Chapter 9

Distillation

INTRODUCTION

This first mass transfer operation chapter receives both preferential and unique treatment relative to the other chapters in Part II. It is no secret that the subject matter of distillation is solely located in the domain of the chemical engineer. In many ways, it is a topic which separates (no pun intended) chemical engineering from other engineering and applied science disciplines. As such, the authors made a conscious decision to provide preferential treatment to distillation and to include developmental material which may be lacking in other chapters. It was also decided to expand upon the concepts of binary distillation, and to include an introductory analysis of multicomponent distillation operations.

Distillation may be defined as the separation of the components of a liquid feed mixture by a process involving partial vaporization through the application of heat. In general, the vapor evolved is recovered in liquid form by condensation. The more volatile (lighter) components of the liquid mixture are obtained in the vapor discharge at a higher concentration. The extent of the separation is governed by two important factors: the properties of the components involved and by the physical arrangement of the unit used for distillation.

In continuous distillation, a feed mixture is introduced to a column where vapor rising up the column is contacted with liquid flowing downward (which is provided by condensing the vapor at the top of the column). This process removes or absorbs the less volatile (heavier) components from the vapor, thus effectively enriching the vapor with the more volatile (lighter) components. This occurs in the section above the feed stream which is referred to as the *enriching* or *rectification section* of the column. The product (liquid or vapor) removed from the top of the column is rich in the more volatile components and is defined as the *distillate*. The section below the feed stream is referred to as the *stripping section* of the column. In this section, the liquid is stripped of the lighter components by the vapor produced in a reboiler at the bottom of the column. The liquid that is removed from the bottom of the column is called the *bottoms*, which is richer in the heavier components.

Mass Transfer Operations for the Practicing Engineer. By Louis Theodore and Francesco Ricci

Distillation columns are used throughout industry when mixtures (primarily in liquid form) must be separated. One such example is the petroleum industry. In such an application, crude oil is fed into a large distillation column and different fractions (oil mixtures of varying composition and volatility) are taken out at different heights in the column. Each fraction, such as jet fuel, home heating oil, gasoline, etc., is used by both industry and the consumer in a variety of ways. The separation achieved in a distillation column depends primarily on the *relative* volatilities of the components to be separated, the number of contacting trays (plates) or packing height, and the ratio of liquid and vapor flow rates.

Distillation columns are rarely designed with packing in large scale production because of the liquid distribution problems that arise with large diameter units and the enormity of the height of many columns. However, where applicable, towers filled with packing are competitive in cost, and are particularly useful in cases where the pressure drop must be low and/or the liquid holdup must be small. Packed towers, an overview of which is available at the end of this chapter, are occasionally used for bench-scale or pilot plant work. In contrast, use of trayed towers extends to many areas of the chemical industry.

The sections to be covered in this chapter are as follows:

1 Flash Distillation

2 Batch Distillation

3 Continuous Distillation with Reflux
  i Equipment and Operation
  ii Equilibrium Considerations
  iii Binary Distillation Design: McCabe–Thiele Graphical Method
  iv Multicomponent Distillation: Fenske–Underwood–Gilliland Method

During the preparation of this chapter, the authors were ably assisted in many ways by a number of graduate students in Manhattan College's chemical engineering program. Several of the illustrative examples provided in this chapter were drawn, in part, from the original work of Marnell.(1)

FLASH DISTILLATION

The separation of a volatile component from a liquid process can be achieved by means of *flash distillation*. This operation is referred to as a "flash" since the more volatile component of a saturated liquid mixture rapidly vaporizes upon entering a tank or drum which is at a lower pressure and/or higher temperature than the incoming feed. If the feed is a sub-cooled liquid, a pump and heater may be required to elevate the pressure and temperature, respectively, to achieve an effective flash (see Fig. 9.1). As the feed enters the flash drum, it impinges against an internal deflector plate which promotes liquid–vapor separation of the feed mixture. The composition of the feed stream (F) is given by the mole fractions belonging to the set $\{z_i\}$. Similarly, the compositions of the vapor and liquid product streams are given by $\{y_i\}$ and $\{x_i\}$, respectively. Alternatively, some processes require that a vapor stream be cooled, so

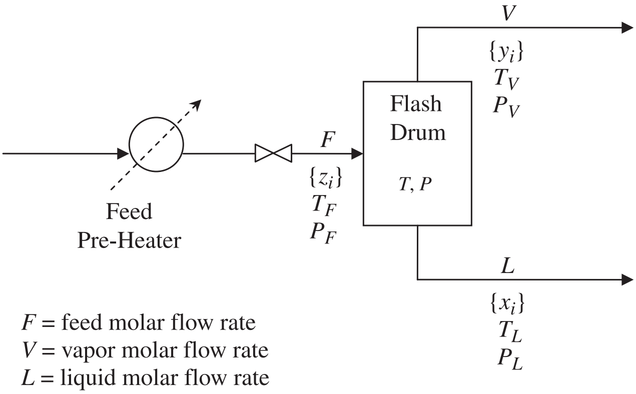


Figure 9.1 Flash distillation system.

as to partially condense the least volatile components in the stream. This process is referred to as a *partial condensation*, and the following development may be adapted to apply to such processes.

As a result of the flash, the vapor phase will be mostly composed of the more volatile components. Typically, flash distillation is not an efficient means of separation when used only once. However, when several flash units are placed in series, much purer products may be achieved. Moreover, it can be a necessary and economical means of separating two or more components with discernible relative volatilities, as is often necessary in the petroleum industry. In a very real sense, an individual flash distillation unit may be seen as analogous to a single tray in a distillation column (as will be explained later in this chapter).

Relative volatility (see Chapter 6) describes the tendency of a particular compound to vaporize, relative to another compound. As is expected, a more volatile component is more likely to vaporize from a mixture (as compared to a compound of lesser volatility) when the mixture's temperature is raised or the pressure is lowered. Relative volatility serves as a quantitative comparison of the volatility difference between two compounds of interest. When a liquid solution may be considered ideal, Raoult's law applies, and hence the relative volatility (α) of component A in an A/B binary mixture may be defined in terms of each component's vapor pressure (p_i')

$$\alpha_{AB} = \frac{K_A}{K_B} = \frac{p_A'}{p_B'} \tag{9.1}$$

where α_{AB} = relative volatility of A with respect to B [dimensionless]

$K_i \equiv y_i/x_i$ = phase equilibrium constant of component i [dimensionless]

Note that the phase equilibrium constant, K_i, is a function of several thermodynamic variables, namely the system's temperature, pressure, and the compositions of each phase. For non-ideal conditions, all three of these considerations must be taken into account, and K values must be determined via fugacity calculations. However, within the scope of this text, one may assume that K is solely a function of temperature and pressure.(2) The concept of relative volatility is of the utmost importance in an operation such as distillation, where two or more components are to be separated based on their differences in boiling point (which is directly correlated to differences in volatility).

The subsequent development refers to the *graphical solution* of flash distilling a binary liquid mixture. As with many process operations, an overall material balance can be written to describe the system illustrated in Figure 9.1. An overall mole balance yields

$$F = L + V \tag{9.2}$$

Based on the above, a componential mole balance can be written for component i, as shown in Equation (9.3):

$$Fz_i = Lx_i + Vy_i \tag{9.3}$$

where z_i = mole fraction of component i in the feed stream [dimensionless]
x_i = mole fraction of component i in the liquid stream [dimensionless]
y_i = mole fraction of component i in the vapor stream [dimensionless]

Since only two components are present in the liquid feed, the subscript i will be omitted, assuming that all mole fractions refer to the lighter component A. As a matter of convenience, Equation (9.3) may be rearranged in terms of the vapor composition to represent a straight line of the form $y = mx + b$ as follows

$$y = -\frac{L}{V}x + \frac{F}{V}z \tag{9.4}$$

where $-L/V$ = the slope of the operating line (m)
$(F/V)z$ = the y-intercept of the operating line (b). (Note that V/F is the fraction of the feed stream which is vaporized)

The above equation defines an operating line for this system, similar to that discussed in Chapter 8. Since the liquid and vapor streams are assumed to be in thermodynamic equilibrium (as is customarily practiced in quick-sizing mass transfer units), the flash is defined as an *equilibrium stage*. The equation therefore relates the liquid and vapor composition leaving the flash drum. One should also note that the vapor molar flow is normally represented by V, not G, in standard *distillation* notation; however, both are used interchangeably for the study of other mass transfer operations in certain chapters to follow.

As shown in Figure 9.2, a plot of the equilibrium data, the $y = x$ line, and the operating line set up a procedure to calculate the unknown variables for this system, typically the outlet liquid and vapor compositions. The use of the $y = x$ line simplifies the graphical solution method and intersects the operating line at the feed composition, z. Thus, at this point, $y = x = z$. The unknown compositions in the vapor and liquid product streams can then determined by the intersection of the operating line and the equilibrium curve.

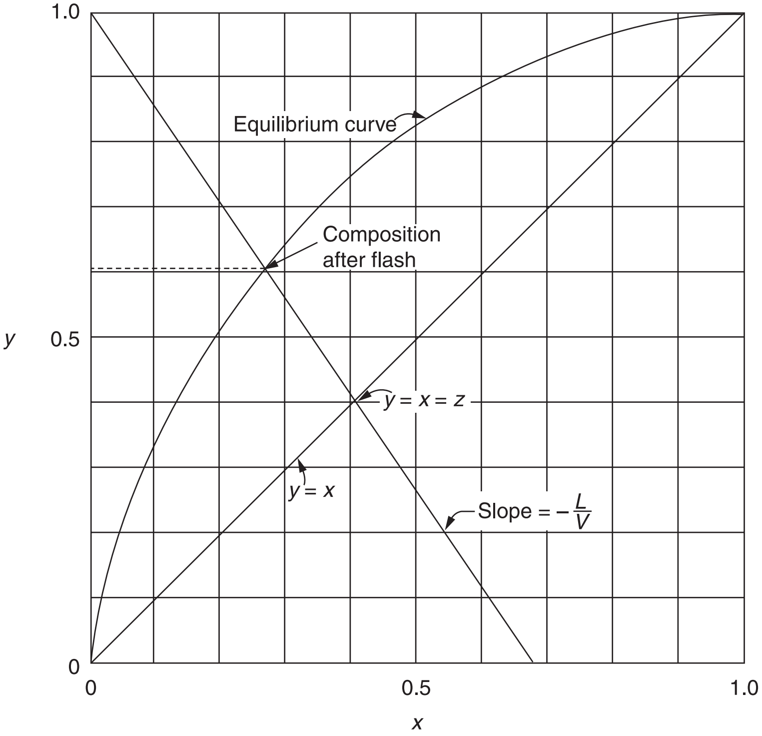


Figure 9.2 Graphical analysis of flash distillation.

ILLUSTRATIVE EXAMPLE 9.1

Dr. Ethyl Ester, an organic chemistry professor performed a flash distillation experiment for her students. A 10 kmol/h liquid feed mixture consisted of 20 mol% ethanol and 80 mol% water at 1 atm. While the professor was able to determine that 30 mol% of the feed vaporized in a small flash drum, she lacked the equipment to measure the liquid and vapor compositions. Determine the liquid and vapor compositions, as well as the percent ethanol recovery in the vapor stream. Equilibrium data for the ethanol/water system were calculated via the Wilson equation$^{(2)}$ at 1 atm, and an x, y diagram is provided in Figure 9.3.

***SOLUTION*:** Superimposed on Figure 9.3 is the $y = x$ line. The describing equation for the operating line is

$$y = -\frac{L}{V}x + \frac{F}{V}z \tag{9.4}$$

The slope of the operating line may be obtained directly from

$$\frac{V}{F} = 0.3$$

$$V = 0.3F$$

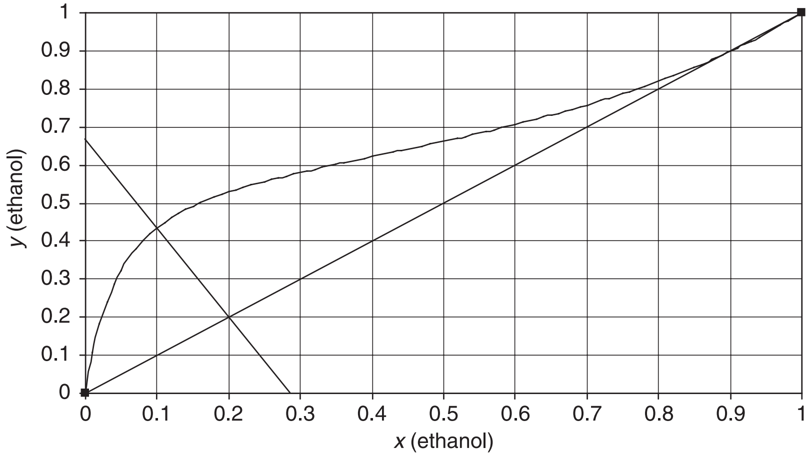


Figure 9.3 Ethanol/Water equilibrium diagram (via Wilson equation, 1 atm).

But since $V = F - L$

$$L = 0.7F$$

$$Slope = -\frac{L}{V}$$

$$= -\frac{0.7F}{0.3F}$$

$$= -2.33$$

The y-intercept is calculated in a similar fashion

$$\frac{F}{V} = 3.33$$

$$y_{\text{int}} = \frac{F}{V}z$$

$$= (3.33)(0.20)$$

$$= 0.666$$

The operating line also appears on the plot. The ethanol liquid and vapor compositions which result from the flash are found from the intersection of the operating line and equilibrium curve:

$$x = 0.10; \quad y = 0.44$$

$$(1 - x) = 0.90; \quad (1 - y) = 0.56$$

Now that the liquid and vapor stream compositions are fixed, the liquid and vapor flow rates may be determined by solving Equations (9.2) and (9.3) simultaneously:

$$F = L + V \tag{9.2}$$

$$Fz_i = Lx_i + Vy_i \tag{9.3}$$

Substituting ($V = F - L$) into Equation (9.3) and substituting mole fractions for ethanol,

$$(10)(0.20) = (L)(0.10) + (10 - L)(0.44)$$

And thus,

$$L = 7.1\,\text{kmol/h}$$
$$V = 2.9\,\text{kmol/h}$$

The percent recovery of ethanol in the vapor stream is calculated as follows:

$$\begin{aligned}\%(RECOVERY)_i &= \left(\frac{Vy_i}{Fz_i}\right)(100); \quad i = \text{ethanol} \\ &= \left[\frac{(2.9)(0.44)}{(10)(0.20)}\right](100) \\ &= 63.8\%\end{aligned}$$

Therefore, 63.8% (by mole) of the ethanol feed is recovered in the vapor product. ■

An iterative procedure is required in order to solve a multicomponent (more than two components) flash problem, the details of which are available in the literature.$^{(2,3)}$ While at least three distinct equations may be derived for multicomponent flash distillation via material balances, one equation in particular is the most convenient. The reason that this equation is so convenient is that it is a monotonically decreasing function (and therefore only has one root, which precludes any extraneous answers). This equation is referred to as the Rachford–Rice (RR) equation, shown in Equation (9.5) below for a mixture of N components,

$$f(\Psi) = \sum_{i=1}^{N} \frac{z_i(K_i - 1)}{1 + (K_i - 1)\Psi} = 0 \tag{9.5}$$

where $\Psi = V/F$ = molar fraction of feed which leaves as vapor [dimensionless]

One should note that the vapor flow rate for a flash distillation is given by $V = F\Psi$, whereas the liquid flow rate is $L = F(1 - \Psi)$. Assuming the feed composition is known, Equation (9.5) may be used for either of two purposes:

1. To calculate the fraction of feed which will vaporize (Ψ) or condense ($1 - \Psi$) at a given flash temperature and pressure.
2. To determine the phase equilibrium constants (K_i) for each species by guessing the flash temperature and/or pressure at a desired value of Ψ.

Regardless of which parameter is to be calculated (Ψ or K_i), an iterative calculation is carried out until the sum in Equation (9.5) is sufficiently close to zero. Once the RR equation has been solved, the compositions of the liquid and vapor streams are calculated by utilizing material balances, and the definition of the phase equilibrium constant, $K_i \equiv y_i/x_i$. The resulting equations are given below:

$$x_i = \frac{z_i}{1 + (K_i - 1)\Psi} \tag{9.6}$$

$$y_i = \frac{z_i K_i}{1 + (K_i - 1)\Psi} \tag{9.7}$$

In order to solve for the compositions of the liquid and vapor streams, one stream is chosen (V or L), mole fractions are calculated for that stream via Equation (9.6) or Equation (9.7), and the mole fractions of the subsequent stream are determined via the equilibrium constant, $K_i \equiv y_i / x_i$. Alternatively, the compositions of both streams can be calculated directly from Equations (9.6) and (9.7).

For near-ideal mixtures, such as light hydrocarbons of the same homologous series at low pressures, Raoult's law may be assumed to apply. In this case, the K value of any component i is the ratio of the vapor pressure of i to the total pressure. Alternatively, one may employ the DePriester Charts.(2)

ILLUSTRATIVE EXAMPLE 9.2

Calculate the vapor ratio, Ψ, and the vapor and liquid stream compositions for a multicomponent flash operation. The feed mole fractions and phase equilibrium constants (at the flash temperature and pressure) are provided in Table 9.1. Given that the feed flow is 1250 lbmol/h, what are the liquid and vapor molar flow rates?

Table 9.1 Multicomponent Flash Data for Illustrative Example 9.2

Component	Mole fraction (z_i)	Equilibrium ratio (K_i)
1	0.28	2.93
2	0.24	1.55
3	0.24	0.87
4	0.08	0.49
5	0.16	0.138

***SOLUTION*:** By utilizing the Rachford–Rice flash equation, it is noted that all values have been specified except for the vapor ratio, Ψ. Since the sum of all terms must be equal to zero, the value of the vapor ratio may be calculated by an iterative, trial and error procedure. This may be performed by hand or in a program with iterative solver algorithms.

$$f(\Psi) = \sum_{i=1}^{N} \frac{z_i(K_i - 1)}{1 + (K_i - 1)\Psi} = 0 \tag{9.5}$$

Upon iteration,

$$\Psi = 0.5647$$

The values of x_i are calculated via Equation (9.6), and the specified values of K_i were then used to determine y_i. The results are shown in Table 9.2. Also note $V = F\Psi$ and $L = F(1 - \Psi)$,

Table 9.2 Liquid and Vapor Compositions for Illustrative Example 9.2

Component	x_i	$y_i = K_i x_i$
1	0.134	0.393
2	0.183	0.284
3	0.259	0.225
4	0.112	0.055
5	0.312	0.043
SUM	1.000	1.000

$$V = (1250)(0.5647) = 706\,\text{lbmol/h}$$
$$L = (1250)(1 - 0.5647) = 544\,\text{lbmol/h}$$

■

BATCH DISTILLATION

Although batch distillations are generally more costly than their continuous counterparts, there are certain applications in which batch distillation is the method of choice. Batch distillation is typically chosen when it is not possible to run a continuous process due to limiting process constraints, the need to distill other process streams, or because the low frequency use of distillation does not warrant a unit devoted solely to a specific product.

