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Azeotropic Distillation: A Review of Mathematical Models

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Abstract: Azeotropic distillation as an early and important special distillation process is commonly used in laboratory and industry. It can be used for separating the mixture with close boiling point or forming azeotrope. This paper tries to provide a review on azeotropic distillation for general readers, focusing on entrainer selection and mathematical models. Since the 1950s, along with extractive distillation, azeotropic distillation has gained a wide attention. Like extractive distillation, the entrainer, i.e., the third component added to the system, is also the core of azeotropic distillation. In the process design and synthesis, the graphical method (in most cases refer to as triangular diagram) is often employed. But it is better to take on the results from graphical method as the initial values of rigorous equilibrium (EQ) stage/non-equilibrium (NEQ) stage models. One outstanding characteristic of the EQ/NEQ stage models different from extractive distillation and catalytic distillation is to describe phase split for heterogeneous azeotropic distillation. In general, the operation process is very sensitive to some parameters in the case of more than one azeotrope formed, and thus the phenomenon of multiple steady states (MSS) tends to appear.

Keywords: Azeotropic distillation, entrainer, mathematical models, graphical method, multiple steady state, special distillation process

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INTRODUCTION

Azeotropic distillation is accomplished by adding to the liquid phase, a volatile third component, which changes the volatility of one of the two components more than the other so that the components are separated by distillation. The two components to be separated often are close boiling point components which do or do not azeotrope in the binary mixture, but sometimes they are components that do azeotrope although they are not close boiling point components (1–17). It is likely that in some cases, one system can be separated either by azeotropic distillation or by extractive distillation, for instance, alcohol/water, acid/water, etc.

The added third component, sometimes called the entrainer, may form a ternary azeotrope with the two components being separated. However, it must be sufficiently volatile from the solution so that it is taken overhead with one of the two components in the azeotropic distillation column. If the entrainer and the component taken overhead separate into two liquid phases when the vapor overhead is condensed, the entrainer phase is refluxed back to the column. The other phase can be fractionated to remove the dissolved entrainer and the residual amount of the other component before it is discarded in the solvent (entrainer) recovery column. Alternatively, this second liquid phase is recycled to some appropriate place in the main process scheme.

Azeotropic distillation is usually divided into two types: homogeneous azeotropic distillation and heterogeneous azeotropic distillation. They are illustrated in Figures 1 and 2, respectively. In homogeneous azeotropic distillation, phase split does not appear in the liquid along the whole column. Whereas, in heterogeneous azeotropic distillation, two liquid phases exist in some regions

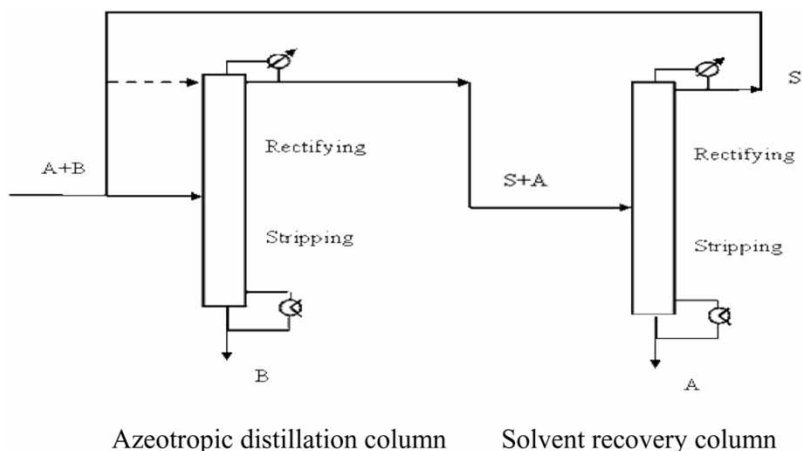


Figure 1. The double-column process for homogeneous azeotropic distillation.

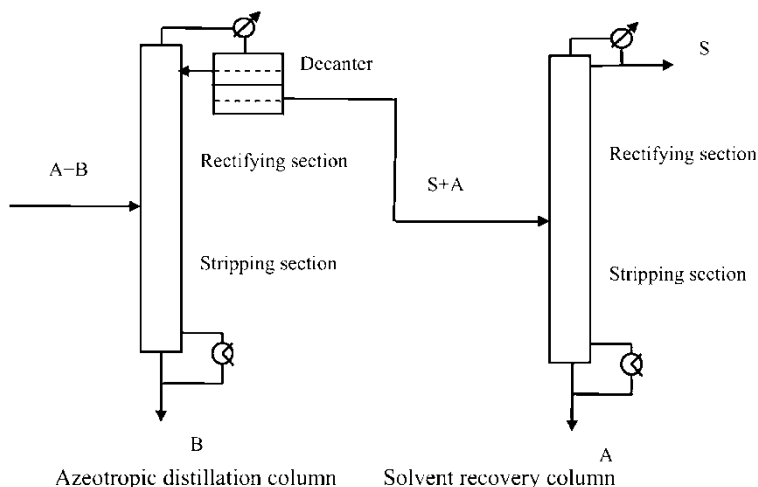


Figure 2. The double-column process for heterogeneous azeotropic distillation.

of the composition space. Heterogeneous azeotropic distillation is more widely used for separating the close boiling point components or azeotropes than homogeneous azeotropic distillation. In particular, the case of heterogeneous mixtures without decanter at the top of azeotropic distillation column can be looked upon as the one of homogeneous mixtures, and at the same time the liquid composition on a tray or a section of packing is replaced by the overall liquid composition. The operation, controlling, and optimization of the azeotropic distillation column have been studied by the researchers (18–23), which is beyond our scope to review this body of references.

For the binary azeotrope to be separated, the typical binary T - x phase diagrams at a fixed pressure are illustrated in Figure 3 for homogeneous azeotrope and in Figure 4 for heterogeneous azeotrope. At an azeotropic point, the relative volatility of binary azeotrope is unity because the overall liquid phase composition $x_i = y_i$. In Figure 3a the L-L two phases region may not exist; or even if they exist, the operating temperature in the distillation column is over the highest temperature of the L-L two-phase region; In Figure 3b the azeotropic boiling point is below the upper critical solution temperature (usual behavior). In Figure 4 two vapor-liquid envelopes ($L_1 - V$ and $L_2 - V$) overlap with liquid-liquid envelop ($L_1 - L_2$) at one line, which is also the tie line of liquid-liquid equilibria. Provided overlapping only at one point (i.e., azeotropic point), which is also the critical point of liquid-liquid equilibria, then the heterogeneous azeotrope becomes the homogeneous azeotrope because in this case $x_1 = x_2 = x_{azeo}$.

Note that forming a homogeneous azeotrope does not mean that the separation method is homogeneous azeotropic distillation, and forming a

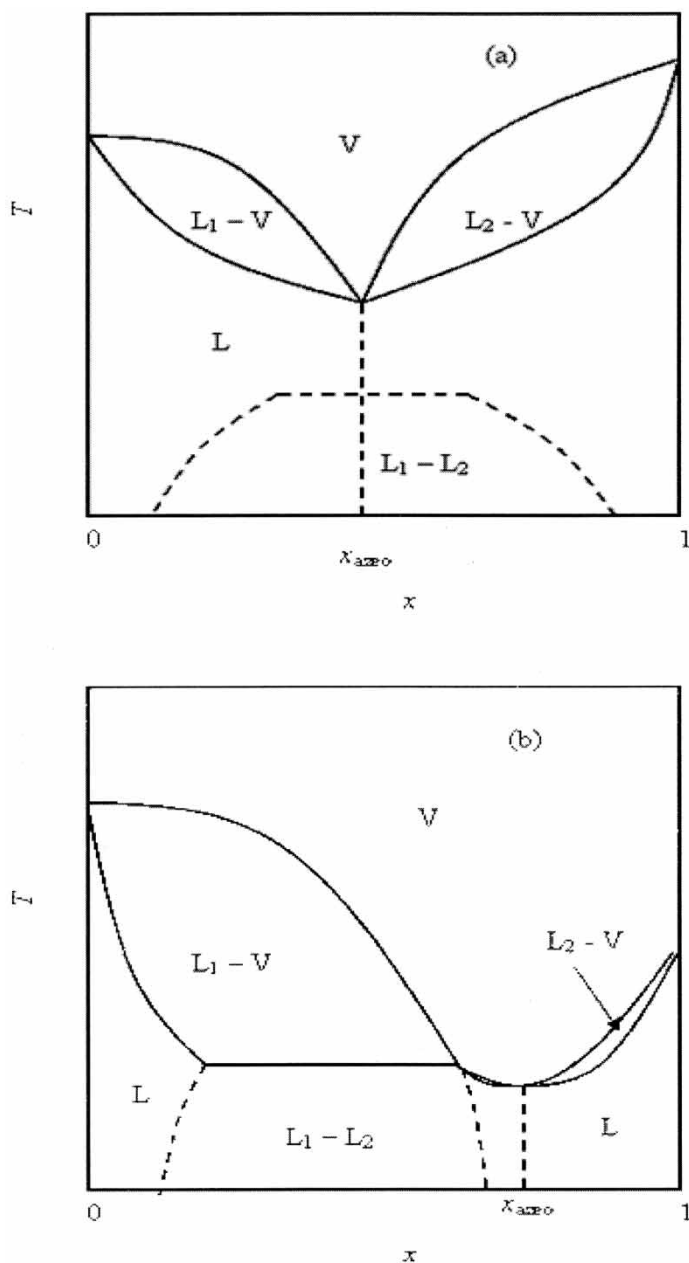


Figure 3. Binary T - x phase diagram at a fixed pressure for homogeneous azeotrope; (a) azeotropic boiling point above but not far from the upper critical solution temperature; adapted (24); (b) azeotropic boiling point below the upper critical solution temperature (usual behavior).

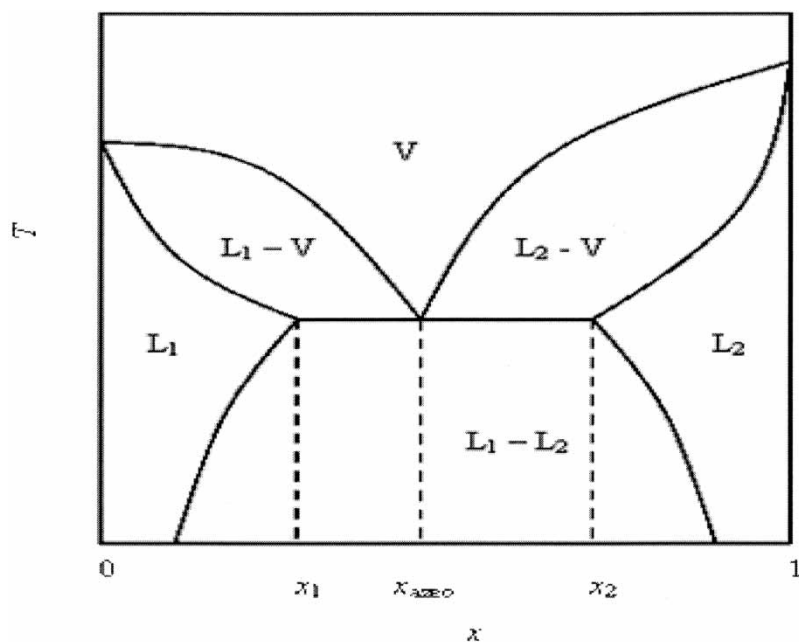


Figure 4. Binary T - x phase diagram at a fixed pressure for heterogeneous azeotrope; adapted from Widagdo (24).

heterogeneous azeotrope also does not mean that the separation method is heterogeneous azeotropic distillation, while depending on physical property of the entrainer used. Homogeneous and heterogeneous azeotropic distillation correspond to the real state of the mixture, consisting of the components to be separated and the entrainer, in the liquid phase on a tray or a section of packing in a distillation column.

