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4

Distillation of Multicomponent Mixtures without Azeotropes

Mixtures containing more than two components complicate the design problem somewhat. The specification of product purities is not as simple as in the binary case and the pinches are different in number and in character. In the first section of this chapter, we summarize the basic relationships, especially differences with binary mixtures. The next section illustrates the application of these models to ternary mixtures, followed by a separate section on mixtures with four and more components. Finally, we discuss tangent pinches in multicomponent mixtures.

4.1 BASIC RELATIONSHIPS

Phase Equilibrium

The generalization of Eq. 2.31 that describes the vapor-liquid equilibrium in a mixture containing c components is

$$y_i = \frac{\alpha_i x_i}{\sum \alpha_j x_j} \tag{4.1}$$

where i is the index of any component and α_i is the volatility of component i. Unless indicated otherwise, the summation is taken over all of the c components present in the mixture. The volatilities are given by $\alpha_i \equiv (\gamma_i P_i^{\text{sat}} \phi_k)/(\gamma_k P_k^{\text{sat}} \phi_i)$ relative to a reference component k. We will usually order the components by decreasing boiling point, with the highest-boiling component as the reference.[1]

These phase equilibrium relationships are nonlinear relations among all of the c mole fractions in each phase. However, we will usually need only $c - 1$ of the mole

[1]The choice of a reference component will sometimes be emphasized with the notation α_{ij}. Note that $\alpha_{ij} = \alpha_{ik}\alpha_{kj}$.

fractions in each phase with the understanding that the remaining mole fractions can be determined from the relations

$$\sum x_i = \sum y_i = 1 \tag{4.2}$$

Even when vapor-phase nonidealities can be neglected, the volatilities may not be constant because of the composition dependence of the activity coefficients or through the variation of the vapor pressures with temperature. In the important, but restrictive, special case where the volatilities can be treated as constants it is simple to find the composition of either phase given that of the other, i.e., to rewrite Eq. 4.1 as

$$x_i = \frac{y_i/\alpha_i}{\sum y_j/\alpha_j} \tag{4.3}$$

Material and Energy Balances

The overall balances for multicomponent separations are more informative than in the binary case. There are c independent balances that can be written

$$F = D + B \tag{4.4}$$

and

$$Fz_{i,F} = Dz_{i,D} + Bz_{i,B} \tag{4.5}$$

where $i = 1, \ldots, c-1$. The analogs of Eqs. 3.3, 3.4, and 3.5 are

$$\frac{D}{F} = \frac{z_{i,F} - z_{i,B}}{z_{i,D} - z_{i,B}} \quad \text{and} \quad \frac{B}{F} = \frac{z_{i,D} - z_{i,F}}{z_{i,D} - z_{i,B}} \tag{4.6}$$

$$\frac{D}{B} = \frac{z_{i,F} - z_{i,B}}{z_{i,D} - z_{i,F}} \tag{4.7}$$

Thus, a specification of the product and feed compositions for any one component is sufficient to determine the ratio of the total product and feed flows and the ratio of the composition differences for every other component.[2]

The energy balances and the definitions of reflux ratio, reboil ratio, and feed quality are identical to the binary case when the composition of the light component in Eqs. 3.19, 3.22, and 3.35 is replaced by the composition of any component in

[2]It is sometimes convenient to relate the fractional recoveries to the mole fractions as follows:

$$f_{i,D} = \frac{z_{i,D}}{z_{i,F}} \frac{z_{j,F} - z_{j,B}}{z_{j,D} - z_{j,B}} \quad \text{and} \quad f_{i,B} = \frac{z_{i,B}}{z_{i,F}} \frac{z_{j,D} - z_{j,F}}{z_{j,D} - z_{j,B}} \tag{4.8}$$

where i and j are component labels and D and B indicate distillate and bottoms. If the fractional recoveries are known, the distillate and bottoms mole fractions are given by

$$z_{i,D} = \frac{f_{i,D} z_{i,F}}{\sum f_{j,D} z_{j,F}} \quad \text{and} \quad z_{i,B} = \frac{f_{i,B} z_{i,F}}{\sum f_{j,B} z_{j,F}} \tag{4.9}$$

With two product streams, $f_{i,D} + f_{i,B} = 1$ and only one of the fractional recoveries for a given component is independent.

the mixture. For example, the constant molar overflow approximation results in the following relationship between the reflux and the reboil ratios (cf. Eq. 3.35):

$$\frac{D}{B} = \frac{s + 1 - q}{r + q} \tag{4.10}$$

With the constant molar overflow assumption, the operating relationships for component i are

$$y_{i,n-1} = \frac{r}{r+1} x_{i,n} + \frac{z_{i,D}}{r+1} \tag{4.11}$$

in the rectifying section and

$$y_{i,n} = \frac{s+1}{s} x_{i,n+1} - \frac{z_{i,B}}{s} \tag{4.12}$$

in the stripping section. Stage-to-stage energy balances may also be needed to account for the variation of the liquid and vapor flows. It is straightforward to add these to the formulation if good models and data for the enthalpies as a function of composition and temperature are available.

4.2
COMPOSITION PROFILES AND PINCHES

The Boundary Value Design Method

It is useful to find a geometric method for mixtures with more than two components. With the addition of more components, the visualization is more difficult, but a complete picture is still possible for three components. This section considers the main geometric ideas for ternary ideal mixtures, and nonideal ternary mixtures are considered in the next section. The general case with four or more components is the subject of Sec. 4.5.

We will use a *triangular diagram* like the one shown in Fig. 4.1 to represent the compositions.[3] Each vertex of the triangle corresponds to a pure component and each edge corresponds to a binary mixture of the two pure components which lie at the vertices joined by that edge. The overall material balance in Eq. 4.7 can be used for any two components, say 1 and 2, to find

$$\frac{z_{2,B} - z_{2,F}}{z_{1,B} - z_{1,F}} = \frac{z_{2,D} - z_{2,F}}{z_{1,D} - z_{1,F}} \tag{4.13}$$

The term on the left is the slope of the line joining the bottoms and feed compositions and on the right is the slope of a line joining the distillate and feed compositions.

[3]Some prefer an equilateral triangle, or mass fractions instead of mole fractions. We use right triangles because rectangular coordinates seem easier to interpret and mole fractions because phase equilibrium models naturally use these variables. Modern computer-aided design tools make the coordinates easy to adjust.