A relatively efficient separation of two or more components may be accomplished through batch distillation in a pot or tank. Although the purity of the distilled product varies throughout the course of batch distillation, it still has its use in industry. As shown in Figure 9.4, a feed is initially charged to a tank, and the vapor generated by boiling the liquid is withdrawn and enters a condenser. The condensed product is collected as distillate, D, with composition x_D, and the liquid remaining in the pot, W, has composition x_W. Total and componential material balances around a batch distillation unit are shown below:

$$F = W + D \tag{9.8}$$

$$Fx_F = Wx_W + Dx_D \tag{9.9}$$

Note that W, x_W, D, and x_D all vary throughout the distillation.

A convenient method for mathematically representing a binary batch distillation process is known as the Rayleigh equation. This equation relates the composition and amount of material remaining in the batch to initial feed charge, F, and composition, x_F:

$$\ln\left(\frac{W}{F}\right) = -\int_{x_W}^{x_F} \frac{dx}{y^* - x} \tag{9.10}$$

where y^* = mole fraction of vapor in equilibrium with liquid of composition x.

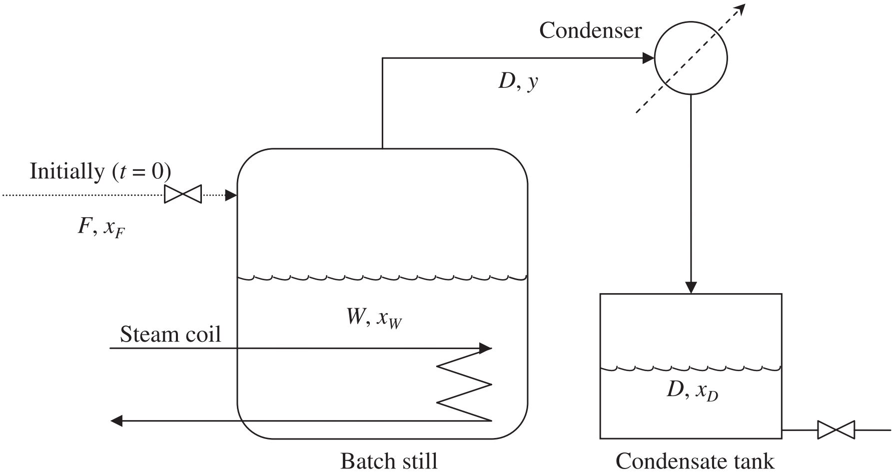


Figure 9.4 Batch distillation diagram.

At the desired distillate composition, the distillation is stopped. At this time, the moles of residue remaining in the still is denoted W_{final}, with composition $x_{W,final}$. As such, Equation (9.10) may be re-written as shown below:

$$W_{final} = F\exp\left[-\int_{x_{W,final}}^{x_F} \frac{dx}{y^* - x}\right] \tag{9.11}$$

This equation may be solved numerically by plotting $1/(y^* - x)$ vs x and integrating between the limits $x_{W,final}$ and x_F to determine the area (A) under the curve (see Fig. 9.5). The above can therefore be written as

$$W_{final} = F\exp[-A] \tag{9.12}$$

where $A =$ area under the curve.

A convenient method for determining the area under a given curve is provided by Simpson's 3-point rule, as described below in Equation (9.13),

$$\begin{aligned} A &= \int_{x_{W,final}}^{x_F} f(x)\,dx \\ &= \int_{x_{W,final}}^{x_F} \frac{dx}{y^* - x} = \frac{x_F - x_{W,final}}{6}\left[f(x_{W,final}) + 4f\left(\frac{x_{W,final} + x_F}{2}\right) + f(x_F)\right] \end{aligned} \tag{9.13}$$

where $f(x) = 1/(y^* - x)$. Instead of relying on Simpson's rule, a more accurate answer may often be calculated by fitting the data points with a polynomial regression as in Figure 9.5. The polynomial may then be integrated directly.

The above integration requires that the function $1/(y^* - x)$ be evaluated at the appropriate x values. Typically, this is a trial-and-error procedure which involves guessing the composition of the material remaining in the tank, $x_{W,final}$, and then determining if Equation (9.11) is satisfied.(4) (See Chapter 19 and Illustrative Example 19.3 for additional details on numerical integration.)

ILLUSTRATIVE EXAMPLE 9.3

A solution containing 50 moles of benzene and 50 moles of toluene is batch distilled at a constant pressure until such time that only 50 moles of liquid is left. Determine the composition of the liquid residue at the conclusion of the distillation process. Benzene/toluene equilibrium data is provided in Table 9.3. (Note that, as is common practice in binary distillation, all mole fractions refer to the lighter component, which in this case is benzene.)

***SOLUTION*:** Write the Rayleigh equation for simple batch distillation.

$$\ln\left(\frac{W_{final}}{F}\right) = -\int_{x_{W,final}}^{x_F} \frac{dx}{y^* - x} \tag{9.10}$$

The initial concentration of benzene (mole fraction) is:

$$\begin{aligned} x_F &= 50/(50 + 50) \\ &= 0.50 \end{aligned}$$

In addition,

$$\ln\left(\frac{W_{final}}{F}\right) = \ln\left(\frac{50}{50 + 50}\right) = \ln(0.5) = -0.693$$

A trial-and-error solution is now required to determine the benzene mole fraction in the liquid. All values are known in Equation (9.10) except for the integral itself, for which $x_W = x_{W,final}$. The area under the curve is determined by guessing values of $x_{W,final}$ until the

Table 9.3 Benzene/Toluene Equilibrium Data

x	y^*	$y^* - x$	$1/(y^* - x)$
0.000	0.000	0.000	–
0.116	0.240	0.124	8.06
0.228	0.418	0.190	5.26
0.336	0.533	0.217	4.61
0.440	0.660	0.221	4.52
0.541	0.747	0.205	4.88
0.639	0.817	0.178	5.62
0.734	0.875	0.142	7.04
0.825	0.924	0.098	10.2
0.914	0.965	0.051	19.6
1.000	1.000	0.000	–

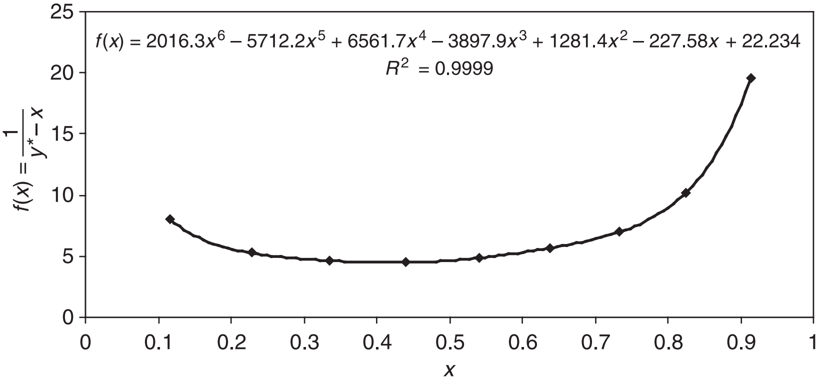


Figure 9.5 Benzene/Toluene equilibrium Rayleigh diagram.

right-hand side of Equation (9.10) is equal to -0.693. If a numerical package is not available, one may plot $1/(y^* - x)$ vs x as in Figure 9.5.

The equation appearing in Figure 9.5 is a polynomial regression fit to the data points, which can facilitate analytical integration. Upon integration of $f(x)$ at varying lower bounds, it can be shown that when $x_{W,final} = 0.35$, the area under the curve is approximately equal to 0.693, which satisfies Equation (9.10). (This calculation is left as an exercise for the reader.) Therefore,

$$x_{W,final} \approx 0.35 \text{ (benzene)}$$
$$1 - x_{W,final} \approx 0.65 \text{ (toluene)}$$

■

ILLUSTRATIVE EXAMPLE 9.4

A chemical manufacturer plans to use methanol as a key solvent in a new batch production process. After conducting an economic analysis, the plant manager has determined that it may be cost effective to use existing equipment to separate methanol from a process water stream which is currently part of another process in the plant. His calculations indicate that the existing equipment can handle a charge of 150 lbmol of aqueous stream which could have a maximum of 75 mol% methanol. The distillate collected must be at least 85% pure in order to be fed directly to the main reactor of the new process. However, he needs to know how much methanol can be recovered from the methanol/water mixture, as well as the amount and concentration of the material (residue) remaining in the tank. Perform the integration found in the Raleigh equation using Simpson's three-point rule. Equilibrium data for the methanol/water mixture is provided in Table 9.4.

***SOLUTION*:** Write the Rayleigh equation for simple batch distillation, as provided in Equation (9.11):

$$W_{final} = F \exp\left[-\int_{x_{W,final}}^{x_F} \frac{dx}{y^* - x}\right]$$

Table 9.4 Methanol/Water Equilibrium Data at 1 atm

x	y
0.80	0.915
0.77	0.895
0.70	0.870
0.65	0.848
0.60	0.830
0.55	0.802
0.50	0.780
0.45	0.754
0.40	0.730

As described in the previous example, plot $1/(y^* - x)$ vs. x as shown in Figure 9.6. As with the previous example, one may obtain a regression equation for the data and integrate to find the area under the curve. Alternatively, one may use Simpson's rule by guessing a value for $x_{W,final}$ and calculating the area. Both procedures require trial and error.

Setting the initial methanol mole fraction to 75%,

$$x_F = 0.75$$

and guess

$$x_{W,final} = 0.59$$

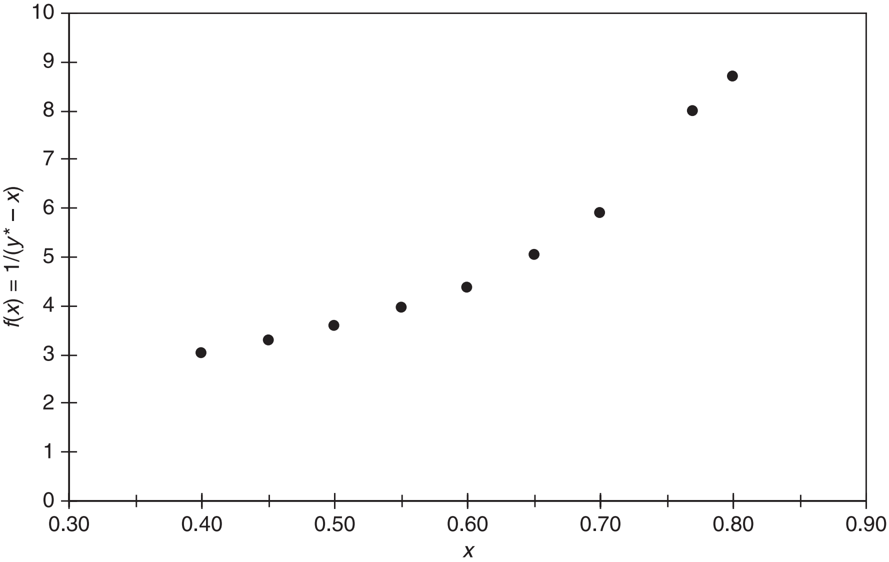


Figure 9.6 Batch distillation analysis.

Employ Simpson's rule with

$$f(x) = \frac{1}{y^* - x}$$

Determine $f(x)$ at the limits of integration by reading the approximate ordinate values from Figure 9.6:

$$f(x_{W,\,final}) = \frac{1}{y^* - x_{W,\,final}} \approx 4.3$$

$$f(x_F) = \frac{1}{y^* - x_F} \approx 7.4$$

Also,

$$f\left(\frac{x_{W,\,final} + x_F}{2}\right) = \frac{1}{y^* - (x_{W,\,final} + x_F)/2} \approx 5.5$$

Therefore,

$$\begin{aligned} A &= \frac{0.16}{6}[4.3 + 4(5.5) + 7.4] \\ &= 0.899 \end{aligned}$$

Calculate the moles of material remaining in the tank and the amount and composition of the distillate collected:

$$\begin{aligned} W &= F \exp(-A) \\ &= 150 \exp(-0.899) \\ &= 61.0 \end{aligned}$$

In addition,

$$\begin{aligned} D &= F - W \\ &= 150 - 61 \\ &= 89 \end{aligned}$$

Thus,

$$\begin{aligned} x_D &= \frac{Fx_F - Wx_{W,\,final}}{D} \\ &= \frac{(150)(0.75) - (61)(0.59)}{89} \\ &= 0.860 \end{aligned}$$

Check if the calculated value of the final distillate composition is within 5% of the given value

$$\begin{aligned} \%Error &= \frac{0.85 - 0.860}{0.85} \times 100 \\ &= 1.2\% \end{aligned}$$

Thus, the initial guess for $x_{W,final}$ may be assumed acceptable.

Should the reader so desire, this example may be solved in the same manner as Illustrative Example 9.3, i.e., by regressing the appropriate Raleigh equilibrium plot, and numerically integrating. With only a fourth-order polynomial fit to the above data, a more accurate answer may be obtained upon performing the iterative guess and check procedure. This is left as an exercise for the reader. ■

In some situations, the degree of separation achieved in a single equilibrium stage (such as a flash distillation column) or in a batch still is often not large enough to obtain the desired distillate and/or bottoms purities. To improve the recovery of the desired product, a multi-staged distillation column may be employed. The analysis of such multi-stage columns will be the focus of the remainder of this chapter.

CONTINUOUS DISTILLATION WITH REFLUX

Equipment and Operation

For large-scale operations, continuous distillation is almost always more economical than batch, especially when a steady supply of feed is available. One of the disadvantages of both batch and flash distillation is the multiplicity of sequential distillations that are often necessary to achieve something approaching “complete” separation of the components. Moreover, it is possible to produce a very pure product by batch distillation. However, in order to obtain a high recovery, the liquid residue must be redistilled multiple times.(5)

A continuous distillation column is analogous to several small flash units in series and effectively circumvents the need for multiple units. Indeed, unless a mixture contains an azeotrope,(2,6) a product stream of any desired purity may be theoretically obtained. In reality, a massive number of trays or an extremely high reflux ratio (to be defined shortly) would be required in the limit of a 100% pure product; these physical constraints on the system design limit the actual recovery possible.

In a continuous distillation column, the mixture to be separated is fed into the column at some predetermined *feed point* between the top and bottom of the column. Vapor flows up the column and liquid flows countercurrently down the column. For the subsequent discussion regarding continuous distillation, a binary (2-component) feed will be assumed. In the case of a binary feed, the more volatile (lower boiling) component will be referred to as the *light component*, whereas the less volatile (higher boiling) component is referred to as the *heavy component*. As is standard practice in binary distillation, all mole fractions (i.e., x_D, x_B, x_F) will be representative of the light component only.

A photograph of a unit operations scale continuous distillation column is provided in Figure 9.7. The ascending vapor and descending liquid are brought into contact on either trays (plates) or packing. The plates/packing serves as a “widget” which allows the liquid and vapor to experience more intimate contact. As described earlier, the vapor at the top of the column enters a condenser. Part of the condensate is returned to the top of the column to provide *reflux*. The reflux descends counter to the rising

Figure 9.7 Photograph of distillation column.

vapors, and in the case of a total condenser, the remainder of the liquid condensate is withdrawn from the condenser as *distillate product*.

Reflux and Boil-up

The molar flow ratio of reflux returned to distillate product collected is defined in this text as the *reflux ratio*, *R*. As the liquid/reflux stream descends, it is progressively stripped of the light constituent by the rising vapor. As a result of both heat and mass transfer effects, the vapor stream tends to vaporize the low-boiling constituent from the liquid and the liquid stream tends to condense the heavy constituent from the vapor. This liquid stream travels from the top tray to the bottom of the column, gradually increasing in the heavy component at each tray. The liquid is then collected by a pump at the bottom of the column, sent to a reboiler where it is partially vaporized (steam is usually employed as the heating medium) and returned to the column to provide an ascending vapor stream in the section of the column below the feed plate. The vapor generated by the reboiler is referred to as the *boil-up*. The other portion of the reboiler liquid is removed as the *bottoms product*. Analogous to the reflux ratio, the *boil-up ratio*, R_B, is defined as the molar flow ratio of vapor generated by the reboiler to bottoms product.

Rectification and Stripping

The vapor stream generated in the reboiler passes up through the portion of the column below the feed tray (the tray onto which the feed stream is admitted). The portion of the column below the feed tray (and including the feed tray itself) is known as the *stripping section*. Upon reaching the top of the stripping section, the rising vapor enters the portion of the column above the feed tray, referred to as the *rectification section*. As this rising vapor stream contacts the descending liquid stream on each plate, its concentration of the lighter component is increased. As previously indicated, the vapor exits from the top of the column and passes into the condenser. The coolant is normally water; however, other cooling fluids may be utilized when the situation warrants. (Additional information on condenser coolant will be discussed shortly.)

As seen in Figure 9.8, which can be compared to the laboratory unit in Figure 9.7, the rectification section is the portion of the column above the feed tray. In this section, there are n-trays; the first tray (tray 1) is at the very top, onto which the reflux is introduced, and the nth tray (tray n) is the tray above the feed tray. In reality, the liquid and

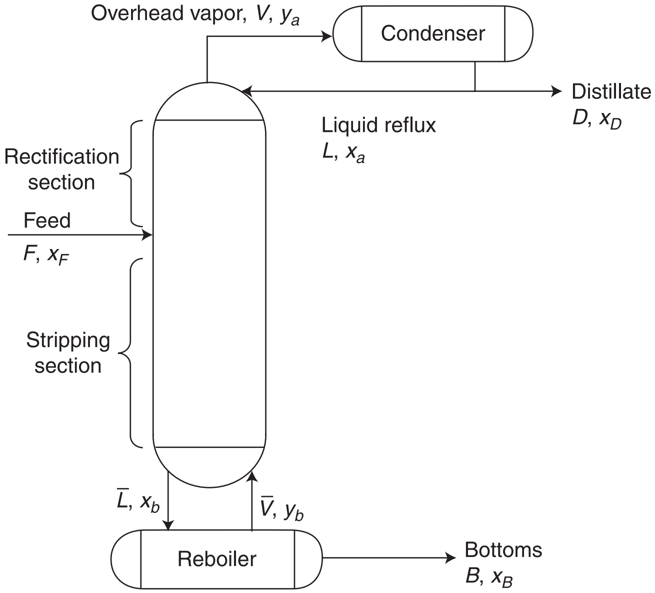


Figure 9.8 Schematic of a trayed distillation column.

vapor molar flow rates each vary from plate to plate because of inevitable differences in the molar enthalpy of vaporization between the light and heavy components. The vapor and liquid molar flow rates leaving the *i*th tray in the rectification section are denoted V_i and L_i with concentrations y_i and x_i, respectively (refer to Fig. 9.9).

Similarly, the stripping section is the portion of the column below the feed tray. The stripping section is said to have *m*-trays (including the feed tray). Thus, the total number of trays in the column is $N = n + m$. The vapor and liquid molar flow rates in the stripping section are differentiated from those in the rectification section by using an overbar. For instance, the vapor and liquid molar flow rates leaving the *j*th tray in the stripping section are denoted $\overline{V}_j$ and $\overline{L}_j$ with concentrations y_j and x_j, respectively.