In addition, for either homogeneous or for heterogeneous azeotropic distillation, the entrainer must be vaporized into the column top, and thus much energy is consumed compared with extractive distillation. For this reason, the cases of azeotropic distillation are used less than those of extractive distillation.

ENTRAINER SELECTION

In principle, any substance can be an entrainer but not every substance can “break” the azeotrope and/or improve relative volatility of the close boiling point mixture. Separation factor (i.e., relative volatility) is an important physical quantity in azeotropic distillation. It is desirable to assess the influence that the entrainer will have on the vapor-liquid equilibrium whenever any column is designed and simulated (25, 26).

In some cases the entrainer and the two components of i and j being separated can produce three-phase (vapor-liquid-liquid) equilibrium. Two liquid phases may be in equilibrium with a vapor phase. For the three-phase equilibrium the solubilities of components i and j in the upper liquid phase are denoted respectively by x_i^I and x_j^I (molar fraction), the solubilities of components A and B in the lower liquid phase respectively by x_i^{II} and x_j^{II} (molar fraction), and the corresponding activity coefficients by γ in the upper liquid phase and Γ in the lower liquid phase, respectively. The relative volatility for components i and j is related to the overall composition X_i according to

$$\alpha_{ij} = \frac{\gamma_i \Gamma_i P_i^0 \theta_i}{\gamma_j \Gamma_j P_j^0 \theta_j} \frac{(x_i^{II} - X_i) \Gamma_j + (X_i - x_i^I) \gamma_j}{(x_i^{II} - X_i) \Gamma_i + (X_i - x_i^I) \gamma_i} \quad (1)$$

where θ_i and θ_j are correction factor for high pressure. At low or even middle pressure, it can be approximately regarded as $\theta_i = \theta_j \approx 1$.

Over the two-liquid phase region Equation (1) gives relative volatilities for three-phase equilibrium. In the composition range where only an upper liquid phase and a vapor phase exist, Equation (1) reduces to

$$\alpha_{ij} = \frac{\gamma_i P_i^0 \theta_j}{\gamma_j P_j^0 \theta_i} \quad (2)$$

When only a lower liquid phase is in equilibrium with a vapor phase, Equation (1) becomes

$$\alpha_{ij} = \frac{\Gamma_i P_i^0 \theta_j}{\Gamma_j P_j^0 \theta_i} \quad (3)$$

where for the low pressure, $\theta_i = \theta_j \approx 1$; and for the middle pressure, $\theta_i = \exp[(V_{iL} - B_{ii})(P - P_i^0)/RT]$ and $\theta_j = \exp[(V_{jL} - B_{jj})(P - P_j^0)/RT]$, in which R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is universal gas constant, T (K) is temperature, P and P_i^0 (Pa) are total pressure and saturated pressure of component i , respectively, V_{iL} ($\text{m}^3 \text{ mol}^{-1}$) is mole volume of component i in the liquid phase, and B_{ii} ($\text{m}^3 \text{ mol}^{-1}$) is the second Virial coefficient.

Equations (2) and (3) are only suitable for vapor-liquid two-phase equilibrium (VLE) where the liquid mixture is miscible and homogeneous. However, Equation (1) is a generalization.

A schematic representation of VLLE is diagrammed in Figure 5. In a closed system, at a fixed temperature, we obtain:

$$y_i = \frac{\gamma_i P_i^0 \theta_i}{P} x_i^I; \quad y_j = \frac{\gamma_j P_j^0 \theta_j}{P} x_j^I \quad (\text{according to VLE}) \quad (4)$$

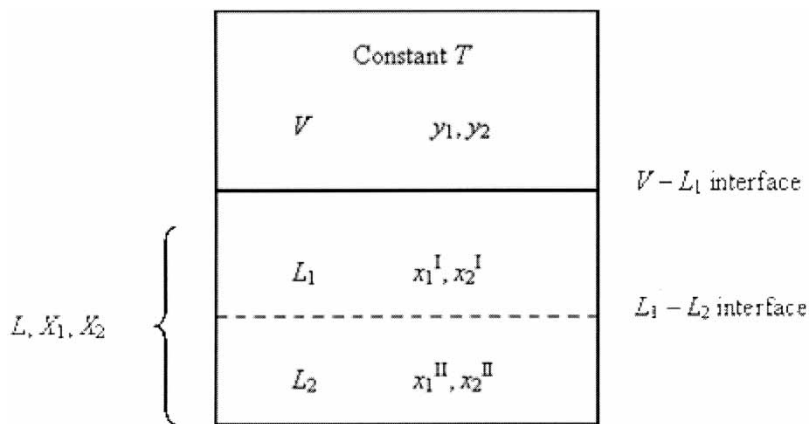


Figure 5. Schematic representation of VLLE (vapor- liquid-liquid three-phase equilibrium) in a closed system.

$$\gamma_i x_i^I = \Gamma_i x_i^{II}, \quad \gamma_j x_j^I = \Gamma_j x_j^{II} \quad (\text{according to LLE and} \quad (5)$$

the equivalence of activities)

$$L = L_1 + L_2, \quad LX_i = L_1 x_i^I + L_2 x_i^{II}; \quad LX_j = L_1 x_j^I + L_2 x_j^{II} \quad (6)$$

(according to material balance)

$$X_i = \frac{L_1 x_i^I + L_2 x_i^{II}}{L_1 + L_2}; \quad X_j = \frac{L_1 x_j^I + L_2 x_j^{II}}{L_1 + L_2} \quad (7)$$

(according to the lever-arm rule)

$$\frac{L_1}{L_2} = \frac{x_i^{II} - X_i}{X_i - x_i^I} = \frac{x_j^{II} - X_j}{X_j - x_j^I} \quad (\text{according to the lever-arm rule}) \quad (8)$$

where L_1 and L_2 are the mass in the upper and lower liquid phase (unit: mole), respectively.

In terms of the definition of relative volatility, it can be derived:

$$\begin{aligned} \alpha_{ij} &= \frac{y_i/X_i}{y_j/X_j} = \frac{\gamma_i P_i^0 \theta_i x_i^I}{\gamma_j P_j^0 \theta_j x_j^I} \frac{X_j}{X_i} = \frac{\gamma_i P_i^0 \theta_i x_i^I}{\gamma_j P_j^0 \theta_j x_j^I} \frac{(L_1 x_j^I + L_2 x_j^{II})}{(L_1 x_i^I + L_2 x_i^{II})} \\ &= \frac{\gamma_i P_i^0 \theta_i x_i^I}{\gamma_j P_j^0 \theta_j x_j^I} \frac{((x_i^{II} - X_i)/(X_i - x_i^I))x_j^I + x_j^{II}}{((x_i^{II} - X_i)/(X_i - x_i^I))x_i^I + x_i^{II}} \end{aligned}$$

$$\begin{aligned}
&= \frac{\gamma_i P_i^0 \theta_i}{\gamma_j P_j^0 \theta_j} \frac{((x_i^H - X_i)/(X_i - x_i^L)) + (x_j^H/x_j^L)}{((x_i^H - X_i)/(X_i - x_i^L)) + (x_i^H/x_i^L)} \\
&= \frac{\gamma_i P_i^0 \theta_i}{\gamma_j P_j^0 \theta_j} \frac{((x_i^H - X_i)/(X_i - x_i^L)) + (\gamma_j/\Gamma_j)}{((x_i^H - X_i)/(X_i - x_i^L)) + (\gamma_i/\Gamma_i)} \\
&= \frac{\gamma_i \Gamma_i P_i^0 \theta_i}{\gamma_j \Gamma_j P_j^0 \theta_j} \frac{(x_i^H - X_i)\Gamma_j + (X_i - x_i^L)\gamma_j}{(x_i^H - X_i)\Gamma_i + (X_i - x_i^L)\gamma_i} \quad (9)
\end{aligned}$$

which is just Equation (1).

Since relative volatility is an important index for evaluating the possible entrainers, it can be seen from Equation (1) that activity coefficient models of both liquid-liquid equilibrium and vapor-liquid equilibrium should be known beforehand in order to predict relative volatility. The liquid composition and activity coefficient in the isothermal liquid-liquid equilibrium are solved by numerical iteration from the equations (Equations (5)–(8)) in order to look for the compositions for which the activities are equal in the two phases for each individual component (Equation (5)). On this basis, the vapor composition in the isothermal vapor-liquid equilibrium is calculated by using Equation (4). However, one problem arises, that is, both one activity coefficient model suitable for VLE and another activity coefficient model suitable for LLE should be utilized in determining the same γ_i and γ_j . In general, one model cannot solve this problem, due to accuracy limitation of activity coefficient models under different conditions. Thus, it adds to some difficulty in calculation. But this contributes to one way to select the potential entrainers, herein, called the calculation method.

Of course, the experimental method is the most reliable in selecting the entrainers, but apparently much time and money must be spent. Only until a limited few possible entrainers are found by means of the calculation method, should the experiments be made.

Besides, simple rules using maps of distillation lines and residue curves (see what follows) have been suggested for screening many possible entrainers. Since drawing distillation lines and residue curves may be very tedious, it is advisable to straightforwardly apply the conclusions generalized by the researchers from many maps. Stichlmair and Herguizuela (27) enumerate some experience rules for entrainer selection, which are given in Table 1.

Some cases using azeotropic distillation as the separation method are listed in Table 2. The interested readers can compare the entrainers used in practice with the rules of selecting entrainers.

Based on computer-aided design, an advanced knowledge integrating system for the selection of solvents for azeotropic distillation is developed by Thomas and Hans (28). The mass separating agents are searched in the system SOLPERT (Solvent Selecting Expert System) by means of

Table 1. Experience rules for entrainer selection

Mixtures with a minimum-boiling azeotrope:

Low boiler (lower than the original azeotrope).

Medium boiler that forms a minimum-boiling azeotrope with the low boiling species.

High boiler that forms minimum-boiling azeotropes with both species. At least one of the new minimum-boiling azeotropes has a lower boiling temperature than the original azeotrope.

Mixtures with a maximum-boiling azeotrope:

Low boiler (lower than the original azeotrope).

Medium boiler that forms a minimum-boiling azeotrope with the low boiling species.

High boiler that forms minimum-boiling azeotropes with both species. At least one of the new maximum-boiling azeotropes has a higher boiling temperature than the original azeotrope.

combining databases, heuristic and numerical methods. Several inherent limitations of solvent screening methods, e.g., database search, empirical methods, and group contribution methods, are circumvented and minimized to gain an maximum of usable information for solvent selection. The solvent selection of SOLPERT consists of four steps, as listed in Table 3.

It is evident that the solvent selection of SOLPERT also holds for extractive distillation. An excellent review about extractive distillation has been presented by Lei et al. (39).