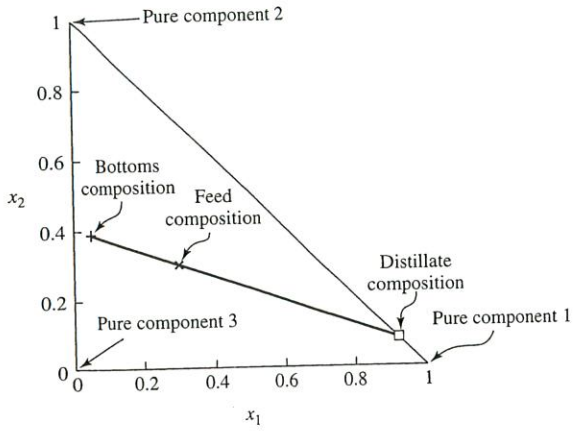


FIGURE 4.1
A composition diagram for ternary mixtures. The abscissa and ordinate represent the mole fractions of the components 1 and 2, respectively. Each vertex represents a pure component and each edge represents a binary mixture. The feed composition is $\mathbf{z}_F = (0.3, 0.3, 0.4)$ and the product compositions are $z_{1,B} = 0.05$, $z_{1,D} = 0.95$, $z_{2,D} = 0.049$. By mass balance $z_{2,B} = 0.397$, $D = 0.626F$, and $B = 0.374F$.

Thus, *on a triangular diagram, the distillate, bottoms, and feed compositions are collinear.*

Unlike the case for binary mixtures, it is necessary to consider the details of the column in order to determine the product distribution for mixtures with three or more components.

The liquid-phase mole fraction in each section of the column will vary from stage to stage according to the dictates of the material and energy balances and the vapor-liquid equilibrium. For ternary mixtures, the profiles of the liquid (and vapor) phase compositions can be determined by solving Eqs. 4.11 and 4.12 along with the appropriate VLE relationships for the two lightest components. Beginning with the distillate and bottoms compositions, the mole fractions on successive stages above the bottom and below the distillate can be computed. This procedure is completely analogous to the approach discussed in Sec. 3.3 for the treatment of binary mixtures. Beginning with some product compositions that satisfy the overall mass balances, we can examine the behavior of the composition profiles.

EXAMPLE 4.1. Figure 4.2 shows profiles of the liquid-phase mole fractions for a mixture of pentane, hexane, and heptane. The feed is a saturated liquid at atmospheric pressure with a composition $\mathbf{x}_F = (0.3, 0.3, 0.4)$; the volatilities are approximately constant at $\alpha_{13} = 6.35$ and $\alpha_{23} = 2.47$. The distillate contains 95% pentane and 4.9% hexane; the balance of 0.1% of the distillate is therefore heptane. If the bottoms is to contain 5% pentane, then the overall balances demand that this product stream also contains 39.7% hexane and 55.3% heptane. Each of the symbols represents the liquid mole fractions on an equilibrium stage; the stripping section requires $n_S = 5.0$ stages (one can be

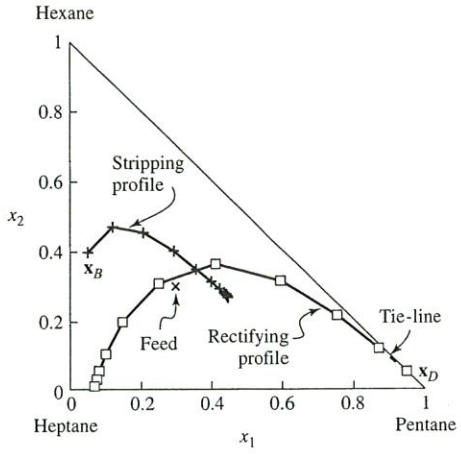


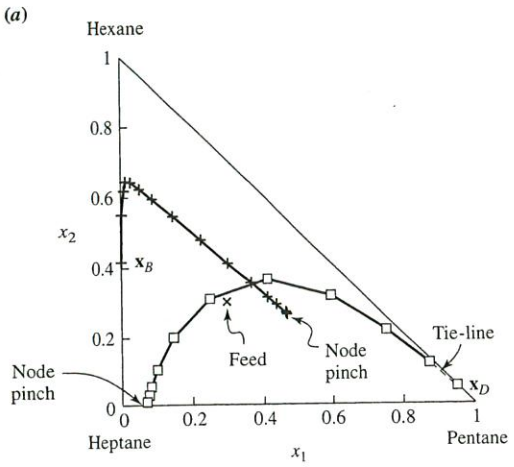
FIGURE 4.2
Composition profiles for a mixture of pentane (1), hexane (2), and heptane (3). The volatilities are taken as $\alpha_{13} = 6.35$, $\alpha_{23} = 2.47$; the pressure is 1 atm and the feed is a saturated liquid. The product specifications are for saturated liquid products with the distillate containing 95 mol % pentane, 4.9% hexane and 0.1% heptane and the bottoms 5% pentane. With a reflux ratio of 2.5, corresponding to a reboil ratio of 1.35, 8.3 theoretical stages are required. The feed is introduced five stages from the bottom as indicated by the intersection of the rectifying (□) and stripping (+) profiles. The dashed line is a vapor-liquid tie-line between the liquid composition on the top stage in the rectifying section and the distillate composition, $\mathbf{x}_D = \mathbf{y}_1$.

an equilibrium reboiler) and the rectifying section contains $n_R = 4.3$ stages. The total number of stages in the column is $n_R + n_S - 1 = 8.3$. (One stage is subtracted to avoid counting the feed stage twice, for both the stripping and rectifying sections.)

Because we specify the product compositions at the *ends* of the column, this is called a "boundary value" design procedure. The location of the feed is now a dependent variable, and it must be introduced at the intersection of the profiles.[4] If only two of the product compositions have specifications that *must* be met, the third composition can be adjusted to minimize the number of stages.

Figure 4.3 shows some profiles for cases where the mole fraction of pentane in the bottoms is reduced. A portion of the stripping profile approaches the ordinate in the lower stages, where the liquid contains little pentane. On successively higher stages, the mole fraction of hexane increases and the mole fraction of heptane drops. Eventually the mole fraction of hexane reaches a maximum, the composition of pentane increases rapidly, and the rate of decrease of the mole fraction of heptane is slowed abruptly. This point has mole fractions of approximately (0.0, 0.676, 0.324). This point is approached asymptotically by the stripping profile with an increasing

[4]Note that the composition of the liquid on the feed stage is generally *not* the same as that of the feed.



