

where ΔH^{vap} = average molar heat of vaporization of the two components being separated. For a partial condenser,

$$Q_C = DR \Delta H^{\text{vap}} \quad (7-33)$$

For a partial reboiler,

$$Q_R = BV_B \Delta H^{\text{vap}} \quad (7-34)$$

When the feed is at the bubble point and a total condenser is used, (7-16) can be arranged to:

$$BV_B = L + D = D(R + 1) \quad (7-35)$$

Comparing this to (7-34) and (7-32), note that $Q_R = Q_C$. When the feed is partially vaporized and a total condenser is used, the heat required by the reboiler is less than the condenser duty and is given by

$$Q_R = Q_C \left[1 - \frac{V_F}{D(R + 1)} \right] \quad (7-36)$$

If saturated steam is the heating medium for the reboiler, the steam rate required is given by an energy balance:

$$m_s = \frac{M_s Q_R}{\Delta H_s^{\text{vap}}} \quad (7-37)$$

where

m_s = mass flow rate of steam

Q_R = reboiler duty (rate of heat transfer)

M_s = molecular weight of steam

ΔH_s^{vap} = molar enthalpy of vaporization of steam

The cooling water rate for the condenser is

$$m_{\text{cw}} = \frac{Q_C}{C_{P_{\text{H}_2\text{O}}} (T_{\text{out}} - T_{\text{in}})} \quad (7-38)$$

where

m_{cw} = mass flow rate of cooling water

Q_C = condenser duty (rate of heat transfer)

$C_{P_{\text{H}_2\text{O}}}$ = specific heat of water

$T_{\text{out}}, T_{\text{in}}$ = temperature of cooling water out of and into the condenser, respectively

Because the annual cost of reboiler steam can be an order of magnitude higher than the annual cost of cooling water, the feed to a distillation column is frequently preheated and partially vaporized to reduce Q_R , in comparison to Q_C , as indicated by (7-36).

Feed Preheat

The feed to a distillation column is usually a process feed, an effluent from a reactor, or a liquid product from another separator. The feed pressure must be greater than the pressure in the column at the feed-tray location. If so, any excess feed pressure is dropped across a valve, which may cause the feed to partially vaporize before entering the column; if not, additional pressure is added with a pump.

The temperature of the feed as it enters the column does not necessarily equal the temperature in the column at the feed-tray location. However, such equality will increase second-law efficiency. It is usually best to avoid a subcooled liquid or superheated vapor feed and supply a partially vaporized feed. This is achieved by preheating the feed in a heat exchanger with the bottoms product or some other process stream that possesses a suitably high temperature, to ensure a reasonable ΔT driving force for heat transfer, and a sufficient available enthalpy.

Optimal Reflux Ratio

An industrial distillation column must be operated between the two limiting conditions of minimum reflux and total reflux. As shown in Table 7.3, for a typical case adapted from Peters and Timmerhaus [6], as the reflux ratio is increased from the minimum value, the number of plates decreases, the column diameter increases, and the reboiler steam and condenser cooling-water requirements increase. When the annualized fixed investment costs for the column, condenser, reflux drum, reflux pump, and reboiler are added to the annual cost of steam and cooling water, an optimal reflux ratio is established, as shown, for the conditions of Table 7.3, in Figure 7.22. For this example the optimal R/R_{min} is 1.1.

Table 7.3 Effect of Reflux Ratio on Annualized Cost of a Distillation Operation

R/R_{min}	Actual N	Diam., ft	Reboiler Duty, Btu/h	Condenser Duty, Btu/h	Annualized Cost, \$/yr			Total Annualized Cost, \$/yr
					Equipment	Cooling Water	Steam	
1.00	Infinite	6.7	9,510,160	9,416,000	Infinite	17,340	132,900	Infinite
1.05	29	6.8	9,776,800	9,680,000	44,640	17,820	136,500	198,960
1.14	21	7.0	10,221,200	10,120,000	38,100	18,600	142,500	199,200
1.23	18	7.1	10,665,600	10,560,000	36,480	19,410	148,800	204,690
1.32	16	7.3	11,110,000	11,000,000	35,640	20,220	155,100	210,960
1.49	14	7.7	11,998,800	11,880,000	35,940	21,870	167,100	224,910
1.75	13	8.0	13,332,000	13,200,000	36,870	24,300	185,400	246,570

(Adapted from an example by Peters and Timmerhaus [6].)

