Fractionation of Straight-Run Pennsylvania Gasoline

M. R. Fenske, School of Chemistry and Physics, Pennsylvania State College, State College, Pa.

DURING the past two years a research program has been conducted at this college relating to problems in the refining and improvement of products of Pennsylvania petroleum. Recently a petroleum refining laboratory was established where the work is to be continued and expanded on a larger and more effective scale. One of the first problems studied was the composition and knock characteristics of straight-run Pennsylvania gasoline. The most logical method for determining the composition, as well as the amounts of the various hydrocarbons present, is fractional distillation. However, this is not a simple problem, for the gasoline is known to consist of a large variety of hydrocarbons, each one being present to the extent of only a few per cent. Since special equipment is needed for such a fractionation, it is always better if some method or data are available for the design of this equipment.

Design of Fractionating Columns

Considerable information is available on the design of fractionating columns (1, 2, 5, 7). For binary mixtures, the graphical method for calculating the change in composition from plate to plate will readily give the number of perfect plates for any given separation, provided data are available on the vapor-liquid equilibria. For mixtures of more than two components, or for mixtures in which the actual chemical compounds are not readily identified, as in petroleum, the stepwise method of calculating from plate to plate by means of equilibrium data and material balances is used. This method was developed and used on the fractionation of petroleum by Lewis and co-workers (3, 4). They introduced the conception of key components, which are the components between which the cut or fractionation is being made.

Since the fractionation of the straight-run Pennsylvania gasoline was intended to separate the constituents so that their identification might be possible, a degree of separation much greater than anything heretofore required was necessary. To get any significant separation of such a complex mixture, obviously a great number of plates (or their equivalent if a packed column is used) is needed. To calculate by the stepwise method the number of perfect plates needed for this degree of separation, when such a large number of components is present in the gasoline, is an almost impossible task. Fortunately, using the conception of key components, the problem becomes relatively simple no matter how complex the mixture, granting the validity of the usual simplifying assumptions used in designing fractionating columns.

These simplifying assumptions are that the moles of overflow and moles of vapor ascending the column are constant, that the operation of the column is continuous and adiabatic,

The equations and relationships derived for the separation of complex mixtures are considerably more convenient than the usual stepwise method for calculating the plates in a fractionating column, and it is believed they are sufficiently accurate for design purposes. It becomes practically impossible to use the stepwise method for unusually close separations in complex mixtures. Equations for the minimum number of perfect plates, and minimum reflux ratios are derived. Certain relationships are developed so that it appears that the separation of a complex mixture may be treated as the separation of a simple binary mixture of the key components, using the same ratios for the binary mixture as occur with the key components in the case of the complex mixture.

Fractionating columns, in agreement with the design indicated by these equations, are found to be effective in separating straight-run Pennsylvania gasoline.

that there is no heat of mixing of any of the components, and that Raoult's law may be used in determining vapor-liquid equilibria. Lewis and co-workers have made an extensive study of the application of Raoult's law to petroleum hydrocarbon mixtures, and this assumption, as well as the others, appears to be justified in the fractionation of petroleum.

Minimum Plates When Operating under Total Reflux

In the design of any column it is important to know at least two things. One is the minimum number of plates required for the separation if no product, or practically no product, is withdrawn from the column. This is the condition of total reflux. The other point is the minimum reflux that can be used to accomplish the desired separation. While this case requires the minimum expenditure of heat, it necessitates a column of infinite height. Obviously, all other cases of practical operation lie in between these two conditions.

Consider the two components, A and B, which are two hydrocarbons present in the gasoline. These are to be the key components; that is, B is the component boiling next higher than A, and it is desired that everything boiling below A, together with practically all of A and a small amount of B, be taken overhead as a distillate; that everything boiling higher than B, together with practically all of B and a small amount of A, be taken off as the still bottoms.