Anyway, data bank search, for its convenience and reliability, is no less a good method (40–42). A successful work has been done by Gmehling (43, 44), where a computerized bank of azeotropic data is now available. Data from the references have been tested before storage. Newly measured azeotropic and azeotropic data are also included. This data bank now contains approximately 36,000 entries (information) on azeotropic or azeotropic behavior or approximately 19,000 non-electrolyte systems involving approximately 1,700 compounds. It can be used reliably in process synthesis computations, e.g.,

Table 2. Some azeotropic distillation cases

No.	Components to be separated	Entrainers
1	Ethanol/water; isopropanol/water, <i>tert</i> -butanol/water	Benzene, toluene, hexane, cyclohexane, methanol, diethylether, methyl-ethyl-ketone (MEK) (29–35)
2	Acetone/ <i>n</i> -heptane	Toluene (36)
3	Acetic acid/water	<i>n</i> -butyl acetate (37)
4	Isopropanol/toluene	Acetone (38)

Table 3. The steps in SOLPERT for selecting entrainer; adapted from Thomas and Hans (28)

Steps	Criteria	Applied methods
1. Selection of classes	Hydrogen bonding Polarity	Heuristic rules Empirical approaches Databases
2. Selection of chemical similar groups	Hildebrand's solubility parameter Snyder's classes Solvatochromic parameters	Heuristic rules Generalization to structural groups Databases
3. Proposal of suitable solvents	Lower and upper limit of boiling point Miscibility azeotropy	Heuristic rules Empirical approaches Numerical methods Group contribution methods Databases
4. Ranking of proposed solvents	Selectivity Miscibility Relative volatility Performance of entrainers for azeotropic distillation	Heuristic rules Numerical methods Group contribution methods Databases

for design calculations of distillation columns, selection of the best solvents for azeotropic distillation and also for further development of group contribution methods or for fitting reliable g^E -model parameters.

MATHEMATICAL MODELS

To describe the azeotropic distillation process, especially for the azeotropic distillation column, it is necessary to set up the reliable mathematical models. Once the mathematical model is determined, it is possible to extend to the synthesis of distillation column sequence. Formerly, the graphical method was popular for

the analysis of azeotropic distillation column. Recently, the equilibrium (EQ) stage and non-equilibrium (NEQ) stage models, similar as those in extractive distillation and catalytic distillation, have received more attention.

Graphical Method

The principal concern in the graphical method is how to construct the maps of residual curve, distillation line and their boundaries so that the feasible composition space can be examined. After these are finished, the actual operating line with a certain reflux ratio between minimum and total reflux is plotted in the composition space. Consequently, the feasibility of a given separation process can be evaluated and the possible multiple steady state may be found.

Residual Curves

Residual-curve maps have been widely used to characterize azeotropic mixture, establish feasible splits by distillation at total reflux and for the synthesis and design of column sequences that separate azeotropic mixture. Schreinemakers (45, 46) defined a residual curve as the locus of the liquid composition during a simple distillation process. Residue curves are conceived for n -component systems, but can be plotted only for ternary or, with more powerful graphical tools and some imagination, quaternary systems.

Since the residual curve is the locus of the liquid composition remaining from a differential vaporization process, we write by a stepwise procedure for a simple distillation still with only one theoretical stage:

$$L_0 = L + V \quad (12)$$

$$L_0 x_{i,0} = Lx_i + Vy_i \quad (13)$$

where L_0 is the amount of liquid in still at start of vaporization increment; L is the amount of liquid in still at end of vaporization increment; y_i is mean equilibrium vapor composition over increment. A schematic representation of a simple distillation is diagrammed in Figure 6.

In a difference time dt , we have

$$-dL = dV \quad (14)$$

$$-d(Lx_i) = y_i dV \quad (15)$$

$$\text{or } -Ldx_i - x_i dL = y_i dV, \quad (16)$$

which arranges to

$$-Ldx_i = (y_i - x_i)dV \quad (17)$$

$$\text{or } Ldx_i = (y_i - x_i)dL. \quad (18)$$

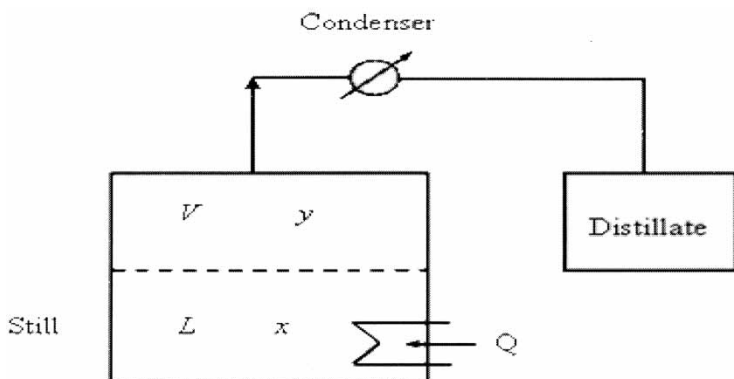


Figure 6. Schematic representation of a simple distillation still.

That is,

$$\frac{dx_i}{dL/L} = y_i - x_i = (K_i - 1)x_i \quad (19)$$

and for any two components i and j ,

$$\frac{dx_i}{dx_j} = \frac{y_i - x_i}{y_j - x_j}. \quad (20)$$

Introduce a dimensionless time $dt = dL/L$, Equation (19) becomes

$$\frac{dx_i}{dt} = y_i - x_i = (K_i - 1)x_i, \quad (21)$$

which is the residual curve equation. Note that it is established under a fixed pressure.

In fact, Equation (21) represents a group of ordinary (constant-coefficient) difference equations, and thus can be solved by such mathematical tools as Gear, Runge-Kutta (L-K) methods, etc. During the calculation, the bubble point subroutine should be called as a sub-function in every dt advance to solve the temperature, because the equilibrium ratio K_i is the function of temperature and liquid composition.

Map representation of residual curves in composition space for three-component systems may be drawn in orthogonal or equilateral cartesian coordinates; or transformations can be made in the coordinate system as long as the linear appearance of straight lines remains invariant. The two types of coordinate systems will be used interchangeably throughout.

As examples, Figures 7 and 8 respectively show the residual curves for the methanol/ethanol/water system at 101.3 kPa in the homogeneous

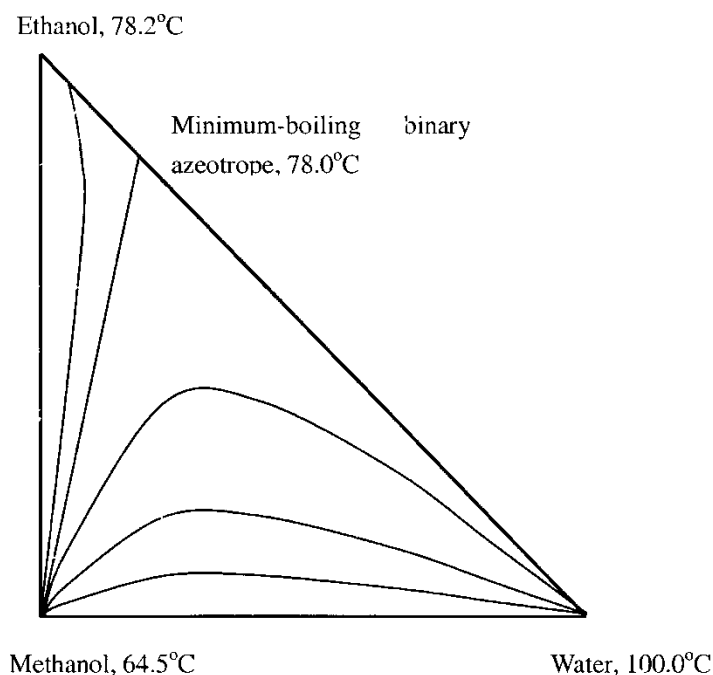


Figure 7. The residual curves for the methanol/ethanol/water system at 101.3 kPa in the homogeneous mixture; adapted from Castillo and Towler (34).

mixture and for the ethanol/water/benzene at 101.3 kPa in the heterogeneous mixture. It can be seen that arrows may be assigned. The arrows are in the direction of time increasing (or temperature increasing) because the concentration of heavy components in the simple distillation still will become higher and higher as time goes on, which results in increasing temperature.

Operating Lines

Similar as the x – y diagram for two-component system, if composition space is only used to perform the calculations, it is necessary to assume constant molar overflow. As shown in Figure 9, both x_D (the distillate composition) and x_B (the bottom composition) are predetermined as a given separation task, and the line DFB represents a limiting overall material balance. The operating lines in Figure 9 are composed of real lines with arrows representing VLE and dashed lines without arrows representing material balance. Real lines and dashed lines are arranged alternately. The number of arrows is equivalent to the separation stages including reboiler, but excluding condenser. This means that there are six separation stages in Figure 9.

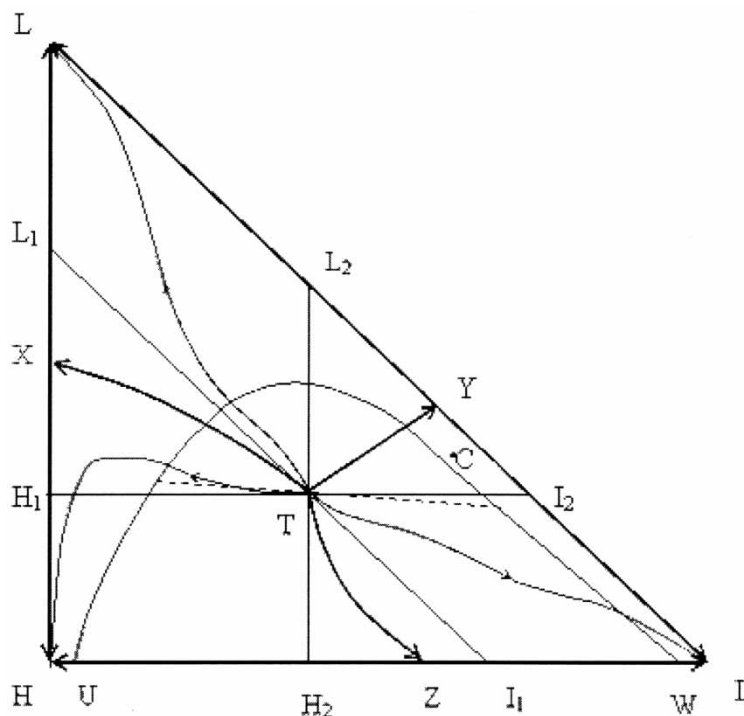


Figure 8. The residual curves for the ethanol (L)/water (H)/benzene (I) system at 101.3 kPa in the heterogeneous mixture; adapted from Bekiaris et al. (47).

Figure 10 illustrates how to draw operating lines in the homogeneous azeotropic distillation column. The operating lines are also identical to those in the heterogeneous azeotropic distillation column, but without the decanter at the top.