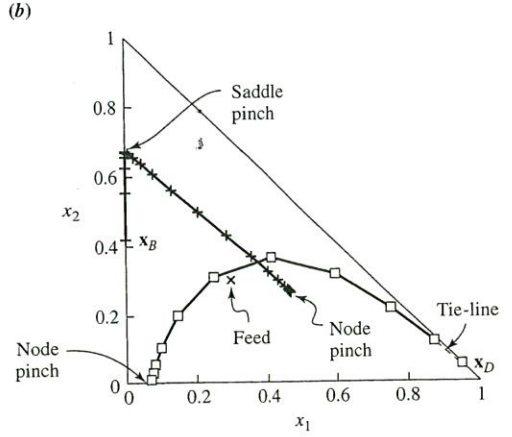


FIGURE 4.3
The effect of product purity on the liquid composition profiles for a mixture of the normal alkanes pentane, hexane, and heptane. The distillate contains 95% pentane, 4.9% hexane, and 0.1% heptane; the bottoms purity is (*a*) 0.1% pentane and (*b*) 0.0001% pentane. Both profiles show a *node* pinch. A *saddle pinch* in the stripping profile is apparent at the composition (0.0, 0.676, 0.324).

number of stages as $z_{1,B} \to 0$. That is, there is a large number of stages for which the composition is essentially constant; this is a *pinch*. The *asymptotic* approach to this point corresponds to a new behavior called a *saddle pinch* or simply a *saddle*. This has no analog in binary mixtures, but it is a common and extremely important feature in the separation of mixtures containing three or more components.[5] The pinches that appear at the end of the upper and the lower operating lines for binary

[5]Another pinch that does have a binary analog is the tangent pinch; this is found in nonideal mixtures, which are discussed in Sec. 4.6.

mixtures do have an analog in the ternary case; these *node pinches* or *nodes* are also shown in Figs. 4.2 and 4.3.[6]

As for the case of binary mixtures, the pinches can be used to find the minimum flows. However, for ternary mixtures there are several possibilities for the relative positions of the pinches. It is useful to classify these possibilities systematically once we consider the degrees of freedom.

We consider rectifying and stripping profiles which satisfy Eqs. 4.11 and 4.12 and cases where the feed composition, feed quality, and the pressure are known. The remaining variables are the distillate and bottoms compositions, along with the reflux and reboil ratios, for a total of $2(c-1)+2 = 2c$ variables.[7] The energy balance in Eq. 4.10 provides one relationship between r and s, and there are also $c-2$ independent versions of the mass balances Eq. 4.13 relating the product compositions. This gives $(2c-2)-(c-2) = c$ degrees of freedom in the product compositions and one degree of freedom between r and s for a total of $c+1$ degrees of freedom from the overall mass and energy balances. For a feasible column, we must also have an intersection of the profiles at the feed stage. If we denote the liquid-phase compositions in the stripping profile as $\mathbf{x}^s$ and in the rectifying profile as $\mathbf{x}^r$, then after n_T stages in the top of the column and n_B stages in the bottom we must have the $c-1$ additional constraints

$$\mathbf{x}^r_{n_T} = \mathbf{x}^s_{n_B} \tag{4.14}$$

and two additional variables n_T and n_B.

Thus, there are $(c+1)-(c-1)+2 = 4$ *degrees of freedom.* Common design specifications for binary mixtures consist of two product compositions (or fractional recoveries), a reflux *or* reboil ratio, and the condition that the feed stage location be optimal. In ternary mixtures, we might first choose the distillate and the bottoms composition for one of the components. Then, a specification of one more product composition and the reflux ratio will provide sufficient information to determine the composition profiles throughout the column, as well as the feed stage location. For a *performance* model, we might choose the number of stages in each column section and the reflux and reboil ratios. Then, the product compositions and flows are calculated. Iterative schemes can be devised to adjust these specifications with the goal of achieving certain desired products, but this is often inefficient, especially in nonideal mixtures.

Minimum Flows and Classification of Splits

In binary mixtures, a node pinch or a tangent pinch determines the minimum flows, but in multicomponent mixtures a saddle pinch may also be important. The node

[6]The terms "saddle" and "node" originate from a consideration of the composition diagram as a phase plane for Eqs. 4.11 and 4.12 and from further considerations for azeotropic mixtures, discussed in Chap. 5.

[7]We presume that Eqs. 4.2 can be trivially satisfied and therefore that there are $c-1$ independent compositions.

pinch is usually obvious, but the influence of the saddle pinch may not be immediately apparent in the profile. The position of the node usually depends most strongly on the ratio of vapor to liquid flows (reflux or reboil ratio), while the location of the saddle is more sensitive to the purity.

Figure 4.4 shows a few profiles for different values of the reflux ratio and product purities. Only the nodes are evident in Fig. 4.4*a*. Figure 4.4*b* shows a rectifying saddle

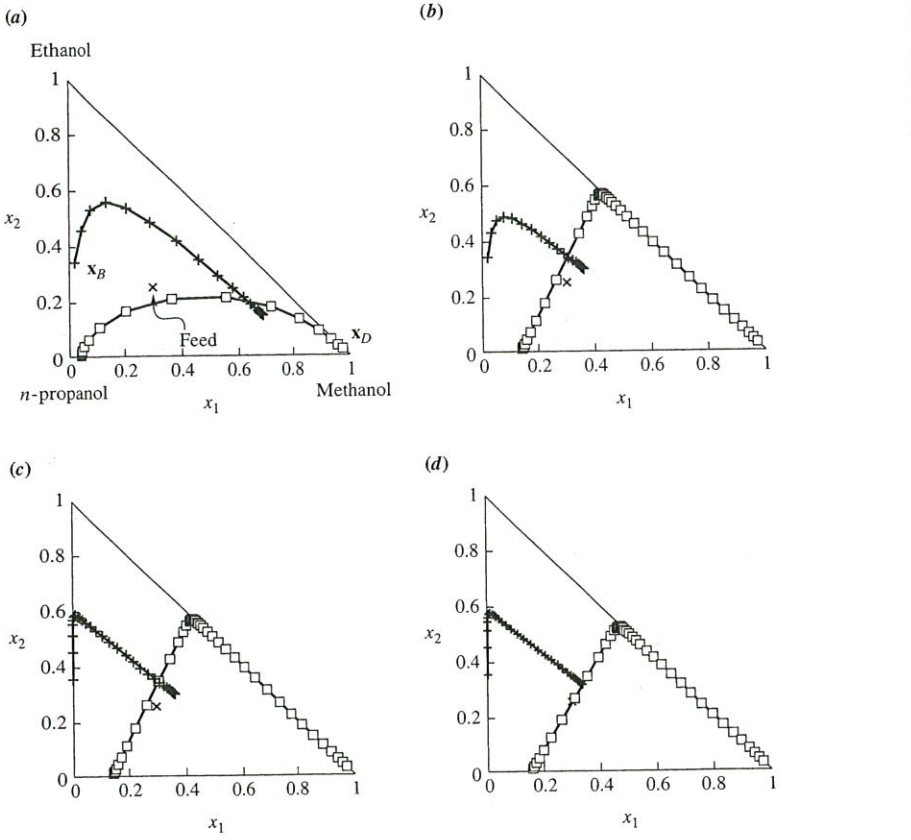


FIGURE 4.4
Column profiles and pinches for a ternary mixture of methanol, ethanol, and *n*-propanol at a pressure of 1 atm. The relative volatilities are 3.25, 1.90, and 1.00, the feed is a saturated liquid with a composition of (0.30, 0.25, 0.45), and the distillate contains 98% methanol. The reflux ratio and the mole fractions of methanol in the bottoms and propanol in the distillate are (*a*) 10, 0.02, 5×10^{-4}, (*b*) 3, 0.02, 5×10^{-11}, (*c*) 3, 5×10^{-4}, 5×10^{-11}, and (*d*) 2.7, 5×10^{-4}, 5×10^{-11}. The rectifying profile (□) and the stripping profile (+) each show a node pinch. The visibility of the saddle pinch depends primarily on the product purity.