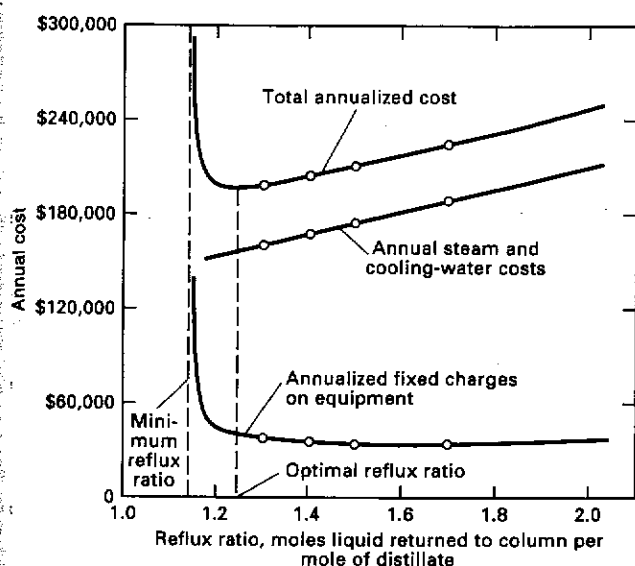


Figure 7.22 Optimal reflux ratio for a representative distillation operation.

[Adapted from M.S. Peters and K.D. Timmerhaus, *Plant Design and Economics for Chemical Engineers*, 4th ed., McGraw-Hill, New York (1991).]

The data in Table 7.3 show that although the condenser and reboiler duties are almost identical for a given reflux ratio, the annual cost of steam for the reboiler is almost eight times that of the cost of condenser cooling water. The total annual cost is dominated by the cost of steam except at the minimum-reflux condition. At the optimal reflux ratio, the cost of steam is 70% of the total annualized cost. Because the cost of steam is dominant, the optimal reflux ratio is sensitive to the steam cost. For example, at the extreme of zero cost for steam, the optimal R/R_{\min} for this example is shifted from 1.1 to 1.32. This example assumes that the heat removed by cooling water in the condenser has no value.

The range of optimal ratio of reflux to minimum reflux often is from 1.05 to 1.50, with the lower value applying to a difficult separation (e.g., $\alpha = 1.2$) and the higher value applying to an easy separation (e.g., $\alpha = 5$). However, as seen

in Figure 7.22, the optimal reflux ratio is not sharply defined. Accordingly, to achieve greater operating flexibility, columns are often designed for reflux ratios greater than the optimum.

Large Number of Stages

The McCabe-Thiele graphical construction is difficult to apply when conditions of relative volatility and/or product purities are such that a large number of stages must be stepped off. In that event, one of the following techniques can be used to determine the stage requirements.

1. Separate plots of expanded scales and/or larger dimensions are used for stepping off stages at the ends of the y - x diagram. For example, the additional plots might cover just the regions (1) 0.95 to 1.0 and (2) 0 to 0.05.
2. As described by Horvath and Schubert [7] and shown in Figure 7.23, a plot based on logarithmic coordinates is used for the low (bottoms) end of the y - x diagram, while for the high (distillate) end, the log-log graph is turned upside down and rotated 90° . Unfortunately, as seen in Figure 7.23, the operating lines become curved, but they can be plotted from a few points computed from (7-9) and (7-14). The 45° line remains straight and the normally curved equilibrium curve becomes nearly straight at the two ends.
3. The stages at the two ends are computed algebraically in the manner of part (b) of Example 7.2. This is readily done with a spreadsheet computer program.
4. If the equilibrium data are given in analytical form, commercially available McCabe-Thiele computer programs can be used.
5. The stages are determined by combining the McCabe-Thiele graphical construction, for a suitable region in the middle, with the Kremser equations of Section 5.4 for the low and/or high ends, where absorption and stripping factors are almost constant. This technique, which is often preferred, is illustrated in the following example.