The relationship between the vapor and liquid compositions for A and B are written directly from Raoult's law.

$$y_A (\pi) = x_A (P_{0_A})$$
$$y_B (\pi) = x_B (P_{0_B})$$

where x and y = mole fractions in liquid and vapor, respectively
π = total pressure
P_{0_A} and P_{0_B} = vapor pressures of pure A and B at temperature at which this mixture happens to be boiling under pressure, π

Dividing one equation by the other, and substituting mole ratios for the mole fraction ratios, and α for the ratio of P_{0_A} to P_{0_B}, there results the familiar equation:

$$\frac{Y_A}{Y_B} = \alpha \frac{X_A}{X_B}$$

Here, α denotes the relative volatility and is assumed constant at the temperature range over which the column is operating.

The usual material balances around any plate above the feed give:

$$Y_{n_A} = X_{n+1_A} + X_{e_A}$$
$$Y_{n_B} = X_{n+1_B} + X_{e_B}$$

where X = moles of liquid
           Y = moles of vapor
X_{c_A} and X_{c_B} = moles of A and B withdrawn as distillate
n and n + 1 = any plate and the one just above it, respectively

However, under total reflux, X_{c_A} and X_{c_B} are zero, so dividing one equation by the other gives:

$$\frac{Y_{n_A}}{Y_{n_B}} = \frac{X_{n+1_A}}{X_{n+1_B}}$$

Substituting this in the equation above, which contains α, gives:

$$\frac{X_{n+1_A}}{X_{n+1_B}} = \alpha\, \frac{X_{n_A}}{X_{n_B}}$$

This equation gives the ratio between the components A and B in the liquid on any plate and their ratio in the liquid on the next plate above it. The general equation then follows:

$$\frac{X_{n_A}}{X_{n_B}} = (\alpha^{n-1})\frac{X_{1_A}}{X_{1_B}} \tag{1}$$

The ratio $\frac{X_{1_A}}{X_{1_B}}$ denotes the molal ratio of A to B on any plate, while $\frac{X_{n_A}}{X_{n_B}}$ denotes the molal ratio of A to B on any plate, n plates removed from the first; n, the exponent of α, is the number of perfect plates required for this separation.

This equation, then, gives the minimum number of plates required to go from one ratio of A to B to another, for it is based on operation under total reflux. In addition, it should be noted that the presence of any number of other components is not involved in this equation, which makes it applicable to the separation of any mixture where A and B are the key components (granting the simplifying assumptions made earlier).

Minimum Reflux Ratio for a Column of Infinite Height

It is important to know the minimum reflux ratio in the design of a column, for this quantity will give the lowest possible amount of heat necessary for the separation desired. To get this minimum consumption of heat, there is needed a column of infinite height. While this is not a practical case, it is nevertheless very useful in determining the performance and efficiency of any actual column.

Equations are given in the standard references (1, 2, 5, 7) for minimum reflux ratio. However, they require the vapor and liquid compositions at the feed plate. These are not readily known for a complex mixture, because the temperature of the feed plate has first to be calculated. This difficulty can be avoided by grouping the terms as ratios of the key components. Writing the usual material balances for plates above the feed for the two components, A and B, gives:

$$Vy_{n_A} = Ox_{n+1_A} + Px_{c_A}$$
$$Vy_{n_B} = Ox_{n+1_B} + Px_{c_B}$$

where x and y = mole fractions of liquid and vapor, respectively
V, O, and P = total moles of vapor, overflow or reflux, and product, respectively
n and n + 1 = any plate and the plate just above it, respectively
x_c = mole fraction in condensate

These equations show the relationship between the vapor rising into a plate and the composition of the liquid on that same plate. If, at any time, the composition of the liquid on the nth plate should become equal to that on the n + 1th plate, then at this point no separation would occur. It also happens that as the reflux ratio (O/P) in a column is reduced, the difference in composition between the nth and n + 1th plate is reduced. That is, the composition on the n + 1th plate approaches that on the nth plate. If it should become only differentially greater, then the column would have to be infinitely high to get the separation required, for the enrichment per plate would be only differential in amount. These conditions are those prevailing at the minimum reflux ratio—namely, the composition on the n + 1th plate becomes equal to that on the nth plate (6).