and Fig. 4.4*c* shows both a node and a saddle in each profile. The saddle pinches in Fig. 4.4*c* correspond to a nearly infinite number of stages and a zone of nearly constant composition in each column section, so it may seem that this corresponds to the minimum reflux, but the reflux ratio can be further reduced, as shown in Fig. 4.4*d*. It is this case that corresponds to the minimum reflux (and flows). This is because the profiles do not intersect for lower values of the reflux ratio so that the product purities cannot be met even with an infinite number of stages. Also see Fig. 4.18*a*.

Valuable intuition is gained by generating these profiles yourself as the product compositions are systematically varied. Exercises 1, 2, and 3 are strongly recommended.

Figure 4.5 shows three possibilities for the minimum flow conditions, depending on the product specifications. When the node pinch in the stripping section controls,[8] the distillate may contain very little of the heaviest component, and this could be written symbolically as "AB/ABC." More specialized (but common) cases have a high purity and recovery of the lightest component in a *direct* or "A/BC" split; see Fig. 4.5*a* and Exercise 1. Conversely, when the node in the rectifying section controls, as in Fig. 4.5*b*, we produce a bottoms with a high purity and recovery of the heaviest component in an *indirect* or "AB/C" split. There is also a special case where the nodes from each section meet at the feed composition as in Fig. 4.5*c*; this is a *transition* or "AB/BC" split, since it marks the division between the direct and indirect geometries. Notice that the smallest value for $r_{\min}$ occurs for the transition split; see Exercise 3. This is sometimes used to develop novel systems of columns where the first column performs the AB/BC split, followed by other columns that split A from B and B from C. See Chap. 7 for more details.

In the direct split, the minimum reflux ratio is independent of the bottoms composition, although the *reboil* ratio will change for different values of the bottoms composition.[9] Consequently, the stripping profile will be somewhat different, although its node will still (just) meet the rectifying profile. Likewise, a variety of distillate purities could be specified for a separation like the one shown in Fig. 4.5*b* and the minimum reboil ratio along with the composition profile in the stripping section remain unchanged if the bottoms and feed compositions are constant.

This leads to a procedure for finding the minimum flows. The reflux or reboil ratio is adjusted until the liquid composition profiles meet in one of the three possible configurations. In fact, we can efficiently compute the minimum reflux (or reboil) knowing only the pinches. For instance, the pinches in the controlling profile, the node pinch in the other profile, and the feed composition are collinear for constant volatilities and high purities. When the volatilities are not constant, this collinearity is still a useful approximation, as discussed later. This method for finding the minimum flows will be discussed in more detail later in this chapter.

[8] "Control" by a pinch means that it is this pinch point which must align with the saddle in the opposite profile and the feed composition.
[9] The reflux and reboil ratios are related by Eq. 4.10.

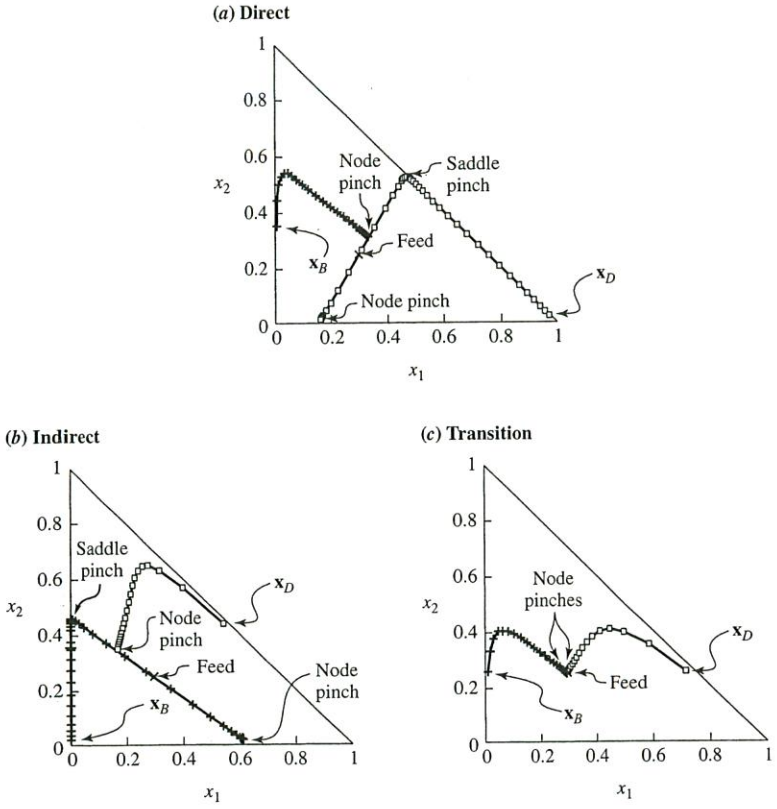


FIGURE 4.5
Composition profiles in (*a*) the direct, (*b*) the indirect, and (*c*) the transition splits. The feed is identical to the case described in Fig. 4.4, and we use $\alpha_{13} = 3.25$ $\alpha_{23} = 1.9$. In (*a*), the product compositions are $\mathbf{x}_D = (0.98, 0.02, 5 \times 10^{-11})$ and $\mathbf{x}_B = (0.005, 0.350, 0.645)$ while the reflux ratio is $r_{\min}$ =2.7. For case (*b*) these variables are (0.55, 0.44, 0.01), $(5 \times 10^{-11}, 0.022, 0.978)$ and 1.35. Case (*c*) is a transition or "AB/BC" split where the pinch in each section is adjacent to the feed stage; for this case, $\mathbf{x}_B = (0.01, 0.25, 0.74)$, $\mathbf{x}_D = (0.73, 0.25, 0.02)$, and $r = r_{\min} = 1.02$.

Minimum Stages

The minimum number of theoretical stages required for a separation can be found from a consideration of the limiting case of total reflux. Figure 3.6*a* shows an example for a binary mixture. For binary mixtures with a constant volatility, Fenske's equation 3.48 can also be used.