A column may consist of one or more feeds and may produce two or more product streams. Any product drawn off at various stages between the top and bottom are referred to as *side streams*. Multiple feeds and product streams do not alter the

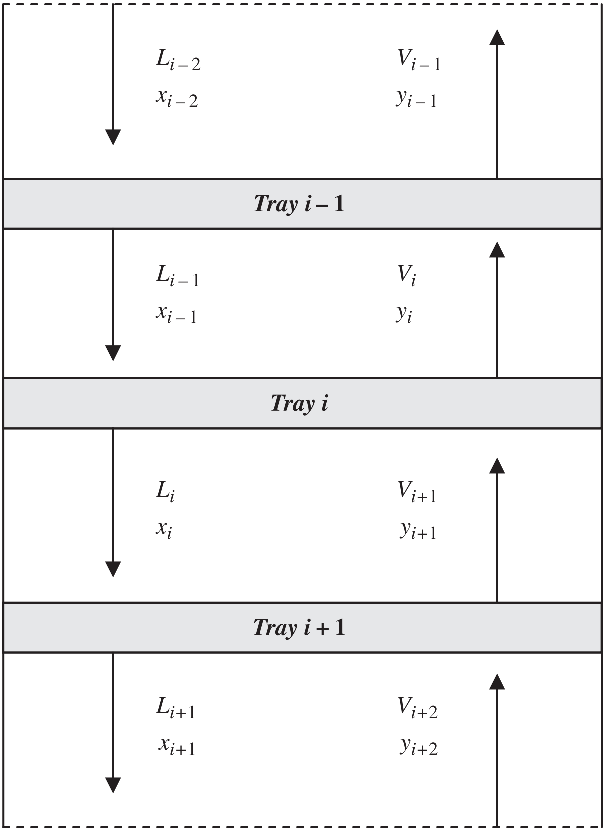


Figure 9.9 Qualitative examination of rectification trays.

basic operation of a column, but they do complicate the analysis of the process to some extent. Not all distillation columns contain both a rectification and stripping section, depending on its prospective use. For instance, if the process requirement is to strip a volatile component from a relatively nonvolatile solvent, the rectification section may be omitted; the unit is then referred to as a *stripping column*.

Tray Designs

Many tray designs are in use today, but one of the early favorites was the *bubble-cap tray* shown qualitatively in Figure 9.10. The descending liquid stream arrives on the plate via the downcomer which can be a short piece of pipe welded into position on the plate or simply a fraction of the plate which has been cut away. While several flow patterns are possible, the liquid generally is guided by the downcomer onto one side of the circular bubble-cap tray below, flows across the middle "capped" section of the tray and leaves by the next downcomer. This flow pattern is referred to as *single crossflow*; the details of various other flow patterns are available in the literature.(7) Referring to Figure 9.10, it is evident that the length of downcomer pipe protruding above the plate fixes the maximum depth of liquid on a tray. It thus acts as an *overflow weir*, which will be discussed shortly. The exit to each downcomer must be located below the liquid level on the plate below to create a vapor lock, preventing vapor from rising in the downcomer.

The contacting device on a bubble-cap tray is the bubble cap, which consists of two parts—the riser and the cap. The riser is a short piece of pipe welded in place

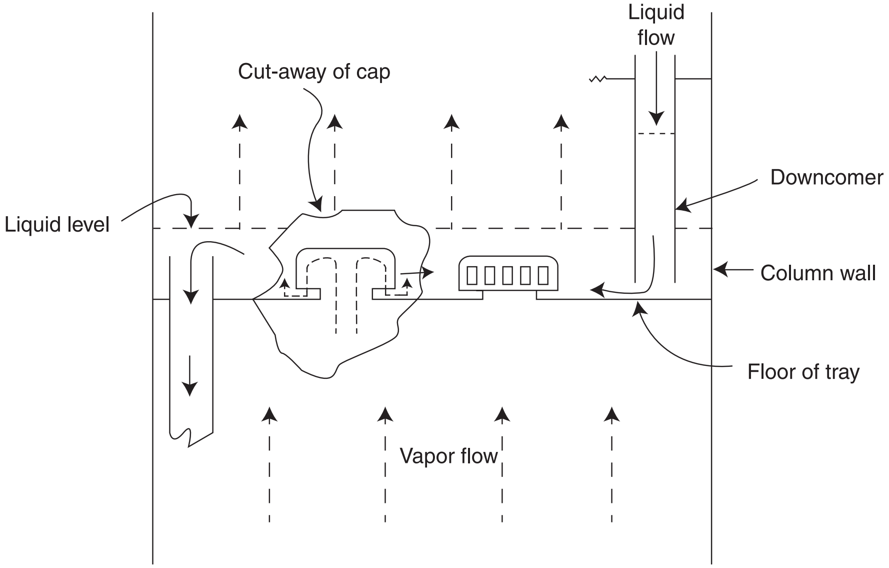


Figure 9.10 Simplified bubble-cap tray.

over a hole in the plate. The cap, which surrounds the riser, is a bell-shaped piece containing vertical slots around the lower periphery. The liquid level on the tray should be maintained so as to submerge each cap, which also ensures a vapor lock between trays. The vapor flows upward through the riser, makes a 180° turn, and is forced under the cap and through the slots to produce intimate contact with the liquid. In order for the vapor to ascend properly, the pressure drop over a given plate must be slightly greater than the head of liquid on said plate.

Another type of tray is the *sieve tray*, which simply consists of a perforated metal plate that has about a 10–15% portion of its cross sectional area removed in order to provide a downcomer (see Figs. 9.11–9.12). A short metal "dam" at the end of the tray acts as an overflow weir which maintains the liquid height and guides the flowing liquid off of the plate and into the downcomer. In this arrangement, the vapor rises from the tray below and passes up through small holes in the tray above. The downcoming liquid flows across this plate and is allowed to achieve intimate contact with the rising vapor. The vapor and liquid come together and are engaged vigorously to form froth. This contact allows for increased rates of mass transfer between phases. Once again, the vapor becomes enriched in the more volatile component while the liquid becomes enriched in the less volatile component.

Information on the third major type of tray, the *valve tray*, is available in the literature.(3)

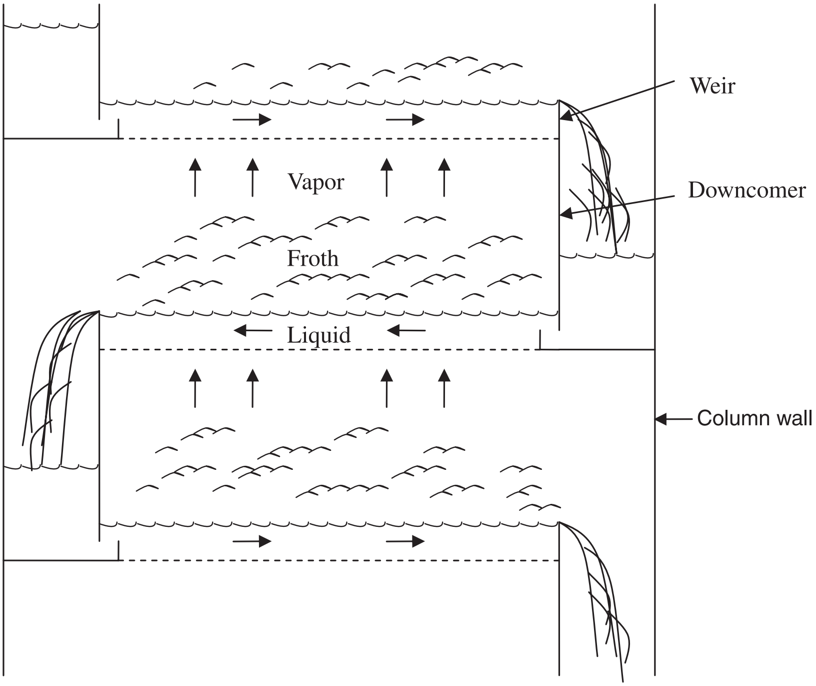


Figure 9.11 Sieve tray column (single crossflow).

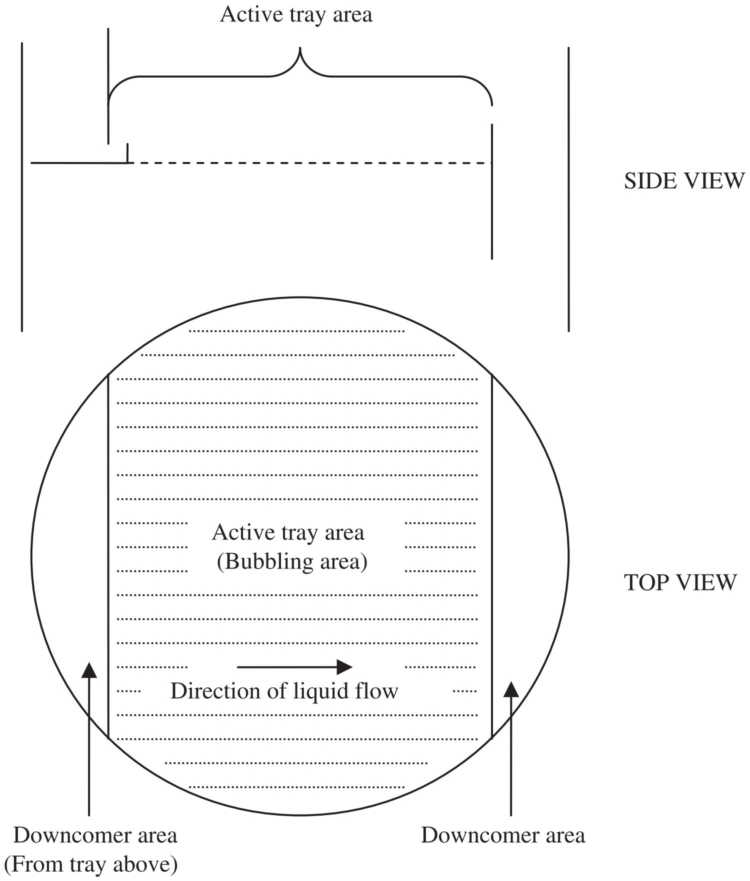


Figure 9.12 Sieve tray column (single crossflow).

Procedures for designing trays involve two major stages: a basic design procedure, and a detailed mechanical layout of the components for the trays. In the first stage, the following design parameters are usually established:

1. Tray diameter and area
2. Type of tray
3. Bubbling area and hole area
4. Hole diameter for sieve trays, key dimensions for bubble caps, and the type of valve in the case of valve trays.

In the second stage, factors such as tray layout and mechanical design are set.

Pressure Drop and Flooding

There are numerous semi-empirical equations that are available for predicting the pressure drop across tray columns. As a *preliminary* estimate, one may assume the pressure drop is given by the height of liquid supported on the tray. Typically, this liquid height is in the 4–6 inch range. Therefore, a reasonable approximation for pressure drop may be 4–6 inches of H_2O per tray, which is approximately 0.1–0.2 psi per tray. The lower value applies to smaller diameter columns and the upper value applying to larger diameter units.(8)

It is important that the vapor stream has the correct superficial velocity (linear average velocity, calculated as if the column conduit was empty) as it flows upwards in the column. Should the vapor flow too slowly, liquid may pass down through the tray perforations instead of over the weir, a condition known as *weeping*. However, if the vapor has a velocity that is too high, some liquid may be carried from the froth to the tray above by the rapidly flowing vapor. This condition is known as *entrainment*. Should the vapor velocity be increased further, entrainment may become excessive such that the liquid level in the downcomer will reach the plate above. At this point, liquid flow from the tray(s) in question becomes hindered, and the column's *entrainment flooding point* has been reached. When calculating the allowable superficial velocity of a vapor, certain effects such as the foaming tendency of a distillation mixture are often taken into account, as foaming increases the likelihood of entrainment. Both excessive entrainment and weeping greatly influence tray efficiency, and negatively impact overall column performance.

Condensers and Reboilers

In some operations where the top product is required as a vapor, the liquid condensed is sufficient only to produce reflux to the column, and the condenser is referred to as a *partial condenser*. In a partial condenser, the reflux will be in equilibrium with the vapor leaving the condenser, and the condenser is considered to be a theoretical stage (an equilibrium stage) when estimating the column height. However, in actual practice it may be advisable not to rely on the action of a partial condenser as an extra stage, but instead to add extra plates to the column in order to effect the desired separation. In contrast, when the vapor is totally condensed, the liquid returned to the column will have the same composition as the distillate product and the condenser is not considered to be a theoretical stage.

A partial reboiler is generally used at the bottom of the column in order to operate the column and produce vapor which flows upwards through the stripping section and into the rectification section. The liquid in the reboiler generally exits as bottoms product. Since both the liquid and vapor are considered to be in thermodynamic equilibrium, the partial reboiler is usually considered a theoretical stage.

Equilibrium Considerations

At this point in the development, each tray in the column is assumed to approach equilibrium conditions, so that the liquid and vapor leaving each tray are in perfect thermodynamic equilibrium. In other words, the contact between the liquid and vapor on a tray is assumed sufficient such that the vapor leaving said tray has the same composition as vapor in equilibrium with the liquid overflow from the tray. This simplifying design assumption defines each tray as a *theoretical* (*ideal*) *tray*, or a *theoretical stage*. Referring to Figure 9.9, V_i and L_i are in thermodynamic equilibrium such that $y_i = K_i x_i$. Distillation columns designed with this simplifying assumption in mind serve as a standard for comparison to actual columns. It is then possible to determine the number of actual trays that is equivalent to a theoretical tray, and by such comparisons, apply this information when designing real columns.

In the case of a binary mixture, the aforementioned equilibrium curve may be constructed by either of two methods. The first method is more general, but also more rigorous. It consists of either empirically measuring *vapor–liquid equilibrium* (VLE) data (such as x, y composition data) in the laboratory, or calculating the data based on thermodynamic VLE equations such as Henry's and Raoult's law, the Wilson equation, the NRTL equation, etc.(2,9) This method is considered more rigorous because it requires compiling a table of x, y values from the aforementioned VLE equations.

The second method is much simpler in application; however, it applies only to ideal mixtures. Note that, while the ideality of a gaseous mixture is determined based on the pressure of the system, a liquid mixture may be considered nearly ideal when each constituent has similar chemical properties (i.e., similar molecular weight, structure, reactivity, etc.) such as isomers or organic species of the same homologous series. This second method employs the relative volatility, defined earlier in Equation (9.1):

$$\alpha_{AB} = \frac{K_A}{K_B} = \frac{y_A/x_A}{y_B/x_B} \tag{9.14}$$

where y_i, x_i = vapor and liquid mole fractions of component i at equilibrium.

For binary mixtures, subscripts are usually omitted for convenience, and all mole fractions refer to the more volatile component, such that

$$\alpha_{AB} = \frac{y/x}{(1-y)/(1-x)} \tag{9.15}$$

where y, x = mole fractions of the lighter component (A) at equilibrium and $(1-y)$, $(1-x)$ = mole fractions of the heavier component (B) at equilibrium.

Equation (9.15) may be rearranged into a more convenient form, which relates y as a function of x:

$$y = \frac{\alpha_{AB}\, x}{1 + (\alpha_{AB} - 1)x} \tag{9.16}$$

This simple formula may be used for ideal mixtures in order to quickly plot an equilibrium curve, assuming α is known and relatively *constant* over the temperature range encountered in the column. When Raoult's law applies, the relative volatility between two compounds is given by a ratio of the vapor pressures of each component. While vapor pressure is a strong function of temperature, the ratios of vapor pressures do not vary as much with temperature change.

Constant Molal Overflow

As previously mentioned, the liquid and vapor molar flow rates do in fact vary from tray to tray in an actual column. However, a major simplifying assumption which is readily employed in continuous distillation calculations is that the liquid and vapor molar flow rates are invariant within the rectification section, and are also invariant (though perhaps of different values) in the stripping section as well. Examining Figure 9.9, the subscripts on V_i, L_i, V_{i+1}, etc., may all be dropped such that the liquid and vapor molar flows for the rectification section are L and V, respectively, while the liquid and vapor molar flow rates in the stripping section are $\overline{L}$ and $\overline{V}$, respectively. This condition is referred to as *constant molal overflow*, and it is an accurate assumption to make when the components to be separated are chemically similar, with approximately similar molar enthalpies of vaporization.

Taking benzene and toluene as an example, benzene's molar latent heat of vaporization is 7360 cal/gmol, whereas toluene's molar latent heat of vaporization is 7960 cal/gmol. Thus, for every 1.0 moles of toluene that is condensed from vapor to liquid, 1.08 moles of benzene may be vaporized, maintaining quasi-constant liquid and vapor molar flow rates in each section of the column.

Without assuming constant molal overflow, the column's operating lines would be non-linear, and enthalpy balances would be required in order to perform design calculations. However, constant molal overflow, when combined with other simplifying assumptions, serves as one of the basic principles that allows simple graphical and analytical methods to be employed to determine the number of theoretical stages in a binary column.

Binary Distillation Design: McCabe–Thiele Graphical Method

When designing a binary distillation column, laborious tray-by-tray thermodynamic calculations may be circumvented by utilizing the McCabe–Thiele graphical method. The major simplifying assumptions which are generally employed with the McCabe–Thiele method are:

1. each tray, a partial condenser and/or partial reboiler all serve as theoretical stages,
2. constant molal overflow applies, and
3. Raoult's law is valid.

While these assumptions are not necessary for completing the graphical sizing of a column, they vastly simplify quick-sizing procedures for ideal or near-ideal systems.

Note that assumption (3) is the assumption most subject to question; however, it may be circumvented by obtaining more accurate equilibrium data.

The aforementioned assumptions allow one to determine several important design parameters by simply constructing a McCabe–Thiele diagram. These parameters include the number of theoretical stages, the minimum number of theoretical stages, and minimum reflux ratio. This method is perhaps the most easy to learn and apply to binary systems since it does not require iterative calculations, nor does it include enthalpy balances (though it may be modified to include them when constant molal overflow is not assumed). In fact, this approach is fundamentally a convenient graphical representation of more drawn out calculations.

Calculation of Operating Lines

As previously discussed, an equilibrium curve may be developed to describe the equilibrium relation between the liquid and vapor components leaving each stage. However, in the graphical design of a staged column, it is necessary to develop an operating line which relates the passing liquid and vapor streams between each stage. In effect, it is the operating line that provides a mathematical relationship describing the operating conditions within the column. The following analysis will develop operating lines for both the rectification section and the stripping section.