Dividing the two equations above, and substituting compositions on the nth plate there results:

$$\frac{y_{n_A}}{y_{n_B}} = \frac{Ox_{n_A} + Px_{c_A}}{Ox_{n_B} + Px_{c_B}}$$

Substituting for $\frac{y_{n_A}}{y_{n_B}}$ its equivalent $\alpha\, \frac{x_{n_A}}{x_{n_B}}$, and rearranging the terms, gives:

$$\left(\frac{O}{P}\right)_{min.} = \frac{1}{\alpha - 1}\left(\frac{x_{c_A}}{x_{n_A}} - \alpha\, \frac{x_{c_B}}{x_{n_B}}\right)$$

While this equation shows that there is a minimum reflux ratio for every plate, the minimum reflux, which is really wanted, is that which, when slightly exceeded, would make the separation possible in a column unusually long. This value is obtained if the feed plate is made the nth plate (6). Accordingly,

$$\left(\frac{O}{P}\right)_{min.} = \frac{1}{\alpha - 1}\left(\frac{x_{c_A}}{x_{f_A}} - \alpha\, \frac{x_{c_B}}{x_{f_B}}\right) \tag{2}$$

where x_f = concentration (in mole fractions) on feed plate

Since it can be proved that the feed entering a column should be introduced on a plate having the same composition as the feed (1), and this is independent of the other components present, it follows that Equation 2 will give the minimum reflux ratio for separation of the key components, A and B, in a mixture, when the molal compositions of A and B in the entering feed and the distillate are known. In this equation it is not necessary to know the temperature of the liquid on the feed plate.

An example may serve to illustrate the use of Equations 1 and 2. Straight-run Pennsylvania gasoline contains about 5 mole per cent normal heptane and 5 mole per cent methylcyclohexane. Contrary to data given in the literature (8), normal heptane and methylcyclohexane do not form a constant-boiling mixture. These two hydrocarbons boil about 3° C. apart; and, in the gasoline, methylcyclohexane is the hydrocarbon next higher boiling than normal heptane. Furthermore, the 50 per cent point of the gasoline comes approximately between heptane and methylcyclohexane. That is, about half the gasoline is lower boiling than heptane, and half is higher boiling. Supposing it is desired to take all the components boiling below heptane, plus 90 per cent of the heptane and 10 per cent of the methylcyclohexane overhead as distillate, and withdraw as bottoms all the components higher boiling than methylcyclohexane plus 90 per cent of the methylcyclohexane and 10 per cent of the heptane. These two hydrocarbons are then the key components. From the ratio of the vapor pressure of normal heptane to that of methylcyclohexane at the same temperature, α is found to be 1.14.

Referring to Equation 1 and the data given above, the ratio of heptane to methylcyclohexane in the feed is 1:1, and in the distillate it is to be 9:1. Substituting and solving for n, the minimum number of perfect plates above the feed is 18.

$$\left(\frac{9}{1}\right) = (1.14)^{n-1}\left(\frac{1}{1}\right)$$
$$n = 18$$

Likewise, assuming α to have the same value for below the feed, the plates in this location are also 18, the total minimum number of perfect plates for the above separation being 36. It is further seen that the feed plate is at the mid-point in the column. With mixtures which require a considerable number of plates for separation, the proportion of plates above the feed to the total is reasonably constant for other reflux ratios; so, in separating this mixture in a column containing more than 36 plates, the feed plate will still be about midway in the column. It is seen that for the above gasoline mixture, or for the simple binary mixture of pure normal heptane and pure methylcyclohexane, the minimum number of perfect plates is the same, if α is constant in the two cases. Since, in the case of the gasoline mixture, the temperatures above the feed plate will be lower than for the simple binary mixture, and the temperatures below the feed plate will be higher, it is possible for α to be somewhat different in these two cases. However, it is only the change in α which would affect the number of plates; and, for cutting between two liquids boiling as closely together as heptane and methylcyclohexane, α is substantially constant.

From a simple material balance on the column, on the basis of 100 moles of feed, there are 50 moles of distillate, and 50 moles of bottoms. The distillate contains 4.5 moles of heptane or a concentration of 9 mole per cent. The concentration of methylcyclohexane in the distillate is then 1 mole per cent. Using Equation 2 and the value of 1.14 for α, the minimum reflux ratio is found:

$$\left(\frac{O}{P}\right)_{min.} = \frac{1}{1.14-1}\left[\frac{0.09}{0.05} - 1.14\left(\frac{0.01}{0.05}\right)\right] = \frac{11}{1}$$

To separate the gasoline according to the above conditions, a reflux ratio (O/P) of at least 11 to 1 must be used, and no fewer than 36 perfect plates are needed.