However, when the mixture contains more than two components, the minimum number of stages also corresponds to certain specific product compositions for some

of the components. For total reflux and total reboil we have $r \to \infty$ and $s \to \infty$, respectively, so that the operating line in each section approaches $x_n = y_{n-1}$. In fact, the rectifying and stripping sections are indistinguishable. Two degrees of freedom remain; we can specify (only) two product compositions and the others must be computed, along with the number of stages.

Ternary mixtures can be understood from a consideration of the liquid-phase composition profiles as the reflux ratio is increased (Fidkowski et al., 1993, especially Fig. 2); also see Fig. 5.12. Figure 4.6 shows the composition profiles at $r = 1{,}000$ for the ternary mixture of normal alkanes discussed above. For each profile, the feed

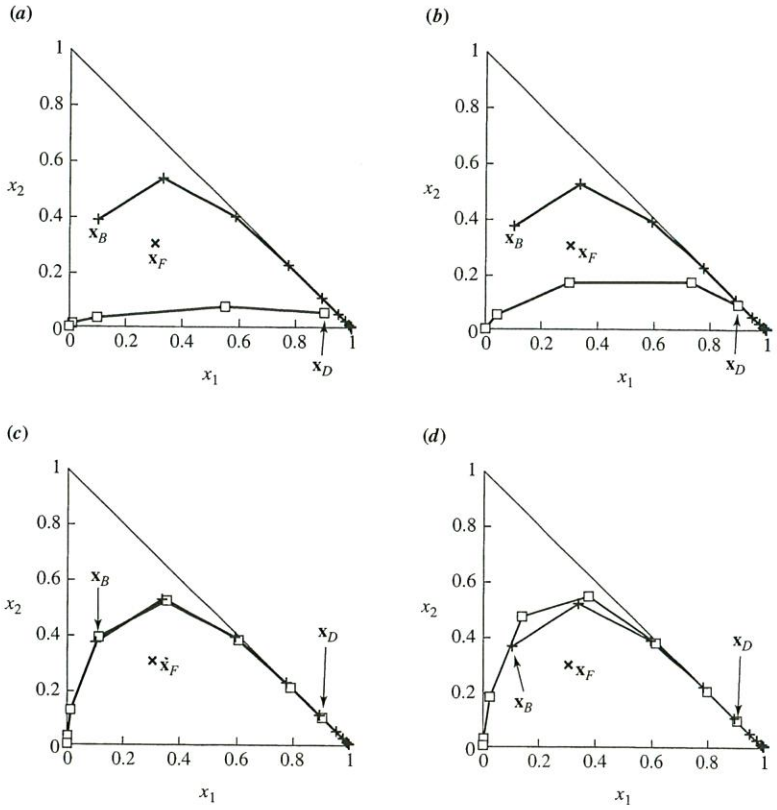


FIGURE 4.6
Composition profiles and the minimum number of stages for a ternary mixture. The feed is a mixture of hexane, heptane, and nonane with a composition of (0.3, 0.3, 0.4). The distillate contains 90% hexane and the bottoms contains 10%. The liquid-phase composition profiles in the rectifying (□) and stripping (+) sections are shown for distillates containing (*a*) 5.00%, (*b*) 1.00%, (*c*) 0.016%, and (*d*) 0.010% nonane. Case (*c*) corresponds to the minimum number of stages, which is slightly greater than 4.

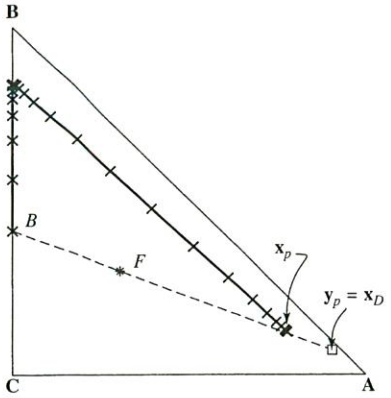


FIGURE 4.14
Stripping profile showing collinearity of the tie-line at a pinch with the product and feed compositions.

Equation 4.64 along with 4.1 and 4.2 is solved for $y_{1,p}$, $y_{2,p}$, and $x_{2,p}$ as a function of $x_{1,p}$. *The limiting distillate compositions are given by the locus of vapor pinch points. These values are independent of the bottoms composition, which affects only the reboil ratio in Eq. 4.63.* Similar expressions for the reflux ratio and the bottoms composition of the second component can be found from Eqs. 4.59, 4.60, 4.1, and 4.2 as

$$r + 1 = \frac{x_{1,D} - x_{1,B}}{y_{1,B} - x_{1,B}} \tag{4.65}$$

and

$$\frac{y_{2,p} - x_{2,p}}{y_{1,p} - x_{1,p}} = \frac{x_{2,F} - x_{2,p}}{x_{1,F} - x_{1,p}} \tag{4.66}$$

Instead of tracking all of the solutions of Eqs. 4.64 and 4.66 a trial-and-error approach using composition profiles can be used to find these limits for product compositions. This is discussed in Exercise 1; that approach is more practical when one of the desired product purities is known, and the limits for the other compositions are sought.

The curves defined by Eqs. 4.64 and 4.66 are shown in Fig. 4.15*a* for a mixture of normal alkanes. Product purities below these curves cannot be accomplished by distillation in a single feed column. For a saturated liquid feed, it can also be shown that the two curves meet at the feed composition $\mathbf{x}_F$, that the tangent to the liquid pinch curve at this point is a tie-line through the feed composition, i.e., through the point $\mathbf{y}_F$, which is the composition of a vapor in equilibrium with the liquid feed. This tie-line is simple to compute and is also shown in the figure. The construction of this tie-line and its extension to the binary edges identifies the product compositions for which the composition profiles in *each* section have a node pinch at the feed composition at the minimum reflux; cf. Fig. 4.5*c*. This is the special case of a transition split, and we will refer to the result of this construction as the *transition line*.