To accomplish the following analysis, refer to Figure 9.13. An overall material balance is written for envelope I in the rectification section as:

$$V = L + D \tag{9.2}$$

This equation relates the vapor (V) flowing up the column, the liquid reflux (L) flowing down the column, and the distillate (D) collected. A componential material balance for the light component, A, is written as

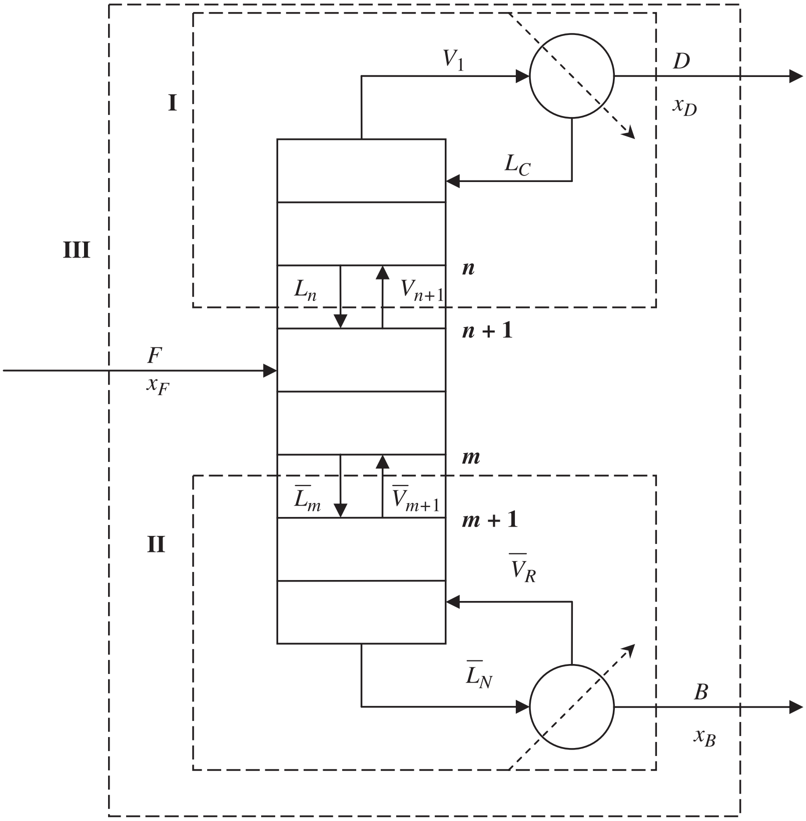
$$Vy_{n+1} = Lx_n + Dx_D \tag{9.17}$$

This can be rearranged to form the equation of a straight line, $y = mx + b$,

$$y_{n+1} = \frac{L}{V}x_n + \frac{D}{V}x_D \tag{9.18}$$

where L/V = the slope of the operating line [dimensionless].

The value L/V is defined as the *internal reflux ratio*, which is the ratio of the liquid reflux molar flow (returned to the top of the column) to the vapor molar flow (exiting the top of the column). By substituting Equation (9.2) into Equation (9.18), then dividing both the numerator and denominator of the terms on the right-hand side by the distillate flow, D, and finally substituting in the definition of the reflux ratio,



I – Material balance around rectification section.
II – Material balance around stripping section.
III – Material balance around column.

Figure 9.13 Material balances around a distillation column.

$R = L/D$, one obtains

$$y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1} \tag{9.19}$$

which is the final result for the operating line of the rectification section.

The corresponding operating line for the stripping section may be developed in a similar manner. The overall material balance around envelope II in the stripping section is

$$\overline{L} = \overline{V} + B \tag{9.20}$$

A componential balance on the lighter component in the stripping section may be rearranged to form an equation analogous to that of Equation (9.18). Note once again that the overbars are reminders that the flow is occurring in the stripping section:

$$y_{m+1} = \frac{\overline{L}}{\overline{V}} x_m + \frac{B}{\overline{V}} x_B \tag{9.21}$$

By performing similar substitutions, and by utilizing the definition of the boil-up ratio, $R_B = \overline{V}/B$, an equation analogous to that of Equation (9.19) may be developed:

$$y_{m+1} = \frac{R_B + 1}{R_B} x_m + \frac{x_B}{R_B} \tag{9.22}$$

which is the final result for the operating line of the stripping section.

Thermal Condition of the Feed (q-factor)

The thermal condition of the feed has a major impact on how a column operates. It has been found advantageous to represent the effect of the thermal condition of the feed graphically on a McCabe–Thiele diagram.(10) If the feed is subcooled, it will condense some of the vapor rising through the stripping section; if it is superheated, it will evaporate some of the liquid cascading down the rectifying section. In most applications, the feed is either a saturated liquid, saturated vapor, or a saturated two-phase mixture. Therefore, only these three scenarios will receive a detailed treatment in this text.

Figure 9.14 illustrates the operation of a standard feed tray with a saturated feed, where F_L is the molar flow rate of the liquid portion of the feed and F_V is the molar flow

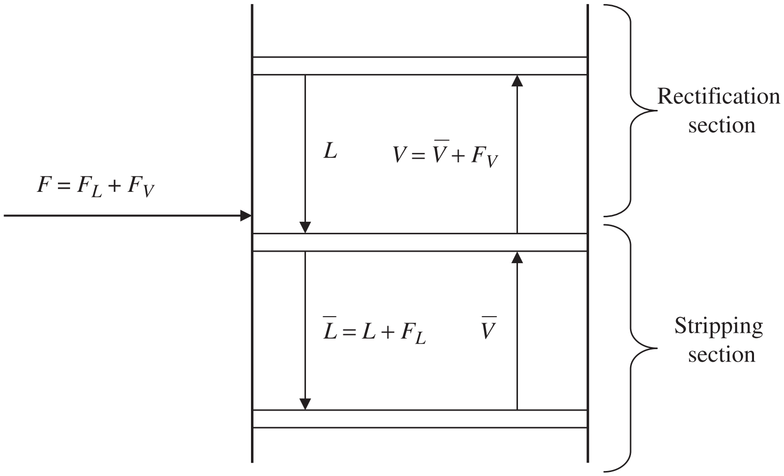


Figure 9.14 Action on a feed tray: saturated feed.

rate of the vapor portion of the feed. For the purposes of this discussion (as noted above), the feed stream may be saturated liquid ($F_V = 0$), saturated vapor ($F_L = 0$), or a saturated two-phase mixture ($F = F_L + F_V$). When the feed is a saturated liquid ($F_V = 0$) and has an enthalpy equal to that of the mixture on the feed plate, the feed will flow completely into the stripping section such that $V = \overline{V}$ and $\overline{L} = L + F_L$. When the feed is a saturated vapor ($F_L = 0$), the feed will completely flash into the rectification section such that $\overline{L} = L$ and $V = \overline{V} + F_V$. When the feed is a saturated two-phase mixture ($F = F_L + F_V$), the resulting liquid and vapor streams leaving the feed tray are given by $\overline{L} = L + F_L$ and $V = \overline{V} + F_V$, respectively.

One can now define a factor which may be used to quantitatively represent the thermal condition of the feed on a McCabe–Thiele diagram. An overall material balance around the feed tray is given by,

$$F + \overline{V} + L = V + \overline{L} \tag{9.23}$$

Rearranging,

$$F + (\overline{V} - V) = (\overline{L} - L) \tag{9.24}$$

An enthalpy (H) balance, neglecting heat losses to the surroundings and any enthalpy of mixing effects, yields

$$FH_F + \overline{V}H_{\overline{V}} + LH_L = VH_V + \overline{L}H_{\overline{L}} \tag{9.25}$$

where H_i = molar enthalpy of stream i at the stream's temperature and pressure about the feed tray.

Since $H_V \approx H_{\overline{V}}$ and $H_L \approx H_{\overline{L}}$, Equation (9.25) becomes

$$FH_F + H_V(\overline{V} - V) = H_L(\overline{L} - L) \tag{9.26}$$

Substituting $(\overline{V} - V)$ from Equation (9.24) into Equation (9.26), one may rearrange the resulting equation to define the *feed condition factor*, q:

$$q = \frac{\overline{L} - L}{F} = \frac{H_V - H_F}{H_V - H_L} \tag{9.27}$$

Note that the term q was employed earlier to represent the volumetric flowrate.

The factor q is defined as the moles of liquid flowing in the stripping section which *resulted from* one mole of feed entering the column. For example, when the feed is a saturated liquid, each mole of feed entering the column adds directly to the stripping section's liquid flow. Hence, the q factor is equal to unity. Conversely, when the feed is a saturated vapor, each mole of feed entering the column adds directly to the vapor flowing up the rectification section. In this case, none (of the one mole) of the feed adds to the stripping section's liquid flow and the q factor is equal to zero. By substituting $\overline{L} = L + F_L$ into Equation (9.27), the L terms cancel, leaving the result that for any type of *saturated feed*, $q = F_L/F$, which is equivalent to the fraction of the feed that is liquid.

In the case of a subcooled liquid feed, the value of q is determined by:

$$q = 1 + \frac{\overline{C}_{P,L}(T_b - T_F)}{\lambda} \tag{9.28}$$

where T_F = the temperature of the feed, T_b = the bubble point temperature of the feed, $\overline{C}_{P,L}$ = average constant pressure heat capacity of the liquid feed, and λ = latent enthalpy of vaporization of the feed at T_F. Ensure that consistent units are employed throughout.

Analogously, the value of q may be calculated for a superheated feed by Equation (9.29),

$$q = -\frac{\overline{C}_{P,V}(T_F - T_d)}{\lambda} \tag{9.29}$$

where T_d = the dew point temperature of the feed and $\overline{C}_{P,V}$ = average constant pressure heat capacity of the vapor feed.

Note that some practitioners prefer to employ a factor, *f*, defined as:

$$f = 1 - q \tag{9.30}$$

Values of q and f are summarized and provided in Table 9.5.

Table 9.5 Values of q and f for the Five General Feed Conditions

Feed condition	q	f
Subcooled liquid	>1	<0
Saturated liquid	1	0
Saturated 2-phase mixture	$>0, <1$	$>0, <1$
Saturated vapor	0	1
Superheated vapor	<0	>1

The term q also defines the point of intersection between the two operating lines on the McCabe–Thiele diagram. The operating line equations at the point of intersection are:

$$Vy_n = Lx_{n-1} + Dx_D \tag{9.31}$$

for the rectification section and

$$\overline{V}y_m = \overline{L}x_{m-1} + Bx_B \tag{9.32}$$

for the stripping section. Letting ($y_n = y_m = y$), ($x_{n-1} = x_{m-1} = x$) at the feed point, and subtracting the latter equation from the former gives (omitting subscripts)

$$y(V - \overline{V}) = x(L - \overline{L}) + Dx_D + Bx_B \tag{9.33}$$

An overall componential balance on the column gives

$$Fx_F = Dx_D + Bx_B \tag{9.34}$$

such that,

$$y(V - \overline{V}) = x(L - \overline{L}) + Fx_F \tag{9.35}$$

Since $(L - \overline{L}) = -qF$ and $(V - \overline{V}) = F(1 - q)$, substituting into Equation (9.35) yields

$$Fy(1 - q) = x(-qF) + Fx_F \tag{9.36}$$

which may be rearranged to give

$$y = \frac{q}{q-1}x - \frac{x_F}{q-1} \tag{9.37}$$

For a given feed condition (x_F and q are fixed), Equation (9.37) plots as a straight line on the McCabe–Thiele diagram and is referred to as the q-line. Substituting x_F for x in Equation (9.37) results in $y = x_F$, indicating that the q-line crosses the $y = x$ diagonal line at the point (x_F, y). The two operating lines and the q-line intersect at a common point which is generally taken to be the feed tray location. Examples of the slope and y-intercept for the five general feed conditions in Table 9.5 are summarized and provided in Table 9.6.

Table 9.6 Values of q-line Slope and Intercept for the Five General Feed Conditions

Feed condition	q-line slope	y-intercept
Subcooled liquid	$<\infty$, >1	<0
Saturated liquid	∞	∞
Saturated 2-phase mixture	<0	$>x_F$
Saturated vapor	0	x_F
Superheated vapor	>0, <1	>0, $<x_F$

A q-line for each of the above five general cases is plotted in Figure 9.15. It should be noted that for a given rectification operating line, decreasing the enthalpy of the feed increases q, which will change the number of theoretical stages required in each section. For example, it can be shown that with an increasingly superheated feed, a larger number of trays are required in the rectification section as opposed to the stripping section. In the case of an increasingly sub-cooled liquid feed, more trays are required in the stripping section.

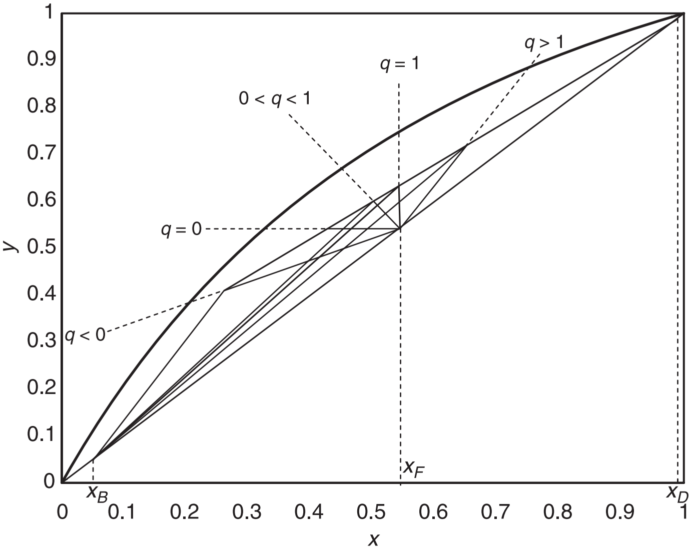


Figure 9.15 Examples of q-lines.

Graphical Location of the Feed Tray

The optimum theoretical feed plate is identified as the step on the McCabe–Thiele diagram which straddles the intersection of the two operating lines. Figure 9.16 represents a typical McCabe–Thiele diagram, the details of which will be explained in the next section. Notice that since the q-line is vertical, the feed is a saturated liquid, and thus the feed must be introduced on the seventh theoretical tray from the top of the column. In any application, the feed should be introduced on the tray where it will cause the least change in concentration of the process streams. This almost always means that the tray which crosses the q-line is designated the *feed tray*. Failure to observe this rule will result in extra "work" for the column, i.e., extra theoretical stages will be required for the separation.

Minimum Number of Theoretical Stages: Total Reflux

The notion of *total* (*infinite*) *reflux* is used in order to determine the theoretical minimum number of stages possible for a given separation. At this condition, the reflux ratio, $R = L/D$ is set equal to infinity since the distillate flow approaches zero. The boil-up ratio, $R_B = \overline{V}/B$ also becomes infinity since the bottoms flow approaches zero. As a result, the feed flowrate, F, also equals zero.

At total reflux, the number of trays in the column achieves its minimum value. The physical interpretation for this occurrence is that, as the amount of reflux and boilup increases, the ability of the column to perform rectification and stripping is enhanced. This increased rectification and stripping results in needing less trays for the liquid and vapor streams to contact on. In the limit, at total reflux, the number of trays necessary reaches its minimum value.

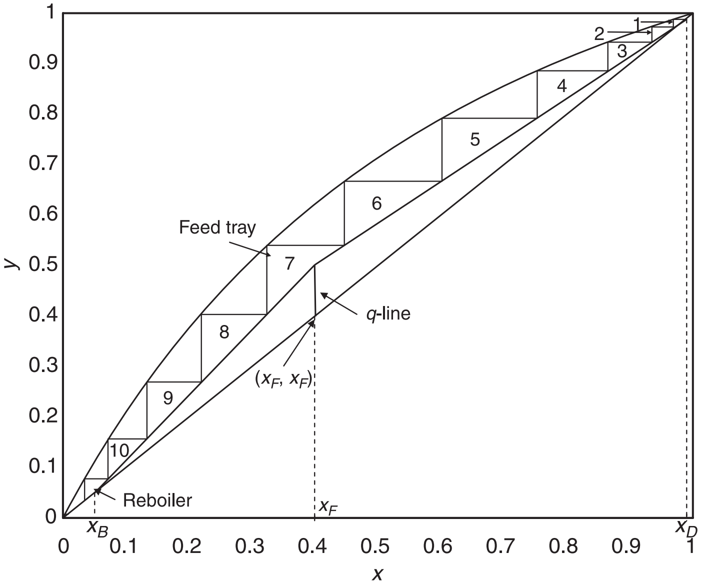


Figure 9.16 Typical McCabe–Thiele diagram.

In order to appreciate the graphical interpretation of this phenomena, one should first note that each of the triangles formed between the equilibrium curve and the operating line on a McCabe–Thiele diagram represents one theoretical stage (see Fig. 9.16). As R and R_B approach infinity, Equations (9.19) and (9.22) both approach $y_{n+1} = x_n$. Hence, the operating lines for both the rectification and stripping section "collapse" to the line $y = x$. As a result, the q-line disappears, and the theoretical stages are stepped off between the equilibrium curve and the 45° line producing the minimum number of theoretical stages. Because the flow rates of the feed, distillate and bottoms are all zero when operating under total reflux, this minimum number is not used in actual applications; instead, it should be viewed as representing a limiting case.

Minimum Reflux Ratio

The case of *minimum reflux ratio* (R_{min}) represents the alternative extreme of total reflux. At this condition, the reflux ratio is at its lowest possible value. Hence, the rectification and stripping abilities of the column are diminished to such a point that it would take an infinite number of trays above and below the feed tray in order to effect the desired separation of products. Once again, this analysis is simply a limiting case; however, it is a concept of great importance in distillation column design.

Heat Duty

In addition to mole balances, one may also perform energy balances across parts of the system. The duty of the condenser can be calculated with the knowledge of the flow rate of coolant (usually water) entering the condenser plus the inlet and outlet temperatures. From a design point of view, the duty may be calculated based on the enthalpy change of the condensing vapor, assuming that the temperature at the top of the column, along with the distillate temperature and pressure are fixed.

The condenser heat duty for a total condenser (in a column with light component A, and heavy component, B) may be calculated by assuming that the condenser is adiabatic. First note that enthalpy is a *state function*,$^{(2)}$ and therefore, the change in enthalpy is independent of the actual process path. As a result, if the entering vapor stream at T_1 is condensed and cooled to T_2, it does not matter thermodynamically whether the condensation took place at T_1, T_2, or any temperature in between. Therefore, one may assume that the vapor condenses at T_1, which is the temperature at the top tray of the column. This saturated liquid is then cooled further to T_2 which is the condenser's exit temperature, T_C (look ahead to Fig. 9.19 for a qualitative condenser schematic).

By performing an enthalpy balance around the total condenser, the condenser heat duty, Q_C, is equal to the enthalpy change of the condensing vapor stream. Thus,

$$Q_C = V[x_D(\lambda_A + \overline{C}_{P,L(A)}(T_1 - T_2)) + (1 - x_D)(\lambda_B + \overline{C}_{P,L(B)}(T_1 - T_2))] \tag{9.38}$$

where $\overline{C}_{P,L(i)}$ = average molar heat capacity of liquid component i (constant P), λ_i = molar latent enthalpy of vaporization of i at T_1.

Assuming sensible enthalpy changes are negligible, the heat load may be calculated by summing the latent enthalpy contributions of each species:

$$Q_C = V[x_D\lambda_A + (1 - x_D)\lambda_B] \tag{9.39}$$

The molar flow rate of vapor may be found from the material balance:

$$V = D + L \tag{9.40}$$

Utilizing $R = L/D$, one may substitute $L = RD$ to obtain,

$$V = D(R + 1) \tag{9.41}$$

Lastly, the distillate flow, D, may be calculated when the distillate and bottoms compositions are specified. Equation (9.42) is a result of combining the total and componential material balance equations on the column:

$$\frac{D}{F} = \frac{x_F - x_B}{x_D - x_B} \tag{9.42}$$

The condenser heat duty may now be readily calculated from either Equation (9.38) or Equation (9.39).

Once the theoretical reboiler temperature is calculated, one may calculate the reboiler duty, the mass flow rate of heating medium (usually steam) entering the reboiler, and the inlet/outlet temperatures of the steam and/or the required heat exchanger area. A more thorough presentation of how to set the column temperatures and pressures is provided in the section on multicomponent distillation.