PRACTICAL OPERATING CONDITIONS

While the equations given above tell the limiting conditions, they do not show directly the actual working conditions. It is possible, starting with the three following equations, to work out the number of plates for various reflux ratios for mixtures which are too complex to be handled in the usual stepwise method. It is believed that these results give, with sufficient accuracy, the necessary relationships between reflux ratio and number of plates:

$$\frac{Y_{n_B}}{Y_{n_A}} = \frac{1}{\alpha}\frac{X_{n_B}}{X_{n_A}} \tag{3}$$

$$Y_{n_B} = X_{n+1_B} + X_{c_B} \tag{4}$$

$$Y_{n_A} = X_{n+1_A} + X_{c_A} \tag{5}$$

where X and Y = molal quantities in liquid and vapor, respectively

n and $n+1$ = nth plate in column and plate immediately above nth plate, respectively (all plates are above feed plate)

X_c = moles of A or B drawn off as product

Dividing Equation 5 by Y_{n_A}, gives, on rearranging:

$$1 - \frac{X_{c_A}}{Y_{n_A}} = \frac{X_{n+1_A}}{Y_{n_A}} = a \tag{6}$$

The quantity $\frac{X_{n+1_A}}{Y_{n_A}}$ which is called a is quite constant even when the reflux ratio is not unusually high. It becomes

more nearly a constant as the reflux ratio is increased, approaching unity as the limit.

Dividing Equation 4 by Y_{n_A}, combining the resulting equation with Equation 3 and substituting the value of Y_{n_A} found in Equation 6, $Y_{n_A} = \left(\frac{X_{n+1_A}}{a}\right)$, there results:

$$\frac{X_{n_B}}{X_{n_A}} = a\alpha\frac{X_{n+1_B}}{X_{n+1_A}} + \alpha\frac{X_{c_B}}{Y_{n_A}} \tag{7}$$

This equation relates the ratio of the two components on one plate to the ratio on the next plate. The last term, $\frac{X_{c_B}}{Y_{n_A}}$ may be considered to result from multiplying the two ratios, $\frac{X_{c_B}}{X_{c_A}}$ and $\frac{X_{c_A}}{Y_{n_A}}$, so that,

$$\frac{X_{c_B}}{Y_{n_A}} = \left(\frac{X_{c_A}}{Y_{n_A}}\right)\left(\frac{X_{c_B}}{X_{c_A}}\right)$$

and from Equation 6,

$$\frac{X_{c_A}}{Y_{n_A}} = 1 - a$$

Combining these two equations and substituting in Equation 7, there results:

$$\frac{X_{n_B}}{X_{n_A}} = a\alpha\frac{X_{n+1_B}}{X_{n+1_A}} + (1-a)(\alpha)\frac{X_{c_B}}{X_{c_A}} \tag{8}$$

This equation shows that a linear relation exists between $\frac{X_{n_B}}{X_{n_A}}$ and $\frac{X_{n+1_B}}{X_{n+1_A}}$, granting the constancy of a.

Applying Equation 8 successively to relate the molal ratios on one plate to the plate next above it, and working out the series which results, there is obtained a general equation for conditions above the feed plate:

$$\frac{X_B}{X_A} = (a\alpha)^{n-1}\left[\frac{X_{n_B}}{X_{n_A}} + \frac{(1-a)(\alpha)}{a\alpha-1}\left(\frac{X_{c_B}}{X_{c_A}}\right)\right] - \frac{(1-a)(\alpha)}{(a\alpha-1)}\left(\frac{X_{c_B}}{X_{c_A}}\right) \tag{9}$$

For the interval between the feed plate and the condenser, then, $\frac{X_{n_B}}{X_{n_A}}$ equals $\frac{X_{c_B}}{X_{c_A}}$, and there results:

$$\frac{X_{f_B}}{X_{f_A}} = (a\alpha)^{n-1}\left(\frac{X_{c_B}}{X_{c_A}}\right)\left(\frac{\alpha-1}{a\alpha-1}\right) - \frac{(1-a)(\alpha)}{a\alpha-1}\left(\frac{X_{c_B}}{X_{c_A}}\right) \tag{10}$$

