Chapter 6: Approximate Shortcut Methods for Multi-component Distillation

6.1 Total Reflux: Fenske Equation

For a *multi-component* (*i.e.* > 1) distillation with the **total reflux** as shown Figure 6.1, the equation for vapour-liquid equilibrium (VLE) at the **re-boiler** for any 2 components (*e.g.*, species A and B) can be formulated as follows

$$\left(\frac{y_A}{y_B}\right)_R = \alpha_R \left(\frac{x_A}{x_B}\right)_R \qquad (6.1)$$

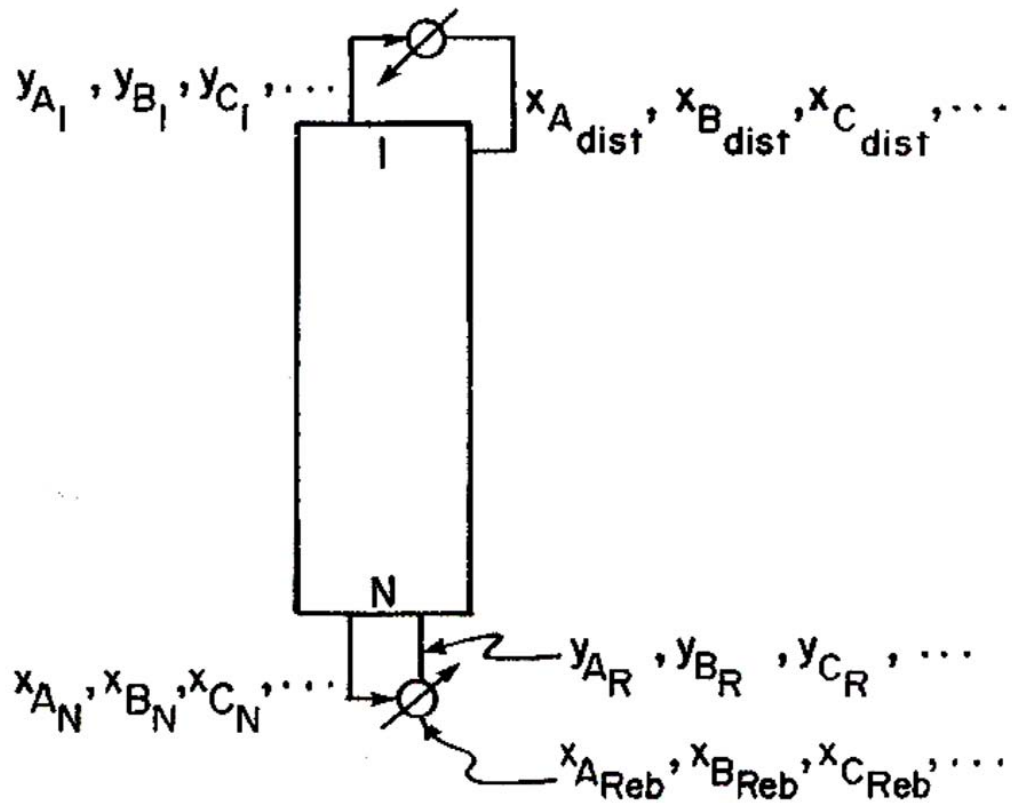(note that sub-script $\boldsymbol{R}$ denotes a **re-boiler**)

Figure 6.1: A distillation column with the total reflux

(from "Separation Process Engineering" by Wankat, 2007)

Eq. 6.1 is, in fact, the relationship that represents the relative volatility of species A and B $\left(\alpha_{AB}\right)$ we have learned previously:

$$\alpha_{AB} = \frac{y_A \, / \, x_A}{y_B \, / \, x_B} \qquad (6.2)$$

Performing the material balances for species A (assuming that **species A** is the **more volatile component**: **MVC**) around the re-boiler gives

$$\overline{L}x_{A,N} = \overline{V}y_{A,R} + Bx_{A,R}$$

or

$$\overline{V}y_{A,R} = \overline{L}x_{A,N} - Bx_{A,R} \qquad (6.3)$$

Doing the same for species B yields

$$\overline{V}y_{B,R} = \overline{L}x_{B,N} - Bx_{B,R} \qquad (6.4)$$

Since this is a *total reflux* distillation,

$$B = 0$$

which results in the fact that

$$\overline{V} = \overline{L}$$

With the above facts, Eq. 6.3 becomes

$$\overline{V}y_{A,R} = \overline{L}x_{A,N}$$

$$\frac{y_{A,R}}{x_{A,N}} = \frac{\overline{L}}{\overline{V}} = 1$$

$$y_{A,R} = x_{A,N} \qquad (6.5)$$

Doing the same for Eq. 6.4 results in

$$y_{B,R} = x_{B,N} \qquad (6.6)$$

Eqs 6.5 and 6.6 confirm that the operating line for the total reflux distillation is, in fact, the $y = x$ line

Combining Eqs 6.5:

$$y_{A,R} = x_{A,N} \qquad (6.5)$$

and Eq. 6.6:

$$y_{B,R} = x_{B,N} \qquad (6.6)$$

with Eq. 6.1:

$$\left(\frac{y_A}{y_B} \right)_R = \alpha_R \left(\frac{x_A}{x_B} \right)_R \qquad (6.1)$$

gives

$$\left(\frac{x_A}{x_B} \right)_N = \alpha_R \left(\frac{x_A}{x_B} \right)_R \qquad (6.7)$$

Applying Eq. 6.1 to stage N yields the VLE equation for stage N as follows

$$\left(\frac{y_A}{y_B} \right)_N = \alpha_N \left(\frac{x_A}{x_B} \right)_N \qquad (6.8)$$

Performing material balances for species A and B around stage N (in a similar manner as *per* the re-boiler) results in

$$y_{A,N} = x_{A,N-1} \qquad (6.9)$$

$$y_{B,N} = x_{B,N-1} \qquad (6.10)$$

Once again, combining Eqs. 6.9 and 6.10 with Eq. 6.8 in a similar way as done for Eqs. 6.5 and 6.6 with Eq. 6.1 gives

$$\left(\frac{x_A}{x_B} \right)_{N-1} = \alpha_N \left(\frac{x_A}{x_B} \right)_N \qquad (6.11)$$

Combining Eq. 6.11 with Eq. 6.7 yields

$$\left(\frac{x_A}{x_B} \right)_{N-1} = \alpha_N \alpha_R \left(\frac{x_A}{x_B} \right)_R \qquad (6.12)$$

By doing the same for stage $N-1$, we obtain

$$\left(\frac{x_A}{x_B}\right)_{N-2} = \alpha_{N-1}\alpha_N\alpha_R\left(\frac{x_A}{x_B}\right)_R \qquad (6.13)$$

Hence, by performing the similar derivations until we reach the top of the distillation (*i.e.* stage 1) with the output of $x_{A,\text{dist}}$ and $x_{B,\text{dist}}$, we obtain the following equation:

$$\left(\frac{x_A}{x_B}\right)_{\text{dist}} = \alpha_1\alpha_2\alpha_3...\alpha_{N-1}\alpha_N\alpha_R\left(\frac{x_A}{x_B}\right)_R$$

$$(6.14)$$

Let's define α_{AB} as the *geometric-average* relative volatility, with can be written mathematically as follows

$$\alpha_{AB} = \left(\alpha_1 \alpha_2 \alpha_3 \ldots \alpha_{N-1} \alpha_N \alpha_R \right)^{\frac{1}{N_{\min}}}$$

where $N_{\min}$ is the number of of *equilibrium* stages for the *total reflux* distillation