Constructing a McCabe–Thiele Diagram

A detailed step-by-step procedure for designing a binary (trayed) distillation column via the McCabe–Thiele graphical method is provided below. In order to construct a McCabe–Thiele diagram, certain simplifying assumptions are generally made:

1. Each tray acts as an ideal stage, from which the exiting vapor and liquid are in thermodynamic vapor–liquid equilibrium.
2. *Constant molal overflow* applies (to circumvent enthalpy balances and curved operating lines).
3. Raoult's law is valid (when the binary mixture is ideal).

In order to apply the McCabe–Thiele graphical method, one must first construct a y vs x equilibrium plot. Once an x, y plot is constructed, one should follow these instructions:

1. Plot the line $y = x$ (the 45° line) and locate the exit composition points (x_D, x_D) and (x_B, x_B).
2. Plot the q-line. This line is given by

$$y = \frac{q}{q-1}x - \frac{x_F}{q-1} \tag{9.37}$$

   The q-line is plotted by starting at the point (x_F, x_F) on the 45° line, and extending it until it touches the equilibrium curve.

3. Determine $R_{\min}$ by drawing a straight line between the point (x_D, x_D) and the point at which the q-line intersects the equilibrium curve. This represents the *pinch point* and also corresponds to the minimum reflux ratio at the given feed condition and desired distillate composition. At minimum reflux, the number of ideal trays approaches infinity. The value of $R_{\min}$ may be determined by noting that the y intercept (y_{int}) of this line [given by Equation (9.19)] is,

$$y_{\text{int}} = \frac{x_D}{R_{\min} + 1} \tag{9.43}$$

   which may be rearranged to:

$$R_{\min} = \frac{x_D}{y_{\text{int}}} - 1 \tag{9.44}$$

4. Now that $R_{\min}$ has been determined, the optimum reflux ratio may be calculated with Equation (9.45)

$$R = mR_{\min} \tag{9.45}$$

Table 9.7 Reflux Ratio Optimization Multipliers

Type of coolant	Optimization multiplier, m
Water ($\approx$100°F)	1.3
Refrigerant ($<$100°F)	1.1
Air (hot conditions)	1.5

where $m =$ an optimization multiplier (which, of necessity is always >1.0)
$R =$ the optimum reflux ratio

The value of m is generally dependent upon the type of cooling fluid used in the condenser. Three pertinent values are provided in Table 9.7. These values are approximations, which have been based on both economic considerations and experience. More detailed tabulations and methodologies are available in the literature.(6)

5 Having determined the optimum value of R, the rectification section operating line (ROL) may be drawn. The simplest way of graphing this line is to first calculate its y-intercept, given by

$$y_{\mathrm{int(ROL)}} = \frac{x_D}{R+1} \tag{9.46}$$

A straight line is then drawn between this y-intercept and the point (x_D, x_D).

6 The last portion of the diagram's basic "frame" is the stripping section operating line (SOL). The simplest way to construct this line is to draw a straight line between (x_B, x_B) and the point where the ROL intersects the q-line.

7 The best course of action at this point is to erase/delete all lines and segments of lines which may be discarded. This includes the portions of the ROL and q-line which extend past the locus where the q-line, ROL, and SOL all intersect. One should also delete the minimum reflux operating line that intersects the q-line at the pinch point.

8 With the basic outline prepared, it is simply a matter of drawing the rectification stages, starting at point (x_D, x_D) and continuing horizontally leftward, until the line reaches the equilibrium curve. At this point, the next line segment should continue straight down (perpendicular to the previous line segment, until it reaches the ROL). This first triangle represents one ideal stage in the binary distillation column. This procedure is repeated (creating a series of triangles between the equilibrium curve and the ROL), until the intersection point of the ROL, SOL, and q-line is reached. Once a tray *crosses* this locus, the *first possible* vertical line segment should be drawn down to the SOL line. The tray at which the line segments switch from ROL to SOL is designated as the feed tray. After this point, all subsequent trays are drawn between the SOL and the equilibrium curve. The last theoretical tray should be drawn such that it just passes the point (x_B, x_B) since it is a rare occurrence that the bottom tray will achieve the exact bottoms composition.

Note that in the case of a partial reboiler, the last (bottommost) triangle is representative of the reboiler. Should a partial condenser be employed, the first (topmost) triangle is representative of the condenser. Should a total reboiler and/or total condenser be utilized, they are not counted as equilibrium stages, and the corresponding triangles are instead counted as theoretical trays.

The McCabe–Thiele method is quite convenient for the sizing of binary distillation columns. It uses vapor–liquid equilibrium curves to determine the theoretical number of stages required to effect the separation of a binary system. Once again, this method generally assumes constant molal overflow, which implies that molar enthalpies of vaporization of the components are approximately the same, such that for every mole of vapor condensed, one mole of liquid is vaporized. For ideal binary mixtures, Raoult's law is often assumed in order to make vapor–liquid equilibrium calculations easier. Lastly, it is always assumed that each tray, as well as a partial reboiler and/or condenser, acts as a theoretical equilibrium stage in the column. The importance of the McCabe–Thiele graphical method cannot be overstated as a training tool in distillation.

Determining the Minimum Number of Theoretical Stages Graphically

At total reflux, R approaches infinity, and the slope of both the ROL and SOL approach unity (the 45° line). The graphical method for determining the minimum number of trays is the same as that for constructing any McCabe–Thiele diagram, i.e., starting at x_D and stepping off triangular stages between the equilibrium curve and the operating lines, *both* of which have collapsed to the 45° line. Thus, the q-line is eliminated (because there is no feed to the column at total reflux).

Tray Efficiency

In order to determine the actual number of trays, the concept of *tray efficiency* must be introduced. One of the preliminary assumptions in constructing the McCabe–Thiele diagram was that each tray would serve as an equilibrium stage. However, this is generally far from true, since the vapor and liquid contacted on a given tray do not have sufficient contact time to reach thermodynamic equilibrium before leaving the tray. Thus, an *overall efficiency* for the plates in a column can be defined. There are several types of efficiencies, including the *Murphree* (individual tray) *efficiency*, and *local* (location on an individual tray) *efficiency*. However, only the overall efficiency will be discussed here.

The overall efficiency, denoted E_0, generally ranges between 0.4 and 0.8, with an upper limit of unity. Overall efficiency is affected by a host of factors such as the tray type, tray spacing, operating conditions, and so on (see *O'Connell correlation*, Fig. 9.21 for more details). In order to calculate the actual number of trays, the number of ideal trays is divided by the overall efficiency:

$$N_{trays} = \frac{N_{trays,ideal}}{E_0} \tag{9.47}$$

Note that, in the case of the McCabe–Thiele graphical method, $N_{trays,ideal}$ is the number of theoretical stages (represented as triangles on the diagram) minus the partial reboiler and/or partial condenser stage(s).

ILLUSTRATIVE EXAMPLE 9.5

Determine the number of stages required to separate a mixture of benzene and toluene containing 40 mole% benzene into a distillate containing 99 mole% benzene and a bottoms containing 1 mole% benzene. The feed is a two-phase mixture consisting of 50 mole% liquid. The process is carried out at 1 atm, the condenser employs cooling water at 100°F, and the overall column efficiency is approximately 50%. Employ the step-by-step method provided above. Refer to Figure 9.17 for equilibrium data (curve).

***SOLUTION*:** Refer to Figure 9.17 in the development to follow.

1 Plot the line $y = x$ (also known as the 45° line) and locate the exit composition points (x_D, x_D) and (x_B, x_B).

2 Plot the q-line

$$y = \frac{q}{q-1}x - \frac{x_F}{q-1} \tag{9.37}$$

For this particular construction, the feed is a 2-phase mixture, which is 50 mole% liquid. Thus, $q = 0.50$, $x_F = 0.40$, and the q-line equation becomes

$$y = -x + 0.8$$

Once again, this line is plotted by starting at the point (x_F, x_F) on the 45° line, and extending it until it touches the equilibrium curve.

3 The value of $R_{\min}$ may be determined by drawing a straight line between (x_D, x_D) and the point at which the q-line touches the equilibrium curve. Observing the y intercept of this line:

$$y_{\text{int}} = \frac{x_D}{R_{\min} + 1} \tag{9.43}$$

which may be rearranged to:

$$R_{\min} = \frac{x_D}{y_{\text{int}}} - 1 \tag{9.44}$$

Since $y_{\text{int}} = 0.298$,

$$R_{\min} = \frac{0.99}{0.298} - 1$$
$$= 2.32$$

4 Now that $R_{\min}$ has been determined, the optimum reflux ratio may be calculated from Table 9.7:

$$R = 1.3\,R_{\min} \tag{9.45}$$
$$R = 1.3(2.32)$$
$$= 3.02$$

5 The ROL can be drawn using the optimum value of R. The simplest way of graphing this line is to first calculate its y-intercept:

$$y_{\text{int(ROL)}} = \frac{x_D}{R+1} \tag{9.46}$$

$$y_{\text{int(ROL)}} = \frac{0.99}{3.02+1}$$

$$= 0.246$$

Then, a straight line is drawn between this y-intercept and the point (x_D, x_D).

6 Draw the SOL. The simplest way to construct this line is to draw a straight line between (x_B, x_B) and the point where the ROL intersects the q-line.

7 Erase all lines and segments that can be discarded.

8 Step off the theoretical stages.

Number of Theoretical Stages = 18 Trays + Partial Reboiler

Calculate the actual number of trays by dividing the ideal trays by $E_0 = 0.50$:

$$N_{trays} = \frac{N_{trays,ideal}}{E_0} \tag{9.47}$$

$$N_{trays} = \frac{18}{0.50}$$

$$= 36$$

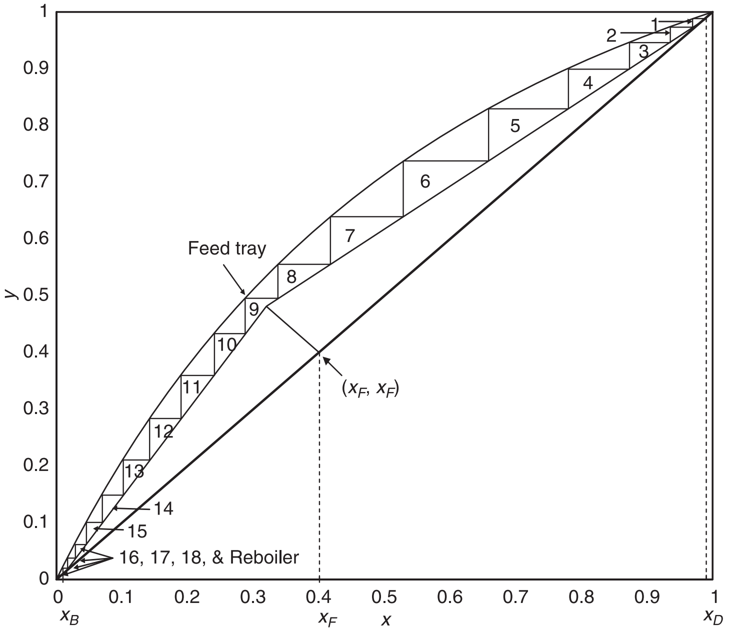


Figure 9.17 McCabe–Thiele diagram—benzene/toluene, 1 atm ($x_D = 0.99$).

The results for this Illustrative Example are summarized below:

Benzene/Toluene system
$P = 1$ atm (absolute)
$x_F = 0.40$
$x_D = 0.99$
$x_B = 0.01$
$R = 1.3R_{\min}$
$q = 0.50$ ($q = F_L/F$, for two-phase mixture)
$E_0 = 0.50$

Number of Required Stages = 36 Trays + Partial Reboiler ■

ILLUSTRATIVE EXAMPLE 9.6

Refer to Illustrative Example 9.5. Calculate the condenser heat duty, neglecting sensible enthalpy effects. The molar latent heat of vaporization for benzene and toluene at the prevailing temperature (at the top of the column) are $\lambda_B = 13{,}251$ Btu/lbmol and $\lambda_T = 14{,}331$ Btu/lbmol, respectively.

***SOLUTION*:** The heat duty for the total condenser is calculated by assuming:

1. sensible enthalpy effects are negligible (in cooling the condensate), and
2. the condenser is adiabatic.

By performing an enthalpy balance around the condenser, the condenser heat duty may be set equal to the enthalpy change of the condensing stream.

$$Q_C = V[x_D\lambda_B + (1 - x_D)\lambda_T] \tag{9.39}$$

However, the vapor molar flow rate must first be calculated. As a result of the material balance:

$$V = D + L \tag{9.40}$$

Noting that $R = L/D$,

$$V = D(R + 1) \tag{9.41}$$

Assuming a basis of 100 lbmol/h of feed:

$$\frac{D}{F} = \frac{x_F - x_B}{x_D - x_B} \tag{9.42}$$

$$D = \left(\frac{0.40 - 0.01}{0.99 - 0.01}\right)(100\,\text{lbmol/h})$$

$$= 39.8\,\text{lbmol/h}$$

Therefore,

$$V = 39.8(3.02 + 1)$$

$$= 160\,\text{lbmol/h}$$

Plugging the necessary values into Equation (9.39):

$$
\begin{aligned}
Q_C &= 160\frac{\text{lbmol}}{\text{h}}\left[0.99\left(13{,}251\frac{\text{Btu}}{\text{lbmol}}\right)+0.01\left(14{,}331\frac{\text{Btu}}{\text{lbmol}}\right)\right]\\
&= 2{,}122{,}000\frac{\text{Btu}}{\text{h}}\\
&= 2{,}122{,}000\frac{\text{Btu}}{\text{h}}\Big/100\frac{\text{lbmol feed}}{\text{h}}\\
&= 21{,}220\,\text{Btu}/\text{lbmol feed}
\end{aligned}
$$

■

ILLUSTRATIVE EXAMPLE 9.7

Once again, refer to Illustrative Example 9.5. Calculate the minimum number of theoretical stages for the given separation.

***SOLUTION*:** The minimum number of theoretical stages is determined by designing the column to operate at total reflux. Recall that, for the condition of total reflux, the ROL and SOL both collapse to the line $y = x$. See Figure 9.18, following a similar procedure to that in Illustrative Example 9.5:

Minimum Number of Theoretical Stages = 10 Trays + Partial Reboiler

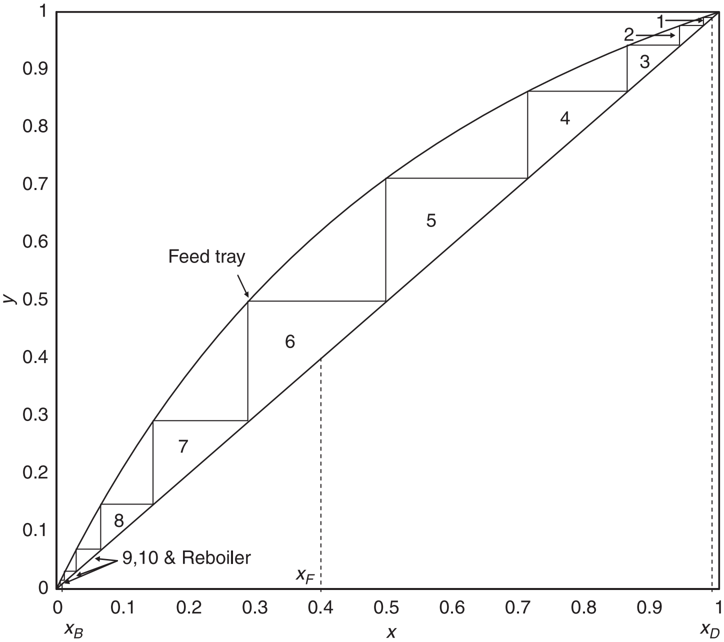


Figure 9.18 McCabe–Thiele diagram (total reflux)—benzene/toluene VLE, 1 atm. ■

Column Diameter

The following discussion regarding column diameter calculation is equally applicable to both binary and multicomponent distillation. Column diameter must generally be calculated before column height since the column diameter affects the choice of tray spacing, which in turn affects column height.

The diameter of a distillation column is generally controlled by the vapor velocity, u. Several factors go into determining an appropriate operating vapor velocity. As previously mentioned, when the velocity is too low in a trayed column, *weeping* occurs. Under these conditions, the liquid passes through the tray perforations instead of frothing and passing over each subsequent overflow weir. Alternatively, should the vapor velocity be too high, the column will experience the aforementioned *entrainment* of liquid from one tray to the tray above. At excessively high vapor velocities, the *entrainment flooding point* may be reached. At this point, the vapor is flowing up the column so rapidly that it effectively prevents the liquid from flowing down the column. Hence, the column will begin to flood with liquid, impacting product purity and perhaps posing a danger to those around the column.

Several correlations have been developed which aid in determining the operational vapor velocity of a column. One such correlation which has withstood the test of time is the Fair flooding correlation (look ahead to Fig. 9.23). This correlation uses data on the liquid and vapor mass flows, mass densities, and surface tension in the general location which is most likely to flood (based in part on feed condition) to determine the flooding velocity, u_F, which may be corrected for foaming considerations. Once corrected, the operating velocity may be calculated. Generally, design engineers may choose a vapor velocity about 60% of the flooding velocity ($u \approx 0.6u_F$). However, the exact value for this fractional *approach to flooding velocity* is left up to the individual protocols for a specific design. Additional details are provided in the next chapter.

The reader should note that, while the values of V and L (which are molar flows) are assumed constant throughout each section of the column, the equivalent mass flow rates of the vapor and liquid streams do in fact vary as their respective molar compositions vary from stage to stage. As molar composition changes, the average molecular weight also changes and hence, the mass flow rate varies even though the molar flow rates are assumed constant. Here, the variation of *mass* flow rates is important because flooding is a fluid mechanics phenomenon, which is more directly related to mass, not moles. As a result, it is important to evaluate certain chemical and physical characteristics (i.e., average molecular weight, density) of the vapor and liquid streams in pertinent sections of the column (i.e., top tray, bottom tray, below and above the feed tray) in order to calculate what the flooding velocity would be in that section.

Once again, flooding correlations such as the Fair flooding correlation are dependent on the liquid and vapor mass flow rates, mass densities and liquid surface tension. Therefore, in calculating the flooding velocity at each section of interest, the local composition, temperature, and pressure must be determined via material balances, and temperature/pressure estimations based on the reboiler and condenser design temperatures. The Fair flooding correlation is demonstrated later in Illustrative Example 9.19 for a multicomponent distillation column.

Once a suitable vapor velocity has been determined, the column diameter may be calculated from the continuity equation, given below:

$$\dot{m} = \rho_V u_B S_B \tag{9.48}$$

where $\dot{m}$ = mass flow rate of vapor, ρ_V = density of the vapor, u_B = vapor velocity (based on bubbling area of tray), and S_B = the *bubbling area* of a given tray.

However, a different form of Equation (9.48) is usually applied in distillation. Dividing the mass flow rate by the density of the vapor yields units of volume per time,

$$q = u_B S_B \tag{9.49}$$

where q = the volumetric flowrate of vapor (not to be confused with the feed thermal condition factor).

The volumetric flowrate of the vapor stream may be determined from the product of molar volume of the vapor (at the local column temperature) and molar flow rate of the vapor, V,

$$q = vV \tag{9.50}$$

where v = molar volume (the inverse of the molar density) of the vapor.

