a packed column, but only if it is filled with efficient packing and operated under adiabatic conditions. Such a column has a lower hold-up and pressure drop but has the disadvantage that when distillation is interrupted the fractionated material in the column drains back to the still. An external source of heat is necessary, except in short columns, to maintain adiabatic conditions. An effective means of doing this is to wrap resistance wire into the asbestos or magnesia lagging in several independently controlled

sections, the number of sections depending upon the length of the column. A thermocouple (or other thermometer) should be placed in the lagging of each section and one should be placed on the external column wall opposite. The heating can then be regulated so that there will be no lateral heat flow.

CONDENSER

TYPE

Partial condenser.—A partial condenser, or dephlegmator, condenses only a portion of the vapors, which is returned to the column as reflux, and the rest of the vapor is delivered to a final condenser. When a mixed vapor is partly condensed, the uncondensed part is enriched in the more volatile component, which assists the column in fractionating the vapors. Peters and Baker (60) found that better separation was obtained with a partial condenser, because with a total condenser—

There is in the partitioning device an appreciable hold-up of distillate, which can hardly be made less than 1 cc. Moreover, by such an arrangement the fractionating effects of the dephlegmator are lost, whereas with the present design the enrichment due to the dephlegmator becomes surprisingly great at the critical points when reaching the point where the last of a certain component is being distilled off.

Furthermore, according to Podbielniak (62, p. 127), the use of a total condenser results in some loss in fractionation, as any separation accomplished in the column is lost by reblending of the separated components before collection. Podbielniak (62, p. 127) states that this reblending results—

When excess holdup occurs within the condensing column section because of unnecessarily large condensing-tube diameter or length, liquid occluding seals or crevices, devices for portioning reflux, etc. While the fractionating column itself may have considerable hold-up of material per unit length, this is usually more than compensated for by the fractionating action of the packing. In the condensing section the fractionating effect drops out, and any appreciable hold-up of material limits and in extreme cases practically destroys the fine separation of components existing at the top of the column packing.

Othmer (55) favors the partial condenser and Young (85, p. 403) states that no plant can be thoroughly efficient without some form of dephlegmator.

Total condenser.—A total condenser liquefies all the vapors, returns a portion to the column as reflux, and delivers the remainder to the product line. Thus, when a total condenser is used, all the fractionation occurs in the column and none occurs in the condenser. This practice is approved by Robinson (68, p. 91), who states:

The function of the usual type of condenser as a fractionating device is a function which should not be allowed to occur, but which, unfortunately, does often occur in many designs of stills.

The contact between liquid and vapor in a condenser is very poor. Most are of tubular design where the cooling medium and the vapor are inside and outside of the tubes, respectively, or the reverse. Under these circumstances, the vapor condensing on the cold surface of the tubes runs down the surface of the tubes while the remaining vapor passes on between the surfaces, keeping out of contact with the condensed vapor as much as possible. This means that one necessary feature of an efficient fractionating device is not complied with in the condenser used for this purpose.

In the second place, condensers must condense differentially and the reflux from the top of the condenser is constantly augmented by additional condensed vapor as it passes down through the condenser until the reflux at the bottom is a maximum. This violates the second rule for efficient fractionating devices.

It is true, therefore, theoretically, and it has been found practically, that by far most efficient results are obtained when as much as possible of the fractionation is required to take place in the fractionating column and as little as possible allowed to occur in the condenser.

Leslie (42) proves mathematically that fractional distillation is more efficient than fractional condensation. Perry (58), Walker, Lewis, and McAdams (82), and Elliott (22) seem to favor the total condenser. Bruun (8), Hill and Ferris (36), Fenske (28), Docksey and May (19) and many others have used total condensers, while Leslie and Geniesse (42, p. 555; 43) have used both types. McIntyre (49) believes the total condenser superior to the partial condenser and should supersede it entirely.

CONCLUSIONS REGARDING CONDENSER

A total condenser is more suitable for most columns, as it requires less attention and the reflux ratio can be held practically constant by a liquid partitioning device with a very small hold-up. A large enough charge should be used so that any reblending of fractionated constituents will not, as a rule, obscure a constituent present in small amount. A partial condenser is suitable when one or more of the components is small and the charge cannot be large.

PACKING

TYPE

Solid packing.—Solid-type packing includes glass beads, balls, and particles of stone, glass, metal, or other inert material. Solid packing was the earliest type used and still finds extensive use in simple laboratory fractionating columns. This packing floods at a low rate of distillation and offers a relatively small surface area per unit volume.

Raschig rings.—Raschig rings are small, thin-walled cylindrical tubes of earthenware, glass, or metal of equal height and diameter. Owing to their dimensions and shape, they make a fairly uniform packing, present a reasonably large surface area and free volume, and form no pockets to hold up liquid.

Chain packing.—Chain packing is used extensively owing to its availability, large surface area, and the ease with which it may be removed from the column. It can be allowed to pack loosely in the column or separate strands can be suspended at the top of the column. The latter method has a greater free volume and allows a greater throughput but has less surface area per unit volume. Schicktanz (73) found that efficiency is increased in going from a single jack chain to a double jack chain to a jeweler's brass locket chain, in accordance with the increase of effective surface exposed in the column. McMillan (50) states that jeweler's-chain packing is less effective than spiral packing and, because of channeling and flooding, adds to the difficulty of control.

Spiral packing.—A spiral coil of wire, which fits the column closely, makes an efficient packing. Podbielniak (61) describes a 3.8-mm. column packed with a spiral of No. 20 wire with six or seven turns to the inch. The coil is ground on the outside to decrease the hold-up of liquid in the interstices between the column and the packing. He describes its operation as follows:

The refluxed liquid is distributed into very thin capillary films supported only at their boundaries by the turns of the wire coil and by the glass walls, instead of simply wetting the very small surface of the packing. This results in maximum contacting between liquid and vapor with least hold-up of liquid on the packing.

Mair, Schick Tanz, and Rose (46) used a spiral of No. 8 copper wire in a 2-cm.-diameter column for the vacuum fractionation of lubricating oil. The spiral offered little resistance to the passage of vapors but retarded the flow of reflux and spread it more evenly over the column. McMillan (50), using a 3.8-mm.-diameter column with an 8-turn-per-inch spiral of No. 22-gage wire, was unable to get satisfactory fractionation. He introduced liquid at the top of the column and gas containing suspended fog particles at the bottom. He noted two currents of ascending vapors—one spiraling slowly up between the turns of the spiral, while the second and by far the larger stream was flowing linearly through the center of the spiral and into the condenser. This central stream contacted the reflux only at its outer edges and was being fractionated only in the partial condenser, which indicates why a longer condenser improves this type fractionating column. As further proof of the inefficiency of spiral-type packing, it was removed from the column and almost identical fractionation was obtained. McMillan found that efficient separation was obtained only after the center space was eliminated. This was done by using either a straight central wire insert or a longitudinal flat spiral of No. 29-gage ribbon $\frac{1}{16}$ inch wide in the free space. Rose (70) found spiral packing gave poorer separation than single-turn wire helices.

Single-turn helices.—A packing consisting of single-turn wire helices was developed by Fenske and his coworkers (79). This packing under certain conditions has a high efficiency and throughput. The efficiency increases and the throughput decreases as the inside diameter of the helix is decreased. Helices made from No. 30 gage wire with an inside diameter of 2.4 mm. were found to be most efficient and have a good throughput. Single-turn helices also have been made of glass (84) to avoid corrosion. Columns of the order of 100 theoretical plates can be built in a laboratory of average height by using this type packing.

Wire-gauze packing.—Stedman (76) got efficiencies as high as 18 plates per foot by using a column packing of rather fine-mesh wire gauze perforated and shaped to give maximum contacting of liquid and vapor. These results, however, were calculated from data obtained with columns only a few inches long.

Carborundum packing.—Midgley (52) used glass beads coated with carborundum and spiral packing coated with the same material. The efficiency of the columns was increased materially by using coated rather than uncoated packing. Farnham (25) confirmed and extended Midgley's observations by using lumps of carborundum and various other porous substances. Hall and Bachman (34), using a column packed with 6-mesh silicon carbide, got height equivalents comparable with those obtained with wire helices, but the distillation rate was lower.

MATERIAL

Farnham (25) surmised that the chemical nature as well as the physical structure of the packing affected the fractional distillation curve. She also suggested that the efficiency of the packing is influ-

enced by its selective adsorption and it is probable, though not proved, that the ideal adsorption curve for a column filling would coincide with the liquidus curve in the boiling-point composition diagram for that pair of liquids. Glasgow and Schicktanz (32), using lead, copper, and glass balls as packing, found the efficiency of separation, the vapor velocity, and hold-up are substantially independent of the heat conductivity or the material of the packing. The condition of the packing, however, is important. Fenske, Tongberg, and Quiggle (29) found that a packing that has corroded slightly behaves very differently from the original packing. Usually, with a corroded packing the H. E. T. P. is greater and the throughput is less than when a noncorroded packing is used. Tongberg, Lawrowski, and Fenske (79) found the dryness of the packing before distillation has a marked effect on its efficiency and if the column is deliberately flooded before distillation is begun, the efficiency is greater.

Apparently when the packing is first wet, the subsequent condensate spreads uniformly over the entire wet surface; on a dry packing, the flow of condensate tends to be somewhat agglomerated or coalesced.

FREE SPACE

The volume of the packed section in a fractionating column not occupied by packing is known as the free space. Generally, the greater the free space, the greater the allowable throughput. Fenske, Tongberg, and Quiggle (29) measured the free space by filling a 100-cc. graduate with packing and noting the volume of kerosene necessary to fill the graduate to the 100-cc. mark. They also found—

The product of the number of square inches of surface area per cubic inch and the percentage of free space, divided by 100, gives a numerical value which parallels the efficiency and over-all utility of the packing.

HOLD-UP

The amount of liquid and vapor in the column while it is operating is termed the hold-up under operating conditions. The importance of a low hold-up was emphasized by Peters and Baker (60), who stated that—

No matter how tall a column is, it cannot give sharp cuts if the amount of liquid held up in the column is too great compared to the size of the cut desired.

According to Podbielniak (62, p. 126)—

Even an infinite increase in column height cannot change the ratio of change of composition accomplished per unit length column to the hold-up of material per the same unit length column.