Thus, Eq. 6.14 can be re-written as

$$\left(\frac{x_A}{x_B} \right)_{\text{dist}} = \alpha_{AB}^{N_{\min}} \left(\frac{x_A}{x_B} \right)_R \qquad (6.15)$$

Solving for $N_{\min}$ results in

$$N_{\min} = \frac{\ln \left[\frac{\left(\frac{x_A}{x_B} \right)_{\text{dist}}}{\left(\frac{x_A}{x_B} \right)_R} \right]}{\ln \alpha_{AB}} \qquad (6.16)$$

Eq. 6.16 can also be written in another form as follows

$$N_{\min} = \frac{\ln\left[\dfrac{\left(\dfrac{Dx_A}{Dx_B}\right)_{\text{dist}}}{\left(\dfrac{Bx_A}{Bx_B}\right)_{\text{R}}}\right]}{\ln \alpha_{AB}} \qquad (6.17)$$

As we have learned from Chapter 5,

$$Dx_{A,\text{ dist}} = \left(FR_A\right)_{\text{dist}} Fz_A \qquad (6.18)$$

(see Eq. 5.6 on Page 8 of Chapter 5)

and

$$Bx_{A,R} = \left[1 - \left(FR_A\right)_{\text{dist}}\right] Fz_A \qquad (6.19)$$

(see Eq. 5.10 on Page 10 of Chapter 5)

Note that $Bx_{A,R} \equiv Bx_{A,\text{bot}}$

We can also write the similar equations as *per* Eqs. 6.18 and 6.19 for species B (try doing it yourself)

Combining Eqs. 6.18 and 6.19 and the corresponding equations for species B with Eq. 6.17, and re-arranging the resulting equation gives

$$N_{\min} = \frac{\ln\left\{\dfrac{\left(FR_A\right)_{\mathrm{dist}}\left(FR_B\right)_{\mathrm{bot}}}{\left[1-\left(FR_A\right)_{\mathrm{dist}}\right]\left[1-\left(FR_B\right)_{\mathrm{bot}}\right]}\right\}}{\ln\alpha_{AB}}$$

(6.20)

Note that $\left(FR_B\right)_{\mathrm{bot}}$ is the fractional recovery of species B in the bottom product

When there are *only* **2 components** (*i.e.* a *binary* **mixture**), Eq. 6.16 can be written as follows

$$N_{\min} = \frac{\ln\left\{ \frac{\left[x_A / \left(1 - x_A\right) \right]_{\mathrm{dist}}}{\left[x_A / \left(1 - x_A\right) \right]_{\mathrm{bot}}} \right\}}{\ln \alpha_{AB}}$$

(6.21)

Eq. 6.20 can also be written for species C and B in the multi-component system (where C is a *non-key* component, but B is a *key* component) as follows

$$N_{\min} = \frac{\ln\left\{ \frac{\left(FR_C\right)_{\mathrm{dist}} \left(FR_B\right)_{\mathrm{bot}}}{\left[1 - \left(FR_C\right)_{\mathrm{dist}} \right]\left[1 - \left(FR_B\right)_{\mathrm{bot}} \right]} \right\}}{\ln \alpha_{CB}}$$

(6.22)

Solving Eq. 6.22 for $\left(FR_C\right)_{\text{dist}}$ results in

$$\left(FR_C\right)_{\text{dist}} = \frac{\alpha_{CB}^{N_{\min}}}{\left[\dfrac{\left(FR_B\right)_{\text{bot}}}{1 - \left(FR_B\right)_{\text{bot}}}\right] + \alpha_{CB}^{N_{\min}}}$$

$$(6.23)$$

The derivations and the resulting equations above were proposed by Merrell Fenske, a Chemical Engineering Professor at the Pennsylvania State University (published in *Industrial and Engineering Chemistry*, Vol. 24, under the topic of "*Fractionation of straight-run Pensylvania gasoline*" in 1932)

The following Example illustrates the application of the **Fenske equation** to the *multi-component* distillation with the total reflux

Example An atmospheric distillation column with a *total* condenser and a *partial* re-boiler is used to separate a mixture of 40 mol% benzene, 30% toluene, and 30% cumene, in which the *feed* is input as a *saturated vapour*

It is required that **95% of toluene** be in the **distillate** and that **95% of cumene** be in the **bottom**

If the CMO is assumed and the *reflux* is a *saturated liquid*, determine **a)** the number of equilibrium stage for *total reflux* distillation and **b)** the fractional recovery of benzene in the distillate $\left[\left(FR_{\text{benzene}}\right)_{\text{dist}}\right]$

Given the constant volatilities with respect to toluene as $\alpha_{\text{benz-tol}} = 2.25$ and $\alpha_{\text{cume-tol}} = 0.21$

Since the *fractional recoveries* of *toluene* (in the distillate–95%) and *cumene* (in the bottom–95%) are specified, both *toluene* and *cumene* are the **key** *components*

By considering the relative volatilities of toluene ($= 1.0$ – with *respect to* toluene *itself*) and cumeme ($= 0.21$ – with respect to toluene), it is evident that toluene is more volatile than cumene

Accordingly,

- *toluene* is the *light* key component (**LK**)
- *cumene* is the *heavy* key component (**HK**)

Therefore, *benzene* is the *non-key* component

As the relative volatility of benzene is higher than that of toluene, which is the LK, *benzene* is the *light non-key* component (**LNK**)

It is given, in the problem statement, that

- $z_{\text{toluene}} = 0.30$
- $z_{\text{cumene}} = 0.30$
- $z_{\text{benzene}} = 0.40$
- $\left(FR_{\text{toluene}}\right)_{\text{dist}} = 0.95$
- $\left(FR_{\text{cumene}}\right)_{\text{bot}} = 0.95$

Let's denote

- toluene $\equiv A$ (the LK)
- cumene $\equiv B$ (the HK)
- benzene $\equiv C$ (the LNK)