The molar volume of vapor at a given point in the column may be readily approximated by the commonly employed ideal gas law ratio(2):

$$v = v_{std}\left(\frac{P_{std}}{P}\right)\left(\frac{T}{T_{std}}\right) \tag{9.51}$$

where T_{std}, P_{std} = standard temperature and pressure, for which v_{std} is known
v_{std} = molar volume of vapor at T_{std} and P_{std}
T, P = temperature and pressure at the area most likely to flood first
v = molar volume of vapor at T and P

A simple form of the column diameter equation may be expressed as

$$D_{column} = \frac{2}{\sqrt{\pi}}\left(\frac{q}{(1-\eta)u}\right)^{0.5} \tag{9.52}$$

where η represents the fraction of the column cross section which is taken up by one downcomer (e.g., for a tray in which the downcomer accounts for 15% of the column cross section, $\eta = 0.15$). Note that η only represents the area of one downcomer because the aforementioned Fair flooding correlation, and hence the calculated vapor velocity u, is based on a tray's *net area*. Referring to Figure 9.12, the net area is here defined as the bubbling area plus the cross sectional area of *one* downcomer. With other correlations, the actual bubbling area may be the basis, for which $(1-2\eta)$ should be employed in Equation 9.52. The interested reader is referred to the literature for a more detailed analysis.(7,11)

As previously mentioned, different sections of a column have liquid and vapor streams of differing densities, average molecular weights, and mass flow rates. As a result, one should consider calculating the flooding velocity at different points in the column. The location with the *lowest* flooding velocity serves as the limiting vapor velocity in the column, and hence, the column diameter should be calculated based on that velocity. However, it is a common practice to design a distillation column of varying diameter based on calculated flooding velocities in each section of the column. In some instances, the diameter of a column changes about the feed tray, such that the rectification and stripping sections may each be operated at their optimal vapor velocities.

Column Height

Once again, the subsequent discussion of column height applies equally well to binary and multicomponent distillation. Column height is mainly determined by two factors: the number of trays and the spacing between the trays. The number of actual trays necessary may be determined from the overall column efficiency; however, the tray spacing may vary with column diameter as well as the nature of the distillation mixture. Components with a tendency to foam excessively should be allowed greater tray spacing, both to prevent entrainment and, in the case of larger columns, to allow for a technician to climb into the column for maintenance. Typical tray spacings are 18, 24, or 36 inches. Generally, larger tray spacing is employed with increasing column diameter. In certain types of columns such as those which separate liquefied air components at cryogenic temperatures, smaller tray spacings of 4 to 8 inches may be employed.

The bulk of the actual column height is determined by multiplying the number of trays times the tray spacing. After this initial height is determined, various considerations are often employed such as designing a *surge volume* at the bottom of the column which allows the column extra space to collect liquid should a pump malfunction. It is also customary to allow extra space in the column so that more trays may be added if necessary.

Multicomponent Distillation: Fenske–Underwood–Gilliland (FUG) Method

Multicomponent distillation is classified as a distillation in which the feed stream contains more than two components. There are several methods of calculation which have been developed for multicomponent distillation. Among these, there are both *rigorous* and *shortcut* column design methods. In this text, the *Fenske–Underwood–Gilliland* (FUG) shortcut method will be developed. It is important for the reader to note that the FUG method consists of three main parts:

1. the Fenske equation, which calculates the minimum number of theoretical stages and the recoveries of the non-key components,
2. the Underwood equations, which calculate the minimum reflux ratio, and
3. the Gilliland correlation, which allows one to determine the number of theoretical stages necessary to produce a desired separation.

Almost all of the principles which find application in multicomponent distillation may also be applied to the limited case of binary distillation. Hence, the FUG method may be applied to a binary column just as well as it could to a multicomponent mixture. However, the McCabe–Thiele method is often preferred for binary systems due to its simplicity. After the FUG method is explored, additional pertinent correlations are introduced in order to facilitate a complete column quick-sizing. However, before proceeding to the three individual components of the FUG method, some introductory material is discussed.

Multicomponent distillation differs from binary in that the entire composition of the product streams may generally not be defined. When a feed consists of three or more components, it is generally impossible to exactly specify the mole fractions of all the components in the distillate and bottoms, as one can in binary distillation. For instance, if a design engineer was to specify all of the mole fractions in the distillate for a ternary (three-component) mixture consisting of A, B, and C, only one mole fraction specification in the distillate could be met exactly by changing the reflux ratio and/or the number of trays. Suppose that the mole fractions for A, B, and C in the distillate were set as 0.60, 0.25, and 0.15, respectively. When the column is designed such that any one of the above mole fractions is obtained (i.e., $x_{D,A} = 0.60$), the mole fractions in the distillate of components B and C are solely dependent upon the thermodynamics in the column which allowed $x_{D,A} = 0.60$. Any chance of $x_{D,B}$ and $x_{D,C}$ equaling their specified design values would be purely coincidental. Thus, the mole fractions of B and C are independent of the mole fraction of A. In contrast, a specified distillate composition of A for a binary feed would automatically fix the amount of the second component in the distillate. Moreover, the thermodynamics that govern multicomponent vapor–liquid equilibrium is much more complex and often produces intricate concentration profiles. As a result of such difficulties, the practice of sizing and designing actual multicomponent distillation columns is often performed by computer programs, which are iterative in nature. These programs are designed to perform tedious thermodynamic calculations on a stage-by-stage basis, while attempting to converge at the desired result. The FUG method is utilized as an efficient means of quick-sizing a multicomponent column without such computer programs. Indeed, some of the more robust distillation programs need large amounts of user-specified inputs regarding the number of trays, reflux ratio, condenser and reboiler temperatures and pressures, feed tray location, etc. Hence, the FUG method still serves a purpose for obtaining necessary ballpark figures.

Key Components

Since not all of the mole fractions in the distillate and bottoms may be specified, the column designer generally specifies two components whose mole fractions or fractional recoveries in the distillate and bottoms streams will serve as the basis for column design. These two components are referred to as the *key components*, with the more volatile of the two being referred to as the *light key* (LK) and the less volatile of the two being referred to as the *heavy key* (HK). With a feed of n components, any two species may be chosen as the key components. However, it is generally useful to choose a *sharp separation*, for which two components of adjacent volatility are labeled as the keys. Here, the volatilities of each component may be compared by observing their respective normal boiling points. If the components are listed in order of increasing boiling point (decreasing volatility), any two sequential pairs of components are of adjacent volatility.

By choosing a sharp separation, the column will be able to specifically divide the feed between the two adjacent key components. With a proper design, the LK, along with all components lighter than the LK will proceed almost completely to the distillate. Similarly, the HK, and all components heavier than the HK will proceed almost completely to the bottoms. In reality, minute amounts of the component(s) lighter than the LK do end up in the bottoms stream and minute amounts of the component(s) heavier than the HK do end up in the distillate product. Hence, all components (not just the keys) are technically *distributed components*, in that they are distributed between the distillate and bottoms. However, the concentrations are often so small for non-keys that they may be considered insignificant and are assumed to be *undistributed components.*

Generally, unless stage-by-stage calculations are employed in which a *finite* value of each species must be present on each tray, all non-key components may be assumed to be undistributed, assuming that there are no components between the keys (sharp separation). Of course, this is not always the case with multicomponent mixtures, since it is possible that a given component may be more volatile than the average mixture in one part of the column, yet less volatile than the average mixture in another part of the column.(12) Moreover, when non-keys have relative volatilities which are very similar to that of the key components, they may be distributed in some appreciable quantity. Great care should be exercised in making assumptions regarding distribution with non-ideal chemical mixtures. A more detailed example of the undistributed components assumption will be discussed whilst examining the Fenske equation.

ILLUSTRATIVE EXAMPLE 9.8

Assuming a *sharp separation* is desired, suggest any set of key components for the following feed composition:

Component	Feed Mole Fraction
Propane	0.05
n-Butane	0.06
i-Butane	0.06
Hexane	0.20
Heptane	0.23
Nonane	0.40

***SOLUTION*:** The given six feed compounds are already listed in order of increasing boiling point (decreasing volatility). Hence, any two sequential pairs may be chosen as the LK and HK in order to effect a sharp separation. Depending on the desired product streams, the five possible pairs are shown below:

Pair #	LK	HK
1	Propane	n-Butane
2	*n*-Butane	*i*-Butane
3	*i*-Butane	Hexane
4	Hexane	Heptane
5	Heptane	Nonane

■

Fractional Recovery

As previously mentioned, in multicomponent distillation, either the fractional recoveries or mole fractions of the key components may be specified in the distillate and bottoms streams. In this text, specification of the fractional recoveries will take precedence over mole fractions. The most convenient definition of *fractional recovery*, *r*, from a design point of view is expressed in Equations (9.53) and (9.54) for the LK and HK, respectively,

$$r_{\mathrm{LK}} = \frac{Dx_{D,\mathrm{LK}}}{Fx_{F,\mathrm{LK}}} \tag{9.53}$$

$$r_{\mathrm{HK}} = \frac{Bx_{B,\mathrm{HK}}}{Fx_{F,\mathrm{HK}}} \tag{9.54}$$

Note that other authors may define the fractional recovery of the HK, r_{HK}, with respect to the distillate stream, in a similar manner to Equation (9.53). This definition is equally valid; however, the reader should be cautioned that utilizing this alternative definition would require that the Fenske equation (see later section) be rearranged. When defined as in Equations (9.53) and (9.54), a typical range of values for the recoveries of each key might be between 0.9 and 0.999, depending on the circumstances.

While there are a wide variety of methods for quick-sizing a multicomponent distillation column, what follows is one particular interpretation of the FUG method. This series of procedures may be used in sequence in order to efficiently quick-size a typical distillation column.

Setting the Column Pressure

Before proceeding to explain the FUG method, it is of primary importance to understand how a design engineer sets the column operating pressure, since this is generally performed first. The condenser is important because it determines the operating pressure of the column. If one assumes that the liquid distillate product is a saturated liquid at its bubble point, then knowledge of the distillate temperature and composition allows the calculation of the condenser pressure, P_C.(2)

If cooling water is the condensing medium of choice, as it usually is, there are certain considerations which must be integrated into the condenser design. Cooling water may be available at a variety of temperatures; however, it is important to not allow the exit temperature of the cooling water to increase well beyond 120°F. This requirement

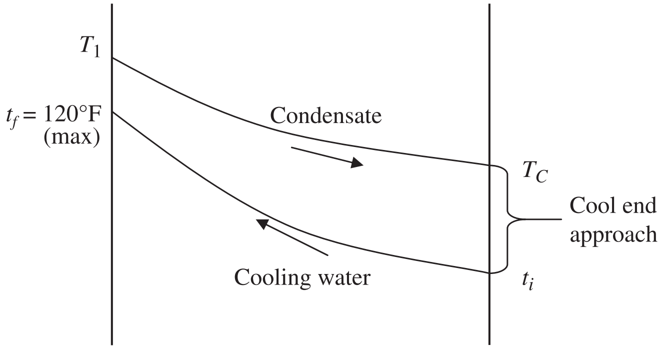


Figure 9.19 Total condenser schematic.

arises because normal process water may contain considerable amounts of naturally occurring calcium carbonate and calcium sulfate salts, the solubilities of which *decrease* with increasing water temperature. Hence, allowing the water temperature to be in excess of 120°F poses a serious problem with respect to salt deposition and subsequent condenser maintenance. Figure 9.19 shows a basic line diagram for a condenser where T_1 = temperature at the top tray of the column, T_C = condenser temperature, and t_i, t_f = inlet and final cooling water temperatures, respectively.

Based on the available cooling water temperature, a *cool end approach* of approximately 20°F may be employed in order to set a reasonable temperature for T_C. By setting T_C, both the distillate temperature and composition are fixed. Therefore, for a total condenser, by assuming the distillate is a saturated liquid at its bubble point, a bubble point pressure calculation may be performed in order to determine the condenser pressure, P_C. Bubble point calculations(2) are carried out with the equation

$$\sum_{i=1}^{N} K_i x_{D,i} = 1.0 \tag{9.55}$$

where N = the number of components in the feed

K_i = equilibrium ratio of the ith component (y_i/x_i)

$x_{D,i}$ = distillate mole fraction of component i

When Raoult's law is assumed applicable, the K values for each species may be approximated by the ratio of that species' vapor pressure to the total pressure. This reduces Equation (9.55) to(2)

$$\sum_{i=1}^{N} \frac{p_i'(T_C)}{P_C} x_{D,i} = 1.0 \tag{9.56}$$

$$\sum_{i=1}^{N} p_i'(T_C)\, x_{D,i} = P_C \tag{9.57}$$

When the Antoine equation is used to calculate vapor pressures, a convenient bubble point pressure equation can be derived:

$$\sum_{i=1}^{N} 10^{a_i-[b_i/(c_i+T_C)]}\, x_{D,i} = P_C \tag{9.58}$$

where P_C = condenser pressure and T_C = condenser temperature.

ILLUSTRATIVE EXAMPLE 9.9

A total condenser produces saturated liquid condensate containing 96% *n*-heptane, 3% *n*-octane, and 1% *i*-octane (mole%). If the condenser temperature has been set to 392°F, calculate the condenser pressure in psia (assume Raoult's law is valid for this ideal liquid mixture).

***SOLUTION*:** Since Raoult's law is valid, Equation (9.58) may be employed in order to calculate P_C. The Antoine equation coefficients are given in Table 9.8, with T [°C] and P [mm Hg].

Table 9.8 Antoine Equation Coefficients for Illustrative Example 9.9

Antoine coefficient	*n*-heptane	*n*-octane	*i*-octane
a_i	6.90253	6.91857	6.88814
b_i	1267.828	1351.756	1319.529
c_i	216.823	209.100	211.625

Employing Equation (9.58),

$$\sum_{i=1}^{N} 10^{a_i-[b_i/(c_i+T_C)]} x_{D,i}$$

Substituting

$$T_C = 200°\text{C}$$

and

$$x_{D,1} = 0.96$$
$$x_{D,2} = 0.03$$

along with the appropriate coefficients provided in Table 9.8, gives

$$P_C = 7140.4\,\text{mm Hg} = 138\,\text{psia}$$

■

Use of the Antoine equation is preferred here because Equation (9.58) does not require a trial-and-error solution and the condenser pressure can be calculated at any condenser temperature. Depending on the type of Antoine coefficients used, one should be sure to employ the correct units in Equation (9.58).(2)

Upon determining P_C, it is up to the designer's discretion as to whether or not the condenser pressure is too low or too high. In most applications, $P_C < 30$ psia is too low such that the condenser pressure should be reset to a value of 30 psia. At this new P_C, the condenser temperature T_C must then be re-calculated with a bubble point temperature calculation. Alternatively, if $P_C > 215$ psia, the condenser pressure is so high that cooling water may not completely condense the vapor. In this case, switching the condenser design to a partial condenser is recommended. At very high condenser pressures, for example, $P_C > 365$ psia, use of a partial condenser cooled with refrigerant is suggested. In this case, the condenser pressure should be reset to 415 psia. At this new P_C, the condenser temperature T_C must then be re-calculated by a dew point temperature calculation. In summary, if 30 psia $< P_C <$ 215 psia, a total condenser is recommended which operates at the calculated P_C. However, for values of P_C outside of this range, the aforementioned adjustments should be made.

Once a suitable condenser pressure has been calculated, the pressure at the top of the column may be assumed by adding a slight pressure drop across the condenser, denoted ΔP_{cond},

$$P_1 = P_C + \Delta P_{cond} \tag{9.59}$$

where $P_1 =$ the pressure at the top tray of the column.

A reasonable value for ΔP_{cond} would be approximately 2 psia.

The next step is to approximate the reboiler pressure by assuming a reasonable number of trays and a corresponding pressure drop per tray. In practice, one may first assume 50 trays with a reasonable pressure drop such as 0.1 psi/tray. In this event, the pressure drop across the actual column would be 50 times 0.1 or 5 psi. This pressure drop between the reboiler and top tray may be denoted as ΔP_{column}. Thus, the reboiler pressure may be approximated by

$$P_R = P_C + \Delta P_{cond} + \Delta P_{column} \tag{9.60}$$

This is obviously a gross approximation; however, it is a useful technique in obtaining preliminary values for quick-sizing the column.

With an approximate reboiler pressure and known bottoms composition, the temperature of the reboiler, T_R, may be calculated using a bubble point temperature calculation(2) analogous to Equation (9.55):

$$\sum_{i=1}^{N} K_i x_{B,i} = 1.0 \tag{9.61}$$

Mean Relative Volatilities

Before the Fenske equation is utilized, the relative volatilities of all components should be calculated based on the condenser and reboiler temperatures and pressures. When Raoult's law is valid, a form of Equation (9.1) may be applied. However, in multicomponent distillation, all relative volatilities are generally calculated with respect to the HK, such that

$$\alpha_i = \frac{K_i}{K_{\mathrm{HK}}} = \frac{p'_i}{p'_{\mathrm{HK}}} \tag{9.62}$$

where $i =$ any component in the feed.

Since the temperatures vary from the condenser to the reboiler, the relative volatilities may also vary slightly. Hence, a relative volatility for each component can be calculated at the condenser and reboiler temperature and pressure. In order to average the differences in relative volatility, a *geometric mean relative volatility*(13) may be calculated for each component, as given by

$$\overline{\alpha_i} = \sqrt{\alpha_{D,i}\ \alpha_{B,i}} \tag{9.63}$$

where $\overline{\alpha_i}$ = geometric mean relative volatility of component i

$\alpha_{D,i}$ = relative volatility of component i in the distillate at T_C and P_C

$\alpha_{B,i}$ = relative volatility of component i in the bottoms at T_R and P_R

The Fenske Equation

The Fenske equation is used to calculate the minimum number of theoretical stages when the column is being operated under total reflux. While many forms of the Fenske equation have been presented in the literature, Equation (9.64) is preferred because it is highly useful from a design perspective,

$$N_{\min} = \frac{\ln\left[\left(\frac{r_{\mathrm{LK}}}{1 - r_{\mathrm{LK}}}\right)\left(\frac{r_{\mathrm{HK}}}{1 - r_{\mathrm{HK}}}\right)\right]}{\ln \overline{\alpha_{\mathrm{LK}}}} \tag{9.64}$$

where $N_{\min}$ = minimum number of theoretical stages (including partial reboiler)

$\overline{\alpha_{\mathrm{LK}}} = \sqrt{\alpha_{\mathrm{D,LK}}\alpha_{\mathrm{B,LK}}}$, a geometric mean of light key relative volatilities

Note that $N_{\min}$ may also be considered to include a partial condenser if the design engineer decides to count a partial condenser as a theoretical stage. This will be the case for all subsequent discussion when referring to the number of theoretical *stages*, since "stages" does not refer explicitly to trays. As previously mentioned, this form of the Fenske equation is based on the definitions of fractional recovery given in Equations (9.53) and (9.54). In the case of a binary mixture, Equation (9.64) may be employed where LK refers to the lighter component of the feed and HK refers to the heavier component of the feed.

In the event that the non-keys of a multicomponent feed are assumed to be distributed (as when non-keys have boiling points similar to a key component), the Fenske equation takes on another important use: to determine the approximate recoveries of the non-keys. In order to determine the fractional recovery of non-key component i, $N_{\min}$ is determined in the usual manner with Equation (9.64). $N_{\min}$ is then substituted back into Equation (9.64), at which time all r_{LK} terms may be replaced by the recovery of any non-key component i, r_i, which is unknown. Similarly, the $\overline{\alpha_{\mathrm{LK}}}$ term in the denominator is replaced with $\overline{\alpha_i}$, which is calculated from Equation (9.63). Hence, the unknown ratio $r_i/(1 - r_i)$ may be determined and the fractional recovery (in the distillate) of non-key i may ultimately be calculated. This procedure is repeated for all non-key components in order to obtain estimates for their respective recoveries in the distillate stream.