As an example, there are six separation stages ($n = 6$) in Figure 10. The stages are counted downward along the column. At the bottom the liquid composition vector $\underline{x}_6$ is in equilibrium with the vapor composition vector, which is denoted by an arrow with a starting point $B(\underline{x}_6)$ to an ending point $V_6(\underline{y}_6)$. Due to the limiting material balance among B , V_6 and L_5 , point $L_5(\underline{x}_5)$ lies in the line connecting $B(\underline{x}_6) - V_6(\underline{y}_6)$. Then, an equilibrium line with arrow is drawn from point $L_5(\underline{x}_5)$ to point $V_5(\underline{y}_5)$. Similarly, due to the limiting material balance among B , V_5 and L_4 , point $L_4(\underline{x}_4)$ lies in the dashed line connecting $B(\underline{x}_6) - V_5(\underline{y}_5)$. In the same way, other operating lines can be drawn. Therefore, it is easy to obtain that at the feed tray,

$$J = J + F \quad (22)$$

$$V_3 + L_3 = L_2 + V_4 + F. \quad (23)$$

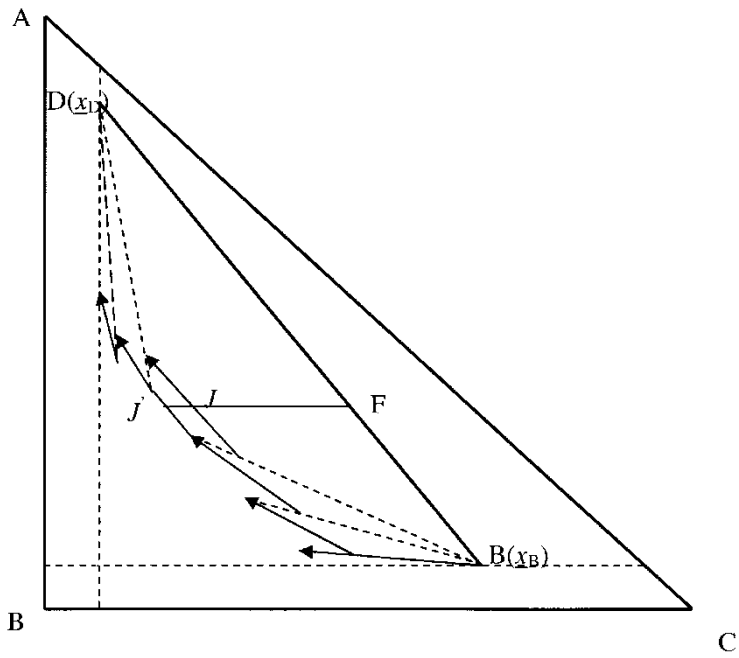


Figure 9. Operating lines in the azeotropic distillation column; reflux ratio is between minimum and total reflux ratios.

On the other hand, the above material balance also can be derived from Figure 11 by constraining the region at plane A1–plane A2.

Operating lines in the heterogeneous azeotropic distillation column are illustrated in Figure 12, where the vector $\underline{x}$ is the overall liquid composition, except $\underline{x}_{D1}$ and $\underline{x}_{D2}$. Note that although the foregoing operating lines are discussed just for tray column, it can be extended to packing column by transformation with the concept of HETP (height equivalent of a theoretical plate).

Distillation Lines

Like the two-component system, in the multi-component azeotropic distillation, there still exists a minimum reflux ratio (corresponding to infinite number of stages) and total reflux (corresponding to minimum stages). It can be imagined that in the composition space, as shown in Figure 9, while reflux ratio is becoming larger, the operating lines are far away from the line DFB. This implies that at minimum reflux ratio at least one operating line lies in the line DFB and thus it is difficult to further draw other operating lines. For example, Figure 13 shows one case at minimum reflux ratio.

However, at total reflux where there is no feed and no products, operating lines are composed of consecutive real lines with arrows because in this case

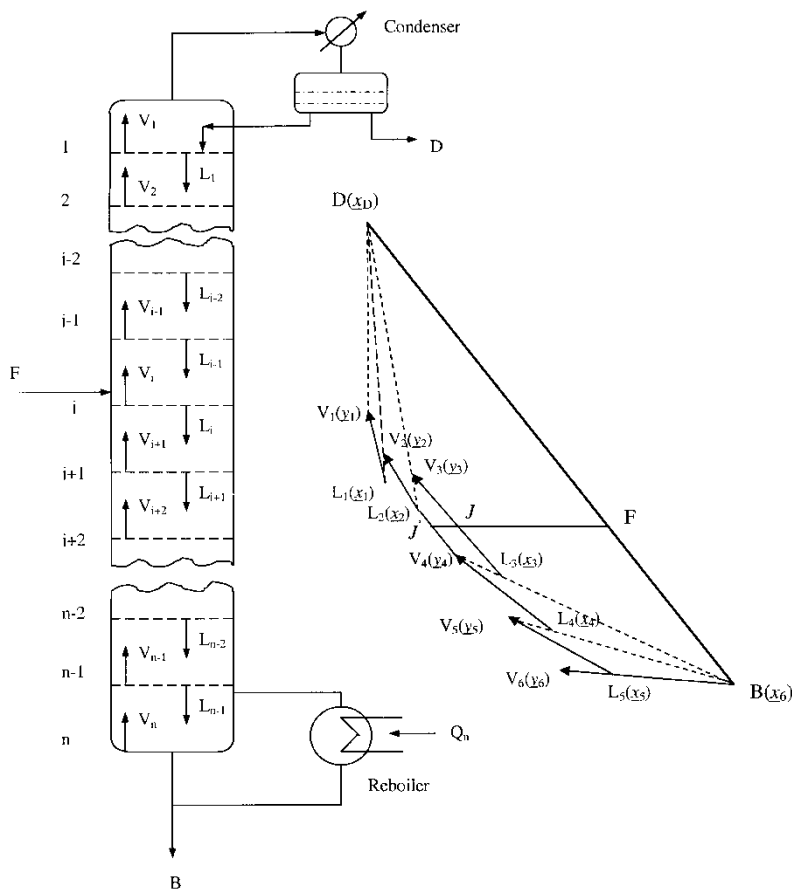


Figure 10. Operating lines in the homogeneous azeotropic distillation column; reflux ratio is between minimum and total reflux ratios.

$y_{n+1} = x_n$. The operating lines at total reflux are called distillation lines. However, we often like to take on the smooth curves fitting the tie points connecting real lines with arrows as distillation lines (as shown in Figure 14).

Now we investigate the difference between residual curves and distillation lines for the tray and packing columns:

For the packing column, Equations (14), (18), and (21) used for plotting residual curves are also strictly satisfied because its composition change along the whole column is continuous, not abrupt as the tray column.

As shown in Figure 15, for a dh differential section of packing column, the total material balance is:

$$-dL = dV. \quad (24)$$

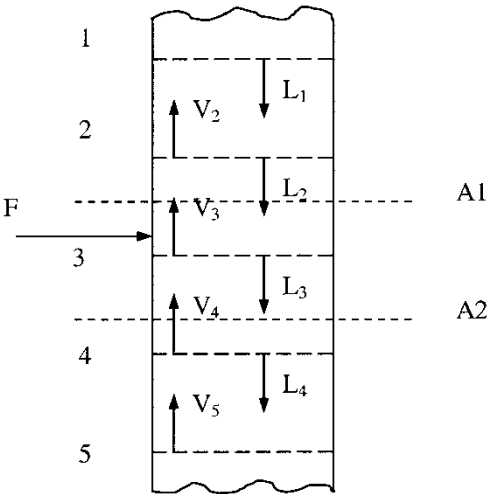


Figure 11. Material balance at the feed tray.

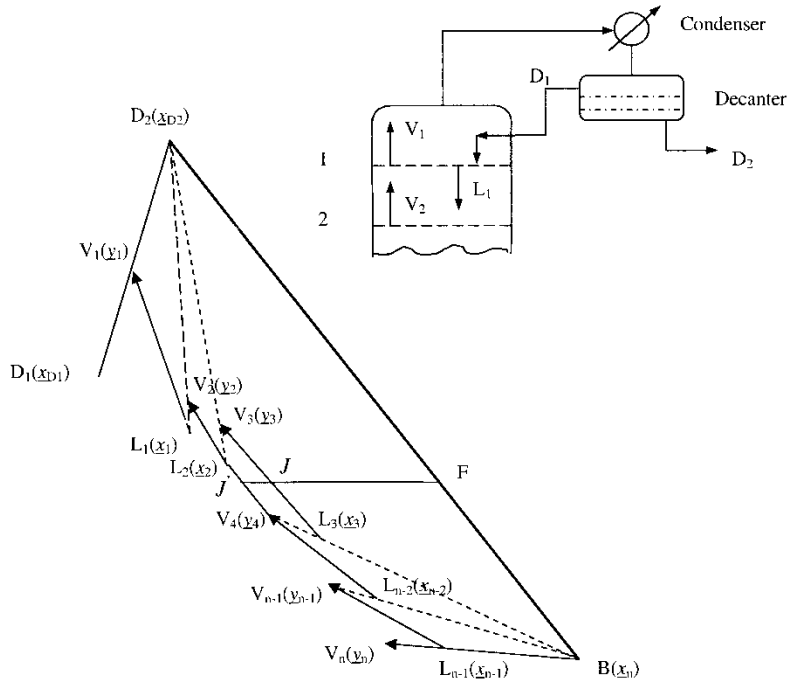


Figure 12. Operating lines in the heterogeneous azeotropic distillation column; reflux ratio is between minimum and total reflux ratios.

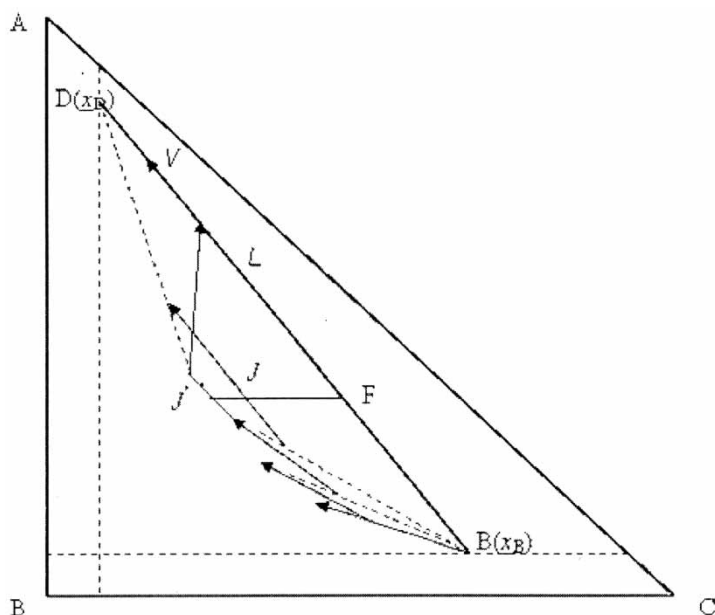


Figure 13. Operating lines at minimum reflux ratio.

The component material balance is:

$$Ldx_i = (y_i - x_i)dL \quad (25)$$

and

$$\frac{dx_i}{dt} = y_i - x_i = (K_i - 1)x_i, \quad (26)$$

which correspond with Equations (14), (18), and (21) in the form, respectively.

Here the subtle difference from simple distillation is only that L and V represent the flowrate of liquid and vapor phases, respectively. Consequently, distillation lines are exactly the residual curves for the packing column. Note that Equation (24) implies that the packing column is at total reflux in order to ensure the equality $-dL = dV$ because if having any feed, $-dL \neq dV$ in the vicinity of the feed position. Moreover, here the assumption of constant molar flow for the vapor and liquid phases is not imposed because the equation of $-dL = dV$ already indicates that there is the change of the flowrate of L and V along the column.

For the tray column, distillation lines are slightly different from residual curves. The main reason is that its composition change along the whole column is stepwise, not continuous as the packing column.