Hence, the number of *minimum* equilibrium stages $\left(N_{\min} \right)$ for the distillation with the total reflux can be computed, using Eq. 6.20, as follows

$$N_{\min} = \frac{\ln \left\{ \dfrac{\left(FR_A \right)_{\text{dist}} \left(FR_B \right)_{\text{bot}}}{\left[1 - \left(FR_A \right)_{\text{dist}} \right] \left[1 - \left(FR_B \right)_{\text{bot}} \right]} \right\}}{\ln \alpha_{AB}}$$

$$N_{\min} = \frac{\ln \left\{ \dfrac{\left(FR_A \right)_{\text{dist}} \left(FR_B \right)_{\text{bot}}}{\left[1 - \left(FR_A \right)_{\text{dist}} \right] \left[1 - \left(FR_B \right)_{\text{bot}} \right]} \right\}}{\ln \left(\dfrac{1}{\alpha_{BA}} \right)}$$

or

$$N_{\min} = \frac{\ln \left\{ \dfrac{\left(FR_{\text{toluene}} \right)_{\text{dist}} \left(FR_{\text{cumene}} \right)_{\text{bot}}}{\left[1 - \left(FR_{\text{toluene}} \right)_{\text{dist}} \right] \left[1 - \left(FR_{\text{cumene}} \right)_{\text{bot}} \right]} \right\}}{\ln \left(\dfrac{1}{\alpha_{\text{cume-tol}}} \right)}$$

$$(6.24)$$

Note that, as α_{AB} is defined as

$$\alpha_{AB} = \frac{y_A \, / \, x_A}{y_B \, / \, x_B}$$

by using the same principle, we obtain the fact that

$$\alpha_{BA} = \frac{y_B \, / \, x_B}{y_A \, / \, x_A}$$

Accordingly,

$$\alpha_{BA} = \frac{1}{\alpha_{AB}}$$

Substituting corresponding numerical values into Eq. 6.24:

$$N_{\text{min}} = \frac{\ln\left\{ \dfrac{\left(FR_{\text{toluene}}\right)_{\text{dist}}\left(FR_{\text{cumene}}\right)_{\text{bot}}}{\left[1-\left(FR_{\text{toluene}}\right)_{\text{dist}}\right]\left[1-\left(FR_{\text{cumene}}\right)_{\text{bot}}\right]} \right\}}{\ln\left(\dfrac{1}{\alpha_{\text{cume-tol}}}\right)}$$

yields

$$N_{\text{min}} = \frac{\ln\left\{ \dfrac{\left(0.95\right)\left(0.95\right)}{\left[1-\left(0.95\right)\right]\left[1-\left(0.95\right)\right]} \right\}}{\ln\left(\dfrac{1}{0.21}\right)}$$

$$N_{\text{min}} = 3.8$$

Then, Eq. 6.23:

$$\left(FR_C\right)_{\text{dist}} = \frac{\alpha_{CB}^{N_{\text{min}}}}{\left[\dfrac{\left(FR_B\right)_{\text{bot}}}{1-\left(FR_B\right)_{\text{bot}}}\right] + \alpha_{CB}^{N_{\text{min}}}}$$

$$\tag{6.23}$$

is employed to compute the fractional recovery of the **LNK** (= *benzene* in this Example) in the **distillate**

Note that α_{CB} in this Example is $\alpha_{\text{benz-cume}}$, but from the given data, we do NOT have the value of $\alpha_{\text{benz-cume}}$

How can we determine this value?

We are the given the values of

- $\alpha_{\text{benz-tol}} = \dfrac{y_{\text{benz}} \,/\, x_{\text{benz}}}{y_{\text{tol}} \,/\, x_{\text{tol}}} = 2.25$ \hfill (6.25)

- $\alpha_{\text{cume-tol}} = \dfrac{y_{\text{cume}} \,/\, x_{\text{cume}}}{y_{\text{tol}} \,/\, x_{\text{tol}}} = 0.21$ \hfill (6.26)

(6.25)/(6.26) gives

$$\frac{\alpha_{\text{benz-tol}}}{\alpha_{\text{cume-tol}}} = \frac{\dfrac{y_{\text{benz}} \, / \, x_{\text{benz}}}{y_{\text{tol}} \, / \, x_{\text{tol}}}}{\dfrac{y_{\text{cume}} \, / \, x_{\text{cume}}}{y_{\text{tol}} \, / \, x_{\text{tol}}}} = \frac{y_{\text{benz}} \, / \, x_{\text{benz}}}{y_{\text{cume}} \, / \, x_{\text{cume}}} = \alpha_{\text{benz-cume}}$$

(6.27)

Substituting corresponding numerical values into Eq. 6.27 results in

$$\alpha_{\text{benz-cume}} = \frac{y_{\text{benz}} \, / \, x_{\text{benz}}}{y_{\text{cume}} \, / \, x_{\text{cume}}} = \frac{\alpha_{\text{benz-tol}}}{\alpha_{\text{cume-tol}}}$$

$$\alpha_{\text{benz-cume}} = \frac{\alpha_{\text{benz-tol}}}{\alpha_{\text{cume-tol}}}$$

$$\alpha_{\text{benz-cume}} = \frac{\alpha_{\text{benz-tol}}}{\alpha_{\text{cume-tol}}} = \frac{2.25}{0.21} = 10.7$$

Thus, the fractional recovery of benzene $\left(\text{species } C\right)$ in the distillate $\left(FR_C\right)_{\text{dist}}$ can be computed, using Eq. 6.23, as follows

$$\left(FR_C\right)_{\text{dist}} = \frac{\alpha_{CB}^{N_{\text{min}}}}{\left[\dfrac{\left(FR_B\right)_{\text{bot}}}{1-\left(FR_B\right)_{\text{bot}}}\right] + \alpha_{CB}^{N_{\text{min}}}}$$

$$= \frac{\alpha_{\text{benz-cume}}^{N_{\text{min}}}}{\left[\dfrac{\left(FR_{\text{cume}}\right)_{\text{bot}}}{1-\left(FR_{\text{cume}}\right)_{\text{bot}}}\right] + \alpha_{\text{benz-cume}}^{N_{\text{min}}}}$$

$$= \frac{\left(10.7\right)^{3.8}}{\left[\dfrac{\left(0.95\right)}{1-\left(0.95\right)}\right] + \left(10.7\right)^{3.8}}$$

$$\left(FR_C\right)_{\text{dist}} = \left(FR_{\text{benz}}\right)_{\text{dist}} = 0.998$$

It is evident that the *fractional recovery* of the *LNK* in this *distillate* is close to **unity** (**1.0**)

6.2 Minimum Reflux: Underwood Equations

We have just learned how to calculate important variables [*e.g.*, $N_{\min}$, $\left(FR_i\right)_{\text{dist}}$] numerically for the case of *total reflux* using an approximate shortcut technique of Fenske (1932)

Is there such a technique for the case of *minimum reflux*?