The Underwood Equations

While the Fenske equation calculates the minimum number of equilibrium stages required for separation at total reflux, Underwood developed equations that estimate the minimum reflux ratio. The Underwood equations are a set of two mathematical expressions which are generally solved sequentially (unless there are one or more components in between the light and heavy keys, in which case they should be solved simultaneously in order to determine the correct root). These equations are listed below:

$$\sum_{i=1}^{N} \frac{\overline{\alpha_i} x_{F,i}}{\overline{\alpha_i} - \Theta} = 1 - q; \quad (1 < \Theta < \overline{\alpha_{LK}}) \tag{9.65}$$

$$R_{\min} = \sum_{i=1}^{N} \frac{\overline{\alpha_i} x_{D,i}}{\overline{\alpha_i} - \Theta} - 1 \tag{9.66}$$

where q = the q-factor, dependent upon the thermal condition of the feed

Θ = root of the first Underwood equation (9.65)

$\overline{\alpha_i} = \sqrt{\alpha_{D,i}\alpha_{B,i}}$, mean relative volatility of the ith component

Equation (9.65) should first be solved for the correct value of Θ, which must lie between the relative volatility of the heavy key (1.0) and the relative volatility of the light key ($\overline{\alpha_{\text{LK}}}$). All other roots of Equation (9.65) are erroneous and have no physical interpretation. Once the correct value of Θ has been determined, it is substituted into Equation (9.66) and $R_{\min}$ is calculated directly.

As previously mentioned, if the designer does not choose a sharp separation, and there are one or more components in between the keys, Equations (9.65) and (9.66) should be solved in a slightly different manner. Instead of being solved sequentially, Equations (9.65) and (9.66) must be solved simultaneously since there are at least two values of Θ which both satisfy Equation (9.65) and are between unity and $\overline{\alpha_{\text{LK}}}$. Solving simultaneously will ensure that the correct value of Θ is calculated.

The Gilliland Correlation

Now that both the Fenske and Underwood equations have been utilized to determine $N_{\min}$ and $R_{\min}$, respectively, the last step in the FUG procedure is to employ the Gilliland correlation in order to determine the number of theoretical trays. The Gilliland correlation is shown in Figure 9.20.(14)

As is evidenced by Figure 9.20, one need only know the minimum reflux ratio and the operating reflux ratio in order to compute the abscissa of the correlation. The corresponding ordinate is then read from the plot. Since the minimum number of theoretical stages is known, the actual number of theoretical stages, N_t, may be calculated. However, it should be noted that the Gilliland correlation was derived for systems with nearly constant relative volatilities throughout the column.(12) Therefore, the Gilliland correlation may not be a suitable short-cut method for non-ideal systems, in which relative volatilities may vary drastically.

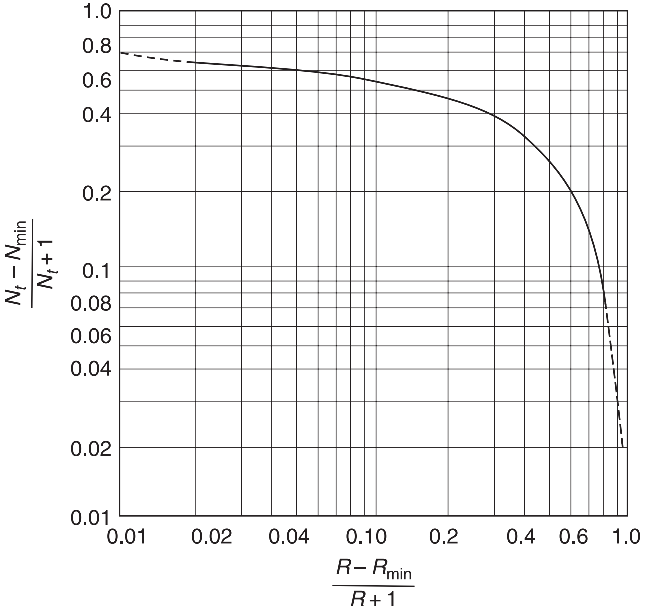


Figure 9.20 Gilliland correlation.

While the Gilliland correlation itself is immensely useful for use as a shortcut method in column quick-sizing, it is inconvenient in that the graph must be read manually. In order to make the Gilliland correlation more applicable to computer programming, several analytical expressions have been developed. One such outstanding correlation, as suggested by Chang,(15) is provided in Equation (9.67) below:

$$Y = 1 - \exp\left[1.490 + 0.315X - \frac{1.805}{X^{0.1}}\right] \tag{9.67}$$

where X is the abscissa (x-axis) of this correlation, given by

$$X = \frac{R - R_{\min}}{R + 1} \tag{9.68}$$

and Y is the ordinate (y-axis) of the correlation,

$$Y = \frac{N_t - N_{\min}}{N_t + 1} \tag{9.69}$$

which may be rearranged to:

$$N_t = \frac{N_{\min} + Y}{1 - Y} \tag{9.70}$$

where N_t = the number of theoretical stages.

Thus, Gilliland's graphical correlation may be replaced by using Chang's convenient mathematical expression.

The calculation of the number of theoretical trays is the last step in the FUG procedure. However, the sizing of distillation columns does not end there. To the contrary, as discussed earlier, there are several other considerations which must be taken into account in order to completely quick-size a distillation column, including: theoretical location of the feed tray, calculation of the actual number of trays, calculation of column diameter, calculation of column height, etc. While the last two considerations have already been discussed in detail, the remaining topics will be further developed in the analysis to follow.

The Kirkbride Equation

The Kirkbride equation may be employed to determine the location of the *theoretical feed tray*. The Kirkbride equation is given by Equation (9.71) below,

$$\frac{N_R}{N_S} = \left[\frac{B}{D}\left(\frac{x_{F,\mathrm{HK}}}{x_{F,\mathrm{LK}}}\right)\left(\frac{x_{B,\mathrm{LK}}}{x_{D,\mathrm{HK}}}\right)^2\right]^{0.206} \tag{9.71}$$

where N_R = number of theoretical stages above the feed tray and N_S = number of theoretical stages below the feed tray.

Equation (9.71) does not directly give the feed tray location, but rather provides a ratio of theoretical stages above and below the feed tray. In order to find the feed tray location, Equation (9.71) must be solved simultaneously with

$$N_R + N_S = N_t - 1 \tag{9.72}$$

where N_t = the number of theoretical stages.

Note that the right-hand side of Equation (9.72) contains a minus one in order to account for the feed tray. In practice, Equation (9.72) is solved for either N_R or N_S and the result is then inserted into the Kirkbride equation. All known values are substituted and the unknown (either N_R or N_S) is calculated. If on solving the Kirkbride equation for N_R one obtains the value n, then there are n theoretical stages above the feed tray in the rectification section. Hence, the theoretical feed tray location would be tray $n + 1$ from the top of the column if a total condenser is employed, or tray n from the top of the column if a partial condenser is employed *and* considered a theoretical stage.

The O'Connell Correlation

As noted above, three major types of tray efficiency exist: the *overall efficiency* which is a single value pertaining to the entire column, the *Murphee efficiency* which pertains to a single tray, and the *local efficiency* which provides an efficiency at a particular location on a single tray. Equation (9.47) demonstrates how one calculates a column's actual number of trays given the overall efficiency, E_0. The O'Connell correlation, as shown in Figure 9.21,(16) may be used to obtain a column's overall efficiency, given

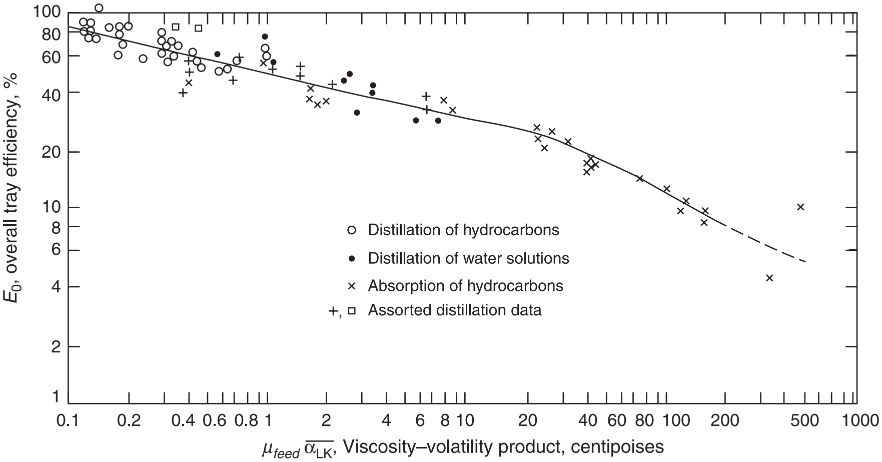


Figure 9.21 Lockhart and Leggett version of the *O'Connell correlation* for overall tray efficiency. (Adapted from F. J. Lockhart and C. W. Leggett, *Advances in Petroleum Chemistry and Refining*, Vol. 1, K. A. Kobe and John J. McKetta, Jr., (eds), Interscience Publishers, Inc., New York City, NY, 1958, 323–326.)

the product of two pertinent quantities: the feed's average viscosity and the average relative volatility of the LK. Note that, the O'Connell correlation applies equally well to a binary mixture where the LK is simply the light component.

The viscosity of a liquid or gas is strongly dependent upon temperature. Therefore, if the feed temperature is not specified, an approximate temperature for the entering feed may be calculated by taking the arithmetic mean of the condenser and reboiler temperatures

$$T_{feed} \approx \frac{T_C + T_R}{2} \tag{9.73}$$

While calculating the actual average viscosity of a multicomponent mixture is best left to a thermodynamicist, taking a mole fraction weighted-average of each component's viscosity can be used as a bare-minimum approximation for quick-sizing purposes:

$$\mu_{feed} \approx \sum_{i=1}^{N} \mu_i(T_{feed}) \cdot x_{F,i} \tag{9.74}$$

Note that approximation may be subject to large error in some feed mixtures. Once a suitable feed viscosity has been calculated, the abscissa of the O'Connell correlation is found via

$$\mu_{feed}\overline{\alpha_{\mathrm{LK}}} \tag{9.75}$$

Lastly, the overall efficiency is read off of the ordinate. $N_{trays,ideal}$ is found by calculating either $N_t - 1$, which subtracts out the partial reboiler, or $N_t - 2$, if both a partial reboiler and partial condenser are considered theoretical stages. Equation (9.47) is then readily employed in order to calculate N_{trays}, the actual number of trays in the multicomponent distillation column.

ILLUSTRATIVE EXAMPLE 9.10

Calculate the condenser pressure in a multicomponent distillation column intended to perform a sharp separation of *n*-pentane and *i*-octane in a *saturated liquid* feed, described in Table 9.9. Pertinent information is found below:

Table 9.9 Feed Flows

	Component (#)	F_i, lbmol/h
	n-Butane (1)	50
LK	*n*-Pentane (2)	200
HK	*i*-Octane (3)	150
	n-Nonane (4)	50
	n-Decane (5)	50
	Total	**500**

- $r_{\mathrm{LK}} = 0.99$
- $r_{\mathrm{HK}} = 0.99$
- Cooling water is available at 90°F
- The non-keys are undistributed such that all keys lighter than the LK appear exclusively in the distillate and those heavier than the HK appear exclusively in the bottoms
- The liquid density is approximately 58 $\mathrm{lb/ft^3}$
- The column is operated at 75% of its flooding velocity
- Raoult's law may be considered valid for calculating the relative volatilities: use the three coefficient Antoine equation to calculate vapor pressures. (Note that differences in the Antoine coefficients employed may lead to noticeable deviation from the answers presented here; be sure to check that the Antoine data utilized is as accurate as possible over the temperature range of interest.)

***SOLUTION*:** Much of the information given above is extraneous, but will be utilized in subsequent Illustrative Examples. The recoveries of the keys are defined as follows:

$$r_{\mathrm{LK}} = \frac{Dx_{D,\mathrm{LK}}}{Fx_{F,\mathrm{LK}}} \tag{9.53}$$

$$r_{\mathrm{HK}} = \frac{Bx_{B,\mathrm{HK}}}{Fx_{F,\mathrm{HK}}} \tag{9.54}$$

When the 0.99 recoveries are employed and the non-keys are assumed undistributed, the resulting distillate and bottoms flows are given in Table 9.10.

Table 9.10 Column Flows

Component (#)	F_i, lbmol/h	D_i, lbmol/h	B_i, lbmol/h
n-Butane (1)	50	50	0
LK *n*-Pentane (2)	200	198	2
HK *i*-Octane (3)	150	1.5	148.5
n-Nonane (4)	50	0	50
n-Decane (5)	50	0	50
Total	**500**	**249.5**	**250.5**

Component mole fractions need to be calculated in order to be used in subsequent distillation equations. These results are given in Table 9.11.

Table 9.11 Mole Fractions

Component (#)	$x_{F,i}$	$x_{D,i}$	$x_{B,i}$
n-Butane (1)	0.1000	0.2004	0.0000
LK *n*-Pentane (2)	0.4000	0.7936	0.0080
HK *i*-Octane (3)	0.3000	0.0060	0.5928
n-Nonane (4)	0.1000	0.0000	0.1996
n-Decane (5)	0.1000	0.0000	0.1996

First, one should note that the cooling water is available at 90°F. By assuming a 20°F approach, the exit distillate temperature is set to 110°F. See Figure 9.22 for the condenser schematic.

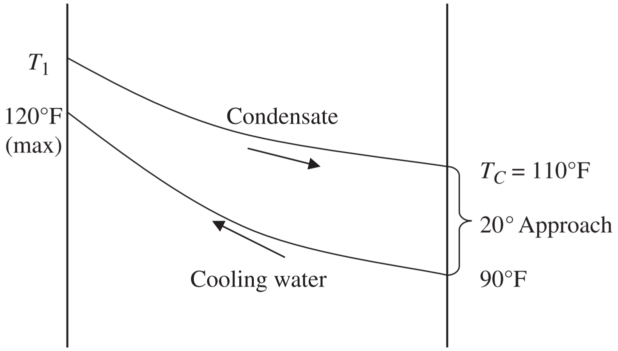


Figure 9.22 Condenser schematic.

The condenser temperature is therefore set to 110°F (43.33°C). Since the temperature and composition of the liquid distillate are known (which is specified to be a saturated liquid), one may perform a bubble point pressure (BPP) calculation in order to determine the condenser pressure:

$$\sum_{i=1}^{N} K_i x_{D,i} = 1.0 \tag{9.55}$$

Since Raoult's law is assumed applicable, the K values for each species may be approximated by the ratio of that species' vapor pressure to the total pressure. When the Antoine equation is used to calculate vapor pressures, one may employ:

$$\sum_{i=1}^{N} 10^{a_i-[b_i/(c_i+T_C)]}\, x_{D,i} = P_C \tag{9.58}$$

$$P_C = 1389.48\,\text{mm Hg}\left(\frac{14.7\,\text{psi}}{760\,\text{mm Hg}}\right) = 26.9\,\text{psia}$$

Since this pressure is below 30 psia, the condenser pressure is reset at 30 psia (this is done in order to avoid a too low of a column pressure that would result in a larger vapor volumetric flow rate, which in turn would lead to a larger and less economical column diameter). Now that the total condenser has a pressure of 30 psia, the new condenser temperature must be determined by a trial-and-error bubble point temperature (BPT) calculation, as described in Equation (9.53). This may be performed by hand or with a computer package. The final result is

$$T_C = 47.0^\circ\text{C} \quad \text{at } P_C = 30\,\text{psia}$$

■

ILLUSTRATIVE EXAMPLE 9.11

Refer to Illustrative Example 9.10. Calculate the relative volatilities of each component at the condenser temperature.

***SOLUTION*:** When Raoult's law is valid, the relative volatility of a component may be expressed in terms of vapor pressures:

$$\alpha_i = \frac{K_i}{K_{\text{HK}}} = \frac{p'_i}{p'_{\text{HK}}} \tag{9.62}$$

The relative volatilities of each species at the condenser temperature are tabulated in Table 9.12. ■

ILLUSTRATIVE EXAMPLE 9.12

Refer to Illustrative Examples 9.10–9.11. Calculate the reboiler temperature and pressure.

***SOLUTION*:** First, it is assumed that the pressure drop across the condenser is ~2 psi. For initial design purposes, it may be assumed that approximately 50 trays will be employed in the column, each having a pressure drop of 0.1 psi. The pressure drop across the column (from the reboiler to condenser) is calculated as in Equation (9.60):

$$\begin{aligned} P_R &= P_C + 2\,\text{psi} + (0.1\,\text{psi/tray})(50\,\text{trays}) \\ &= 30 + 2 + 5 \\ &= 37\,\text{psia} \end{aligned}$$

which equates to 1912.93 mm Hg.

Last, the reboiler temperature is calculated by observing that the liquid in the reboiler is a saturated liquid at its bubble point. Therefore, a BPT calculation is performed to find T_R, assuming Raoult's law. To perform this calculation, Equation (9.58) can be modified for the reboiler, as shown below:

$$\sum_{i=1}^{N} 10^{a_i - [b_i/(c_i + T_R)]}\, x_{B,i} = P_R \tag{9.76}$$

Upon iteratively solving for T_R with the appropriate Antoine coefficients:

$$T_R = 165.5^\circ\text{C} \quad \text{at } P_R = 37\,\text{psia}$$ ■

ILLUSTRATIVE EXAMPLE 9.13

Refer to Illustrative Examples 9.10–9.12. Calculate the relative volatilities of each component at the reboiler temperature. Then, use these results coupled with those of Illustrative Example 9.11 to calculate the geometric mean relative volatilities of each component.

***SOLUTION*:** The relative volatilities are now calculated for each component at T_R. Once again, these relative volatilities are based on the HK:

$$\alpha_i = \frac{K_i}{K_{\text{HK}}} = \frac{p'_i}{p'_{\text{HK}}} \tag{9.56}$$

The distillate, bottoms, and geometric mean relative volatilities are tabulated in Table 9.12. ■

Table 9.12 Distillate, Bottoms, and Mean Relative Volatilities

Component (#)	$\alpha_{D,i}$	$\alpha_{B,i}$	$\overline{\alpha_i}$
n-Butane (1)	55.95	12.80	26.77
LK *n*-Pentane (2)	17.78	6.08	10.40
HK *i*-Octane (3)	1.00	1.00	1.00
n-Nonane (4)	0.25	0.45	0.34
n-Decane (5)	0.09	0.25	0.15

ILLUSTRATIVE EXAMPLE 9.14

Refer to Illustrative Examples 9.10–9.13. Calculate the minimum number of trays.

***SOLUTION*:** Employ the Fenske equation as provided by

$$N_{\min} = \frac{\ln\left[\left(\frac{r_{\mathrm{LK}}}{1 - r_{\mathrm{LK}}}\right)\left(\frac{r_{\mathrm{HK}}}{1 - r_{\mathrm{HK}}}\right)\right]}{\ln \overline{\alpha_{\mathrm{LK}}}} \tag{9.64}$$

Upon substitution,

$$N_{\min} = \frac{\ln\left[\left(\frac{0.99}{0.01}\right)\left(\frac{0.99}{0.01}\right)\right]}{\ln(10.40)}$$

$$= 3.9251$$

Thus, if rounded, the minimum number of theoretical stages is four (three plus a partial reboiler).