Tongberg, Quiggle, and Fenske (78) describe the following procedure as a satisfactory means of determining the hold-up under operating conditions. A definite amount of a nonvolatile liquid is added to a definite amount of liquid charged to the dry still and column. A known volume of liquid taken from the still while the column is operating at total reflux is evaporated and the nonvolatile material is accurately weighed. The difference in the amount of volatile liquid associated with the nonvolatile liquid before and after the distillation represents the amount held up in the column. Stearic acid (78) and dibutyl phthalate (32) are satisfactory nonvolatile materials for this test.

CONCLUSIONS REGARDING PACKING

A good packing is corrosion-resistant, has a large surface area per unit volume, has a small hold-up, and will accommodate a large volume of vapor per unit time. Consideration of these factors favors single-turn glass or wire helices. More data are desirable concerning wire-gauze and carborundum packing.

OPERATING CONDITIONS

VAPORIZATION RATE

The amount of vapor evaporated in the still per unit time is known as vaporization rate and represents the forward flow of vapor in the column.

PRODUCT RATE

The product rate is often called the distillation rate. With a particular apparatus, there is an optimum value for this factor, above which there will be insufficient separation and below which the increase in separation does not warrant the extra time required.

The usual distillation practice is to keep the distillation rate constant. Glasgow and Schicktanz (32) used a mechanical device for this purpose. Some operators, however, increase the rate when collecting a pure component and decrease the rate between components. According to Podbielniak (64), this procedure decreases the time necessary for a distillation with no loss in accuracy.

REFLUX RATIO

Most investigators use the term "reflux ratio" to designate the quantity of reflux per unit weight of product. A study of the principles of fractionation (2, p. 365; 35; 83) shows the greater the reflux ratio, the fewer plates are required for a given separation; conversely, the greater the number of plates, the smaller the reflux ratio required. However, Marshall and Sutherland (47), Leslie and Geniesse (43), and Peters (59) concluded that a variation in the reflux ratio had no marked effect on the H. E. T. P. McMillan's (50) results show higher efficiency with medium rather than high or low reflux. Calingaert and Huggins (12), with a coke-packed column, found the efficiency was proportional to the reflux ratio at constant vapor velocity. Meyer (51) concluded the more plates in a column the greater the reflux ratio necessary to make full use of the plates. The usual practice is to maintain a constant reflux ratio; however, some investigators decrease the reflux while collecting pure compounds and increase it at the critical points between compounds. Podbielniak (62) stated that this practice decreases the distillation time with no loss in rectification. Judging from their results, Hill and Ferris (36) concluded the peak efficiency of a packed column was at a rate just below flooding. Tongberg, Quiggle, and Fenske (78) operated columns at maximum reflux by maintaining them just below the flooding point. Podbielniak (63) found maximum efficiency when the packing is barely wet. This is verified by Bruun and Schicktanz (11), whose results show efficiency decreased materially near the flooding point. It is apparent that the hold-up is increased under these conditions. The reflux ratio should be kept as low as possible

and still make the required separation, because any increase in reflux ratio increases the distillation time and the heat consumption.

Reflux ratio control.—Reflux usually is controlled in partial condensers by varying the rate of flow of the cooling water or air (42, p. 555) or by changing the height of water in the condenser (42, p. 555). In total condensers, the reflux ratio usually is controlled by either a vapor- or liquid-partitioning device. Calibrated orifices (36), stopcocks (43), and ground-glass valves (74) are used to proportion the vapors. Liquid-partitioning devices use stopcocks (45), needle valves (28), capillary tubes (8), pinch cocks (47), reflux pockets (24), and ground-glass plugs (74).

Reflux ratio determination.—Several methods are used to determine the reflux ratio. Among the more common methods are determining temperature rise in the condenser water (28), using a calibrated reflux siphoning cup (78), counting drops from the base of the column and from the product line (63), and using a reflux flow meter (43). The calibrated-orifice and capillary-tube type proportioning devices have a constant reflux ratio.

VAPOR VELOCITY

Vapor velocity is expressed in a number of ways by various investigators. Glasgow and Schicktanz (32) determine values of vapor velocity from throughput and free space. Fenske (29) uses both superficial linear vapor velocity at the top of the column and cubic inches per hour of liquid condensed at the top of the column. Docksey and May (19) express vapor velocity in terms of linear velocity for a plain tube without packing. Calingaert and Huggins (12) prefer calories of heat in the vapor passing up the column per second. Rose (70) uses cubic centimeters of liquid per minute at the base of the column, and Gadwa (31) uses mass velocity in pounds of vapor per square foot of packing.

There is some disagreement as to the effect of vapor velocity. Marshall and Sutherland (47) and Leslie and Geniesse (43) report vapor velocity has little effect on the effectiveness of the column. Calingaert and Huggins (12) found the effectiveness inversely proportional to the vapor velocity at constant reflux, and experiments by Hill and Ferris (36) indicate an increase in efficiency with increased vapor velocity. Docksey and May (19) and Rose (70) found the effectiveness inversely proportional to the vapor velocity at low rates, becoming more nearly constant at higher rates. Kirschbaum and Andrews' (40) experiments showed that with increasing vapor velocity the effectiveness reached a maximum, declined rapidly at first and then more slowly. Experiments cited by Robinson (68, p. 90) show that efficiency in plate columns is increased if the vapor velocity, where the liquid and vapor are contacted, is increased.

PRESSURE DROP

Bubble-plate columns generally have a greater pressure drop than columns of the same dimensions with efficient packing. Columns having a low pressure drop are preferred in high-vacuum distillation because the increase in pressure through the column raises the boiling point of the material in the still materially. Pressure drop in plate

columns is due to the head of liquid on the plates and resistance to flow of vapor through the vapor slots and through the liquid. In packed columns, pressure drop is a function of the packing, vapor velocity, and reflux. Chilton and Colburn (14) estimate only 10 percent of the resistance in a packed column is due to frictional resistance and the rest is due to contraction and expansion losses in the vapor flow through the irregular orifices formed by the packing particles. They found contraction, expansion, and friction losses are approximately proportional to the square of the vapor velocity. Since the reflux flows through the same interstices as the vapor, an increase in reflux necessarily increases the pressure drop. Schick Tanz (73) used the pressure drop from the stillpot to the stillhead as a measure of the throughput. In a later publication, Glasgow and Schick Tanz (32) showed how the pressure drop from pot to head was used to control the energy input to the stillpot and thence the throughput.

CONCLUSIONS REGARDING OPERATING CONDITIONS

A column should be operated to make the best possible separation without too great expenditure of heat and time, which can be accomplished only by having the operating variables under control. The rate of vaporization and the reflux ratio are especially important, since the vapor velocity, product rate, and pressure drop depend upon them. Rate of vaporization can be controlled by heat input and the reflux ratio by a liquid-partitioning device with a very low hold-up. The column should be operated at several vaporization rates and reflux ratios to determine the maximum throughput without sacrificing too much loss in fractionation.

TEST CONDITIONS

VAPORIZATION RATE

The column under this heading in table 6 records the rate of vaporization per unit time in the still under test conditions. When the data are available, the maximum rate of vaporization under total reflux is given, as it is a measure of the capacity of the column. In other words, the higher the rate of vaporization under total reflux without flooding, the greater the capacity of the column.

H. E. T. P.

The H. E. T. P. (height of equivalent theoretical plate) is the length of column necessary to make the same separation as would be made by a perfect plate. It is the reciprocal of the effectiveness of the column; that is, the lower the H. E. T. P., the more effective the column.

NUMBER OF THEORETICAL PLATES

The number of theoretical plates is a measure of the separation possible with the column under the test conditions. It means that under test conditions the column will make the same separation as a theoretical column with that number of perfect plates.

TABLE 6.—Tabular summary of laboratory fractionating columns

Reference No.¹	Stillpot			Column						Condenser type	Packing			
	Material	Capacity, ml.	Heating	Insulation²	Type	Material	Diameter, mm.³	Length, cm.	Heating		Insulation	Type	Material	Free volume
43	Glass	2,000	Internal electric.	-----	Packed	Glass	(22.9)	(122)	Hot air	Asbestos, iron pipe, and air jacket.	Total	5.6-mm. Lessing rings.	Sheet metal	-----
	do	2,000	do	-----	do	do	(22.9)	(122)	do	do	do	6.5-mm. Lessing rings.	do	-----
47	do	1,000	do	Asbestos	do	do	21	99	None	Air jacket	do	5.4-mm. beads	Glass	-----
11	do	-----	Electric	-----	Bubble cap	do	-----	250	Electric	Asbestos	do	-----	-----	150
28	-----	5,000	do	-----	Packed	Brass	(19)	(15,850)	do	do	do	Rings and helices.	Glass and wire.	-----
78	Glass	100	do	-----	do	Glass	10	41	Hot vapors	Air jacket	do	1-turn helices	Glass	-----
	Steel	11,000	do	Asbestos and pipe lagging.	do	Nickel	33	274	Electric	Asbestos paper and pipe lagging.	do	4-mm. helices	Nickel wire	86%
	do	11,000	do	do	do	do	33	274	do	do	do	do	do	86%
	do	11,000	do	do	do	do	33	274	do	do	do	do	do	86%
	do	11,000	do	do	do	do	33	274	do	do	do	do	do	86%
	do	11,000	do	do	do	do	33	274	do	do	do	do	do	86%
	do	11,000	do	do	do	do	33	274	do	do	do	Carding staples.	0.5-mm. iron wire.	72%
	do	11,000	do	do	do	do	33	274	do	do	do	do	do	72%
	do	11,000	do	do	do	do	33	274	do	do	do	do	do	72%
	do	11,000	do	do	do	do	33	274	do	do	do	do	do	72%
19	Glass	400	do	Asbestos	do	Glass	8	100	do	-----	do	Spiral	Copper	-----
	do	400	do	do	do	do	8	100	do	-----	do	do	-----	-----
	do	5,000	do	do	do	do	(50.8)	(91.4)	do	Asbestos	do	Lessing rings	-----	-----
	do	5,000	do	do	do	do	(50.8)	(91.4)	do	do	do	do	-----	-----
	do	5,000	do	do	do	do	(50.8)	(91.4)	do	do	do	do	-----	-----
	do	5,000	do	do	do	do	(50.8)	(91.4)	do	do	do	do	-----	-----
	Iron	do	do	do	do	Iron	(47.6)	(58.4)	do	do	do	do	-----	-----
	do	do	do	do	do	do	(47.6)	(73.7)	do	do	do	do	-----	-----
	do	do	do	do	do	do	(47.6)	(88.9)	do	do	do	do	-----	-----
do	do	do	do	do	do	(47.6)	(83.9)	do	do	do	do	-----	-----	