For a *binary* (*i.e.* 2-component) mixture, the *pinch* point *usually* (but **NOT *always***) *occurs* when the *top* and the *bottom operating* lines *cross each other on* the *equilibrium line* as shown in Figure 6.2
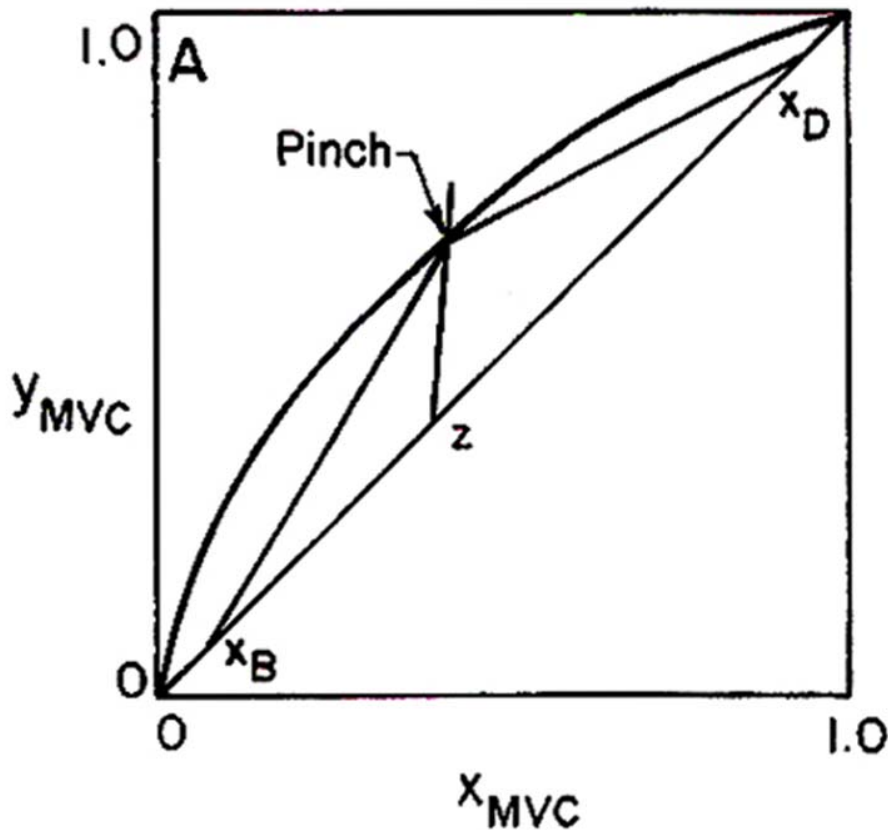
Figure 6.2: The pinch point for a binary mixture without the azeotrope

(from "Separation Process Engineering" by Wankat, 2007)

Note that an *exception* that the *pinch point* is **not** at the *intersection* of the *top* operating line, the *bottom* operating line, and the *equilibrium* line is as illustrated in Figure 6.3
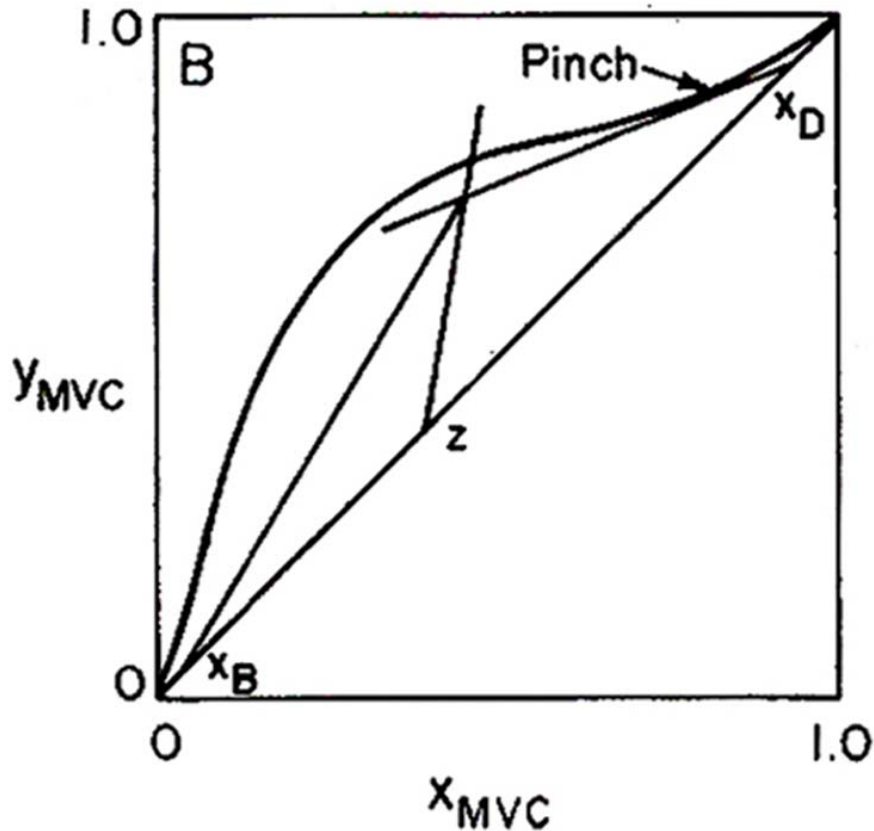
Figure 6.3: The pinch point for a binary mixture with the azeotrope

(from "Separation Process Engineering" by Wankat, 2007)

The case that the *pinch point* is the *intersection* point of the intersection of the *top* operating line, the *bottom* operating line, and the *equilibrium* line as illustrated by Figure 6.2 can also be *extended* to the *multi-component* systems

A.J.V. Underwood developed a procedure to calculate the minimum reflux ratio (published in *Chemical Engineering Progress*, Vol. 34, under the topic of *"Fractional distillation of multi-component mixtures"* in 1948), which comprises a number of equations

The development of *Underwood equations* is rather *complex*, and it is not necessary, especially for *practicing engineers*, to understand all the details of the development/derivations

To be *practical*, we shall follow an *approximate* derivation of R.E. Thompson (published in *AIChE Modular Instructions*, Series B, Vol. 2, under the topic of *"Shortcut design method-minimum reflux"* in 1980), which is *good enough* for *engineering calculations*

Consider the enriching/rectifying section of a distillation column as shown in Figure 6.4
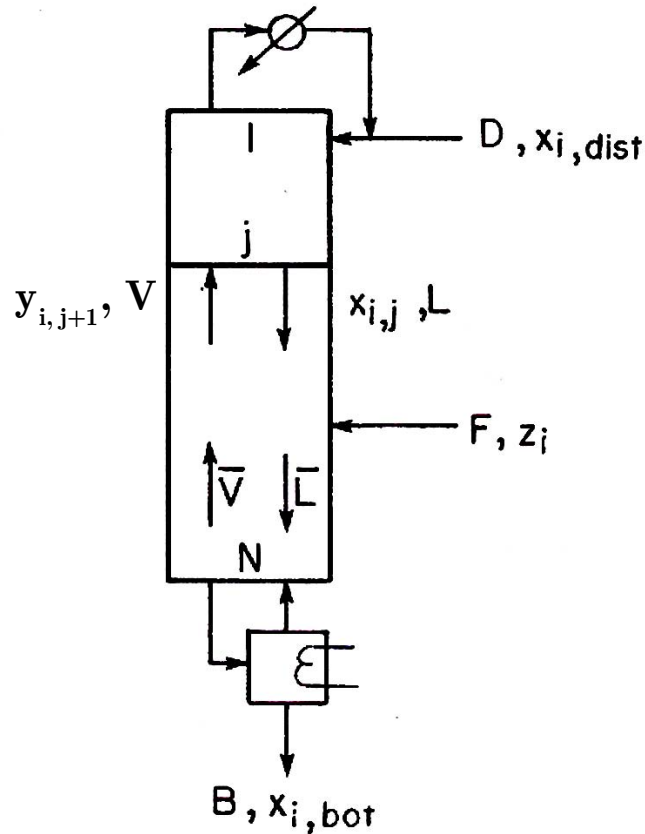

Figure 6.4: The enriching or rectifying section of the distillation column

(from "Separation Process Engineering" by Wankat, 2007)

Performing a *material balance* for species i for the *enriching/rectifying section* in the case of *minimum reflux ratio* gives

$$y_{i,\,j+1} V_{\min} = x_{i,\,j} L_{\min} + x_{i,\,\text{dist}} D \qquad (6.28)$$