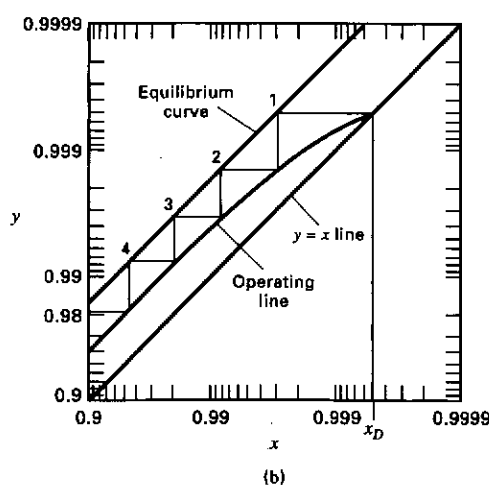
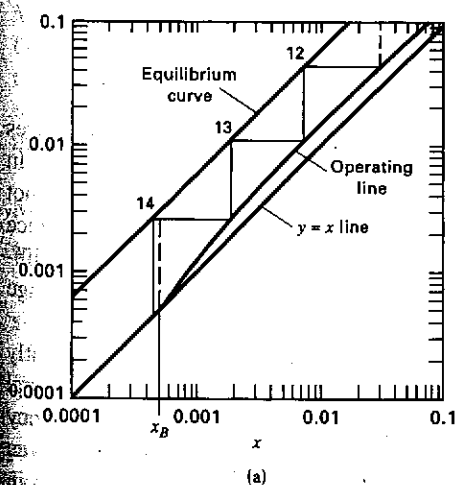


Figure 7.23 Use of log-log coordinates for McCabe-Thiele construction: (a) bottoms end of column; (b) distillate end of column.

Repeat part (c) of Example 7.1 for benzene distillate and bottoms purities of 99.9 and 0.1 mol%, respectively, using a reflux ratio of 1.88, which is about 30% higher than the minimum reflux of 1.44 for these new purities. At the top of the column, $\alpha = 2.52$; at the bottom, $\alpha = 2.26$.

SOLUTION

Figure 7.24 shows the McCabe–Thiele construction for the region of x from 0.028 to 0.956, where the stages have been stepped off in two directions, starting from the feed stage. In this middle region, seven stages are stepped off above the feed stage and eight below the feed stage, for a total of 16 stages, including the feed stage. The Kremser equations can now be applied to determine the remaining stages needed to achieve the desired high purities for the distillate and bottoms.

Additional stages for the rectifying section. With respect to Figure 5.8a, counting stages from the top down, from Figure 7.24:

From (7-3), for $(x_N)_{\text{benzene}} = 0.956$,

$$(y_{N+1})_{\text{benzene}} = 0.982 \quad \text{and} \quad (y_{N+1})_{\text{toluene}} = 0.018$$

Also, $(x_0)_{\text{benzene}} = (y_1)_{\text{benzene}} = 0.999$ and $(x_0)_{\text{toluene}} = (y_1)_{\text{toluene}} = 0.001$

Combining the Kremser equations (5.55), (5-34), (5-35), (5-48), and (5-50) and performing a number of algebraic manipulations:

$$N_R = \frac{\log \left[\frac{1}{\bar{A}} + \left(1 - \frac{1}{\bar{A}} \right) \left(\frac{y_{N+1} - x_0 K}{y_1 - x_0 K} \right) \right]}{\log \bar{A}} \quad (7-39)$$

where N_R = additional equilibrium stages for the rectifying section. For that section, which is like an absorption section, it is best to apply (7-39) to toluene, the heavy key. Because $\alpha = 2.52$ at the top of the column, where K_{benzene} is close to one, take $K_{\text{toluene}} = 1/2.52 = 0.397$. Since $R = 1.88$, $L/V = R/(R + 1) = 0.653$.