7	Glass			Bubble cap	Glass	25	10	Electric	Air jacket				3.5
	do			do	do	25	20	do	do				7.0
	do			do	do	25	40	do	do				22.0
	do			do	do	25	10	do	do				3.5
	do			do	do	25	20	do	do				7.0
	do			do	do	25	40	do	do				22.0
30			Liquid bath	Packed	Nickel	33	1,250	do				3-m m. 1-turn helices.	Nickel wire
			do	do	do	33	1,250	do				do	do
			do	do	do	33	1,250	do				do	do
	Iron	12,000	Electric	do	do	33	1,160	do				4-mm. 1-turn helices.	Steel
70	Glass		Internal electric.	Empty	Glass	6	30.3	None	Silvered vacuum jacket.	Total	None		
	do		do	do	do	6	30.3	do	do	do	do		
	do		do	Packed	do	6	30.3	do	do	do	Spiral	Nickel	
	do		do	do	do	6	30.3	do	do	do	do	do	
	do		do	do	do	6	30.3	do	do	do	Helices	do	
	do		do	do	do	6	30.3	do	do	do	do	do	
	do		do	do	do	6	30.3	do	do	do	Carding teeth		
	do		do	do	do	6	30.3	do	do	do	do		
	do		do	do	do	6	30.3	do	do	do	do		
	do		do	Empty	do	3	30.3	do	do	do	None		
	do		do	do	do	3	30.3	do	do	do	None		
	do		do	Packed	do	3	30.3	do	do	do	Spiral	Nickel	
	do		do	do	do	3	30.3	do	do	do	do	do	
10	Glass		Electric	Bubble cap	do		200	Electric	Transite jacket and asbestos.	do			
38	do	1,000	do	Packed	do	25.8	120	None	Vacuum jacket	Partial	3.8-mm. balls	Glass	238 ml.
	do	1,000	do	do	do	25.8	120	do	do	do	do	do	
	do	1,000	do	do	do	25.8	120	do	do	do	4.0-mm. balls	Copper	
	do	1,000	do	do	do	25.8	120	do	do	do	do	do	244 ml.
	do	1,000	do	do	do	25.8	120	do	do	do	2.95-mm. balls	Glass	233 ml.
	do	1,000	do	do	do	25.8	120	do	do	do	2.05-mm. balls	Lead	238 ml.
	do	1,000	do	do	do	25.8	120	do	do	do	Locket chain	Brass	413 ml.
79				do	do	20	60				2.4-mm. single-turn helices.	#30 B&S gage wire.	
				do	do	20	60				do	do	
				do	do	20	282				do	do	
				do	do	20	282				do	do	

¹ Reference numbers refer to bibliography at end of paper.

² Blank spaces indicate no data were given.

³ Numbers in parentheses are values calculated by author.

TABLE 6.—*Tabular summary of laboratory fractionating columns—Continued*

Reference No. 1	Operating conditions						Test conditions					Miscellaneous	
	Vaporization rate, ml./min.	Product rate, ml./min.	Reflux ratio			Vapor velocity, cm./sec.	Pressure drop, mm. Hg.	Vaporization rate, ml./min.	Reflux ratio	H. E. T. P., cm.	Theoretical plates, no.		Reference liquids
			Amount	Control	How determined								
45	-----	-----	1.5:1 1.2:1	Stopcock do	Flow meter do	(15.2) (18.0)	-----	1.5:1 1.2:1	(13.7) (18.6)	(8.9) (6.6)	Chloroform and toluene do	-----	
47	-----	-----	-----	Pinchcock	-----	-----	-----	Infinite	9.96	9.9	Ethanol and water	-----	
11	-----	1.0	20:1	Stopcock	-----	-----	-----	20:1	-----	26	Benzene and ethylene chloride.	-----	
28	-----	(0.5-0.67)	30:1	-----	Δt. of cond. water.	-----	-----	-----	App. 15	App. 100	Benzene and carbon tetrachloride.	Manometer used to warn of flooding.	
78	(7.0) (86.7)	-----	-----	Stopcock do	Siphon cup Δt. of cond. water.	-----	-----	Infinite do	3.7 13.5	12 21.5	n-heptane and toluene n-heptane and methylcyclohexane.	do	
	(105) (70)	-----	-----	do do	do do	-----	-----	do do	9.7 17.0	29.5 17.0	do Carbon tetrachloride and benzene.	-----	
	(95) (71.7)	-----	-----	do do	do do	-----	-----	do do	16.0 15.0	18.0 19.5	do Methylcyclohexane and toluene.	-----	
	(93.3) (30)	-----	-----	do do	do do	-----	-----	do do	13.5 7.4	21.0 38.0	do n-heptane and methylcyclohexane.	Maximum vaporization rate was 78 ml./min. when packing was new.	
	(83.3) (26.7)	-----	-----	do do	do do	-----	-----	do do	3.1 3.1	35.5 35.5	do Carbon tetrachloride and benzene.	Do.	
	(80.0)	-----	-----	do	do	-----	-----	do	10.0	27.5	do	-----	
	-----	-----	-----	do	Reflux meter	125	-----	-----	-----	-----	4+	Benzene and toluene	-----
	-----	0.8	14.3 : 1	do	do	24	-----	-----	-----	-----	7-	do	-----
-----	-----	38.5 : 1	do	do	296	-----	-----	-----	15.8	5.8	Nitrobenzene and aniline	Operated with 8 mm. pressure.	
-----	-----	-----	-----	-----	13.3	-----	-----	-----	11.05	8.3	do	Operated with 253.5 mm. pressure.	

		26.5 :1	do.		9.7			24.7	3.7	do.	58.5 percent N ₂ gas as diluent. Operated with 263.5 mm. pressure. Do. Do. 56.5 percent N ₂ gas as diluent.
		17.2 :1			15.5			12.45	5.1	do.	
		17.9 :1			15.4			11.9	6.2	do.	
		16.95:1			15.4			10.45	8.5	do.	
		33:1			15.4			22.8	3.9	do.	
7							5.1	Infinite.	1.9	5.4	Carbon tetrachloride and benzene.
							4.5	do.	4.5	4.4	do.
							4.8	do.	7.1	5.7	do.
							5.1	do.	2.1	4.7	n-heptane and toluene.
							7.5	do.	4.3	4.7	do.
							7.3	do.	8.0	5.0	do.
30	(50)					79		do.	11.7	108	n-heptane and methylcyclohexane.
	(41.7)					39		do.	13.5	94	do.
	(70)					80		do.	10.4	122	do.
	(56.7)					45	91.7	do.	(11.5)	101	do.
70					8			70:1	(30.3)	1	Benzene and carbon tetrachloride.
					1			do.	(3.9)	8.0	do.
					1			do.	(4.7)	6.5	do.
					5			do.	(7.6)	4.0	do.
					5			do.	(3.8)	8.0	do.
					1			do.	(2.8)	11.0	do.
					3.6			do.	(9.2)	3.3	do.
					2.6			do.	(5.1)	6.0	do.
					3.0			do.	(30.3)	1.0	do.
					5.6			do.	(3.4)	9.0	do.
					2.2			do.	(3.8)	8.0	do.
					5.6			do.	(3.8)	8.0	do.
10	0.1-0.5	20-100:1	Micrometer regulator.			30		Infinite.	2.8	70-72	n-heptane and methylcyclohexane.

¹ Reference numbers refer to bibliography at end of paper.

⁴ Maximum with total reflux.

⁵ Liquid velocity, cc./min.

TABLE 6.—Tabular summary of laboratory fractionating columns—Continued

Reference No.	Operating conditions						Test conditions					Miscellaneous	
	Vaporization rate, ml./min.	Product rate, ml./min.	Reflux ratio			Vapor velocity, cm./sec.	Pressure drop, mm. Hg.	Vaporization rate, ml./min.	Reflux ratio	H. E. T. P., cm.	Theoretical plates, no.		Reference liquids
			Amount	Control	How determined								
38	20	2.0	9:1	Cooling water.	-----	(53.3)	10	20	Infinite	5.5	21.5	Benzene and ethylene chloride.	Constant rate maintained by manometer measuring back pressure and controlling heat input.
	21	2.1	9:1	do.	-----		10	21	do.	6.0	20	do.	
	18	1.8	9:1	do.	-----	(46.7)	10	18	do.	5.8	19.5	do.	
	15.5	2.1	9:1	do.	-----	(42.8)	12	15.5	do.	4.2	28.0	do.	
	15.0	1.5	9:1	do.	-----	(40.8)	15	15.0	do.	3.2	36.5	do.	
	21.5	2.1	9:1	do.	-----	(33.8)	10	21.5	do.	3.5	34.0	do.	
79	(22.5)	-----	-----	-----	-----	-----	(4.8)	(22.5)	do.	3.7	16.0	<i>n</i> -heptane and methylcyclohexane.	
	(6.0)	-----	-----	-----	-----	-----	(6.8)	(22.5)	do.	2.7	22.5	do.	
	(21.0)	-----	-----	-----	-----	-----	(30.6)	(21.0)	do.	2.8	102	do.	
	(14.3)	-----	-----	-----	-----	-----	(33.9)	(21.0)	do.	2.5	113	do.	

BINARY MIXTURES

A suitable method of testing a column is to distill a binary mixture and analyze the distillate and still liquid. Some of the preferred characteristics of such a mixture as given by Fenske (27) are:

(1) The liquids should be obtainable in a high state of purity; (2) they should be of the same type as those regularly used in the column; (3) they should be stable and noncorrosive in the column; (4) the mixture should be capable of easy and accurate analysis; and (5) the vapor-liquid equilibrium diagram for atmospheric pressure should be available if a perfect solution is not formed.