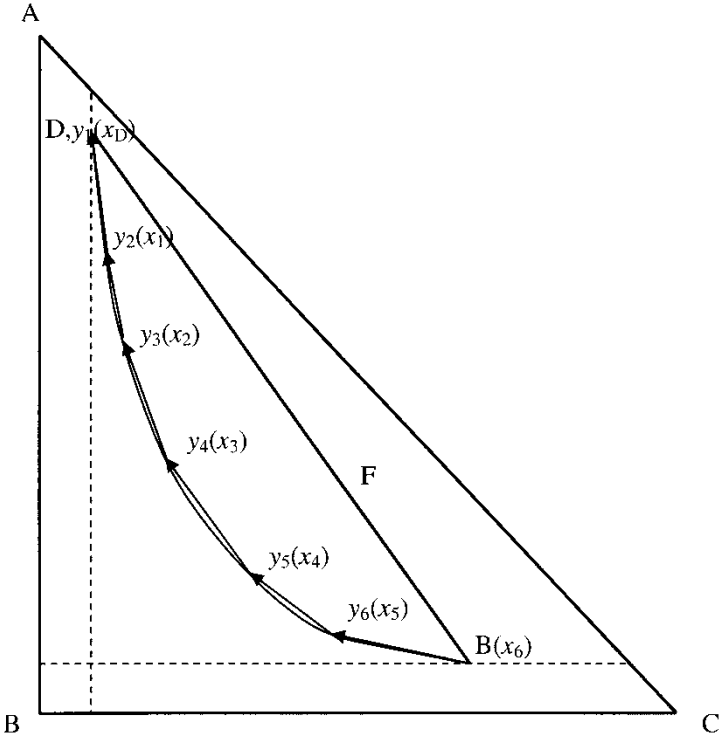


Figure 14. Operating lines at total reflux (i.e., distillation lines).

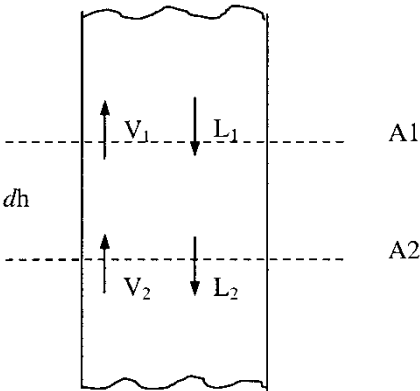


Figure 15. A dh differential section of packing column.

Suppose that at total reflux the mathematical differential element is enlarged enough to be in the vicinity of one tray, as shown in Figure 11 (A1 plane–A2 plane but no feed), and the following equations analogous to Equations (14), (18), and (21) are satisfied:

$$-\Delta L = \Delta V \quad (27)$$

$$L\Delta x_i = (y_i - x_i)\Delta L \quad (28)$$

$$\frac{\Delta x_i}{\Delta L/L} = y_i - x_i = (K_i - 1)x_i. \quad (29)$$

For this reason, the residual curves are a good approximation to the operating lines at total reflux. Then, what arises at a limited reflux ratio (and having feed)? In this case, the difference equation is identical to that at total reflux except on the feed tray. That is why the operating lines at different reflux ratio have the similar shape.

Since the mathematical differential element for the tray column is enlarged not to be a limit, real lines with arrows are the chords of distillation lines, e.g., $\underline{y} - \underline{x}$ (the tie line BM_1 vector), as shown in Figure 16. But in accordance with Equation (21), $\underline{y} - \underline{x}$ should be tangent to residual curves at point B. Note that when the residual curve is linear (e.g., for binary mixtures), the chords and residual curves are collinear (i.e., distillation lines overlap with residual curves).

Simple Distillation and Distillation Line Boundaries

In composition space, one or more residue curves (or distillation lines) divide the whole into regions with distinct pairs of starting and terminal points. Hence, the lines separating two or more distillation regions are called simple distillation boundaries (correspond to residue curves) or distillation lines boundaries (correspond to distillation lines). For homogeneous mixture, the simple distillation and distillation line boundaries cannot be crossed; but for heterogeneous mixture, these boundaries may be crossed because in this case phase split occurs in LLE regions and thus two liquid phases may fall into different distillation regions.

As illustrated in Figure 8 where it is supposed there is no decanter at the top of distillation column and LLE curve is not utilized, the system forms three binary azeotropes representing with points X, Y, and Z, and one ternary azeotropes representing with point T. Points X, Y, Z, as well as the vertices L, H, and I, are called the singular (fixed) points in which the driving force for change in the liquid composition is zero; that is, $dx_i/dt = 0$ or $y_i = x_i$. Lines TX, TY, TZ divide the whole into three regions (LXTYL, HZTXH, IYTZI) with distinct pairs of starting and terminal points; for instance, in region LXTYL the starting point is T and the terminal point is L. So, lines TX, TY, and TZ are simple distillation boundaries or distillation lines boundaries.

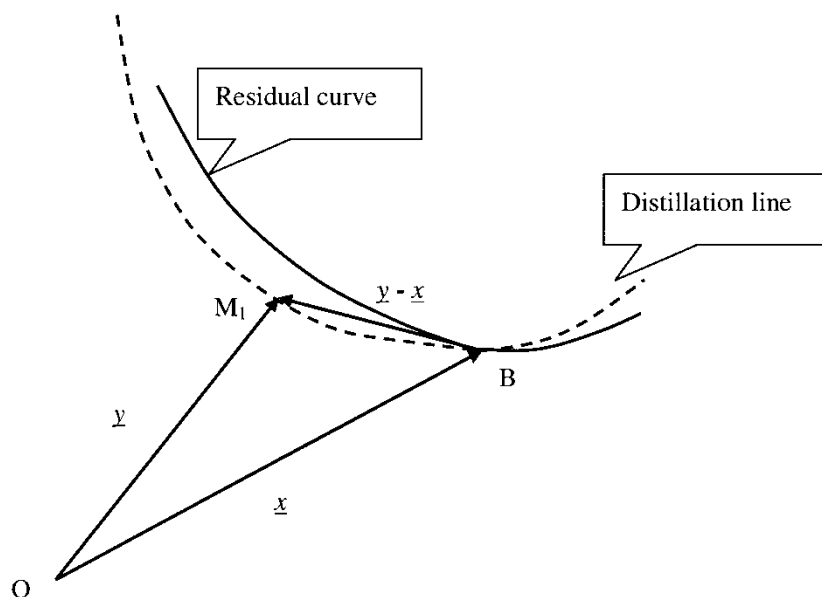


Figure 16. Difference between residual curve and distillation line for the tray column.

But if one point lies in LLE region (UCWU), the boundaries may be crossed due to phase split.

It is believed that the residual curves are a good approximation to the operating lines at total reflux. Rather, as discussed before, the distillation lines are equivalent to the operating lines at total reflux. For the packing column, simple distillation boundaries are exactly the distillation line boundaries; for the tray column, the appropriate boundaries are the separatrices on the maps of distillation lines (48). In the case of infinite reflux and infinite number of trays (or infinitely high columns), the product compositions can reside on the simple distillation or distillation line boundaries.

EQ and NEQ Stage Models

The equilibrium (EQ) stage model is widely applied to analyze and design the columns for either homogeneous or heterogeneous azeotropic distillation. However, as pointed out by Krishnamurthy and Taylor (49–51), concentration profiles predicted by the non-equilibrium (NEQ) (or rate-based model) stage model may be different from those by the EQ stage model even with revisions to tray efficiency. The difference is caused by the difference in mass transfer resistances and the diffusional interaction effects especially

for heterogeneous azeotropic distillation. Sometimes the mass transfer resistance in the liquid phase cannot be neglected in the two-liquid region for heterogeneous azeotropic distillation. Therefore, the EQ stage model which essentially excludes the liquid phase mass transfer, may be an improper model for predicting the exact profiles of concentration and flowrate in the azeotropic distillation column. Alternatively, the NEQ stage model has recently been applied to analyze and design the azeotropic distillation column (31, 52). However, for homogeneous and heterogeneous azeotropic distillation, the equation forms are different when using the EQ or NEQ stage model.

Homogeneous Azeotropic Distillation

Either for the EQ stage model or for the NEQ stage model, the equation forms of homogeneous azeotropic distillation are the same as those as in extractive distillation and catalytic distillation. But it is known that the amount of entrainer plays an important in the simulation of separation performance of homogeneous azeotropic distillation column. It can be obtained from the graphical method, which is shown in Figure 17 where point *N* represents the feed composition consisting of the components *A* and *B* to be separated and point *M* represents the azeotropic composition with minimum boiling point.

In terms of lever-arm rule, the relation of the flowrates of entrainer *S* and feed *F* is written as

$$\frac{S}{F} = \frac{AN \cdot BM}{AB \cdot CM} = \frac{EN}{CM} = \frac{ON}{OC}. \quad (30)$$

The value of the flowrate of entrainer *S* can be used as an initial guess in the rigorous EQ and/or NEQ stage models.

Model Equation of EQ Stage

The schematic diagrams of a tray column for EQ stage model are shown in Figure 18. In general, the assumptions adopted are as follows (53–55):

1. Operation reaches steady state;
2. System reaches mechanical equilibrium in every tray;
3. The vapor and liquid bulks are mixed perfectly and assumed to be at thermodynamic equilibrium;
4. Heat of mixing can be neglected;
5. Reactions, if possible, take place in the liquid phase; if reactions take place in the vapor phase, the actual vapor compositions are replaced by transformed superficial compositions;
6. The condenser and reboiler are considered as an equilibrium tray;

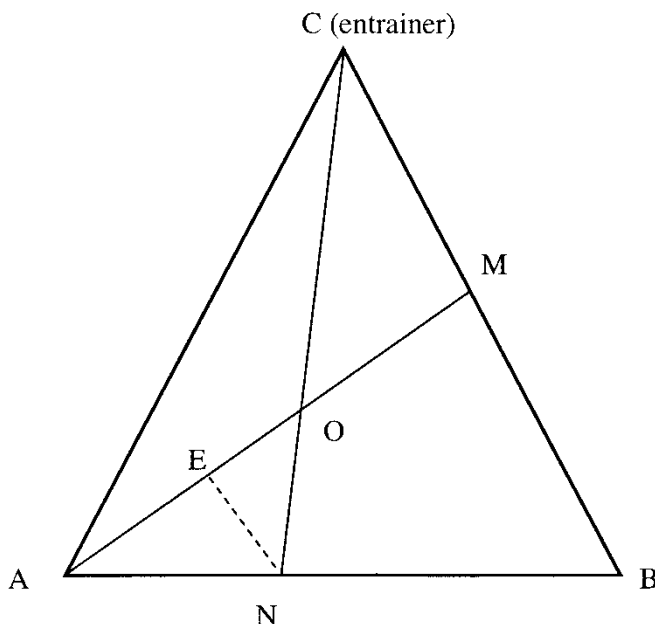


Figure 17. Graphical method for calculating the amount of entrainer for homogeneous azeotropic distillation with one minimum boiling point azeotrope.

7. If the catalyst is used, then the amount of catalyst in each tray of reaction section is equal;
8. If the catalyst is used, then the influence of catalyst on the mass and energy balance is neglected because the catalyst concentration in the liquid phase is often low.