Since the *pinch* point is at the *intersection* of the *top* operating line, the *bottom* operating line, and the *equilibrium* line, the *compositions* (around the pinch point) are *constant; i.e.*

$$x_{i,\,j-1} = x_{i,\,j} = x_{i,\,j+1} \qquad (6.29\text{a})$$

and

$$y_{i,\,j-1} = y_{i,\,j} = y_{i,\,j+1} \qquad (6.29\text{b})$$

The *equilibrium* equation of species i at stage $j+1$ can be written as follows

$$y_{i,\,j+1} = K_i x_{i,\,j+1} \qquad (6.30)$$

Combining Eq. 6.28 with Eqs. 6.29 (a & b) and 6.30 results in

$$V_{\min} y_{i,\,j+1} = L_{\min} \frac{y_{i,\,j+1}}{K_i} + D x_{i,\,\text{dist}}$$

$$(6.31)$$

Let's define the relative volatility of species i, α_i, as

$$\alpha_i = \frac{K_i}{K_{\text{ref}}} \qquad (6.32)$$

where K_{ref} is the K value of the *reference* species

Eq. 6.32 can be re-arranged to

$$K_i = \alpha_i K_{\text{ref}} \qquad (6.33)$$

Combining Eq. 6.33 with Eq. 6.31 and re-arranging the resulting equation yields

$$V_{\min} y_{i,\,j+1} = \frac{L_{\min}}{\alpha_i K_{\text{ref}}} y_{i,\,j+1} + D x_{i,\,\text{dist}}$$

$$V_{\min} y_{i,\,j+1} - \frac{L_{\min}}{\alpha_i K_{\mathrm{ref}}} y_{i,\,j+1} = Dx_{i,\,\mathrm{dist}}$$

$$V_{\min} y_{i,\,j+1} \left(1 - \frac{L_{\min}}{V_{\min} \alpha_i K_{\mathrm{ref}}} \right) = Dx_{i,\,\mathrm{dist}}$$

$$V_{\min} y_{i,\,j+1} = \frac{Dx_{i,\,\mathrm{dist}}}{\left(1 - \dfrac{L_{\min}}{V_{\min} \alpha_i K_{\mathrm{ref}}} \right)}$$

$$(6.34)$$

Multiplying both numerator and denominator of the right hand side (RHS) of Eq. 6.34 with α_i gives

$$V_{\min} y_{i,\,j+1} = \frac{\alpha_i Dx_{i,\,\mathrm{dist}}}{\left(\alpha_i - \dfrac{L_{\min}}{V_{\min} K_{\mathrm{ref}}} \right)}$$

$$(6.35)$$

Taking a summation of Eq. 6.35 for all species results in

$$\sum V_{\min} y_{i,\,j+1} = V_{\min}\left(1\right) = V_{\min} = \sum \frac{\alpha_i D x_{i,\,\text{dist}}}{\left(\alpha_i - \dfrac{L_{\min}}{V_{\min} K_{\text{ref}}}\right)}$$

$$(6.36)$$

Performing the similar derivations for the *stripping* section (*i.e.* under the feed stage) yields

$$-\bar{V}_{\min} = \sum \frac{\bar{\alpha}_i B x_{i,\,\text{bot}}}{\left(\bar{\alpha}_i - \dfrac{\bar{L}_{\min}}{\bar{V}_{\min} \bar{K}_{\text{ref}}}\right)} \qquad (6.37)$$

It is important to note that, since the conditions in the enriching/rectifying section are different from those in the stripping section, we obtain the fact that, *generally,*

$$\alpha_i \neq \overline{\alpha}_i$$

and

$$K_{\text{ref}} \neq \overline{K}_{\text{ref}}$$

Underwood also defined the following terms:

$$\phi = \frac{L_{\text{min}}}{V_{\text{min}} K_{\text{ref}}} \qquad (6.38a)$$

and

$$\overline{\phi} = \frac{\overline{L}_{\text{min}}}{\overline{V}_{\text{min}} \overline{K}_{\text{ref}}} \qquad (6.38b)$$

Combining Eqs. 6.38 (a & b) with Eqs. 6.36 and 6.37 results in

$$V_{\text{min}} = \sum \frac{\alpha_i D x_{i,\text{ dist}}}{\left(\alpha_i - \phi\right)} \qquad (6.39)$$

and

$$-\overline{V}_{\min} = \sum \frac{\overline{\alpha}_i B x_{i,\,\text{bot}}}{\left(\overline{\alpha}_i - \overline{\phi}\right)} \qquad (6.40)$$

(6.39) + (6.40) gives

$$V_{\min} - \overline{V}_{\min} = \sum \left[\frac{\alpha_i D x_{i,\,\text{dist}}}{\left(\alpha_i - \phi\right)} + \frac{\overline{\alpha}_i B x_{i,\,\text{bot}}}{\left(\overline{\alpha}_i - \overline{\phi}\right)}\right]$$

$$(6.41)$$

When the *CMO* and the *constant relative volatilities* (*i.e.* $\alpha_i = \overline{\alpha}_i$) can be *assumed*, there are *common* values of ϕ and $\overline{\phi}$ (*i.e.* $\phi = \overline{\phi}$) that satisfy both Eqs. 6.39 and 6.40, thus making Eq. 6.41 become

$$V_{\min} - \overline{V}_{\min} = \sum \left[\frac{\alpha_i D x_{i,\,\text{dist}}}{\left(\alpha_i - \phi\right)} + \frac{\alpha_i B x_{i,\,\text{bot}}}{\left(\alpha_i - \phi\right)}\right]$$

$$(6.42)$$

or

$$V_{\text{min}} - \bar{V}_{\text{min}} = \sum \left[\frac{\alpha_i \left(Dx_{i,\text{ dist}} + Bx_{i,\text{ bot}} \right)}{\left(\alpha_i - \phi \right)} \right]$$

(6.43)

By performing an *overall* or *external* material balance around the whole column, we obtain the following equation:

$$Fz_i = Dx_{i,\text{ dist}} + Bx_{i,\text{ bot}}$$ (6.44)

Combining Eq. 6.44 with Eq. 6.43 yields

$$V_{\text{min}} - \bar{V}_{\text{min}} = V_{F,\text{ min}} = \Delta V_{\text{feed}} = \sum \frac{\alpha_i F z_i}{\left(\alpha_i - \phi \right)}$$

(6.45)

Note that ΔV_{feed} or $V_{F,\text{ min}}$ is the *change* in the *vapour* flow rate at the *feed stage*

If the value of q, which is defined as

$$\frac{\Delta V_{\text{feed}}}{F} = \frac{V_F}{F} = f = 1 - q$$

is known, ΔV_{feed} or V_F can be calculated from the following equation:

$$\Delta V_{\text{feed}} = \left(1 - q\right) F \qquad (6.46)$$

Eq. 6.45 is the *first* Underwood equation, used to estimate the value of ϕ

Eq. 6.39:

$$V_{\text{min}} = \sum \frac{\alpha_i D x_{i,\,\text{dist}}}{\left(\alpha_i - \phi\right)} \qquad (6.39)$$

is the *second* Underwood equation, used to compute the value of V_{min}

Once V_{min} is known, the value of L_{min} can then be calculated from the material balance equation at the condenser as follows

$$L_{\text{min}} = V_{\text{min}} - D \qquad (6.47)$$

Note that D can be obtained from the following equation:

$$D = \sum \left(D x_{i,\text{ dist}} \right) \qquad (6.48)$$

Note also that, if there are C species (components), there will be C values (roots) of ϕ