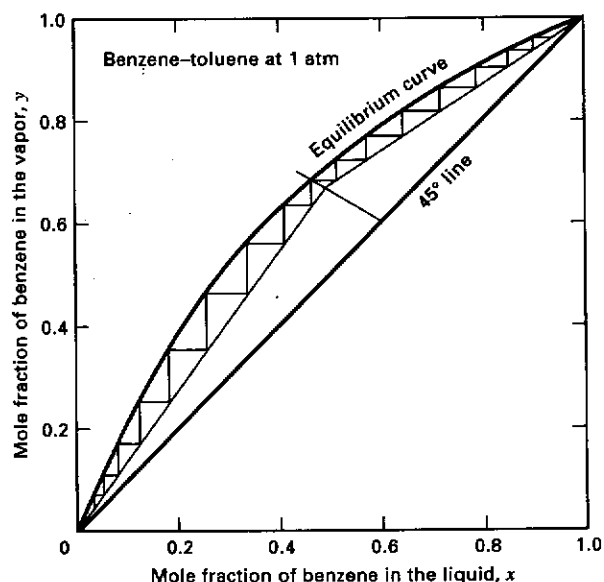


Figure 7.24 McCabe–Thiele construction for Example 7.4 from $x = 0.028$ to $x = 0.956$.

Therefore, the absorption factor for toluene is $A_{\text{toluene}} = L/(VK_{\text{toluene}}) = 0.653/0.397 = 1.64$ which is assumed to remain constant in the uppermost part of the rectifying section. Therefore, from (7-39) for toluene,

$$N_R = \frac{\log \left[\frac{1}{1.64} + \left(1 - \frac{1}{1.64} \right) \left(\frac{0.018 - 0.001(0.397)}{0.001 - 0.001(0.397)} \right) \right]}{\log 1.64} = 5.0$$

Additional stages for the stripping section. With respect to Figure 5.8b, counting stages from the bottom up, we have from Figure 7.24: $(x_{N+1})_{\text{benzene}} = 0.048$. Also, $(x_1)_{\text{benzene}} = (x_B)_{\text{benzene}} = 0.001$. Combining the Kremser equations for a stripping section gives

$$N_S = \frac{\log \left[\bar{A} + (1 - \bar{A}) \left(\frac{x_{N+1} - x_1/K}{x_1 - x_1/K} \right) \right]}{\log(1/\bar{A})} \quad (7-40)$$

where

N_S = additional equilibrium stages for the stripping section

\bar{A} = absorption factor in the stripping section = $\bar{L}/K\bar{V}$

Because benzene is being stripped in the stripping section, it is best to apply (7-40) to the benzene. At the bottom of the column, where K_{toluene} is approximately 1.0, $\alpha = 2.26$, and therefore $K_{\text{benzene}} = 2.26$. By material balance, with flows in lbmol/h, $D = 270.1$. For $R = 1.88$, $L = 507.8$, and $V = 270.1 + 507.8 = 777.9$. From Example 7.1, $V_F = D = 270.1$ and $L_F = 450 - 270.1 = 179.9$. Therefore, $\bar{L} = L + L_F = 507.8 + 179.9 = 687.7$ lbmol/h and $\bar{V} = V - V_F = 777.9 - 270.1 = 507.8$ lbmol/h.

$$\bar{L}/\bar{V} = 687.7/507.8 = 1.354;$$

$$\bar{A}_{\text{benzene}} = \bar{L}/K\bar{V} = 1.354/2.26 = 0.599$$

Substitution into (7-40) gives

$$N_S = \frac{\log \left[0.599 + (1 - 0.599) \left(\frac{0.028 - 0.001/2.26}{0.001 - 0.001/2.26} \right) \right]}{\log(1/0.599)} = 5.9$$

This value includes the partial reboiler. Accordingly, the total number of equilibrium stages starting from the bottom is: partial reboiler + 5.9 + 8 + feed stage + 7 + 5.0 = 26.9.

Use of Murphree Efficiency

The McCabe–Thiele method assumes that the two phases leaving each stage are in thermodynamic equilibrium. In industrial, countercurrent, multistage equipment, it is not always practical to provide the combination of residence time and intimacy of contact required to approach equilibrium closely. Hence, concentration changes for a given stage are usually less than predicted by equilibrium.