The equations that model EQ stages are known as the MESHR equations. MESHR is an acronym referring to the different types of equation. The M equations are the material balance equations. The total material balance takes the form

$$\frac{dM_j}{dt} = V_{j+1} + L_{j-1} + F_j - (1 + r_j^V)V_j - (1 + r_j^L)L_j + \sum_{k=1}^r \sum_{i=1}^c v_{i,k} R_{k,j} \varepsilon_j \quad (31)$$

where F , V , L (mol s^{-1}) are feed, vapor, and liquid flowrates, respectively, t (s) is time, $R_{k,j}$ ($\text{mol s}^{-1} \text{kg}^{-1} \text{cat.}$) is reaction rate, $v_{i,k}$ is the stoichiometric coefficient of component i in reaction k , ε (kg or m^3) is reaction volume or amount of catalyst, and M_j is the hold-up on stage j . With very few exceptions, M_j is considered to be the hold-up only of the liquid phase. It is more important to

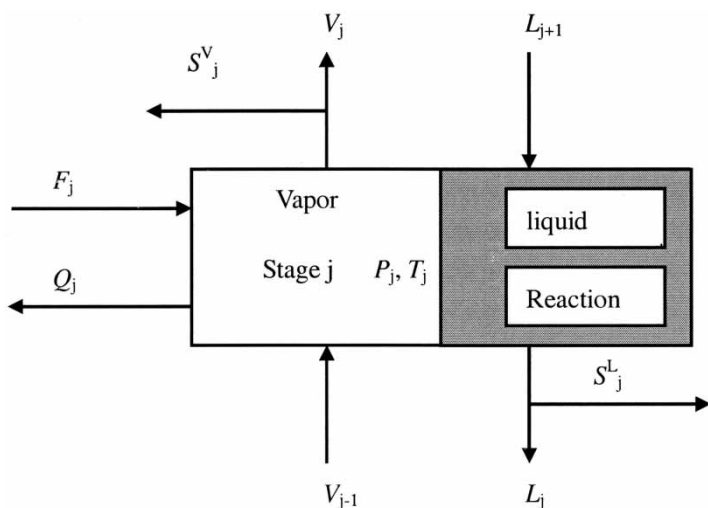


Figure 18. Schematic representation of an EQ stage.

include the hold-up of the vapor phase at higher pressures. The component material balance (neglecting the vapor hold-up) is:

$$\begin{aligned} \frac{dM_j x_{i,j}}{dt} = & V_{j+1} y_{i,j+1} + L_{j-1} x_{i,j-1} + F_j z_{i,j} - (1 + r_j^V) V_j y_{i,j} \\ & - (1 + r_j^L) L_j x_{i,j} + \sum_{k=1}^r v_{i,k} R_{k,j} \epsilon_j \end{aligned} \quad (32)$$

where x, y are mole fraction in the liquid and vapor phases, respectively.

In the material balance equations given above r_j is the ratio of sidestream flow to interstage flow:

$$r_j^V = S_j^V / V_j, \quad r_j^L = S_j^L / L_j \quad (33)$$

The E equations are the phase equilibrium relations:

$$y_{i,j} = K_{i,j} x_{i,j} \quad (34)$$

where $K_{i,j}$ is the chemical equilibrium constant.

The S equations are the summation equations:

$$\sum_{i=1}^c x_{i,j} = 1, \quad \sum_{i=1}^c y_{i,j} = 1. \quad (35)$$

The enthalpy balance is given by

$$\begin{aligned} \frac{dM_j H_j}{dt} = & V_{j+1} H_{j+1}^V + L_{j-1} H_{j-1}^L + F_j H_j^F - (1 + r_j^V) V_j H_j^V \\ & - (1 + r_j^L) L_j H_j^L - Q_j \end{aligned} \quad (36)$$

where H is molar enthalpy, and Q is heat duty.

There is no need to take separate account in Equation (36) of the heat generated due to chemical reaction since the computed enthalpies include the heats of formation.

The R equations are the reaction rate equations. For the reactive extractive distillation it is known that the chemical reaction is reversible, and the reaction rate is assumed to be zero. That is to say, the chemical equilibrium is reached in every tray.

Under steady-state conditions all of the time derivatives in the MESH equations are equal to zero. Newton's method (or a variant thereof) for solving all of the independent equations simultaneously is an approach widely used currently. But other methods also appear frequently, e.g., the relaxation method. In this method the MESH equations are written in unsteady-state form and are integrated numerically until the steady-state solution has been found, is used to solve the above equations.

The EQ stage model is commonly used for the process simulation of azeotropic distillation, and can obtain the necessary information for various purposes. This model has been installed in the commercial simulation software programs, i.e., ASPEN PLUS, PROII, HYSIS, et al.

Model Equation of NEQ Stage

The NEQ stage model for azeotropic distillation should follow the philosophy of rate-based models for conventional distillation. As we know, the NEQ stage model is more complicated than the EQ stage model. In the NEQ stage model, the design information on the column configuration must be specified so that mass transfer coefficients, interfacial areas, liquid hold-ups, etc. can be calculated. Therefore, for any new invented configuration of the column, many experiments have to be done in advance to obtain the necessary model parameters. Evidently, it is too tedious, and much time will be spent on the design of azeotropic distillation process. Fortunately, as pointed out by Lee and Dudukovic (56), a close agreement between the predictions of the EQ and NEQ stage models may be found if tray efficiency or HETP (height equal to a theoretical plate) is known under the condition that the mixture is homogeneous, of course.

The model equations of NEQ stage for azeotropic distillation are similar to those for extractive distillation and catalytic distillation (57–62). Though sophisticated NEQ stage model is available at some time, detailed information on the hydrodynamics and mass transfer parameters for the various hardware

configurations is woefully lacking in the open reference. Moreover, such information may have vital consequences for the calculated results of the distillation column. There is a crying need for research in this area. It is perhaps worth noting here that modern tools of computational fluid dynamics could be invaluable in developing better insights into hydrodynamics and mass transfer in the distillation column. But the computing time may be greatly prolonged.

In the field of reaction distillation (RD), recent NEQ modeling works have exposed the limitations of EQ stage model for final design and for the development of control strategies. The NEQ stage model has been used for commercial RD plant design and simulation. Thus, it is conjecturable that the NEQ stage model would be widely applied in azeotropic distillation, and the EQ stage model only has its place for preliminary design. The research on the NEQ stage model for azeotropic distillation should be strengthened in the near future.

The schematic diagrams of a tray column for the NEQ stage model are shown in Figure 19. In general, the assumptions adopted are as follows:

1. Operation reaches steady state;
2. System reaches mechanical equilibrium in every tray;
3. The vapor and liquid bulks are mixed perfectly and assumed to be at thermodynamic equilibrium;
4. Heat of mixing can be neglected;
5. There is no accumulation of mass and heat at the interface;
6. The condenser and reboiler are considered as an equilibrium tray;
7. Reactions take place in the liquid bulk within the interface ignored; if reactions take place in the vapor phase, the actual vapor compositions are replaced by transformed superficial compositions;
8. The heat generated due to chemical reaction is neglected because heat effect is often not apparent for the reaction concerned.

In addition, in the NEQ stage model it is assumed that the resistance to mass and energy transfer is located in thin film adjacent to the vapor-liquid interface according to the two-film theory; See Figure 20.

The time rate of change of the number of moles of component i in the vapor (M_i^V) and liquid (M_i^L) phases on stage j are given by the following balance relations:

$$\frac{dM_{i,j}^V}{dt} = V_{j+1}y_{i,j+1} - V_jy_{i,j} + z_{i,j}^V F_{i,j}^V - N_{i,j}^V \quad (37)$$

$$\frac{dM_{i,j}^L}{dt} = L_{j-1}x_{i,j-1} - L_jx_{i,j} + z_{i,j}^L F_{i,j}^L + N_{i,j}^L + \sum_{k=1}^r v_{i,k} R_{k,j} \varepsilon_j^L \quad (38)$$

where $N_{i,j}$ (mol s^{-1}) is the interfacial mass transfer rate.

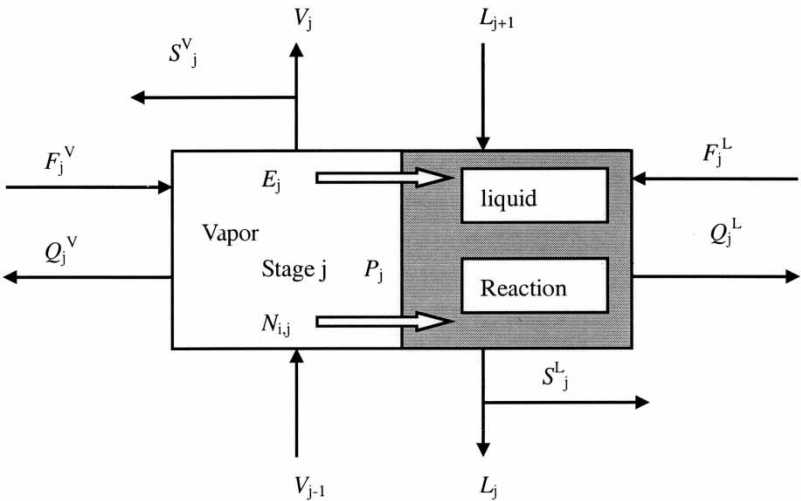


Figure 19. Schematic representation of an NEQ stage.

The overall molar balances are obtained by summing Equations (37) and (38) over the total number of components c in the mixture:

$$\frac{dM_j^V}{dt} = V_{j+1} - V_j + F_j^V - \sum_{k=1}^c N_{k,j}^V \quad (39)$$

$$\frac{dM_j^L}{dt} = L_{j-1} - L_j + F_j^L + \sum_{k=1}^c N_{i,j}^L + \sum_{i=1}^c \sum_{k=1}^r v_{i,k} R_{k,j} \epsilon_j^L. \quad (40)$$

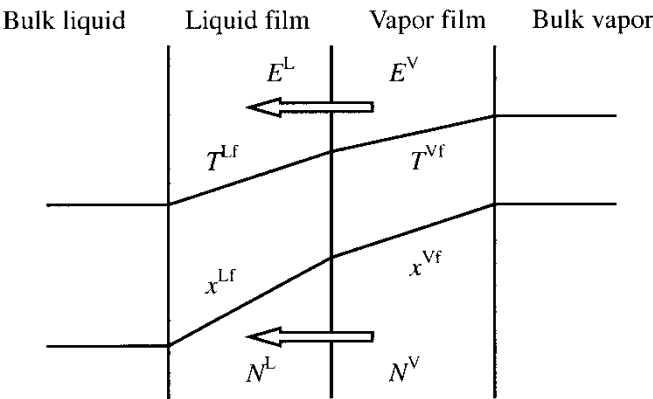


Figure 20. Two-film model of the NEQ stage.

The mole fractions of the vapor and liquid phases are calculated from the respective phase molar hold-ups:

$$y_{i,j} = \frac{M_{i,j}^V}{M_j^V}, \quad x_{i,j} = \frac{M_{i,j}^L}{M_j^L}. \quad (41)$$

Only $c-1$ of these mole fractions are independent because the phase mole fractions sum to unity:

$$\sum_{k=1}^c y_{k,j} = 1, \quad \sum_{k=1}^c x_{k,j} = 1 \quad (42)$$

The energy balance for the vapor and liquid phases are written as follows:

$$\frac{dE_j^V}{dt} = V_{j+1}H_{j+1}^V - V_jH_j^V + F_j^V H_j^{VF} - E_j^V - Q_j^V \quad (43)$$

$$\frac{dE_j^L}{dt} = L_{j-1}H_{j-1}^L - L_jH_j^L + F_j^L H_j^{LF} + E_j^L - Q_j^L \quad (44)$$

where H_j^V and H_j^L represent the molar enthalpy of vapor and liquid phases, respectively.

There is no need to take separate account in Equations (43) and (44) of the heat generated due to chemical reaction since the computed enthalpies include the heats of formation.

As mentioned before, the importance to model the NEQ is to set up the relation of interfacial mass and energy transfer rates. The molar transfer rate N_i^L in the liquid phase is related to the chemical potential gradients by the Maxwell–Stefan equation:

$$\frac{x_i^L}{RT^L} \frac{\partial \mu_i^L}{\partial \eta} = \sum_{k=1}^c \frac{x_i^L N_k^L - x_k^L N_i^L}{C_i^L \kappa_{i,k}^L A} \quad (45)$$

$\kappa_{i,k}^L$ represents the mass transfer coefficient of the $i-k$ pair in the liquid phase; this coefficient is estimated from information on the corresponding Maxwell–Stefan diffusivity $D_{i,k}^L$ (61, 63, 64).