Some of the binary mixtures that have been used are chloroform and toluene (43), ethanol and water (47), acetic acid and water (59), nitrobenzene and aniline (19), ethylene chloride and benzene (32), benzene and carbon tetrachloride (78), benzene and toluene (78), *n*-heptane and toluene (7), *n*-heptane and methylcyclohexane (78), and methylcyclohexane and toluene (78). Some of the more commonly used mixtures were discussed in the section on evaluation of columns. Hydrocarbons are preferred for testing columns used in petroleum distillations, because different hydrocarbon mixtures have been found to give essentially the same results. This is not true, however, of nonhydrocarbons (78).

GENERAL CONCLUSIONS

A review of the literature on laboratory fractionating columns shows there are many necessary details for an efficient fractionating unit that may be overlooked. The following are the principal features that require consideration when designing such a unit:

1. A corrosion-resistant stillpot of proper size for the characteristics of the charge being distilled and of suitable shape to maintain a satisfactory evaporating area for the charge in comparison to the free cross section of the column. The stillpot should be well-insulated and heated over a relatively large surface by external electrical heating units that can be closely controlled.

2. A column with the ratio of height to diameter not less than 15 to 1. It should be well insulated and, in addition, have a closely regulated external source of heat to compensate for that lost to the atmosphere.

3. An effective means for contacting vapor and reflux.

a. Corrosion-resistant packing having a large surface area per unit volume, a small hold-up and pressure drop, and capable of handling a large volume of vapor per unit time.

b. Bubble plates that provide maximum contacting of vapor and reflux and also combine the qualities of a satisfactory throughput with a small hold-up and pressure drop.

4. A stillhead provided with means to condense the vapor and to regulate and maintain the reflux ratio. A total condenser with a small holdup is usually more satisfactory.

LITERATURE CITED

1. ALLEN, I. C., and JACOBS, W. A. Physical and Chemical Properties of the Petroleum of the San Joaquin Valley, Calif. Bureau of Mines Bull. 19, 1911, 60 pp.

2. BADGER, W. L., and McCABE, W. L. Elements of Chemical Engineering. New York, 1936, p. 341.

3. BAKER, THEODORE, CHILTON, T. H., and VERNON, H. C. The Course of Liquor Flow in Packed Towers. Trans. Am. Inst. Chem. Eng., vol. 31, June 25, 1935, p. 302.

4. BEATTY, H. A., and CALINGAERT, GEORGE. Tests for the Accuracy of Vapor-Liquid Equilibrium Data. Ind. Eng. Chem., vol. 26, August 1934, pp. 904-909.

5. ————. Vapor-Liquid Equilibrium of Hydrocarbon Mixtures. Ind. Eng. Chem., vol. 26, May 1934, pp. 504-508.

6. BROMILEY, E. C., and QUIGGLE, D. Vapor-Liquid Equilibria of Hydrocarbon Mixtures. *Ind. Eng. Chem.*, vol. 25, October 1933, pp. 1136-1138.
7. BRUUN, J. H. Laboratory Bubble-Cap Columns of Glass. *Ind. Eng. Chem., Anal. Ed.*, vol. 8, May 15, 1936, pp. 224-226.
8. ———. Convenient Reflux Regulators for Laboratory Stills. *Ind. Eng. Chem., Anal. Ed.*, vol. 2, Apr. 15, 1930, pp. 187-188.
9. ———. Laboratory Rectifying Columns for Nonsiphoning Bubbling-Cap Plates. *Ind. Eng. Chem., Anal. Ed.*, vol. 1, Oct. 15, 1929, pp. 212-213.
10. BRUUN, J. H., and FAULCONER, W. B. M. A 100-Plate Semiautomatic Bubble-Cap Still of Glass. *Ind. Eng. Chem., Anal. Ed.*, vol. 9, April 15, 1937, pp. 192-194.
11. BRUUN, J. H., and SCHICKTANZ, S. T. Laboratory Rectifying Stills of Glass. *Nat. Bur. of Standards Jour. Research*, vol. 7, 1931, p. 871.
12. CALINGAERT, GEORGE, and HUGGINS, F. E., JR. The Efficiency of Fractionating Columns. *Ind. Eng. Chem.*, vol. 16, June 1924, pp. 584-586.
13. CARSWELL, T. S. Fractionating Column Calculations. *Ind. Eng. Chem.*, vol. 18, March 1926, pp. 294-295.
14. CHILTON, T. H., and COLBURN, A. P. Pressure Drop in Packed Tubes. *Ind. Eng. Chem.*, vol. 23, August 1931, p. 917.
15. CLARKE, H. T., and RAHRS, E. J. A "Bubbler" Laboratory Fractionating Column. *Ind. Eng. Chem.*, vol. 18, October 1926, p. 1092.
16. COOKE, M. B. An Experimental Still for the Detailed Study of Crude Petroleum. Bureau of Mines Rept. of Investigations 2632, 1924, 21 pp.
17. COOKE, M. B., and RUE, H. P. Studies in the Fractional Distillation of Crude Petroleum. Bureau of Mines Tech. Paper 431, 1928, 54 pp.
18. DEAN, E. W., HILL, H. H., SMITH, N. A. C., and JACOBS, W. A. The Analytical Distillation of Petroleum and Its Products. Bureau of Mines Bull. 207, 1922, 82 pp.
19. DOCKSEY, P., and MAY, C. J. Relative Efficiencies of Packed Fractionating Columns. *Jour. Inst. Petrol. Technol.*, vol. 21, March 1935, pp. 176-199.
20. DODGE, B. F., and HUFFMAN, J. R. Calculation of the Number of Theoretical Plates for a Rectifying Column. *Ind. Eng. Chem.*, vol. 29, December 1937, pp. 1434-1436.
21. DUPONT, GEORGES. Composition and Commercial Applications of Spirits of Turpentine. *Chimie et industrie*, vol. 8, September 1922, pp. 549-552.
22. ELLIOT, C. Distillation in Practice. London, 1925, p. 74.
23. ESPACH, R. H. A Visible-Action Continuous-Distillation Apparatus for Laboratory Study of Fractionation. Bureau of Mines Rept. of Investigations 2892, 1923, 7 pp.
24. EVANS, H. M., CORNISH, R. E., LEFKOVSKY, S., ARCHIBALD, R. C., and FESKOV, G. Construction and Use of Raschig's Laboratory Fractionating Column. *Ind. Eng. Chem., Anal. Ed.*, vol. 2, July 15, 1930, pp. 339-343.
25. FARNHAM, E. C. Carborundum Fractionating Columns. *Jour. Phys. Chem.*, vol. 35, March 1931, pp. 844-858.
26. FENSKE, M. R. Fractionation of Straight-Run Pennsylvania Gasoline. *Ind. Eng. Chem.*, vol. 24, May 1932, pp. 482-485.
27. ———. Laboratory and Small-Scale Distillation. *The Science of Petroleum*, vol. 2, New York, 1938, p. 1630.
28. FENSKE, M. R., QUIGGLE, D., and TONGBERG, C. O. Composition of Straight-Run Pennsylvania Gasoline. I. *Ind. Eng. Chem.*, vol. 24, April 1932, pp. 408-418.
29. FENSKE, M. R., TONGBERG, C. O., and QUIGGLE, D. Packing Materials for Fractionating Columns. *Ind. Eng. Chem.*, vol. 26, November 1934, pp. 1169-1177.
30. FENSKE, M. R., TONGBERG, C. O., QUIGGLE, D., and CRYDER, D. S. Fractional Distillation Columns. *Ind. Eng. Chem.*, vol. 28, June 1936, pp. 644-645.
31. GADWA, T. A. Thesis. Pennsylvania State College, 1931.
32. GLASGOW, A. R., JR., and SCHICKTANZ, S. T. Study of Ball Packings for Laboratory Rectifying Columns. *Nat. Bur. of Standards Jour. Research*, vol. 19, November 1937, pp. 593-603.
33. GUTHRIE, BOYD, and HIGGINS, RALPH. Laboratory Batch Still and Fractionating Column for Production and Study of Lubricating Distillates Under Vacuum. Bureau of Mines Rept. of Investigations 3159, 1932, 18 pp.
34. HALL, H. J., and BACHMAN, G. B. Laboratory Columns Packed with Silicon Carbide. *Ind. Eng. Chem., Anal. Ed.*, vol. 10, Sept. 15, 1938, pp. 548-549.