As discussed in Section 6.5, a stage efficiency frequently used to describe individual tray performance for individual components is the Murphree plate efficiency. This efficiency can be defined on the basis of either phase and, for a given component, is equal to the change in actual composition in

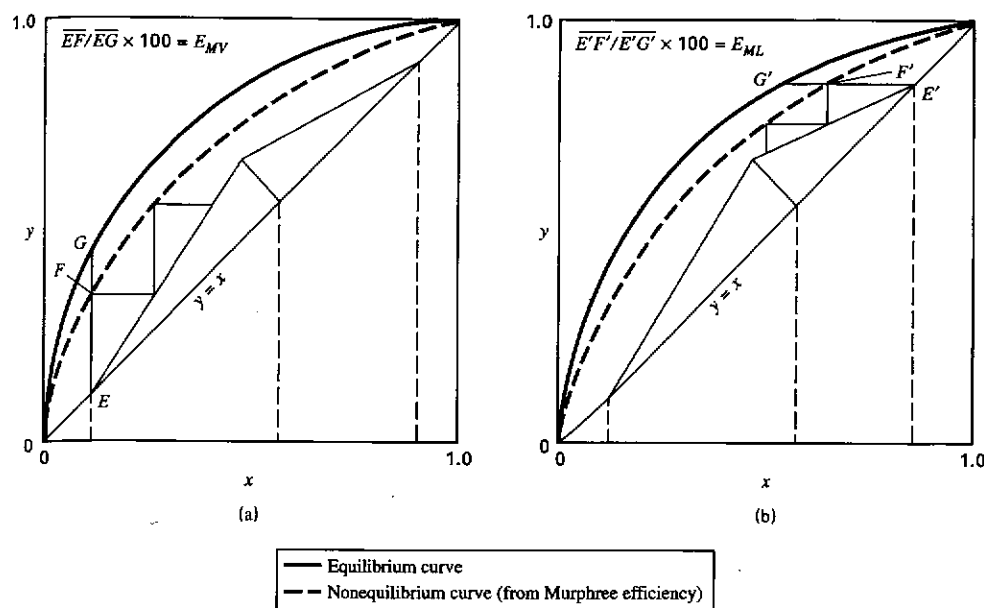


Figure 7.25 Use of Murphree plate efficiencies in McCabe-Thiele construction.

the phase, divided by the change predicted by equilibrium. This definition applied to the vapor phase can be expressed in a manner similar to (6-28):

$$E_{MV} = \frac{y_n - y_{n+1}}{y_n^* - y_{n+1}} \quad (7-41)$$

Where E_{MV} is the Murphree vapor efficiency for stage n , where $n + 1$ is the stage below and y_n^* is the composition in the hypothetical vapor phase in equilibrium with the liquid composition leaving stage n . Values of E_{MV} can be less than or somewhat more than 100%. The component subscript in (7-41) is dropped because values of E_{MV} are equal for the two components of a binary mixture.

In stepping off stages, the Murphree vapor efficiency, if known, can be used to dictate the percentage of the distance taken from the operating line to the equilibrium line; only E_{MV} of the total vertical path is traveled. This is shown in Figure 7.25a for the case of Murphree efficiencies based on the vapor phase. Figure 7.25b shows the case when the Murphree tray efficiency is based on the liquid. In effect, the dashed curve for actual exit-phase composition replaces the thermodynamic equilibrium curve for a particular set of operating lines. In Figure 7.25a, $E_{MV} = \overline{EF}/\overline{EG} = 0.7$ for the bottom stage.

Multiple Feeds, Side Streams, and Open Steam

The McCabe-Thiele method for a single feed and two products is readily extended to the case of multiple feeds and/or side streams by adding one additional operating line for each additional feed or side stream. A multiple-feed arrangement is shown in Figure 7.26. In the absence of side stream L_S , this arrangement has no effect on the material balance associated with the rectifying section of the column above the upper-feed point, F_1 . The section of column between the upper-feed point

and the lower-feed point F_2 (in the absence of feed F) is represented by an operating line of slope L'/V' , this line intersecting the rectifying-section operating line. A similar argument holds for the stripping section of the column. Hence it is possible to apply the McCabe-Thiele graphical construction shown in Figure 7.27a, where feed F_1 is a dew-point vapor, while feed F_2 is a bubble-point liquid. Feed F and side stream L_S of Figure 7.26 are not present. Thus, between the two feed points for this example, the molar vapor flow rate is $V' = V - F_1$ and $\bar{L} = L' + F_2 = L + F_2$. For given x_B, z_{F_2} ,