The summation equations at the interface are:

$$\sum_{k=1}^c y_{i,j}^{Vf} = 1, \quad \sum_{k=1}^c x_{i,j}^{Lf} = 1 \quad (46)$$

The interphase energy transfer rates E^{Lf} have conductive and convective contributions

$$E^{Lf} = -h^{Lf} A \frac{\partial T^{Lf}}{\partial \eta} + \sum_{i=1}^c N_i^{Lf} H_i^{Lf} \quad (47)$$

where A is the interfacial area and h^{Lf} is the heat transfer coefficient in the liquid phase. A relation analogous to Equation (47) holds for the vapor phase.

At the vapor-liquid interface we assume phase equilibrium

$$y_{i,j}|_I = K_{i,j}x_{i,j}|_I. \quad (48)$$

We also have continuity of mass and energy

$$N_i^{Vf}|_I = N_i^{Lf}|_I, \quad E^{Vf}|_I = E^{Lf}|_I. \quad (49)$$

Under steady-state conditions all of the time derivatives in the above equations are equal to zero. Similar to EQ stage model, the model equations can be solved using Newton's method (or a variant thereof). Other methods such as the combination of modified relaxation and Newton-Raphson methods where the equations are written in unsteady-state form and are integrated numerically until the steady-state solution has been found, can also be used to solve the above equations.

But both in the EQ stage model and in the NEQ stage model, the thermodynamic and physical properties are required. Moreover in the NEQ stage model the mass and energy transfer models are also necessary. A list of the thermodynamic, physical properties and mass and energy transfer correlations (63–67) available in our program is provided in Table 4.

Heterogeneous Azeotropic Distillation

In this case it is certain that phase split will occur in some regions of the tray column. The number of liquid phase can be determined by the modified plane phase stability test. If the fluid is split into two liquid phases, the concentration and flowrate of each phase are calculated by LLE calculation. Note that for the packing column, due to the mixing effect of packing on the liquid phase, the concentration and flowrate of two liquid phases can be regarded as a whole.

A fundamental thermodynamic criteria for equilibrium between phases is the equality of chemical potentials for each component in all phases. That is, for component i in two phases, I and II,

$$\mu_i^I = \mu_i^{II} \quad (50)$$

This condition is able to reduce to the well-known iso-activity criterion for liquid-liquid equilibrium, which states

$$a_i^I = a_i^{II}. \quad (51)$$

Table 4. Thermodynamic, physical properties and mass and energy transfer models used in the EQ and NEQ stage models

K-value models	$K_i = \gamma_i P_i^o / P$
Equations of state	Virial equation
Molar volume	Data from the references
Critical temperature, pressure, volume	Data from the references
Heat capacities	Ideal gas heat capacities for the vapor phase
Enthalpy	The modified Peng-Robinson (MPR) equation for the vapor enthalpy The liquid phase enthalpy deduced from vapor phase enthalpy and evaporation heat
Activity coefficient	UNIFAC equation
Vapor pressure	Antoine equation
Viscosity	Orrick-Erbar equation for the liquid phase Wilke equation for the vapor phase
Surface tension	Data from the references
Thermal conductivity	Data from the reference
Binary mass transfer coefficient	AIChE method
Multi-component mass transfer coefficient	The generalized Maxwell-Stefan equation
Binary diffusion coefficient	Fuller-Schettler-Giddings equation for the vapor phase Lusis-Ratliff equation for the liquid phase at infinite dilution; Vignes method for the liquid phase at finite dilution
Heat transfer coefficient	Calculated from the Chilton-Colburn j -factor

The activity of component i (a_i) can be expressed in terms of an activity coefficient (γ_i), which is defined by the relationship:

$$a_i = \gamma_i x_i \quad (52)$$

Equation (51), therefore, becomes

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II} \quad (53)$$

where x_i^I represents the mole fraction and γ_i^I the activity coefficient of component i in phase I. The activity coefficient is, in turn, a function of composition and temperature:

$$\gamma_i = \gamma_i(x_1, x_2, \dots, x_n, T), \quad (54)$$

which can be calculated by using an appropriate activity coefficient model, such as NRTL, Wilson, UNIQUAC, UNIFAC, and so forth (68–72).

The liquid-liquid flash problem that is required to be solved for three-phase distillation is to calculate the equilibrium phase compositions and

phase fractions for a given overall composition (z_i) and system temperature (T). If two equilibrium phases exist under these conditions, then the problem involves $2n + 1$ equilibrium and mass balance equations:

$$x_i^I \gamma_i^I - x_i^{II} \gamma_i^{II} = 0 \quad (55)$$

$$s x_i^I + (1 - s) x_i^{II} = z_i \quad (56)$$

$$\sum_{i=1}^n x_i^I = 1 \quad (57)$$

The unknowns are the phase compositions (x_i^I and x_i^{II}) and the fraction of the overall mixture occupied by phase II (s). The summation of phase I mole fraction has been included in Equation (57), and then excludes the corresponding sum for phase II as it is implicit in the equation group since the feed mole fractions (z_i) are constrained to sum to one.

In principle, it is possible to find the values of x_i^I , x_i^{II} and s that satisfy Equations (55)–(57) for the systems at liquid-liquid two-phase equilibrium. However, the calculation is complicated by the fact that there are multiple solutions to this equation group (73–75).

Classical thermodynamic analysis states that the necessary and sufficient condition of a single stable phase with an initial overall mole fraction, z_1 , is:

$$\left(\frac{\partial^2 G_m}{\partial z_1^2} \right)_{T,P} > 0 \quad (58)$$

where G_m is the Gibbs free energy per mole of mixture (J mol^{-1}). That is to say, G_m is a concave function of composition. Phase split will occur when

$$\left(\frac{\partial^2 G_m}{\partial z_1^2} \right)_{T,P} < 0 \quad (59)$$

and the boundary condition of phase stability is:

$$\left(\frac{\partial^2 G_m}{\partial z_1^2} \right)_{T,P} = 0 \quad (60)$$

The schematic representation of judging phase stability is shown in Figure 21, where at point A the single phase is stable and at point C unstable. The boundary is at point B, which is an inflexion point. Apparently, point D is at equilibrium where the Gibbs free energy per mole of mixture for all phases $G_{m,\min}$ is a minimum.

However, it is not an effective way to judge phase stability by applying Equations (58)–(60), because in general the molar Gibbs free energy is very difficult to obtain directly. In practice, one method of tangent plane stability analysis is often adopted. Besides judging function, the key advantage is to produce excellent initial estimates for the phase split

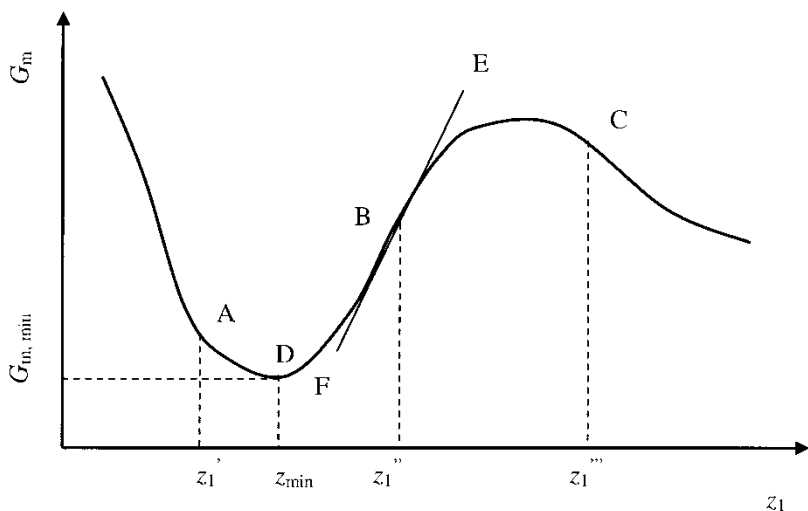


Figure 21. Schematic representation of phase stability; line EF is the tangent of inflexion point B.

calculation. The interested readers can refer to the references (76–79), which presents the extensive algorithms.

The method used for solving Equations (53)–(57) simultaneously is by using the Newton-Raphson method. With respect to the stability test, the equations are written as deviation functions:

$$D_i = x_i^I \gamma_i^I - x_i^{II} \gamma_i^{II} \quad (61)$$

$$D_{i+n} = z_i - s x_i^I - (1-s) x_i^{II} \quad (62)$$

$$D_{2n+1} = 1.0 - \sum_{i=1}^n x_i^I \quad (63)$$

The variable vector is given as

$$x^T = (x_1^I, \dots, x_n^I, x_1^{II}, \dots, x_n^{II}, s), \quad (64)$$

which is revised according to

$$x^{(t+1)} = x^{(t)} + \Delta x \quad (t = \text{iteration number}). \quad (65)$$

The correction vector Δx is calculated by

$$J \Delta x = -D \quad (66)$$

where J is the Jacobian matrix housing the partial derivatives of Equations (61)–(63). The equation group in Equation (66) can be solved by standard

Gaussian elimination. The iterations are continued until the mean square error condition for the residuals (D) satisfies a certain tolerance.

Experience has shown that the step length corrections (Δx) calculated by Equation (66) may be too large, thus forcing the iterations to diverge or converge on the trivial solution. To avoid this, the maximum corrections are limited to $x_{\max}$ for the mole fraction and $s_{\max}$ for the phase fraction:

$$x_{\max} = 0.10 \quad (67)$$

$$s_{\max} = 0.15 \quad (68)$$

Using this scheme and the initial conditions of the stability test usually allow the liquid-phase split to be calculated in less than six-time iterations.

Here the concept of binodal curve and spinodal curve is briefly mentioned. Binodal curve is made up of the points satisfying Equation (53), while spinodal curve satisfying Equation (60). Both separate one-phase and two-phase regions. In the composition space, binodal curve and spinodal curve are close but do not overlap. The interval between binodal curve and spinodal curve is the partially stable region where a little strong external perturbation can lead to phase split. But the region enclosed by spinodal curve is thermodynamically unstable. A schematic representation of binodal curve and spinodal curve (80–82) is illustrated in Figure 22.

For the NEQ stage model, in the heterogeneous liquid (usually two-liquid phase) region, the effect of liquid phase mass and heat transfer resistances near the liquid-liquid interface is considered. However, this effect does not exist in the homogeneous region. Figure 23 illustrates the vapor-liquid-liquid three-phase mass and heat transfers on the tray based on two-film model.

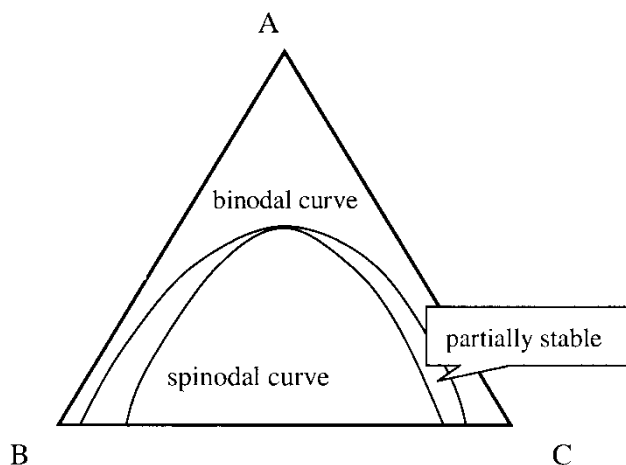


Figure 22. A schematic representation of binodal curve and spinodal curve.