35. HAUSBRAND, E. (Translated by E. H. Tripp.) Principles of Industrial Distillation. New York, 1926, p. 18.
36. HILL, J. B., and FERRIS, S. W. Laboratory Fractionating Columns. *Ind. Eng. Chem.*, vol. 19, March 1927, pp. 379-382.
37. HUFFMAN, J. R., and UREY, H. C. Separation of Oxygen Isotopes by a Fractionating Column. *Ind. Eng. Chem.*, vol. 29, May 1937, pp. 531-535.
38. INTERNATIONAL CRITICAL TABLES. Vol. 3, New York, 1928, p. 287.
39. ———. Vol. 7, New York, 1930, p. 77.
40. KIRSCHBAUM, EMIL, and ANDREWS, C. A. On the Efficiency of Rectification Column Plates. *Jour. Inst. Petrol. Technol.*, vol. 22, December 1936, p. 817.
41. LESESNE, S. D., and LOCHTE, H. L. A New Type of Semimicro Fractionating Column. *Ind. Eng. Chem., Anal. Ed.*, vol. 10, Aug. 15, 1938, p. 450.
42. LESLIE, E. H. Motor Fuels. New York, 1923, p. 120.
43. LESLIE, E. H., and GENESSE, J. C. Distillation Studies. *Ind. Eng. Chem.*, vol. 18, June 1926, pp. 590-596.
44. LEWIS, W. K. The Efficiency and Design of Rectifying Columns. *Ind. Eng. Chem.*, vol. 14, June 1922, pp. 492-497.
45. LOVELESS, A. W. T. An Improved Laboratory Fractionating Column. *Ind. Eng. Chem.*, vol. 18, August 1926, p. 826.
46. MAIR, B. J., SCHICKTANZ, S. T., and ROSE, F. W. Apparatus and Methods for Investigating the Chemical Constitution of Lubricating Oil, and Preliminary Fractionation of the Lubricating Oil Fraction of a Mid-Continent Petroleum. *Nat. Bur. of Standards Jour. Research*, vol. 15, December 1935, pp. 557-573.
47. MARSHALL, M. J., and SUTHERLAND, B. P. Effectiveness of Laboratory Rectifying Columns. *Ind. Eng. Chem.*, vol. 19, June 1927, pp. 735-738.
48. McCABE, W. L., and THIELE, E. W. Graphical Design of Fractionating Columns. *Ind. Eng. Chem.*, vol. 17, June 1925, pp. 605-611.
49. McINTYRE, R. Fractional Distillation. *Jour. Soc. Chem. Ind.*, vol. 52, July 14, 1933, pp. 578-579.
50. McMILLAN, W. A. Analytical Fractionation of Hydrocarbon Gases. *Jour. Inst. Petrol. Technol.*, vol. 22, 1936, pp. 616-645.
51. MEYER, PERCY. A Theoretical Comparison of Petroleum Distillation Systems. *Jour. Inst. Petrol. Technol.*, vol. 19, 1933, p. 834.
52. MIDGLEY, THOMAS. Coated Spiral Fractionating Columns. *Ind. Eng. Chem., Anal. Ed.*, vol. 1, Apr. 15, 1929, pp. 86-88.
53. MURPHEREE, E. V. Graphical Rectifying Column Calculations. *Ind. Eng. Chem.*, vol. 17, September 1925, pp. 960-964.
54. ———. Rectifying Column Calculations. *Ind. Eng. Chem.*, vol. 17, July 1925, pp. 747-750.
55. OTHMER, D. F. Large Glass Distillation Equipment. *Ind. Eng. Chem.*, vol. 22, April 1930, pp. 322-325.
56. PAHLAVOUNI, E. Recherches sur la théorie des solutions concentrées. IV. La méthode de M. A. Rosanoff pour l'étude de la composition de la phase vapeur en équilibre avec un mélange binaire de liquides volatils. *Bull. soc. chim. Belg.*, vol. 36, no. 11, November 1927, pp. 533-547.
57. PALKIN, S. Improved Gauze-Plate Laboratory Rectifying Column. *Ind. Eng. Chem., Anal. Ed.*, vol. 3, Oct. 15, 1931, pp. 377-378.
58. PERRY, J. H. *Chemical Engineers Handbook*. New York, 1934, p. 1202.
59. PETERS, W. A., JR. The Efficiency and Capacity of Fractionating Columns. *Ind. Eng. Chem.*, vol. 14, June 1922, pp. 476-479.
60. PETERS, W. A., JR., and BAKER, THEODORE. High-Precision Fractional Distillation in the Laboratory. *Ind. Eng. Chem.*, vol. 18, January 1926, pp. 69-72.
61. PODBIELNIAK, W. J. Apparatus and Methods for Precise Fractional-Distillation Analysis. *Ind. Eng. Chem., Anal. Ed.*, vol. 3, Apr. 15, 1931, p. 179.
62. ———. Apparatus and Methods for Precise Fractional-Distillation Analysis. II. *Ind. Eng. Chem., Anal. Ed.*, vol. 5, Mar. 15, 1933, p. 121.
63. ———. Apparatus and Methods for Precise Fractional-Distillation Analysis. III. *Ind. Eng. Chem., Anal. Ed.*, vol. 5, Mar. 15, 1933, p. 140.
64. ———. Apparatus and Methods for Precise Fractional-Distillation Analysis. IV. *Ind. Eng. Chem., Anal. Ed.*, vol. 5, May 15, 1933, p. 176.
65. ———. Apparatus for the Centrifugal Fractionation of Materials Such as in Oil Refining. U. S. Patent 2,003,308, June 4, 1935.
66. QUIGGLE, D., and FENSKE, M. R. Vapor-Liquid Equilibria of Methylcyclohexane-Toluene Mixtures. *Jour. Am. Chem. Soc.*, vol. 59, October 1937, pp. 1829-1832.

67. RITTMAN, W. F., and DEAN, E. W. The Analytical Distillation of Petroleum. Bureau of Mines Bull. 125, 1916, 79 pp.
68. ROBINSON, C. S. Elements of Fractional Distillation. New York, 1930, p. 88.
69. ROSANOFF, M. A., and EASLEY, C. W. On the Partial Vapor Pressures of Binary Mixtures. Jour. Am. Chem. Soc., vol. 31, September 1909, pp. 953-987.
70. ROSE, ARTHUR. Distillation Efficiency in 3- and 6-mm. Fractionating Columns. Ind. Eng. Chem., vol. 28, October 1936, pp. 1210-1212.
71. RUE, H. P., and ESPACH, R. H. Refining of Light Petroleum Distillates. Bureau of Mines Bull. 333, 1930, 111 pp.
72. SCHICKTANZ, S. T. A Fractionating Column With Fritted Glass Plates. Nat. Bur. of Standards Jour. Research, vol. 12, February 1934, pp. 259-261.
73. ———. Notes on an Improved Chain-Packed Distilling Column. Nat. Bur. of Standards Jour. Research, vol. 11, July 1933, pp. 89-92.
74. SIMONS, J. H. Designs for Laboratory Fractionating Columns. Ind. Eng. Chem., Anal. Ed., vol. 10, Jan. 15, 1937, pp. 29-31.
75. SMOKER, E. H. Analytic Determination of the Number of Plates in a Fractionating Column. Trans. Am. Inst. Chem. Eng., vol. 34, Apr. 25, 1938, pp. 165-172.
76. STEDMAN, D. F. Fractionating Columns and Packings for Them. Nat. Petrol. News, vol. 29, Aug. 25, 1937, pp. R-125, R-126, R-128.
77. TABLES ANNUELLES DE CONSTANTES ET DONNEES NUMERIQUES, 1927-28. Vol. 8, Paris, 1931.
78. TONGBERG, C. O., QUIGGLE, D., and FENSKE, M. R. Efficient Small-Scale Fractionating Equipment. Ind. Eng. Chem., vol. 26, November 1934, pp. 1213-1217.
79. TONGBERG, C. O., LAWROWSKI, S., and FENSKE, M. R. Packing Material for Fractional Distillation Columns. Ind. Eng. Chem., vol. 29, August 1937, pp. 957-958.
80. UNDERWOOD, A. J. V. The Determination of Plate Efficiency in Fractionating Columns for Complex Mixtures. Jour. Inst. Petrol. Technol., vol. 21, February 1935, pp. 125-131.
81. WADSWORTH, J. M. Removal of the Lighter Hydrocarbons from Petroleum by Continuous Distillation. Bureau of Mines Bull. 162, 1919, 162 pp.
82. WALKER, W. H., LEWIS, W. K., and McADAMS, W. H. Principles of Chemical Engineering. New York, 1927, p. 578.
83. WALKER, W. H., LEWIS, W. K., McADAMS, W. H., and GILLILAND, E. R. Principles of Chemical Engineering. New York, 1937, p. 563.
84. WILSON, C. D., PARKER, G. T., and LAUGHLIN, K. C. A New Glass Packing for Laboratory Fractionating Columns. Jour. Am. Chem. Soc., vol. 55, July 1933, pp. 2795-2796.
85. YOUNG, SYDNEY. Distillation Principles and Processes. London, 1922, p. 141.
86. ZAWIDSKI, JAN VON. Über die Dampfdrücke binärer Flüssigkeitsgemische. Ztschr. physikal. Chem., vol. 35, no. 2, 1900, pp. 129-203.

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Superfractionation Studies

Composition and Octane Numbers of 0.5% Fractions
of an Oklahoma City Naphtha

C. C. WARD, R. M. GOODING, AND B. H. ECCLESTON
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SUPERFRACTIONATION STUDIES

Composition and Octane Numbers of 0.5% Fractions of an Oklahoma City Naphtha

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This paper shows relations between the composition and octane number of narrow-boiling naphtha fractions and shows the changes in octane numbers as the distillation progresses. One hundred gallons of naphtha representing 12% of Oklahoma City crude oil were superfractionated in a pilot plant unit having the equivalent of eighty to ninety theoretical plates. One hundred fifty fractions, each representing 0.5% of the naphtha, were collected between 73° and 258° F. The hydrocarbon composition of each of these fractions was determined by use of specific dispersions and refractivity intercepts, and the F-3 octane number of each fraction with 4.0 ml. of tetraethyllead was obtained. Graphs indicate the relations of composition to distillation temperatures, densities, and octane numbers.

DURING the past six years the Bureau of Mines has made an extensive study of straight-run naphthas as sources of aviation gasoline base stocks, toluene, and other hydrocarbons. When the base-stock content was the objective, these naphthas were fractionated in pilot plant stills, and wide-boiling cuts in the proper boiling ranges were rated in standardized aviation fueling engines to determine the quality of the naphtha as a source of aviation gasoline base stock. Many of these naphthas also were fractionated in laboratory distillation units, and fractions were collected at each 1° F. interval. These fractions were analyzed by specific dispersion (S) and refractivity intercept (R) methods to estimate the composition in terms of individual hydrocarbons. The data from these analyses and the best blending values available for the engine ratings of individual hydrocarbons were used to calculate the octane numbers of some of the cuts from the pilot plant stills. In this study the composition and octane ratings of 0.5% fractions from an Oklahoma City naphtha were determined, and the data were used to estimate the octane numbers of individual hydrocarbons.

The charge stock consisted of 100 gallons of naphtha representing 12% of an Oklahoma City crude oil. Table I presents engine ratings and inspection data for this naphtha. This quantity of charge provided 0.5% fractions sufficiently large for the tests contemplated.

APPARATUS AND PROCEDURE

The still pot of the fractionation unit used in this study had a capacity of only 55 gallons; therefore, the original charge was divided into two parts by preliminary distillations in two 40-gallon stills and one 20-gallon still having columns equivalent to about thirty theoretical plates. These distillations were conducted in such a way that the break between the two parts was on the *n*-heptane plateau. Appropriate cuts from the distillations were combined to give one charge of 55 gallons and one of 36 gallons.

The fractionation unit is shown in Figure 1. The still pot is heated by one or more of ten 220-volt, 1000-watt strip heaters. Each heater is on a separate circuit, and one heater is controlled by a variable transformer. This arrangement provides a variable heat input range of 0 to 10,000 watts. The column is a 3-inch pipe 25 feet long, packed with $\frac{3}{8}$ -inch stainless steel helices, and is surrounded by a 5-inch pipe to provide an insulating air jacket.