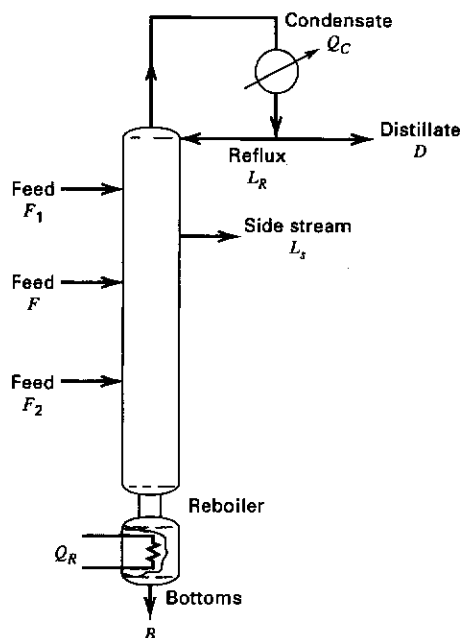


Figure 7.26 Complex distillation column with multiple feeds and side stream.

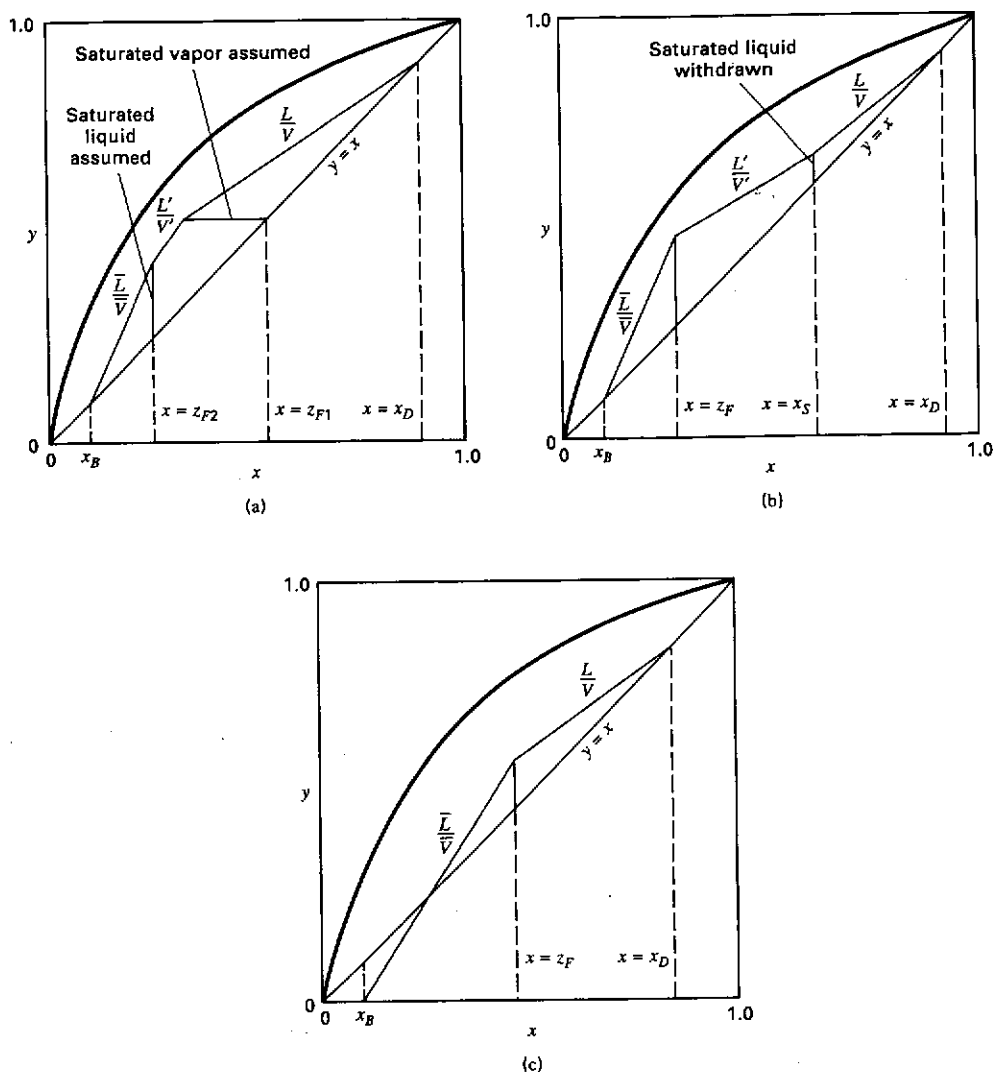


Figure 7.27 McCabe-Thiele construction for complex columns: (a) two feeds (saturated liquid and saturated vapor); (b) one feed, one side stream (saturated liquid); (c) use of open steam.

z_{F1} , x_D , and L/D , the three operating lines in Figure 7.27a are readily constructed.