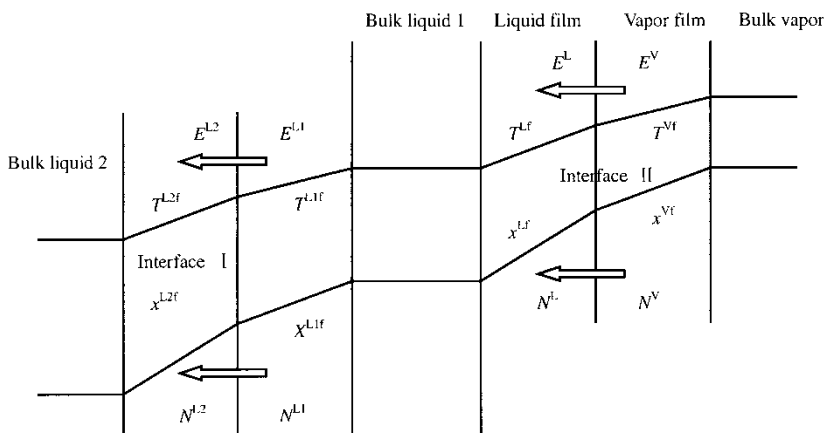


Figure 23. Two-film model of vapor-liquid 1-liquid 2 three-phase mass and heat transfers on the tray (it is supposed that the direction of mass and heat transfers is from the vapor phase to the liquid phase and then from liquid 1 to liquid 2).

Consequently, at steady-state, we have continuity of mass and energy at the interfaces I and II:

$$N_i^{Vf}|_I = N_i^{Lf}|_I, \quad E^{Vf}|_I = E^{Lf}|_I \quad (69)$$

$$N_i^{L1f}|_{II} = N_i^{L2f}|_{II}, \quad E^{L1f}|_{II} = E^{L2f}|_{II} \quad (70)$$

The molar transfer rates N_i^{Vf} , N_i^{Lf} , N_i^{L1f} , and N_i^{L2f} are related to the chemical potential gradients and generally solved by the Maxwell-Stefan equation given in Equation (45). The molar heat transfer rates, E^{Vf} , E^{Lf} , E^{L1f} , and E^{L2f} are often obtained by means of the Reynolds analogy, the Chilton-Colburn analogy, or the Prandtl analogy to derive the heat transfer coefficients.

Case Study

On this basis, an azeotropic distillation column can be simulated by the EQ and/or NEQ stage models. Herein, for the EQ stage model, the ethanol dehydration process by azeotropic distillation with pentane as entrainer was simulated. The result coming from the references (25, 26) is shown in Figures 24 and 25, from which we can find the typical characteristics of azeotropic distillation column, that is, there is a steep change in temperature and composition along the column, often near the bottom or the top. As shown in Figures 24 and 25, this range is near the bottom (between the fourth and eighth trays). The corresponding fourth and eighth trays (or a section of packing) are generally called sensitive trays. The sensitive range is marked in dashed lines. At the same time, the general assumption on constant molar

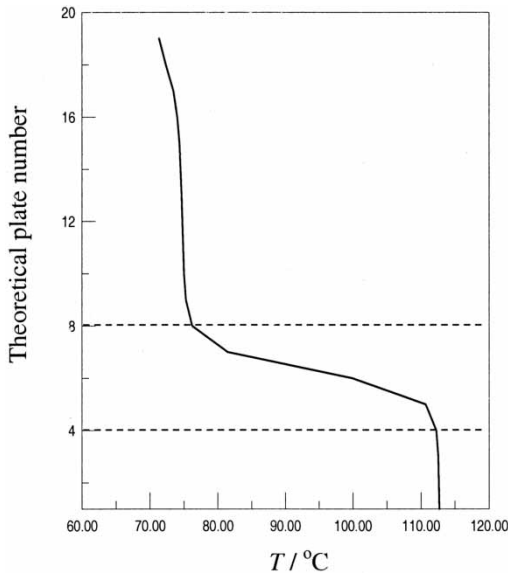


Figure 24. Temperature profile of the ethanol/water/pentane system along the azeotropic distillation column; theoretical plate is numbered from the bottom to the top.

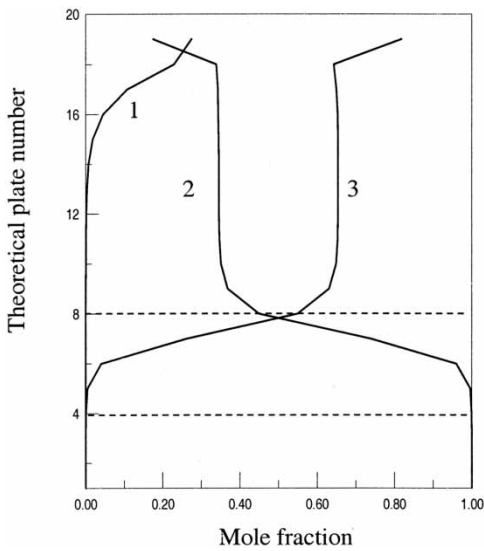


Figure 25. Composition profile of the ethanol/water/pentane system along the azeotropic distillation column; theoretical plate is numbered from the bottom to the top; (1) mole fraction of water in vapor phase (entrainer free); (2) mole fraction of ethanol in liquid phase; (3) mole fraction of pentane as entrainer in the liquid phase.

flowrate adopted in the short-cut method should be cautious because flowrate change for vapor and/or liquid phases sometimes is very high, up to 25% along the column.

For the NEQ stage model, the ethanol dehydration process by azeotropic distillation with benzene as entrainer was simulated by Mortaheb and Kosuge (52). The effect of operating conditions on the separation performance of azeotropic distillation column was studied. But it was also found that there is a steep change in temperature and composition along the column, often near the bottom or the top.

Multiple Steady-State Analysis

The term, multiple steady state (MSS), is referred to as output multiplicities, i.e., columns with the same inputs (the same feed, distillate, bottoms, reflux and boilup molar flows, the same feed composition, number of stages, and feed location) but different outputs (product compositions) and thus different composition profiles.

MSSs in conventional distillation have been known from the simulation and theoretical studies dating back to the 1970s and have been a topic of considerable interest in the distillation community. However, only recently has experimental verification of their existence has been forthcoming. MSS is related to nonlinear analysis along the continuation path. Although the nonlinear analysis is highly mathematical and somewhat sophisticated, it is rapidly gaining acceptance by many practitioners in this field.

In order to explore the occurrence of MSS, the bifurcation parameter should be chosen among the inputs. The common bifurcation parameters are feed location, product flowrate, etc. The mathematical methods have two types: graphical method and numerical simulation.

In the graphical method for the ∞/∞ case (infinite reflux and infinite number of trays or infinite long columns), the geometrical condition for the existence of MSS is as follows (4, 83–85):

1. As illustrated in Figure 8, some lines parallel to the LH edge intersects the interior boundary TX more than once, or
2. Some lines parallel to LI intersects TY more than once, or
3. Some lines parallel to IH intersects TZ more than once.

However, the lines (e.g., L_2H_2 , I_2H_1 , L_1I_1) respectively parallel to LH, LI, and IH intersect TX, TY, or TZ only once. Thus, no MSS is found in Figure 8. In Figure 26 it is supposed that there is no decanter at the top of distillation column and LLE curve is not utilized. Figure 26 illustrates the phenomena of MSS. The lines (e.g., L_1L_2) between lines H_1H_2 and I_1I_2 intersect TX twice, and thus MSS exists. For the ∞/∞ case, the top composition can lie

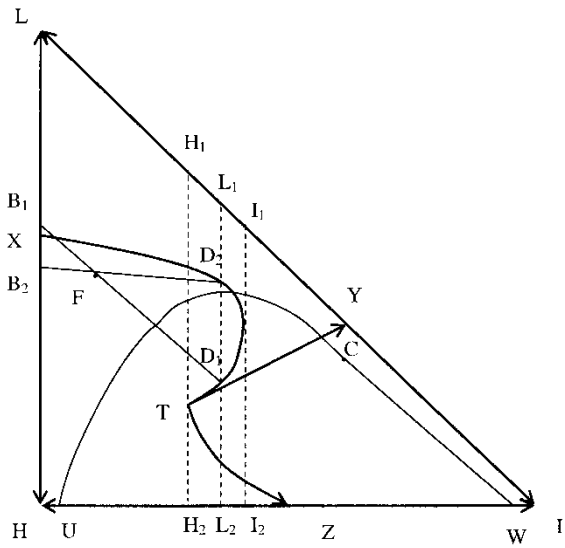


Figure 26. MSS without decanter at the top of distillation column.

in TX boundary and the bottom composition lies in LH boundary. So it is very straightforward to derive: $B_1 = B_2$ (flowrate of bottom product) and $D_1 = D_2$ (flowrate of top product). But in these two cases, the product compositions are different, which indicates that different outputs appear. Evidently, both bottom product and top product can be used as bifurcation parameters. Moreover, MSS often appears in the vicinity of singular (fixed) points, such as the point T.

Note that the boundaries employed may be simple distillation boundaries or distillation line boundaries, depending on the column type. Furthermore, for heterogeneous azeotropic distillation with decanter at the top, the boundaries may include one part of LLE envelope.

In the numerical simulation, continuation methods normally used for finding solutions to “hard” problems, where a very good initial guess is required in order for Newton’s method to converge on that solution. In addition, it has proven to be a valuable tool for finding MSS in distillation columns. The underlying idea of continuation methods is that of path following, whereby a mathematical path is traced from a problem $G(x)$ for which we can obtain a solution relatively easily to the “hard” problem $(F(x))$, thereby keeping track of the changes in the variables. Such a path is implicitly defined by the homotopy equation:

$$H(x, t) = (1 - t)G(x) + tF(x) \tag{71}$$

If our original problem is n -dimensional, this equation describes a curve in $(n + 1)$ dimensional space. Since the solution to $H(x,0) = 0$ coincides with

$G(x) = 0$, we have at least one point on this curve. We now have to evaluate how the variables change along the curve, and correct each accordingly as we walk along the curve. By differentiating the homotopy equation with respect to the arc length and integrating the resulting system of differentiating equations, we can generate an estimate for a new point on the curve, which can then be corrected to give the next point on the curve. For more details about this method, the interested readers can refer to the references (59, 60, 86, 87).

MSSs are located using one of the operational specifications (e.g., reboiler duty, bottom product flowrate, feed rate, conversion) as the continuation parameter (or bifurcation parameter). This results in a system of n equations with $n + 1$ variables, thereby implicitly defining a curve in a $(n + 1)$ dimensional space. If we have a converged solution for a fixed specification, we have a starting point on this curve. We can then apply exactly the same algorithm as described previously to “walk” along the curve. By doing so, we can follow the steady-state solution of the model as a function of that specification. Thus, we can obtain valuable information about steady-state column behavior and MSS regions. An added benefit of this approach is that now we are following a solution that is at any point on the curve describing a physically meaningful situation and not a strictly mathematical artifact. In the latter case, the homotopy path in itself does not have a physical meaning and might go through regions of negative mole fractions, etc. In these regions, the solution is invalid if, for instance, in activity coefficient calculations the logarithm of the mole fractions is required.

Apart from the application of azeotropic distillation in traditional chemical engineering field, it has already been used in such front areas (88–91) as preparation of nanometer-sized $\text{ZrO}_2/\text{Al}_2\text{O}_3$ powders, synthesizing nanoscale powders of yttria-doped ceria electrolyte, removal of byproducts in lipase-catalyzed solid-phase synthesis of sugar fatty acid esters, combining fungal dehydration and lipid extraction, and so on. It manifests that azeotropic distillation has sustained a continuing interest from the past to more recent years.

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