Variable transformers controlling five heating sections on the jacket can be adjusted to provide adiabatic conditions, as indicated by identity of thermocouple temperatures at six different levels in the column and in the jacket. The arrangement of the thermocouples and the insulation is shown in section A-A of Figure 1. The pressure drop through the column is measured by a 100-inch water manometer, and heat to the still pot is adjusted during a distillation to keep the pressure drop constant at 60 inches. A total condenser is used, and all condensate passes through a three-way needle valve where a portion is diverted as product. The remaining condensate is heated by a 750-watt immersion heater to within 3-4° F. of the overhead vapor temperature and returned to the column as reflux. This heater is controlled by a variable transformer. Two three-way valves in the condensate return line allow periodic measurement of condensate rate through a rotameter. Normally the rotameter is by-passed to reduce the holdup between the condenser and the column. The vaporization rate is measured in terms of pressure drop through the column, but the condensate rate is checked with the rotameter every 6 to 8 hours so that vaporization is maintained at the desired rate. The fractionating efficiency of the column was not determined directly, but comparative distillation data from it and a laboratory column equivalent to eighty theoretical plates at total reflux indicate comparable performance.

The first part of the charge (boiling below *n*-heptane) was weighed into the still pot and heated until an overhead temperature of 100° F. was reached; this assured removal of all pentane to reduce loss of this material while the column was being flooded. The depentanized material was then heated sufficiently to flood the column thoroughly; then the heat was adjusted to give a total condensate rate of approximately 400 ml. per minute. After the column had reached equilibrium at total reflux, as evidenced by no change in overhead and column temperatures during a 2-hour period, the product valve was opened and fractions of approximately 0.5% (1750 ml.) were collected at a reflux ratio of not less than 40 to 1, until well into the *n*-heptane plateau. The column was shut down and the still pot allowed to cool. The second part of the charge (boiling above *n*-heptane) was then weighed into the stillpot and added to the residuum from the distillation of the first part. The column was again flooded and brought to equilibrium, and 0.5% fractions were collected until a temperature of 258° F. was reached. The still was shut down and allowed to cool, and the residuum was withdrawn and weighed.

The specific gravity of each of the 150 fractions was determined at 20°/20° C. with a four-place, Chainomatic Westphal balance, the density at 20° C. calculated, and the refractive indices for the mercury g line and the sodium D line measured at 20° C. with a Bausch and Lomb precision oil refractometer. These properties were used to calculate the specific dispersion and refractivity intercept for each fraction. The percentages of individual hydrocarbons in each fraction were calculated from these properties and from the boiling points by a procedure reported in a recent paper (2). Analyses of known mixtures by this method indicate that the probable error of aromatics is $\pm 0.2\%$ and that of paraffins and naphthenes, within 10% of the reported result. The percentages of individual hydrocarbons in the fractions were used to estimate the over-all composition of the naphtha boiling be-

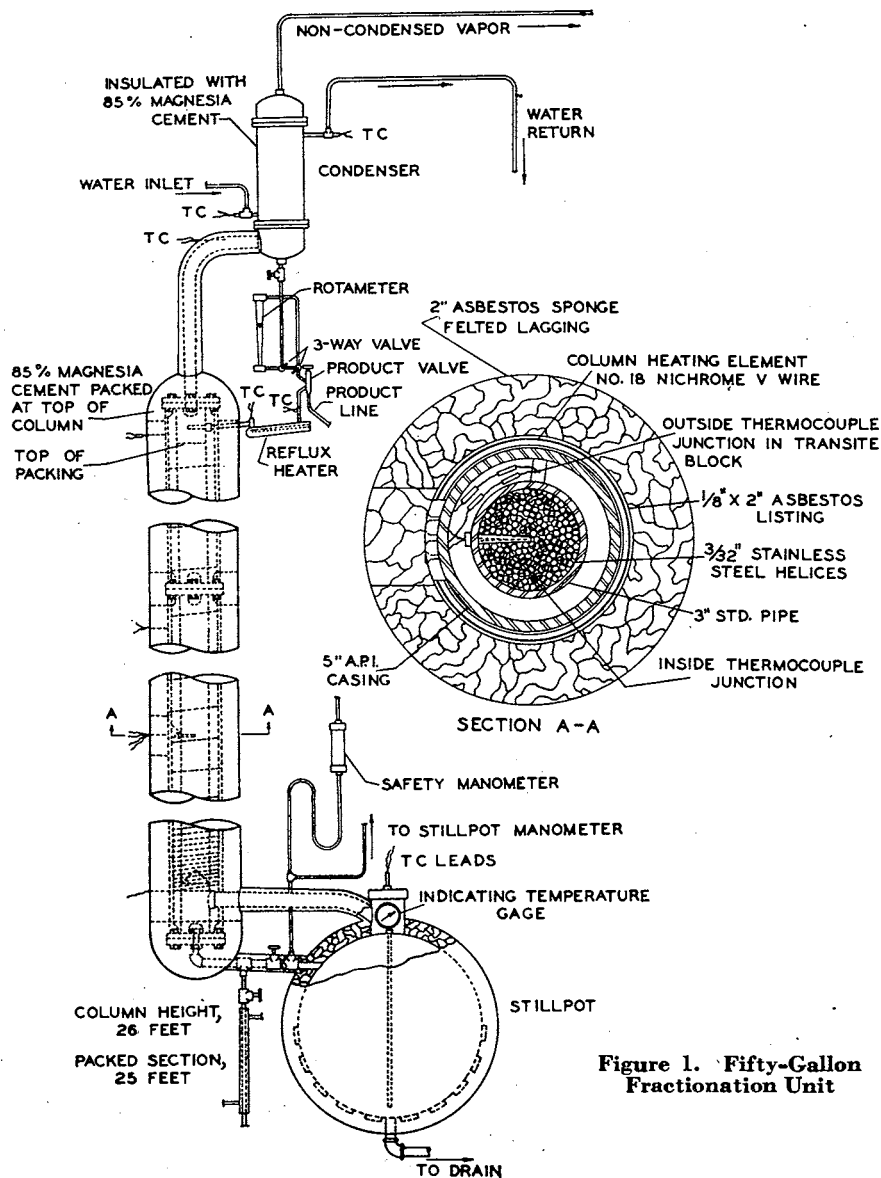


Figure 1. Fifty-Gallon Fractionation Unit

tween 97° and 258° F. Table II presents compositions in terms of percentages of individual hydrocarbons based on the crude oil and on the 97–258° F. naphtha.

The engine rating for each of the 0.5% fractions with 4.0 ml. of tetraethyllead was determined by the CRC-F-3 method. This lead concentration brought most of the fractions within the range of the F-3 method (above 72 octane number), and coincided with the data that were available on ratings of hydrocarbons by that method. The percentages of individual hydrocarbons in each fraction and the reported values for their ratings were used to estimate the octane number of the fraction before it was rated with the engine. Fractions that were estimated to rate above 72 octane number were rated on the engine without blending, and those estimated to rate below 72 octane number were blended 50–50 with a reference fuel blend (38.6% F-6, 61.4% C-13 + 4 ml. tetraethyllead) of octane number 100 to bring them within the range of the F-3 method.

COMPOSITION OF FRACTIONS

Figure 2 shows the overhead temperature and the octane numbers of individual fractions plotted against volume sum percentage distilled. The octane numbers calculated from blends with reference fuels are indicated by broken lines. The bar graph gives the composition of each fraction in terms of paraffins,

naphthenes, and aromatics to indicate relations between octane number and composition. The high octane numbers coincide with the higher concentrations of isoparaffins, naphthenes, and aromatics, whereas the greatest contributors to low octane numbers are the normal paraffins. The effects of some individual hydrocarbons are apparent. Examples of those contributing to high octane number are: 2,3-dimethylbutane (fraction 23), methylcyclopentane (fractions 53–59), 1,1-dimethylcyclopentane (fraction 66), *trans*-1,2- and -1,3-dimethylcyclopentane (fractions 75–77), trimethylcyclopentanes (fraction 114), toluene (fractions 119–121), and *trans*-dimethylcyclohexanes (fractions 136–137). Hydrocarbons contributing to low octane number (in addition to *n*-paraffins) are: cyclohexane (fraction 64), methylcyclohexane (fraction 107–110), and methylheptanes (fractions 124–128).

Experience in calculating octane numbers of fractions from composition and from reported octane numbers of individual hydrocarbons indicated that some of the reported values might be in error; consequently, the compositions and engine ratings obtained in this study were used to calculate the blending octane numbers of the individual hydrocarbons. Most of the fractions contained only two hydrocarbons in addition to benzene, toluene, or ethylbenzene, whose F-3 ratings with 4.0 ml. of tetraethyllead are fairly well established as 97, 100, and 102, respectively. These aromatic values were accepted as accurate, and the octane numbers of the other two constituents were determined graphically, as shown in Figure 3 for methylcyclohexane in *n*-heptane. The octane number that a blend of the nonaromatic components

of a fraction would have if blended in the ratio in which they occur in the fraction was calculated by the following equation:

$$\frac{O_f - X_A O_A}{100 - X_A} = \left(\frac{X_1}{100 - X_A} \right) O_1 + \left(\frac{X_2}{100 - X_A} \right) O_2$$

where X_A = aromatic component in fraction, %
 X_1 = component 1 in fraction, %
 X_2 = component 2 in fraction, %
 O_A = octane number of aromatic component
 O_1 = octane number of component 1
 O_2 = octane number of component 2
 O_f = octane number of fraction

The octane number thus obtained was plotted against the percentage of methylcyclohexane in *n*-heptane. A straight line was drawn through these points using the method of averages; the 100% methylcyclohexane intercept was called the blending octane number of methylcyclohexane, and the 0% methylcyclohexane intercept, the blending octane number of the *n*-heptane. The data points for this mixture defined a fairly good line, but with some other mixtures the two nonaromatic hydrocarbons occurred in only a few fractions and in approximately the same relative percentages, so that the slope of a line through the data points could not be established definitely. However, most of the hydrocarbons for which the data are doubtful were present only