A side stream may be withdrawn from the rectifying section, the stripping section, or between multiple feed points, as a saturated vapor or saturated liquid. Within material-balance constraints, L_S and x_S can both be specified. In Figure 7.27b, a saturated-liquid side stream of composition x_S and molar flow rate L_S is withdrawn from the rectifying section above feed F . In the section of stages between the side stream-withdrawal stage and the feed stage, $L' = L - L_S$, while $V' = V$. The McCabe-Thiele constructions determine the location of the side stream stage. However, if it is not located directly above x_S , the reflux ratio must be varied until it does.

For certain types of distillation, an inert hot gas is introduced directly into the base of the column. Open steam, for example, can be used if one of the components in the mixture is water, or if water can form a second liquid phase, thereby reducing the boiling point, as in the steam distillation of fats, where heat is supplied by live, superheated steam and no reboiler is used. Most commonly, the feed contains water,

which is removed as bottoms. In that application, Q_R of Figure 7.26 is replaced by a stream of composition $y = 0$ (pure steam) which, with $x = x_B$, becomes a point on the operating line, since the passing streams at this point actually exist at the end of the column. With open steam, the bottoms flow rate is increased by the flow rate of the open steam. The use of open steam rather than a reboiler for the operating condition $F_1 = F_2 = L_S = 0$ is represented graphically in Figure 7.27c.

EXAMPLE 7.16

A complex distillation column, equipped with a partial reboiler and total condenser, and operating at steady state with a saturated-liquid feed, has a liquid side stream draw-off in the enriching (rectifying) section. Making the usual simplifying assumptions of the McCabe-Thiele method: (a) Derive an equation for the two operating lines in the enriching section. (b) Find the point of intersection of these operating lines. (c) Find the intersection of the operating line between F and L_S with the diagonal. (d) Show the construction on a y - x diagram.

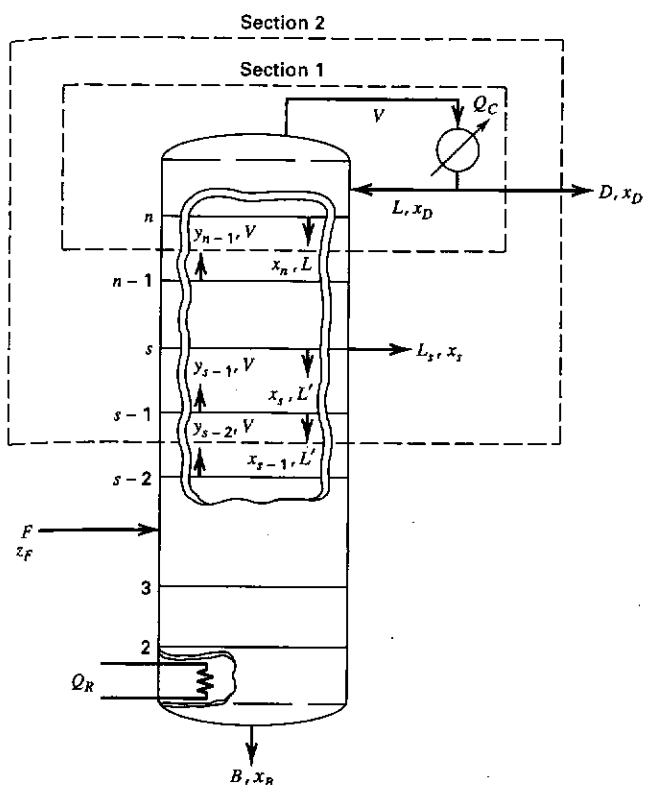


Figure 7.28 Distillation column with side stream for Example 7.5.