The use of **_Underwood_ equations** can be divided into **3 cases** as follows

Case A : Assume that all non-keys (NKs) do not distribute; *i.e.* for the *distillate,*

$$Dx_{\text{HNK, dist}} = 0$$

and

$$Dx_{\text{LNK, dist}} = Fz_{\text{LNK}}$$

while the amounts of key components (both HK and LK) are

$$Dx_{\text{LK, dist}} = \left(FR_{\text{LK}}\right)_{\text{dist}} Fz_{\text{LK}} \qquad (6.49)$$

and

$$Dx_{\text{HK, dist}} = \left(1 - FR_{\text{HK}}\right)_{\text{bot}} Fz_{\text{HK}}$$

$$(6.50)$$

In this case (Case A), Eq. 6.45:

$$\Delta V_{\text{feed}} = \sum \frac{\alpha_i Fz_i}{\left(\alpha_i - \phi\right)} \qquad (6.45)$$

can, thus, be solved for the value of ϕ, which is between the relative volatilities of LK and HK, or $\alpha_{\text{HK}} < \phi < \alpha_{\text{LK}}$

Case B : Assume that the *distributions* of *NKs* obtained from the Fenske equation for the case of *total reflux* are *still valid* or *applicable* for the case of *minimum reflux*

In this case (Case B), the value of ϕ is still between the relative volatilities of LK and HK, or $\alpha_{\mathrm{HK}} < \phi < \alpha_{\mathrm{LK}}$

Case C : In this case, the **exact** solutions (*i.e.* without having to make any assumptions as *per* Cases *A* and *B*) are obtained

As mentioned earlier, if there are C species, there will be C values for ϕ

Thus, we can have $C - 1$ degree of freedoms, which yields $C - 1$ equations for Eq. 6.39:

$$V_{\min} = \sum \frac{\alpha_i Dx_{i, \text{ dist}}}{\left(\alpha_i - \phi\right)} \qquad (6.39)$$

and there are $C - 1$ unknowns (*i.e.* $V_{\min}$ and $Dx_{i, \text{ dist}}$ for all LNK and HNK)

With $C - 1$ unknowns and $C - 1$ equations, the value of ϕ_i for each species can be solved as follows

$$\alpha_{\text{HNK, 1}} < \phi_1 < \alpha_{\text{HNK, 2}} < \phi_2 < \alpha_{\text{HK}} < ... < \alpha_{\text{LK}} < \phi_{\text{C-1}} < \alpha_{\text{LNK, 1}}$$

The following Example is the illustration of the application of the Underwood equations

Example For the same distillation problem on Page 13, determine the *minimum* reflux ratio, based on the feed rate of 100 kmol/h

Since it is given that the feed is a *saturated vapour*, $q = 0$, which results in

$$\Delta V_{\text{feed}} = \left(1 - q\right) F$$
$$= \left(1 - 0\right)\left(100\right)$$
$$\Delta V_{\text{feed}} = 100$$

Hence, Eq. 6.45 becomes

$$\Delta V_{\text{feed}} = \sum \frac{\alpha_i F z_i}{\left(\alpha_i - \phi\right)}$$

$$\Delta V_{\text{feed}} = \frac{\alpha_{\text{benz}} F z_{\text{benz}}}{\left(\alpha_{\text{benz}} - \phi\right)} + \frac{\alpha_{\text{tol}} F z_{\text{tol}}}{\left(\alpha_{\text{tol}} - \phi\right)} + \frac{\alpha_{\text{cume}} F z_{\text{cume}}}{\left(\alpha_{\text{cume}} - \phi\right)}$$

$$(6.51)$$

Substituting corresponding numerical values into Eq. 6.51 gives

$$100 = \frac{2.25(100)(0.40)}{(2.25 - \phi)} + \frac{1.0(100)(0.30)}{(1.0 - \phi)} + \frac{0.21(100)(0.30)}{(0.21 - \phi)} \qquad (6.52)$$

Since the LK = toluene $(\alpha = 1.0)$ and the HK = cumeme $(\alpha = 0.21)$, the value of ϕ is between 0.21 and 1.0

Solving Eq. 6.52 yields

$$\phi = 0.5454$$

The next step is to determine the value of $V_{\min}$ using Eq. 6.39:

$$V_{\min} = \sum \frac{\alpha_i D x_{i,\ \text{dist}}}{(\alpha_i - \phi)}$$

Since all species (including the LNK or benzene) are distributed in both distillate and bottom products, the value of $Dx_{i, \text{dist}}$ of each species can be computed from the following equation:

$$Dx_{i, \text{dist}} = z_i F(FR)_{i, \text{dist}} \qquad (6.53)$$

It given, in the problem statement, (see Page 13) that

- the fraction recovery of toluene in the distillate $(FR)_{\text{tol, dist}}$ is 95% or 0.95
- the fraction recovery of cumeme in the bottom $(FR)_{\text{cume, bot}}$ is 95% or 0.95; thus, $(FR)_{\text{cume, dist}} = 1 - 0.95 = 0.05$

From the previous calculations (see Page 21), the fractional recovery of benzene (the LNK in this Example) or $(FR)_{\text{benz, dist}}$ is found be 0.998

Substituting corresponding numerical values into Eq. 6.53 yields

- $Dx_{\text{benz, dist}} = \left(0.40\right)\left(100\right)\left(0.998\right) = 39.9$
- $Dx_{\text{tol, dist}} = \left(0.30\right)\left(100\right)\left(0.95\right) = 28.5$
- $Dx_{\text{cume, dist}} = \left(0.30\right)\left(100\right)\left(0.05\right) = 1.5$

Thus, the value of V_{min} can be computed as follows

$$V_{\text{min}} = \sum \frac{\alpha_i Dx_{i,\text{ dist}}}{\left(\alpha_i - \phi\right)}$$

$$V_{\text{min}} = \frac{\alpha_{\text{benz}} Dx_{\text{benz, dist}}}{\left(\alpha_{\text{benz}} - \phi\right)} + \frac{\alpha_{\text{tol}} Dx_{\text{tol, dist}}}{\left(\alpha_{\text{tol}} - \phi\right)} + \frac{\alpha_{\text{cume}} Dx_{\text{cume, dist}}}{\left(\alpha_{\text{cume}} - \phi\right)}$$

$$V_{\text{min}} = \frac{(2.25)(39.9)}{(2.25 - 0.5454)} + \frac{(1.0)(28.5)}{(1.0 - 0.5454)}$$
$$+ \frac{(0.21)(1.5)}{(0.21 - 0.5454)}$$

$$V_{\text{min}} = 114.4$$

We have learned that

$$\sum \left(Dx_{i,\text{ dist}} \right) = D \qquad (5.25)$$

Thus, for this Example,

$$D = Dx_{\text{benz, dist}} + Dx_{\text{tol, dist}} + Dx_{\text{cume, dist}}$$
$$= 39.9 + 28.5 + 1.5$$
$$D = 69.9$$