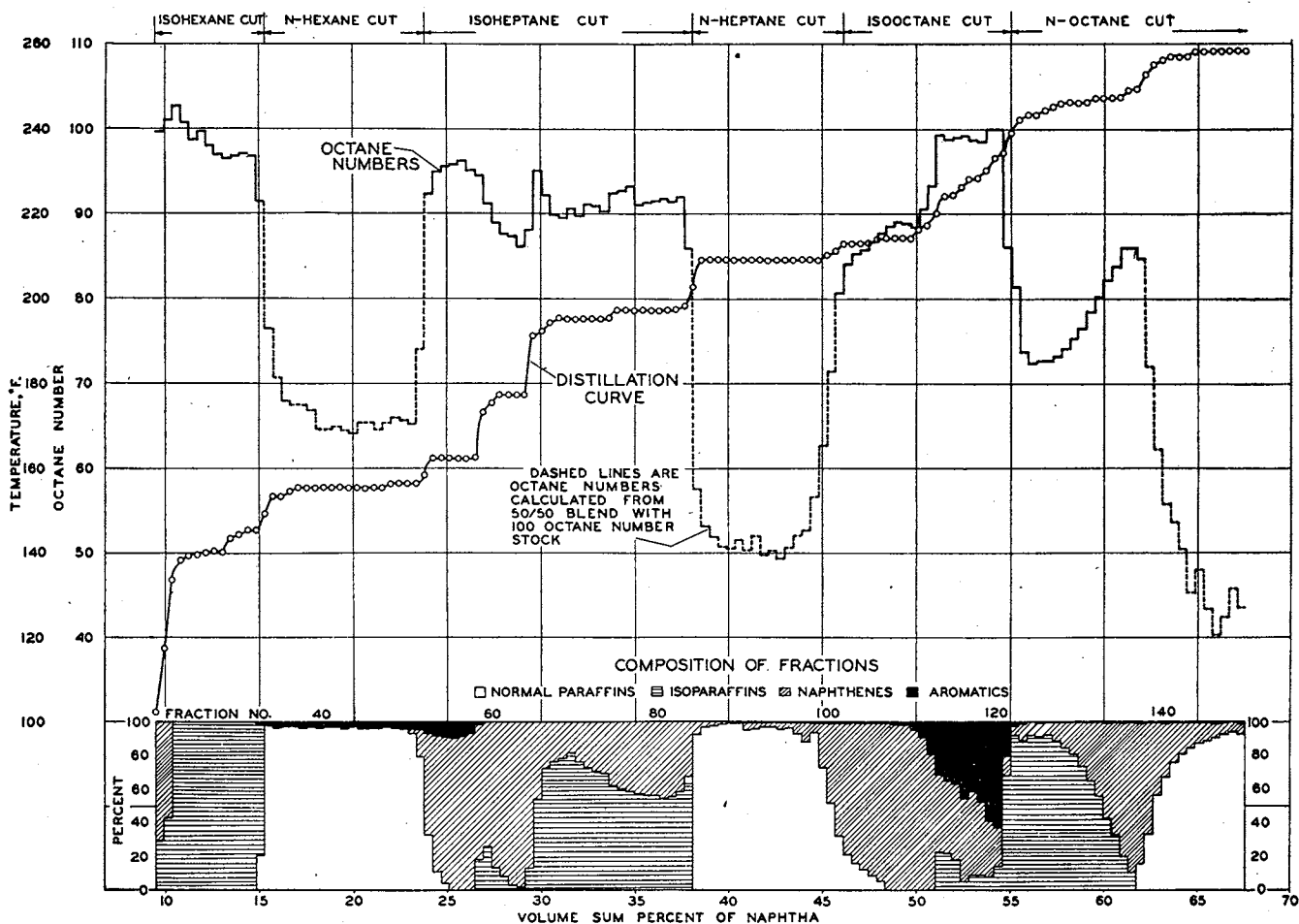


Figure 2. F-3 Octane Numbers of Fractions with 4.0 ml. Tetraethyllead

in small percentages, and the errors are not large enough to affect appreciably octane numbers calculated for the iso cuts or for naphthas. Table III lists the blending octane numbers of the hydrocarbons in this naphtha calculated from the composition and octane numbers of the fractions. Some of these values may be in error by several octane numbers because of the difficulty in establishing a line through the data points and because of errors in analysis of the fractions.

EVALUATION OF ISO CUTS

Although this study provided a means of calculating the blending octane numbers of hydrocarbons from the composition and octane number of the fractions, its original purpose (4) was to determine how much base stock from the Oklahoma City naphtha could be utilized in grade 115/145 aviation fuel. For this reason the octane number 84 with 4.0 ml. of tetraethyllead was arbitrarily selected as the lowest octane number fraction that would be included in a superfractionation iso cut. On this basis consecutive fractions in the appropriate boiling ranges having ratings higher than 84 were combined to provide an isohexane cut, an isoheptane cut, and an iso-octane cut. Two additional cuts were made by combining the isohexane and isoheptane cuts and the isohexane, isoheptane, iso-octane cuts in the same proportions as they were present in the original naphtha, to determine ratings of the base stock after removal of the normal hexane, heptane, and octane from the naphtha. To facilitate the evaluation of the iso cuts as base stock for 115/145 grade fuel, they were adjusted to 7-pound Reid vapor pressure with isopentane and leaded to 4.6 ml; then the CRC-F-3 lean mixture and the CRC-F-4 supercharge ratings were determined. The engine ratings with 4.6 ml.

of tetraethyllead for each of the five base stocks are given in Table IV. A.G.A.C. tables (1) were used to convert F-3 ratings in terms of iso-octane plus tetraethyllead to octane numbers, and to convert F-4 ratings from per cent S/M or S plus tetraethyllead to index numbers. The ratings of each of the 7-pound iso cuts were used with those of 7-pound alkylate and 7-pound toluene to estimate the quantity of the iso cut that could be used in 115/145 grade fuel. For comparison of the iso cuts with the fractions that make up the cuts and with the ratings of the component hydrocarbons in the iso cuts, it appeared more applicable to use the octane number of the iso cuts with 4.0 ml. of tetraethyllead and without isopentane. Large enough samples were not available for these ratings after the other tests had been made; consequently, the ratings with 4.0 ml. of tetraethyllead and with no isopentane were calculated from the 7-pound blend with 4.6 ml. of tetraethyllead. Many base stocks and blends were rated in these laboratories with both 4.0 and 4.6 ml. of tetraethyllead, and these values were plotted to give the curves shown in

TABLE I. SAMPLE IDENTIFICATION BY INSPECTION OF 282° F. END-POINT VIRGIN NAPHTHA FROM CRUDE OIL

(Crude oil source, Oklahoma City field, pipe line sample; naphtha prepared by Deep Rock Refinery, Cushing, Okla.)

CRC-F-3 Octane No.		A.S.T.M. distillation	
Clear	56.3 ^a	Initial, b. p., °F.	87
4 ml. T.E.L.	83.3	10% evapd., °F.	114
4.6 ml. T.E.L.	84.3	50% evapd., °F.	194
Reid vapor pressure, lb.	12.5	90% evapd., °F.	253
Sulfur, %	0.004	End point, °F.	282
Corrosion	Negative	Residue, %	0.5
Doctor test	Sour	Loss, %	5.5
Gravity, °A.P.I.	69.9		

^a Calculated from blend with reference fuel.

TABLE II. COMPOSITION OF NAPHTHA IN BOILING RANGE 97-258° F.

	% of Crude Oil	% of 97-258° F. Naphtha
n-Pentane	0.050	0.97
Cyclopentane	0.047	1.03
2,2-Dimethylbutane	0.006	0.13
2,3-Dimethylbutane	0.047	1.03
2-Methylpentane	0.226	4.88
3-Methylpentane	0.121	2.61
n-Hexane	0.708	15.34
Methylcyclopentane	0.203	4.40
2,2- and 2,4-Dimethylpentane	0.030	0.65
Benzene	0.048	1.06
Cyclohexane	0.234	5.06
1,1-Dimethylcyclopentane	0.017	0.38
2,3-Dimethylpentane	0.236	5.10
2-Methylhexane		
trans-1,3-Dimethylcyclopentane	0.083	1.80
trans-1,2-Dimethylcyclopentane	0.155	3.35
3-Methylhexane	0.216	4.67
n-Heptane	0.611	13.21
Methylcyclohexane	0.349	7.55
Ethylcyclopentane	0.108	2.34
2,2-Dimethylhexane	0.037	0.81
2,6- and 2,4-Dimethylhexane	0.036	0.79
Toluene	0.167	3.62
Trimethylcyclopentanes (?)	0.112	2.41
2,3-Dimethylhexane	0.067	1.46
A trimethylcyclopentane (?)	0.006	0.13
2,4-Dimethylhexane	0.102	2.20
trans-Dimethylcyclohexanes	0.272	5.89
3-Methylheptane	0.203	4.40
Ethylbenzene	0.002	0.04
n-Octane	0.125	2.70
Total	4.624	100.00
Paraffins		61.0
Naphthenes		34.3
Aromatics		4.7
		100.0

Figure 4 for converting ratings of aviation gasoline from one tetraethyllead concentration to the other. These curves were used to calculate the ratings of the iso cut at 4.0 ml. of tetraethyllead from the values at 4.6. The effect of the isopentane was calculated from its percentage in the blend and the blending value of 113.0 octane number and 144.0 index number with 4.0 ml. of tetraethyllead, as determined on the isopentane used in this study. The calculated engine ratings of the unblended iso cuts at 4.0 ml. of tetraethyllead after adjusting for the extra tetraethyllead and the isopentane are given in Table IV, along with inspection data on the unblended iso cuts.

To determine the reliability of the blending octane numbers of the individual hydrocarbons, the approximate composition of each of the iso cuts given in Table V was calculated from the composition of its component fractions. These percentages, when multiplied by the blending octane numbers listed in Table III,

TABLE III. CALCULATED F-3 BLENDING OCTANE NUMBERS OF PURE HYDROCARBONS WITH 4.0 ML. T.E.L.