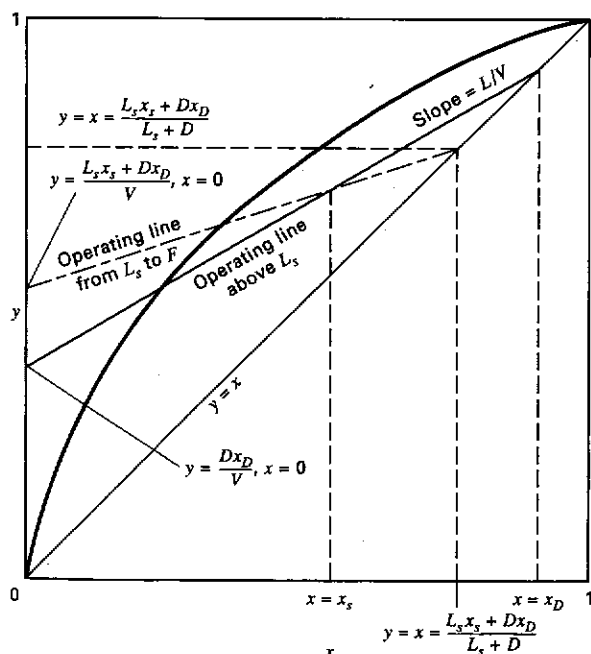


Figure 7.29 McCabe-Thiele diagram for Example 7.5.

SOLUTION

- (a) By material balance over section 1 in Figure 7.28, $V_{n-1}y_{n-1} = L_n x_n + Dx_D$. About section 2, $V_{s-2}y_{s-2} = L'_{s-1}x_{s-1} + L_s x_s + Dx_D$. The two operating lines for conditions of

constant molar overflow become:

$$y = \frac{L}{V}x + \frac{D}{V}x_D \quad \text{and} \quad y = \frac{L'}{V}x + \frac{L_s x_s + Dx_D}{V}$$

- (b) Equating the two operating lines, the intersection occurs at $(L - L')x = L_s x_s$ and since $L - L' = L_s$, the point of intersection becomes $x = x_s$.

- (c) The intersection of the lines

$$y = \frac{L'}{V}x + \frac{L_s x_s + Dx_D}{V}$$

and $y = x$ occurs at $x = \frac{L_s x_s + Dx_D}{L_s + D}$

- (d) The y - x diagram is shown in Figure 7.29.

7.3 ESTIMATION OF STAGE EFFICIENCY

Methods for estimating the stage efficiency for binary distillation are analogous to those for absorption and stripping, presented in Section 6.5. The efficiency is a complex function of tray design, fluid properties, and flow patterns. However, in hydrocarbon absorption and stripping, the liquid phase is often rich in heavy components so that liquid viscosity is high and mass-transfer rates are relatively low. This leads to low stage efficiencies, usually less than 50%. In contrast, for binary distillation, particularly of close-boiling mixtures, liquid viscosity is low, with the result that stage efficiencies, for well-designed trays and optimal operating conditions, are often higher than 70% and can be even higher than 100% for large-diameter columns where a cross-flow effect is present.

Performance Data

As discussed in *AIChE Equipment Testing Procedure* [8], performance data for an industrial distillation column are best obtained at conditions of total reflux (no feed or products) so as to avoid possible column-feed fluctuations, simplify location of the operating line, and avoid discrepancies between feed and feed-tray compositions. However, as shown by Williams, Stigger, and Nichols [9], efficiency measured at total reflux can differ markedly from that at design reflux ratio. Ideally, the column is operated in the range of 50% to 85% of flooding. If liquid samples are taken from the top and bottom of the column, the overall plate efficiency, E_o , can be determined from (6-21), where the number of the theoretical stages required is determined by applying the McCabe-Thiele method at total reflux, as in Figure 7.11. If liquid samples are taken from the downcomers of intermediate trays, Murphree vapor efficiencies, E_{MV} , can be determined using (6-28). If liquid samples are withdrawn from different points on one tray, (6-30) can be applied to obtain point efficiencies, E_{OV} . Reliable values for these efficiencies require the availability of accurate vapor-liquid equilibrium data. For that reason, efficiency data for binary mixtures that form ideal solutions are preferred.