In Fig. 4.15*a*, the shaded regions correspond to compositions that are feasible according to the material balance constraints. Product compositions in either one of

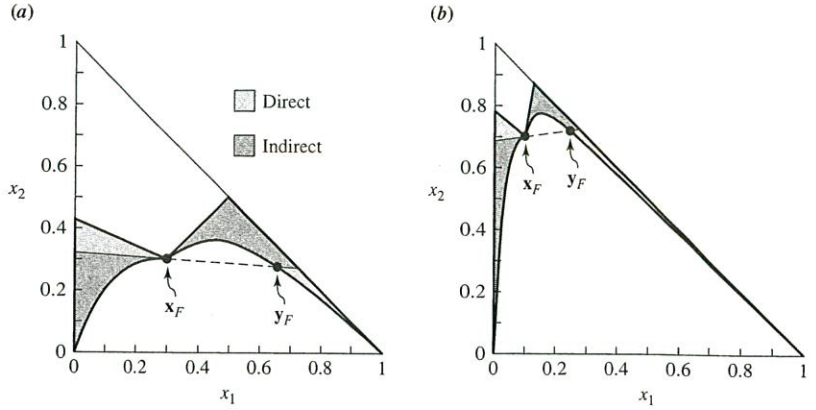


FIGURE 4.15
Feasible regions for product compositions in ternary mixtures. The lower curves are determined from the locus of node pinch compositions in the rectifying (left) and stripping (right) profiles. If the product compositions were chosen on this curve, a single column section could accomplish the separation at minimum flows. The tie-line through the feed composition is tangent to the boundary and marks the transition between the direct and the indirect splits. The volatilities and feed compositions are (*a*) (12.67, 5.35, 1.00) and (0.3, 0.3, 0.4), respectively and (*b*) (12.67, 5.35, 1.00) and (0.1, 0.7, 0.2), respectively.

the two similarly shaded regions in the figure correspond to the direct or indirect splits. Transition splits occur for product compositions on the transition line, with the "sharp" transition split, AB/BC, corresponding to the endpoints of the transition line. The vapor rates increase rapidly as the product composition moves away from the boundary defined by the transition line toward either the lower portion of the hypotenuse or the ordinate in the figure. The lowest possible minimum reflux (or minimum reboil) ratio for any given product compositions of the lightest component are found close to the transition line. Figure 4.15*b* shows the shapes of these feasible regions at another feed composition.

Equations 4.63 to 4.66 are independent of the VLE model, and the same approach can be applied for nonideal mixtures. However, when mixtures have tangent pinches or azeotropes, the pinch tracking is more complicated and distillation boundaries further complicate the picture. In Sec. 4.6 we discuss tangent pinches, and Chap. 5 gives a more detailed analysis of azeotropic mixtures.

Minimum Flows

A useful measure for comparing alternative distillation systems and for setting the vapor rate inside a column is the minimum value for the vapor-to-feed ratio $(V/F)_{\min}$, where V is the vapor rate at the end of the column with the most expensive utility costs. This is normally the vapor rate leaving the reboiler. However, in cryogenic and

other low-temperature distillations that require refrigerated condensers V represents the vapor rate entering the condenser. As a rule, values of $(V/F)_{\min}$ less than 0.5 are considered low (attractive) while values greater than 3 are high. The minimum value for V/F is normally calculated from the minimum reflux or minimum reboil ratio using the relations

$$\left(\frac{V_T}{F}\right)_{\min} = (r_{\min} + 1)\frac{D}{F} \tag{4.67}$$

$$\left(\frac{V_B}{F}\right)_{\min} = s_{\min}\frac{B}{F} \tag{4.68}$$

When the constant molar overflow assumption applies, the ratio $(V_B/F)_{\min}$ is related to $r_{\min}$ as follows:

$$\left(\frac{V_B}{F}\right)_{\min} = (r_{\min} + q)\frac{D}{F} + (q - 1)\frac{B}{F} \tag{4.69}$$

The ratios D/F and B/F are known functions of the specified product compositions.

For binary mixtures, three of the four degrees of freedom for a design can be taken as $x_{D,1}, x_{B,1}$, and r. The composition changes can be represented on a McCabe-Thiele diagram, which is shown in Fig. 4.16 for the separation of hexane (1) and heptane (2).

The composition profiles are also shown in Fig. 4.16 by projection of the liquid mole fractions onto the x_1 axis. The profiles start at product compositions and end at the fixed points (pinches) where the operating lines intersect the equilibrium curve. There are at least two fixed points in each profile, one a stable node and the other an unstable node. For $r < r_{\min}$, the profiles do not intersect. At $r = r_{\min}$, the stable nodes in both profiles occur at the same point. For a saturated liquid feed, this happens exactly at the feed composition. For other values of q the common pinch point can be calculated easily. When $r > r_{\min}$, the profiles overlap and we can choose an optimal feed stage location; this is the fourth degree of freedom.

If we define the *fixed point distance* between the node pinch in the rectifying section and the node pinch in the stripping section as e_1, it follows that on a graph of e_1 versus $r/(r + 1)$ minimum reflux corresponds to the point where the curve goes through zero (see Fig. 4.17). For this example, $r_{\min} = 0.968$, which gives $(V_B/F)_{\min} = 1.084$ from Eq. 4.69.

The utility of this approach is that it generalizes to mixtures with more components. Liquid composition profiles for the separation of benzene from a mixture of benzene (1), toluene (2), and xylene (3) (a direct split) are shown in Fig. 4.18. The profiles start at the product compositions and end at the stable nodes; an additional (saddle) fixed point is present close to the binary edge in each profile. The saddles correspond to points where one of the components almost disappears from the column section, i.e., becomes present only in trace amounts. There is no analog to this in binary mixtures. For $r < r_{\min}$ the profiles do not intersect and the separation cannot be achieved even with an infinite number of stages. For $r > r_{\min}$ the profiles intersect transversely and the separation can be achieved with a finite number of stages. At $r = r_{\min}$, the stripping profile ends (pinches) somewhere on the rectifying profile