Paraffins	
2,3-Dimethylbutane	106
2-Methylpentane	98
3-Methylpentane	97
n-Heptane	64
2,2- and 2,4-Dimethylpentane	97
2,3-Dimethylpentane	89
2-Methylhexane	
3-Methylhexane	92
n-Heptane	50
Dimethylhexanes	80
2- and 4-Methylheptane	71
3-Methylheptane	72
n-Octane	39
Naphthenes	
Methylcyclopentane	97
Cyclohexane	86
trans-1,3-Dimethylcyclopentane	96
Methylcyclohexane	90
Ethylcyclopentane	89
Trimethylcyclopentanes	97
trans-1,3- and 1,4-Dimethylcyclohexanes	91
trans-1,2-Dimethylcyclohexane	91
Aromatics (f)	
Benzene	97
Toluene	100
Ethylbenzene	102

gave the calculated octane numbers shown in Table VI, where they are compared with the determined values. The greatest deviation was only 2 octane numbers. However, the octane numbers used were developed in this study, and it was believed that hydrocarbon compositions from other studies would be a better test of the method for calculating octane numbers. The hydrocarbon compositions and the octane numbers of iso cuts from an East Texas naphtha and a Hull-Silk-Sikes naphtha were available; therefore, the octane numbers of the five iso cuts from each of these naphthas were calculated from the octane number values listed in Table III. The comparison of these values with the determined values also are listed in Table VI. The maximum deviation of these ten iso cuts is 3 octane numbers.

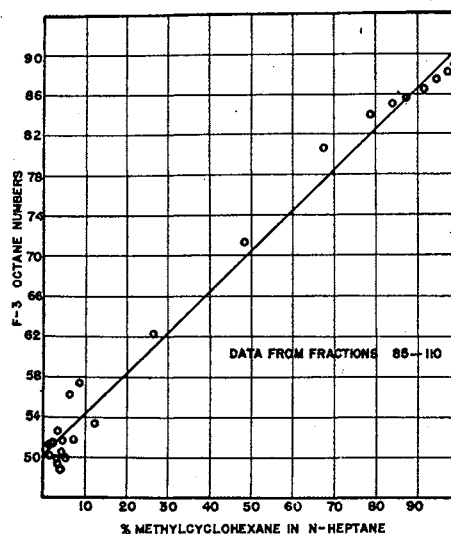


Figure 3. Graphical Determination of Octane Numbers for Methylcyclohexane in n-Heptane

In previous studies of straight-run base stocks several hundred naphthas were fractionated in pilot scale stills to obtain wide-boiling cuts for engine testing to rate their value as base stocks. Some of these cuts corresponded to the 97-243° F. boiling range. Thirteen of the naphthas on which F-3 engine ratings for this boiling range were available also were fractionated in a laboratory fractionation unit of eighty theoretical plates; small fractions were collected and analyzed by refractivity intercept and specific

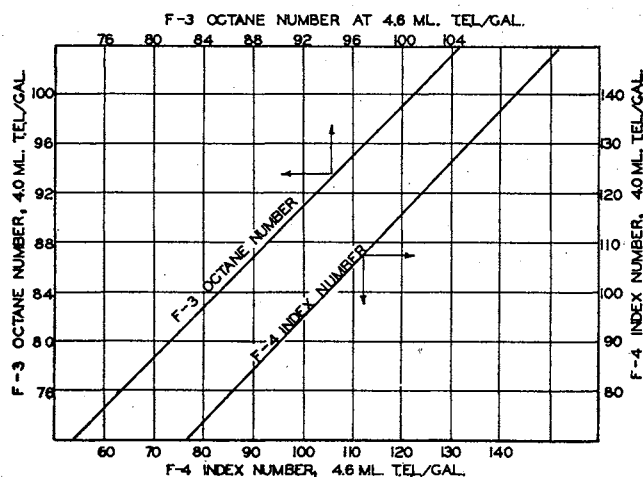


Figure 4. Relation between Engine Ratings at 4.0 and 4.6 Ml. Tetraethyllead per Gallon

TABLE IV. PROPERTIES OF ISO CUTS AND THEIR BLENDS

	C ₆	C ₇	C ₈	(C ₆ + C ₇)	(C ₆ + C ₇ + C ₈)
Crude oil, %	0.70	1.73	1.08	2.43	3.51
Naphtha, %	5.85	14.42	9.03	20.25	29.28
Engine ratings of 7-lb. blends					
F-3 octane No., 4.6 ml. T.E.L.	101.2	96.6	95.9	98.4	98.1
	(iso-octane + 0.09)				
F-4 ratings, 4.6 ml. T.E.L.					
S + T.E.L. Index No.	0.39	1.13	1.13	1.13	1.25
	111	128	128	128	130
Engine ratings of unblended iso cuts, calcd. from 7-lb. blends with 4.6 ml. T.E.L.					
F-3 octane No., 4.0 ml. T.E.L.	100.4	90.8	88.3	94.5	93.2
F-4 index No., 4.0 ml. T.E.L.	106	119	117	121	122
A.S.T.M. D-86 distillation					
Initial b.p., °F.	124	177	210
5% evapd., °F.	135	178	214
10% evapd., °F.	136	178	214
50% evapd., °F.	138	182	216
90% evapd., °F.	140	188	218
End point, °F.	142	192	222
Residue, %	0.4	0.6	0.7
Loss, %	1.3	0.4	0.6
Sp. gr., 60°/60° F.	0.6698	0.7555	0.7780
Gravity, °A.P.I.	79.8	71.4	50.4
Reid vapor pressure, lb.	7.2	3.1	1.5

TABLE V. APPROXIMATE COMPOSITION OF ISO CUTS, VOLUME PER CENT

Isohexane Cut	Isoheptane Cut	Iso-octane Cut
PARAFFINS		
2,2-Dimethylbutane 3.9	n-Hexane 1.4	n-Heptane 3.3
2,3-Dimethylbutane 10.2	2,2-Dimethylpentane } 2.5	2,2-Dimethylhexane 5.3
2-Methylpentane 47.0	2,4-Dimethylpentane }	2,5-Dimethylhexane 1.1
3-Methylpentane 27.4	2,3-Dimethylpentane }	2,4-Dimethylhexane 3.0
n-Hexane 1.6	2-Methylhexane } 21.5	2,3-Dimethylhexane 16.1
	3-Methylhexane } 41.5	
Total paraffins 90.1		12.7
NAPHTHENES		
Cyclopentane 9.8	Methylcyclopentane 18.0	Methylcyclohexane 36.4
	Cyclohexane 17.0	Ethylcyclopentane 12.3
	1,1-Dimethylcyclopentane 1.4	Trimethylcyclopentanes 17.3
	trans-1,3-Dimethylcyclopentane 8.2	
	trans-1,2-Dimethylcyclopentane 12.2	
Total naphthenes 9.8	56.8	66.0
AROMATICS		
Benzene 0.1	Benzene 1.7	Toluene 21.3
Total aromatics 0.1	1.7	21.3
Grand total 100.0	100.0	100.0

TABLE VI. COMPARISON OF CALCULATED AND DETERMINED F-3 OCTANE NUMBERS (4.0 ML. T.E.L. PER GALLON) OF INDIVIDUAL CUTS FROM THREE NAPHTHAS

Fraction	Octane Number		
	Calcd.	Detd.	Difference
Oklahoma City			
Isohexane cut	100	100	0
Isoheptane cut	92	91	+1
Iso-octane cut	90	88	+2
Iso-C ₆ + iso-C ₇ blend	94	95	-1
Iso-C ₆ + iso-C ₇ + iso-C ₈ blend	94	93	+1
East Texas			
Iso-C ₆ cut	99	100	-1
Iso-C ₇ cut	94	91	+3
Iso-C ₈ cut	87	86	+1
Iso-C ₆ + iso-C ₇ blend	94	95	-1
Iso-C ₆ + iso-C ₇ + iso-C ₈ blend	91	91	0
Hull-Silk-Sikes			
Iso-C ₆ cut	98	100	-2
Iso-C ₇ cut	93	93	0
Iso-C ₈ cut	88	86	+2
Iso-C ₆ + iso-C ₇ blend	94	97	-3
Iso-C ₆ + iso-C ₇ + iso-C ₈ blend	91	92	-1

TABLE VII. COMPARISON OF CALCULATED AND DETERMINED F-3 OCTANE NUMBERS (4.0 ML. T.E.L. PER GALLON) OF NAPHTHAS BOILING FROM 97° TO 243° F.

Naphtha	Octane No.		Difference
	Calcd.	Detd.	
Tom O'Conner	88	86	+2
Coslinga	89	89	0
Saxet	91	89	+2
Old Ocean	86	87	-1
K.M.A. Strawn	84	85	-1
Golden Meadow	88	88	0
Chapel Hill	82	83	-1
Conroe	89	89	0
Plymouth	89	90	-1
Segno	88	90	-2
Jennings	85	87	+1
Wade City	91	89	+2
Carthage	84	84	0

dispersion methods to estimate the composition in terms of individual hydrocarbons. The percentages of individual hydrocarbons and the blending octane numbers listed in Table III were used to calculate the octane numbers of the naphtha cuts. The calculated octane numbers and the determined values are compared in Table VII. The maximum deviation is 2 octane numbers.

CONCLUSIONS

A naphtha from an Oklahoma City crude oil was superfractionated, and 0.5% fractions were collected and rated with 4.0 ml. of tetraethyllead by the CRC-F-3 method. A graph of the octane number of fractions plotted against sum per cent distilled indicates boiling points at which cuts should be made on superfractionators and the effect of changing cut points on the volume per cent and engine ratings of the superfractionated base stock. Analyses of the 0.5% fractions and the engine ratings provide a means for calculating the blending octane numbers of individual hydrocarbons blended with the hydrocarbons with which they normally are associated. These blending octane numbers can be used to calculate the octane numbers of naphthas having a boiling range of 97–243° F. to within ±3 octane numbers, from superfractionations made in laboratory distillation units and from analyses of the fractions by specific dispersion and refractivity intercept methods.

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LITERATURE CITED

- (1) Aviation Gasoline Advisory Committee, Subcommittee on Blending Octane Numbers, Rept. No. 5, June 1, 1944.
- (2) Gooding, R. M., Adams, N. G., and Rall, H. T., *IND. ENG. CHEM., ANAL. ED.*, 18, 2–13 (1946).
- (3) Throne, H. M., Murphy, Walter, and Ball, J. S., *Ibid.*, 17, 481–6 (1945).
- (4) U. S. Bur. of Mines, restricted rept., "Preparation of 115/145 Grade Aviation Fuel Using Base Stock Made by Superfractionation of Naphtha from Oklahoma City, Oklahoma Crude Oil", Dec. 1945.

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