Note that as a rule of thumb in distillation design, any decimal answer regarding the number of trays or stages is usually rounded *up* to the nearest whole number, *never down*. However, with the exception of the Kirkbride equation, unrounded values are employed in these calculations until the actual number of trays (N_{trays}) is determined. This is because N_{trays} has a physical interpretation as the actual number of trays needed and is, of necessity, an integer. Employing rounded values in previous calculations (e.g., Gilliland and O'Connell correlations) may propagate error in the final result. ■

ILLUSTRATIVE EXAMPLE 9.15

Refer to Illustrative Examples 9.10–9.14. Calculate the minimum reflux ratio and optimum reflux ratio.

***SOLUTION*:** Employ the Underwood equations, as indicated in the text. Noting that, for a saturated liquid feed, $q = 1$,

$$\sum_{i=1}^{N} \frac{\overline{\alpha_i} x_{F,i}}{\overline{\alpha_i} - \Theta} = 1 - q; \quad (1 < \Theta < \overline{\alpha_{\mathrm{LK}}}) \tag{9.65}$$

One finds the root, Θ,

$$\Theta = 1.5572$$

Substituting into

$$R_{\min} = \sum_{i=1}^{N} \frac{\overline{\alpha_i} x_{D,i}}{\overline{\alpha_i} - \Theta} - 1 \tag{9.66}$$

gives

$$R_{\min} = 0.1354$$

Referring to Table 9.7, since cooling water is used in the condenser, the optimization multiplier is 1.3. Hence, the optimum reflux ratio is $R = 1.3R_{\min}$.

$$R = 0.1760$$

■

ILLUSTRATIVE EXAMPLE 9.16

Refer to Illustrative Examples 9.10–9.15. Calculate the number of theoretical stages necessary to affect the desired separation.

***SOLUTION*:** Using the Chang equation in order to calculate the proper value of the Gilliland correlation abscissa:

$$X = \frac{R - R_{\min}}{R + 1} \tag{9.68}$$

$$X = \frac{0.1760 - 0.1354}{0.1760 + 1}$$

$$= 0.03454$$

The ordinate is given by

$$Y = 1 - \exp\left[1.490 + 0.315X - \frac{1.805}{X^{0.1}}\right] \tag{9.67}$$

for which

$$Y = 0.6417$$

and thus

$$N_t = \frac{N_{\min} + Y}{1 - Y} \tag{9.70}$$

$$N_t = \frac{3.2951 + 0.6417}{1 - 0.6417}$$

$$= 12.7457$$

Therefore, when rounded, this column requires 13 theoretical stages (12 theoretical trays plus a reboiler).

■

ILLUSTRATIVE EXAMPLE 9.17

Refer to Illustrative Examples 9.10–9.16. Determine the theoretical feed tray location for this column.

***SOLUTION*:** Employing the Kirkbride equation [Equation (9.71)] and substituting,

$$\frac{N_R}{N_S} = \left[\frac{B}{D}\left(\frac{x_{\text{F,HK}}}{x_{\text{F,LK}}}\right)\left(\frac{x_{\text{B,LK}}}{x_{\text{D,HK}}}\right)^2\right]^{0.206} \tag{9.71}$$

$$= \left[\frac{250.5}{249.5}\left(\frac{0.30}{0.40}\right)\left(\frac{0.0080}{0.0060}\right)^2\right]^{0.206}$$

$$= 1.062$$

Utilizing the complimentary equation

$$N_R + N_S = N_t - 1; \quad N_t = 13 \tag{9.72}$$

Rearranging and substituting Equation (9.72) into Equation (9.71),

$$\frac{N_R}{N_S} = \frac{N_R}{N_t - N_R - 1} = 1.062$$

Solving for N_R,

$$N_R = 6.18 \rightarrow 7 \text{ theoretical stages}$$

Calculating N_S,

$$\begin{aligned} N_S &= N_t - N_R - 1 \\ &= 13 - 7 - 1 \\ &= 5 \text{ theoretical stages} \end{aligned}$$

Employing integer values for the number of stages, there should be seven theoretical stages above the feed tray (N_R) and five theoretical stages below the feed tray (N_S). Since a total condenser is employed, the feed should be admitted on the eighth tray from the top of the column. ■

ILLUSTRATIVE EXAMPLE 9.18

Refer to Illustrative Examples 9.10–9.17. Determine the *actual* number of trays via the O'Connell correlation.

***SOLUTION*:** Using Equation (9.73), T_{feed} is approximately 106.72°C. Assuming that the average viscosity of the feed at this temperature is taken to be approximately 0.17 centipoise (this approximation is subject to improvement at the reader's discretion), and employing the result given in Table 9.12 gives

$$\begin{aligned} \mu_{feed}\overline{\alpha_{\text{LK}}} &= (0.17)(10.40) \\ &= 1.7673 \end{aligned} \tag{9.75}$$

Reading the corresponding ordinate off of Figure 9.21, the fractional efficiency (ordinate) is approximately 48%. The actual number of trays is calculated by dividing the theoretical number of trays by 0.48:

$$N_{trays} = \frac{N_{trays,ideal}}{E_0} \tag{9.47}$$

$$N_{trays} = \frac{12.7457 - 1}{0.48}$$

$$= 24.47$$

Thus, the final result is that this column requires approximately 25 trays plus a partial reboiler in order to produce the desired separation. ■

ILLUSTRATIVE EXAMPLE 9.19

Refer to Illustrative Examples 9.10–9.18. Calculate the flooding velocity, vapor velocity and column diameter. Assume that the trays to be employed have downcorners which each occupy 10% of the cross sectional area.

***SOLUTION*:** Note that the details of the more lengthy calculations found in this illustrative example are left as an exercise for the reader.

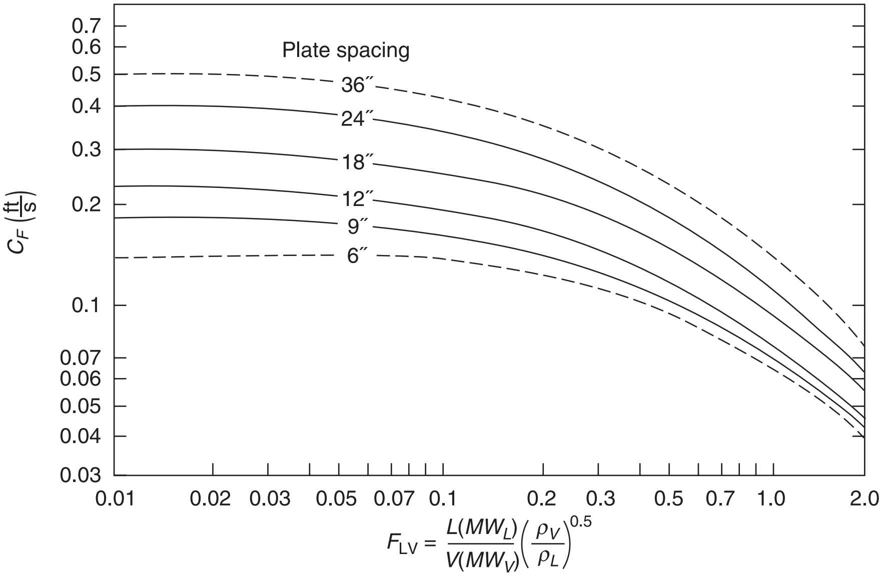


Figure 9.23 Fair flooding correlation for crossflow trays.

The Fair entrainment flooding correlation (see Fig. 9.23)(17) is one of several flooding correlations that can be used to calculate the diameter of a sieve tray distillation column. The abscissa of this correlation of the flow parameter, X_{flood} (dimensionless) is

$$F_{LV}(\text{flooding}) = X_{flood} = \frac{L(MW_L)}{V(MW_V)}\left(\frac{\rho_V}{\rho_L}\right)^{0.5} \tag{9.77}$$

where $L =$ liquid molar flow rate (in the section where flooding first occurs), $V =$ vapor molar flow rate (in the section where flooding first occurs), $MW_L =$ average molecular weight of liquid (where flooding first occurs), and $MW_V =$ average molecular weight of vapor (where flooding first occurs).

Since the feed in this example is a saturated liquid, it may be assumed (due to larger flow rates) that flooding will most likely first occur in the stripping section of the column. Hence $\overline{L}$ and $\overline{V}$ must be calculated. The average molecular weights may be calculated based on the composition of the liquid and vapor leaving the reboiler. In reality, the liquid composition should be that of the liquid leaving the last tray, which is where flooding may first occur; however, using the bottoms composition as an approximation does not normally lead to significant error.

The composition of the boil-up vapor leaving the reboiler is determined by a vapor–liquid equilibrium calculation, with the liquid composition, reboiler temperature, and reboiler pressure all known ($y_{reb,i} = K_i x_{B,i}$). The average molecular weight of the liquid and vapor at the bottom of the column is taken as a mole fraction weighted average

$$MW_V = 115.02, \quad MW_L = 122.28$$

The density of the liquid is given as 58 lb/ft^3, while that of the vapor may be calculated using the ideal gas law:

$$\begin{aligned} \rho_V &= (MW_V)\frac{P_R}{RT_R} \\ &= (115.02)\frac{(1912.93)}{(998.970)(165.5 + 273)} \\ \rho_V &= 0.502\,\text{lb/ft}^3 \end{aligned} \tag{9.78}$$

Note that the reboiler temperature here must be expressed in *absolute* temperature units.(2)

The liquid and vapor molar flow rates in the rectification section may be calculated via material balances (assuming constant molal overflow):

$$\begin{aligned} \overline{L} &= (R)(249.5) + 500 \\ &= 543.9\,\text{lbmol/h} \\ \overline{V} &= (249.5)(R + 1) \\ &= 293.4\,\text{lbmol/h} \end{aligned}$$

The flooding parameter may now be calculated by using Equation (9.77):

$$X_{Flood} = \frac{\overline{L}(MW_L)}{\overline{V}(MW_V)}\left(\frac{\rho_V}{\rho_L}\right)^{0.5}$$

$$= \frac{(543.9)(122.28)}{(293.4)(115.02)}\left(\frac{0.502}{58}\right)^{0.5}$$

$$X_{Flood} = 0.1833$$

This value is now used in order to read the ordinate of the correlation, C_F, which is in ft/s. In order to read the ordinate, a value for tray spacing must be assumed. Initially, choose a 24 inch tray spacing. Treybal$^{(6)}$ presents values of tray spacing per a given range of column diameters, as shown in Table 9.13. Once the column diameter is calculated, it will be compared to the diameter range recommended for 24 inch tray spacing.

Table 9.13 Recommended Tray Spacing*

Column diameter, ft	Tray spacing, inches
≤4	20
4–10	24
10–12	30
≥12	36

*Individual practice may call for tray spacing different than those here described.

From the Fair flooding correlation, with a tray spacing of 24 inches:

$$C_F = 0.30\,\text{ft/s}$$

This value is now used to calculate the vapor flooding velocity u_F via Equation (9.79):

$$u_F = C_F\left(\frac{\rho_L - \rho_V}{\rho_V}\right)^{0.5}\left(\frac{\sigma}{20}\right)^{0.2} \tag{9.79}$$

where σ = surface tension correction factor (dyne/cm).

Hydrocarbon mixtures often have surface tensions of approximately 20 dyne/cm. Therefore, the surface tension correction factor term may be neglected, leading to:

$$u_F = (0.30)\left(\frac{58 - 0.502}{0.502}\right)^{0.5}$$

$$= 3.21\,\text{ft/s}$$

Once the flooding velocity is calculated, the actual velocity is determined by multiplying it by the approach to flooding. In this case, use 0.75.

$$\begin{aligned} u &= (0.75)(3.21\ \text{ft/s}) \\ &= 2.41\ \text{ft/s} \end{aligned}$$

Note that this vapor velocity is based on the aforementioned *net area* of a tray. The column diameter is now calculated based on the vapor velocity, molar flow rate, and tray geometry:

$$\begin{aligned} D_{column} &= \frac{2}{\sqrt{\pi}}\left(\frac{q}{(1-\eta)u}\right)^{0.5} \qquad (9.52) \\ &= \frac{2}{\sqrt{\pi}}\left(\frac{(MW_V)V}{\rho_V(1-\eta)u}\right)^{0.5} \\ &= \frac{2}{\sqrt{\pi}}\left(\frac{(115.02)(293.4)}{(3600)(0.502)(1-0.10)(2.41)}\right)^{0.5} \\ &= 3.31\ \text{ft} \end{aligned}$$

Therefore, the diameter is 3.31 ft in this particular case. Referring to Table 9.13, this diameter is generally considered too small for a tray spacing of 24 inches. Therefore, the calculation is repeated at a tray spacing of 18 inches on the Fair flooding correlation. A new value of C_F is determined and a new vapor velocity calculated. The final result for the new column diameter is calculated as 3.70 ft, which is an acceptable diameter for tray spacing of 18 inches. ■

ILLUSTRATIVE EXAMPLE 9.20

Refer to Illustrative Examples 9.10–9.19. Calculate the column height, taking into account a surge volume that will allow for five minutes of “extra” operation time plus a 5 ft height safety factor.

***SOLUTION*:** These calculations are relatively self-explanatory. Notice that a surge volume is calculated for safety in operation: the factor of (60/5) is to account for a surge volume at the bottom of the column which will take 5 minutes to fill should the bottoms pump fail. Also, an additional 5 ft is added to the column height, which is roughly a 15% height safety factor; this extra height may be used to install more trays for better operation. The three contributions to the *total* height may now be calculated:

$$h_{trays} = \left(18\ \frac{\text{in}}{\text{tray}}\right)\left(\frac{\text{ft}}{12\ \text{in}}\right)(25\ \text{trays}) = 37.5\ \text{ft}$$

The surge volume is:

$$V_{surge} = \frac{(MW_L)\overline{L}}{(60/5)\rho_L} = 95.56\ \text{ft}^3$$

Hence, surge height is:

$$h_{surge} = \frac{V_{surge}}{(\pi D^2_{column}/4)} = 8.9\,\text{ft}$$

Finally,

$$\begin{aligned} h_{column} &= h_{trays} + h_{surge} + 5\,\text{ft} \\ &= 37.5 + 8.9 + 5.0 \\ &= 51.4\,\text{ft} \end{aligned}$$

The column height should be approximately 52 ft. ■

Packed Column Distillation

Packed-bed distillation towers, generally referred to as *packed columns*, are employed commercially in small-scale applications where low throughput and small column diameter make them cost competitive with tray towers. Packed columns generally have a smaller pressure drop, which also decreases operational costs. The calculation of column diameter and pressure drop across packing are calculated in a similar manner to the Fair flooding correlation. Details are available in the literature,(6,7) but information is provided in the next chapter.

The operation of a packed column is similar to that of a trayed column. Indeed, by examining a column from the outside, they may seem virtually identical. However, while trayed columns have discrete stages for separation, the packing in a packed column creates a continuous surface for mass transfer.

In designing packed columns, the column height is based on the number of theoretical plates, and the *height equivalent to a theoretical plate* (HETP). Let the height of a packed zone be denoted by *h*. HETP is then defined as follows:

$$\text{HETP} = \frac{h}{N_p} \tag{9.80}$$

where N_p = the number of theoretical stages achieved in the packed zone.

Hence, the HETP may be physically interpreted as the height of packing that produces a liquid and vapor stream (exiting this height of packing from the bottom and top, respectively), which are in thermodynamic equilibrium as the liquid and vapor streams would be if they contacted on a theoretical plate. Other approaches have been developed in order to determine the height of a packed column, namely that of the *transfer unit*, the details of which are available in the literature.(6)

The two main classes of packing are *random dumped packing* or *structured packing*. There are packings of various shapes and sizes: some of the more typical dumped packing includes *Raschig rings*, *pall rings, Berl saddles* and *Intalox saddles*.(6) The packing (be they structured or dumped) serves the same purpose as trays do in a trayed column, that is, to provide a "widget" for the vapor and liquid to experience more intimate contact and better mass transfer.

As liquid flows through dumped packing, it may preferentially flow in certain channels towards the wall of the column. As a result, liquid distribution is usually degraded. In order to ensure that liquid is spread evenly over the packing, liquid redistributors can be placed intermittently in the column. When the liquid distribution is well maintained, most of the packing tends to wet, creating a thin film of liquid on the surface of the packing. As the rising vapors contact the liquid film, mass transfer occurs.

For a 1.5 or 2 inch size of a common packing, the HETP is generally in the range of 1 to 2 ft. Smaller packing generally gives rise to a smaller HETP. However, it has been noted that structured packing produces a somewhat better separation than random dumped packing.(12) More information regarding the design and operation of packed columns is available in the literature(3,6,12,18) as well as the next chapter.

REFERENCES

1. P. Marnell, adopted from class notes (with permission), 2009.
2. L. Theodore, F. Ricci, and T. Van Vliet, "*Thermodynamics for the Practicing Engineer*," John Wiley & Sons, Hoboken, NJ, 2009.
3. B. D. Smith, "*Design of Equilibrium Stage Processes*," McGraw-Hill, New York City, NY, 1963.
4. L. Theodore and J. Barden, "*Mass Transfer Operations*," Theodore Tutorials, East Williston, NY, 1995.
5. J. Coates and B. Pressburg, "Analyze Material and Heat Balances for Continuous Distillation," *Chem. Eng.*, New York City, NY, 2/20/61.
6. R. Treybal, "*Mass Transfer Operations*," 3rd edition, McGraw-Hill, New York City, NY, 1980.
7. T. R. Fair, "Distillation," chapter 5, in R. W. Rousseau (ed)," *Handbook of Separation Process Technology*," John Wiley & Sons, Hoboken, NJ, 1987.
8. L. Theodore, personal notes, 2009.
9. J. M. Smith, H. C. Van Ness, and M. M. Abbott, "*Introduction to Chemical Engineering Thermodynamics*," 7th edition, McGraw-Hill, New York City, NY, 2005.
10. W. McCabe and E. Thiele, *Ind. Eng. Chem.*, New York City, NY, **17**, 605, 1925.
11. Generalized Pressure Drop Correlation, Chart No. GR-109, Rev 4, U.S. Stoneware Co., Akron, OH, 1963.
12. W. L. McCabe, J. C. Smith, and P. Harriot, "*Unit Operations of Chemical Engineering*," 7th edition, McGraw-Hill, New York City, NY, 2005.
13. S. Shaefer and L. Theodore, "*Probability and Statistics Applications in Environmental Science*," CRC Press/Taylor & Francis Group, Boca Raton, FL, 2007.
14. E. R. Gilliland, *Ind. Eng. Chem.*, New York City, NY, **32**, 1220, 1940.
15. H. Y. Chang, *Hydrocarbon Processing*, New York City, NY, **64(3)**, 48, 1985.
16. H. E. O'Connell, *Trans. AIChE*, New York City, NY, **42**, 741, 1946.
17. J. R. Fair, *Petro/Chem. Eng.*, New York City, NY, **33**(10), 45, 1961.
18. L. Theodore, "*Air Pollution Control Equipment Calculations*," John Wiley & Sons, Hoboken, NJ, 2008.

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