Accordingly, by using Eq. 6.47, the value of L_{min} can be calculated as follows

$$L_{\min} = V_{\min} - D = 114.4 - 69.9 = 44.5$$

Therefore, the minimum reflux ratio $\left(\dfrac{L}{D}\right)_{\min}$ is

$$\frac{44.5}{69.9} = 0.64$$

6.3 Gilliland Correlation for Number of Stages at Finite Reflux Ratio

We have already studied how to *estimate* the *numerical* solutions for 2 *extreme* cases for *multi-component* distillation; *i.e.* the *total reflux* case (proposed by Fenske) and the case of *minimum reflux* (proposed by Underwood)

In order to determine the *number of stages* for *multi-component* distillation at *finite* reflux ratio, there should be a *correlation* that *utilises* the results from both extreme cases (*i.e.* the cases of *total reflux* and *minimum reflux*)

E.R. Gilliland established a technique that *empirically* correlates the number of stages, N, at *finite* reflux ratio $\left(\dfrac{L}{D}\right)$ to the *minimum* number of stages, $N_{\min}$ (at the *total reflux*) and the *minimum* reflux ratio $\left(\dfrac{L}{D}\right)_{\min}$ [which yields the infinite $\left(\infty\right)$ number of stages]

The work was published in *Industrial and Engineering Chemistry*, Vol. 32, under the topic of "*Multicomponent rectification: Estimation of the number of theoretical plates as a function of the reflux ratio*" in 1940

In order to develop the correlation, Gilliland performed a series of accurate *stage-by-stage* calculations and found that there was a correlation between the function $\dfrac{\left(N - N_{\min}\right)}{\left(N + 1\right)}$ and the function $\dfrac{\left[\left(\dfrac{L}{D}\right) - \left(\dfrac{L}{D}\right)_{\min}\right]}{\left[\left(\dfrac{L}{D}\right) + 1\right]}$

The correlation firstly developed by Gilliland was later modified by C.J. Liddle [published in *Chemical Engineering*, Vol. 75(23), under the topic of *"Improved shortcut method for distillation calculations"* in 1968] and could be presented in the form of *chart* as shown in Figure 6.5
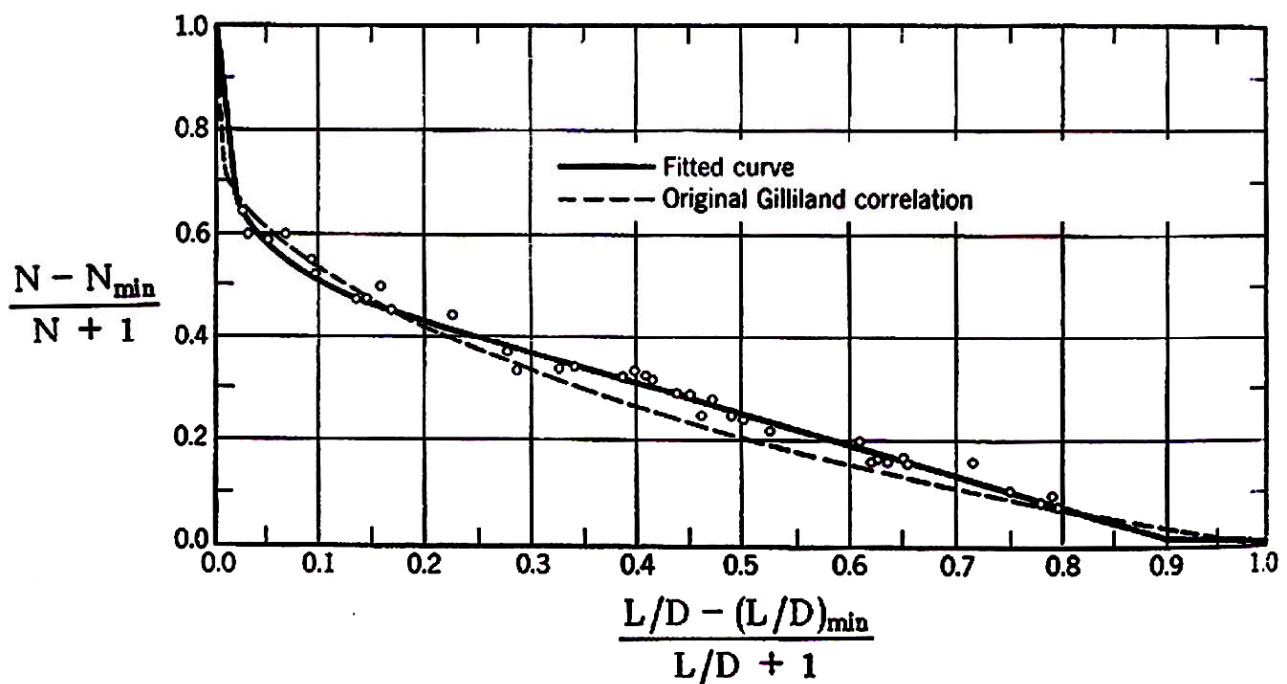

$$\frac{N - N_{min}}{N + 1}$$

Fitted curve

Original Gilliland correlation

$$\frac{L/D - (L/D)_{min}}{L/D + 1}$$

Figure 6.5: The Gilliland correlation (1940) chart, which was modified by Liddle in 1968

(from "Separation Process Engineering" by Wankat, 2007)

The procedure of using the Gilliland's correlation/chart is as follows

1) Calculate N_{min} using the Fenske equation

2) Calculate $\left(\dfrac{L}{D}\right)_{min}$ using the Underwood's equations

3) Choose actual or operating $\dfrac{L}{D}$, which is normally within the range of 1.05 to 1.25 times that of $\left(\dfrac{L}{D}\right)_{min}$ (note the *number* between *1.05* to *1.25* that uses to multiply $\left(\dfrac{L}{D}\right)_{min}$ is called a *multiplier, M*)

4) Calculate the *abscissa* or the value of

$$\frac{\left[\left(\dfrac{L}{D}\right) - \left(\dfrac{L}{D}\right)_{\text{min}}\right]}{\left[\left(\dfrac{L}{D}\right) + 1\right]} \quad \text{(on the } X\text{-}axis)$$

5) Determine the *ordinate* or the value of

$$\frac{\left(N - N_{\text{min}}\right)}{\left(N + 1\right)} \quad \text{(on the } Y\text{-}axis) \text{ using the}$$

correlating line

6) Calculate the actual number of stages,

N from the function $\dfrac{\left(N - N_{\text{min}}\right)}{\left(N + 1\right)}$

It is important to note that the Gilliland's correlation should be used only for ***rough esti-mates*** – **NOT** for the ***exact solutions***

The *optimal* feed stage/plate can also be estimated using the following procedure

First, the *Fenske* equation is used to determine the *minimum number* of *stages*, N_{min}

Then, the *optimal* feed stage can be obtained by *determining the minimum number of stages* required to go *from* the *feed* concentrations to the *distillate* concentrations for the *key* components, $N_{F,\,min}$, using the following equation:

$$N_{F,\,min} = \frac{\ln\left[\dfrac{\left(\dfrac{x_{LK}}{x_{HK}}\right)_{dist}}{\left(\dfrac{z_{LK}}{z_{HK}}\right)}\right]}{\ln \alpha_{LK\text{-}HK}} \qquad (6.54)$$