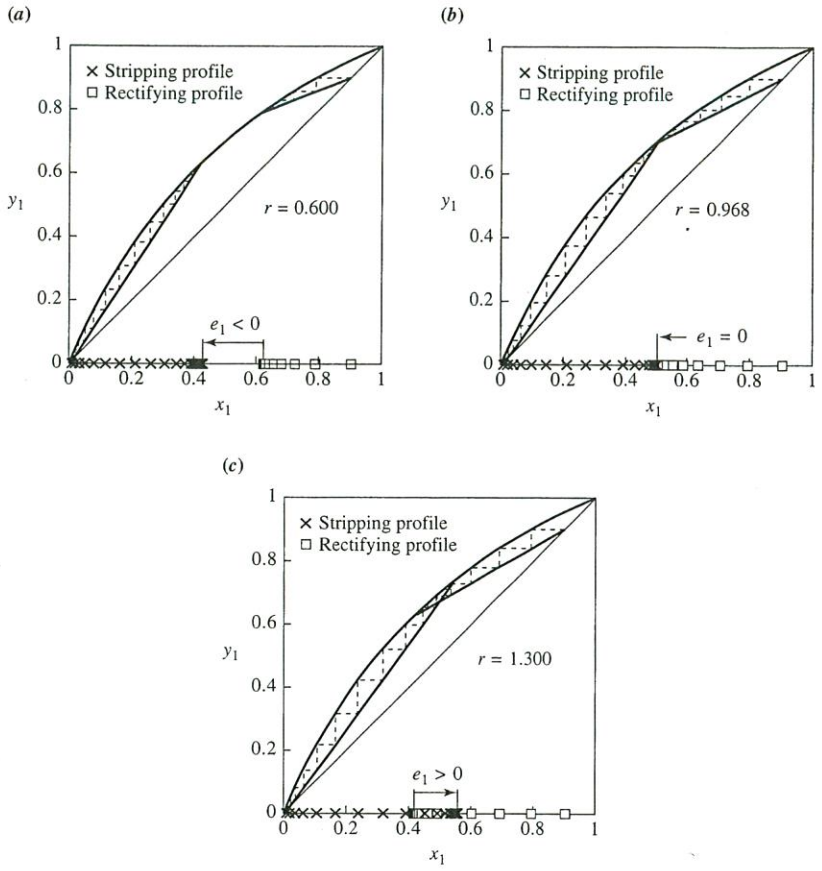


FIGURE 4.16
McCabe–Thiele diagram for a binary separation of hexane (1) and heptane (2) at 1 atm pressure with $x_{F,1} = 0.5$, $x_{D,1} = 0.9$, $x_{B,1} = 0.01$, and $q = 1$. Vapor-liquid equilibrium was calculated with a constant volatility of 2.37: (*a*) $r < r_{\min}$, (*b*) $r = r_{\min}$, (*c*) $r > r_{\min}$.

and the separation can just be accomplished with an infinite number of stages. *Two* pinch zones control the minimum reflux. For a direct split (Fig. 4.18*b*) one occurs in the stripping section below the feed stage (stripping node), and the other occurs in the rectifying section several stages above the feed stage (rectifying saddle).

For the distillation of constant volatility mixtures in columns with constant molar flows and a saturated liquid feed, the stripping node, the rectifying saddle, the rectifying node, and the feed composition (the points $\hat{\mathbf{x}}^{1,s}$, $\hat{\mathbf{x}}^{2,r}$, $\hat{\mathbf{x}}^{3,r}$ and $\mathbf{x}_F$) are *aligned* at minimum reflux for direct splits (Julka and Doherty, 1990). Since the pinches all move as the reflux ratio is varied, we can find minimum reflux by varying r until any three of these points lie on a straight line. The most convenient points to align

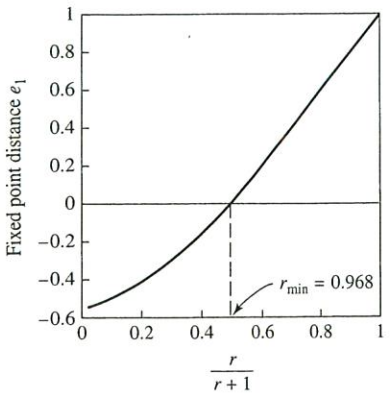


FIGURE 4.17
Fixed point distance as a function of $r/(r+1)$ for the example shown in Fig. 4.16.

are the stripping node, the rectifying saddle, and the feed composition.[21] Aligning these points is accomplished by constructing the following vectors originating from the rectifying saddle

$$\mathbf{e}_1 = \mathbf{x}_F - \hat{\mathbf{x}}^{2,r} \tag{4.70}$$

$$\mathbf{e}_2 = \hat{\mathbf{x}}^{1,s} - \hat{\mathbf{x}}^{2,r} \tag{4.71}$$

These vectors are shown in Fig. 4.18, where it can be seen that minimum reflux occurs when they lie on top of each other, i.e., the vectors are *linearly dependent*. Therefore, the minimum reflux condition is equivalent to

$$\det(\mathbf{e}_1, \mathbf{e}_2) = 0 \tag{4.72}$$

The value of r that solves this equation is the minimum reflux ratio. The absolute value of the determinant represents twice the area spanned between the vectors $\mathbf{e}_1$ and $\mathbf{e}_2$, and therefore the determinant is proportional to the *fixed point area* defined by these vectors. A graph of the fixed point area versus $r/(r+1)$ is shown in Fig. 4.19 for the benzene-toluene-xylene distillation described in Fig. 4.18. The zero in this graph gives a value for r_{min} of 1.518 and a corresponding value for $(V_B/F)_{min} = 0.763$. An efficient and robust method for performing these calculations is given by Fidkowski et al. (1991).

For nonsaturated liquid feeds, the point $\mathbf{x}_F$ should be replaced by $\tilde{\mathbf{x}}$ in the alignment condition (Eq. 4.72), where $\tilde{\mathbf{x}}$ is a linear combination of $\mathbf{z}_F$ and $\hat{\mathbf{x}}^{1,s}$ (Julka and Doherty, 1990).

$$\tilde{\mathbf{x}} = \mathbf{z}_F + (1-q)(\hat{\mathbf{x}}^{1,s} - \hat{\mathbf{y}}^{1,s}) \tag{4.73}$$

and $\hat{\mathbf{x}}^{1,s}$ and $\hat{\mathbf{y}}^{1,s}$ are in vapor–liquid equilibrium.

For nonideal mixtures the minimum reflux condition still requires that the stripping profile ends (pinches) on the rectifying profile for direct splits. However, now the stripping node, the rectifying saddle, and the feed composition lie on a *curve*

[21] We can also pick the rectifying saddle, the rectifying node, and the feed composition because the minimum reflux is *independent* of the bottom composition for direct splits. However, the minimum *vapor rate* will depend on the bottom composition, since the ratios D/F and B/F in Eq. 4.69 both vary with bottom composition.

	Feed	Distillate	Bottoms
1. Benzene	0.3000	0.9900	1.0×10^{-5}
2. Toluene	0.3000	0.0100	0.4261
3. Xylene	0.4000	1.0×10^{-10}	0.5739