The constancy of a which is $\frac{X_{n+1_A}}{Y_{n_A}}$ can be readily determined from the conditions prevailing at the top of the column and at the feed plate. These conditions will give the limiting values of a. In general, the higher the reflux ratio, the more nearly constant a will become. If a is sufficiently constant for the accuracy desired, then either Equations 9 or 10 will enable the number of perfect plates for conditions above the feed to be calculated, for these equations are simply based on equilibrium conditions, assuming Raoult's law, and on material balances. It should be noted that these equations do not depend in any way on the number of other components present, granting the constancy of α. That is, these equations will be valid for a simple binary mixture of the key components or for the case of the key components if they were existing in a complex mixture, such as gasoline, if the condi-

tions of separation are such that α is constant in both cases. Since the term, a, is obtained by the material balance, it is unaffected by the number of other components present. Instead of using Equations 9 or 10 for calculating the number of plates for various reflux ratios for complex mixtures, it appears possible to calculate the plates from a simple binary mixture of the key components by the usual graphical method for a two-component system, choosing a value of α to meet the temperature conditions prevailing in the complex mixture, and using the same ratios for the binary mixture as occur with the key components in the case of the complex mixture. For the binary mixture the vapor-liquid equilibria is readily obtained from the equation:

$$y = \frac{\alpha x}{1 + (\alpha - 1)x}$$

where x and y = mole fractions of the more volatile component of a binary mixture in the liquid and vapor, respectively

This treatment obviates the use of the term "a." However, for separating to a high degree close-boiling materials, Equation 10 is more convenient for the over-all column design, for, with components boiling about $3°$ C. apart, a graph about 4 feet long is needed to get suitable accuracy.

Referring again to the heptane-methylcyclohexane mixture, Equation 10 shows that, with a feed of 50 mole per cent heptane and 50 mole per cent methylcyclohexane, and separating this to a distillate containing 90 mole per cent heptane and 10 mole per cent methylcyclohexane, there are needed for a 14 to 1 reflux ratio (O/P) 34 perfect plates above the feed plate. Calculating this same result by the usual graphical method, using a graph approximately 4×2 feet, there are needed 36 perfect plates. This is also the result for separating between the heptane and methylcyclohexane in the gasoline discussed above, for α is substantially the same for the case of the gasoline or for the simple binary mixture of heptane and methylcyclohexane.

Equations exactly similar to Equations 8 and 9 can be derived for conditions below the feed plate. These equations are:

$$\frac{X_{m_B}}{X_{m_A}} = a'\alpha \left(\frac{X_{m+1_B}}{X_{m+1_A}}\right) + \alpha(1 - a')\left(\frac{X_{w_B}}{X_{w_A}}\right) \qquad (11)$$

$$\frac{X_B}{X_A} = (a'\alpha)^{n-1}\left[\frac{X_{m_B}}{X_{m_A}} + \frac{(1 - a')(\alpha)}{a'\alpha - 1}\left(\frac{X_{w_B}}{X_{w_A}}\right)\right] - \frac{(1 - a')(\alpha)}{(a'\alpha - 1)}\left(\frac{X_{w_B}}{X_{w_A}}\right) \qquad (12)$$

where m = conditions below feed plate
X_w = molal quantities withdrawn as bottoms

Now, a' becomes the ratio, $\dfrac{X_{m+1_A}}{Y_{m_A}}$. Equation 12 may be used where a' is sufficiently constant for conditions below the feed, or a complex mixture may be calculated as a simple binary mixture of the key components using the same ratios for the binary mixture as occur with the key components in the case of the complex mixture.

Packed fractionating columns which are in agreement with the design indicated by these equations have been found to be particularly effective in separating straight-run Pennsylvania gasoline. This work is being reported at the present time in a series of papers. In addition, further development and application of these equations to a variety of distillation problems will be reported in the near future.

ACKNOWLEDGMENT

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Installation of Holmes-Manley Vertical Stills at Port Arthur Works of the Texas Company