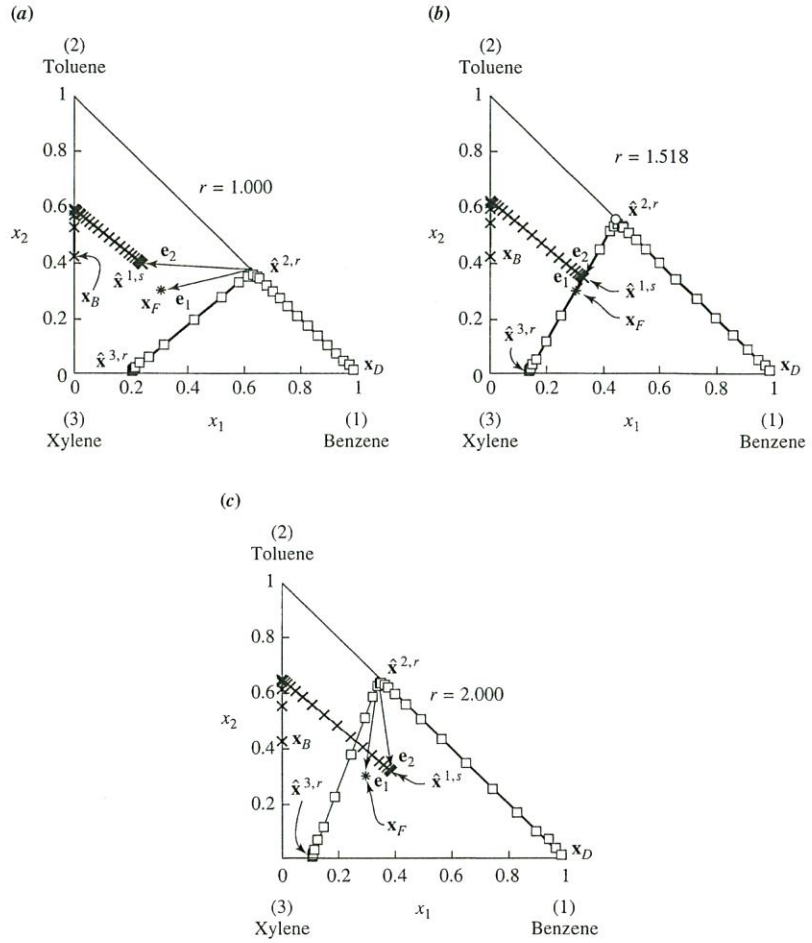


FIGURE 4.18
Liquid composition profiles for a ternary mixture of benzene (1), toluene (2), and xylene (3) at 1 atm pressure and $q = 1$. Vapor-liquid equilibrium was calculated using Raoult's law: (*a*) $r < r_{min}$, (*b*) $r = r_{min}$, (*c*) $r > r_{min}$.

rather than a straight line. Nevertheless, the curve joining these three points is nearly linear even for highly nonideal mixtures (Levy et al., 1985), and the zero area method typically gives values for r_{min} that are within a few percent of the exact value. This is well within the combined error introduced by imperfect physical property models, and by the assumptions of a perfectly adiabatic column and of equilibrium stages.

larger differences among the alternatives mean that less accurate models will not lead to bad decisions. In other words, models need to be sufficiently accurate to discard poor alternatives and yield a smaller number of candidate designs worthy of further attention. A well-known example is the large number of alternative distillation sequences for ideal mixtures. For very nonideal mixtures many of these alternative sequences are infeasible. However, this does not necessarily mean that there are no alternatives, but only that they are different structures and more work is required to find them.

In this chapter, we describe an approach for finding and comparing systems based on distillation that will attain certain design goals. For systems without azeotropic behavior, many separations are feasible for multicomponent mixtures. The task in conceptual design is typically to select from among these alternatives the sequence or sequences that deserve more detailed study. There is a large incentive for speed in this sequencing exercise because the separation system is generally part of a larger processing system that includes a reactor system and possibly additional upstream and downstream plants, e.g., Douglas (1988).

The first part of the chapter considers mixtures without azeotropes, which can be separated in sequences of simple columns. Following that, we discuss sequences containing "complex" columns, which involve multiple feeds, sidestream product withdrawal, or combinations of interconnected rectifying and stripping sections. This is followed by a discussion of sequences for separating azeotropic mixtures, and heat integration.

7.2 SEQUENCES OF SIMPLE COLUMNS

Table 7.1 shows some sequences of splits that can be used to separate nonazeotropic mixtures. These can all be accomplished in "simple" columns, which have a single feed and two products. Each of the splits listed corresponds to one simple column; e.g., each of the 14 simple distillation sequences for 5-component mixtures has 4 columns. The general result is that $n - 1$ simple columns are sufficient to separate an n-component mixture into nearly pure streams. Actually, more columns can be used, and this is sometimes more economical, as discussed later in the context of heat integration. It is not difficult to see that the number of simple column sequences increases dramatically with the number of components (Exercise 3).

Heuristic Approaches

Several early studies on distillation sequencing suggested heuristics for the choice of a sequence. Some of these heuristics are given in Table 7.2.

Some of these heuristics are simply intuitive; others have been suggested by patterns in simulation case studies [e.g., Tedder and Rudd (1978), Nishida et al. (1981)] or can be derived from known assumptions (Wahnschafft et al., 1993). Heuristics have the advantage of speed and minimal data requirements. However, heuristics can

TABLE 7.1
Simple distillation sequences for mixtures without azeotropes. The components are $A, B, C, \ldots$ in order of increasing boiling point

	Sequences for three components	
	Column 1	Column 2
1	A/BC	B/C
2	AB/C	A/B

	Sequences for four components		
	Column 1	Column 2	Column 3
1	A/BCD	B/CD	C/D
2	A/BCD	BC/D	B/C
3	AB/CD	A/B	C/D
4	ABC/D	A/BC	B/C
5	ABC/D	AB/C	A/B

	Sequences for five components			
	Column 1	Column 2	Column 3	Column 4
1	$A/BCDE$	B/CDE	C/DE	D/E
2	$A/BCDE$	B/CDE	CD/E	C/D
3	$A/BCDE$	BC/DE	B/C	D/E
4	$A/BCDE$	BCD/E	B/CD	C/D
5	$A/BCDE$	BCD/E	BC/D	B/C
6	AB/CDE	A/B	C/DE	D/E
7	AB/CDE	A/B	CD/E	C/D
8	ABC/DE	A/BC	D/E	B/C
9	ABC/DE	AB/C	D/E	A/B
10	$ABCD/E$	A/BCD	B/CD	C/D
11	$ABCD/E$	A/BCD	BC/D	B/C
12	$ABCD/E$	AB/CD	A/B	C/D
13	$ABCD/E$	ABC/D	A/BC	B/C
14	$ABCD/E$	ABC/D	AB/C	A/B

TABLE 7.2
Selected heuristics for distillation sequencing

1. **General heuristics**
   - (*a*) Remove corrosive or reactive components as early as possible
   - (*b*) Remove final products as distillates or as vapor streams from total reboilers
   - (*c*) Prefer the direct sequence
   - (*d*) Prefer to reduce the number of columns in a recycle loop
   - (*e*) Lump pairs of components with relative volatilities less than 1.1 and remove these as a single product to be separated using another technology
2. **Heuristics for simple columns**
   - (*a*) Remove the most plentiful component first
   - (*b*) Remove the lightest component first
   - (*c*) Make splits with the highest recoveries last
   - (*d*) Make the most difficult splits last
   - (*e*) Favor splits which give molar flows of distillate and bottoms with the smallest difference
   - (*f*) Make the cheapest split next in selecting a sequence of columns

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To my mother and father,
to my wonderful wife, Margaret,
and to Sarah and Max
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To the people who taught me something else:
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Pepper and the Chief,
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