Next, by assuming that the *relative feed stage* is *constant* as we change from *total reflux* to a *finite* value of *reflux ratio*, we obtain the following equation:

$$\frac{N_{F,\,\text{min}}}{N_{\text{min}}} = \frac{N_F}{N} \qquad (6.55)$$

which is employed to calculate the *optimal* feed location, N_F

Alternatively, a probably *more accurate* equation (proposed by C.G. Kirkbride – in **Separation Process Technology** by J.L. Humphrey and G.E. Keller II, 1997) is used to estimate the optimal feed stage $\left(N_f\right)$ as follows

$$\log\left(\frac{N_f - 1}{N - N_f}\right) = 0.260 \log\left\{\frac{B}{D}\left(\frac{z_{\text{HK}}}{z_{\text{LK}}}\right)\left(\frac{x_{\text{LK, bot}}}{x_{\text{HK, dist}}}\right)^2\right\}$$

$$(6.56)$$

Note, once again, that both **Eqs. 6.55 & 6.56** should be *used only* for a *first guess* for specifying the *optimal* feed location

In addition to the chart (Figure 6.5 on Page 47), the Gilliland's correlation can also be presented in the form of equation as follows (note

that $x = \dfrac{\left[\left(\dfrac{L}{D}\right) - \left(\dfrac{L}{D}\right)_{\text{min}}\right]}{\left[\left(\dfrac{L}{D}\right) + 1\right]})$

For $0 \leq x \leq 0.01$:

$$\frac{\left(N - N_{\min}\right)}{\left(N + 1\right)} = 1.0 - 18.5715x$$

$$(6.57)$$

For $0.01 < x < 0.90$:

$$\frac{\left(N - N_{\min}\right)}{\left(N + 1\right)} = 0.545827 - 0.591422x + \frac{0.002743}{x}$$

$$(6.58)$$

For $0.90 < x < 1.0$:

$$\frac{\left(N - N_{\min}\right)}{\left(N + 1\right)} = 0.16595 - 0.16595x$$

$$(6.59)$$

The use of the *Gilliland's correlation* to estimate the *total number* of *stages* and the *optimal feed stage* is illustrated in the following Example

Example Estimate the total number of equilibrium stages $\left(N\right)$ and the optimal feed stage $\left(N_F\right)$ for the same Example on Pages 13 & 39 if the *actual* reflux ratio $\left(\dfrac{L}{D}\right)$ is set at 2.0

To obtain the solutions for this Example, we follow the following procedure:

1) Calculate the value of $N_{\min}$

From the Example on Page 13, we obtain

$$N_{\min} = 3.8$$

2) Calculate the value of $\left(\dfrac{L}{D}\right)_{\min}$

From the Example on Page 39, we obtain

$$\left(\frac{L}{D}\right)_{\text{min}} = 0.64$$

3) Choose the value of the actual $\dfrac{L}{D}$

It is given that the actual or operating $\dfrac{L}{D}$ is set as 2.0

4) Calculate the *abscissa* (the *X-axis* of the Gilliland's chart)

The *abscissa* can be computed using the values of $\left(\dfrac{L}{D}\right)_{\text{min}}$ and the actual $\dfrac{L}{D}$ as follows

$$\frac{\left[\left(\dfrac{L}{D}\right) - \left(\dfrac{L}{D}\right)_{\text{min}}\right]}{\left[\left(\dfrac{L}{D}\right) + 1\right]} = \frac{[2.0 - 0.64]}{[2.0 + 1]} = 0.453$$

5) Determine the value of ordinate (the *Y-axis* of the Gilliland's chart)

The *ordinate* can be *read* from the chart when the *abscissa* is *known*

With the abscissa, $\dfrac{\left[\left(\dfrac{L}{D}\right) - \left(\dfrac{L}{D}\right)_{\min}\right]}{\left[\left(\dfrac{L}{D}\right) + 1\right]}$ of 0.453,

the ordinate is found to be

$$\frac{\left(N - N_{\min}\right)}{\left(N + 1\right)} \approx 0.27$$

Alternatively, we can use Eq. 6.58 to compute the value of the ordinate, $\dfrac{\left(N - N_{\min}\right)}{\left(N + 1\right)}$, as follows

$$\frac{\left(N - N_{\text{min}}\right)}{\left(N + 1\right)} = 0.545827 - 0.591422\left(0.453\right) + \frac{0.002743}{0.453}$$

$$\frac{\left(N - N_{\text{min}}\right)}{\left(N + 1\right)} = 0.284$$

Note that Eq. 6.58 is used because the value of the abscissa is between 0.01-0.90 (*i.e.*

$$x = \frac{\left[\left(\dfrac{L}{D}\right) - \left(\dfrac{L}{D}\right)_{\text{min}}\right]}{\left[\left(\dfrac{L}{D}\right) + 1\right]} = 0.453)$$

6) Calculate the value of N

The *number* of *equilibrium stages*, N, can be computed using the values of the ordinate and N_{min} as follows

$$\frac{\left(N - N_{\min}\right)}{\left(N + 1\right)} = 0.27$$

$$\frac{\left(N - 3.8\right)}{\left(N + 1\right)} = 0.27$$

$$N - 3.8 = 0.27\left(N + 1\right)$$

$$N - 3.8 = 0.27N + 0.27$$

$$0.73N = 4.07$$

$$N = 5.58$$

The *optimal* feed location (stage), N_F, can then be obtained using Eqs. 6.54 and 6.55 as follows

It is given that (see Page 13)

- $z_{\mathrm{LK}} = z_{\mathrm{tol}} = 0.30$
- $z_{\mathrm{HK}} = z_{\mathrm{cume}} = 0.30$

From the Example on Pages 39-44, we obtained the following:

- $Dx_{\text{tol, dist}} = 28.5$
- $Dx_{\text{cume, dist}} = 1.5$
- $D = \sum \left(Dx_{i, \text{ dist}} \right) = 69.9$

Thus, the values of $x_{\text{tol, dist}}$ and $x_{\text{cume, dist}}$ can be computed as follows

- $x_{\text{tol, dist}} = \dfrac{Dx_{\text{tol, dist}}}{D} = \dfrac{28.5}{69.9} = 0.408$

- $x_{\text{cume, dist}} = \dfrac{Dx_{\text{cume, dist}}}{D} = \dfrac{1.5}{69.9} = 0.021$

Substituting corresponding numerical values into Eq. 6.54 results in

$$N_{F,\ min} = \frac{\ln\left[\dfrac{\left(\dfrac{0.408}{0.021}\right)}{\left(\dfrac{0.30}{0.30}\right)}\right]}{\ln\left(\dfrac{1}{0.21}\right)} = 1.90$$

Hence, the *optimal* feed stage for the case of *finite reflux ratio* ($\dfrac{L}{D} = 2.0$ in this Example) can be calculated using Eq. 6.55 as follows

$$\frac{N_{F,\ min}}{N_{min}} = \frac{N_F}{N}$$

$$N_F = \left(\frac{N_{F,\ min}}{N_{min}}\right)N = \left(\frac{1.90}{3.8}\right)5.58$$
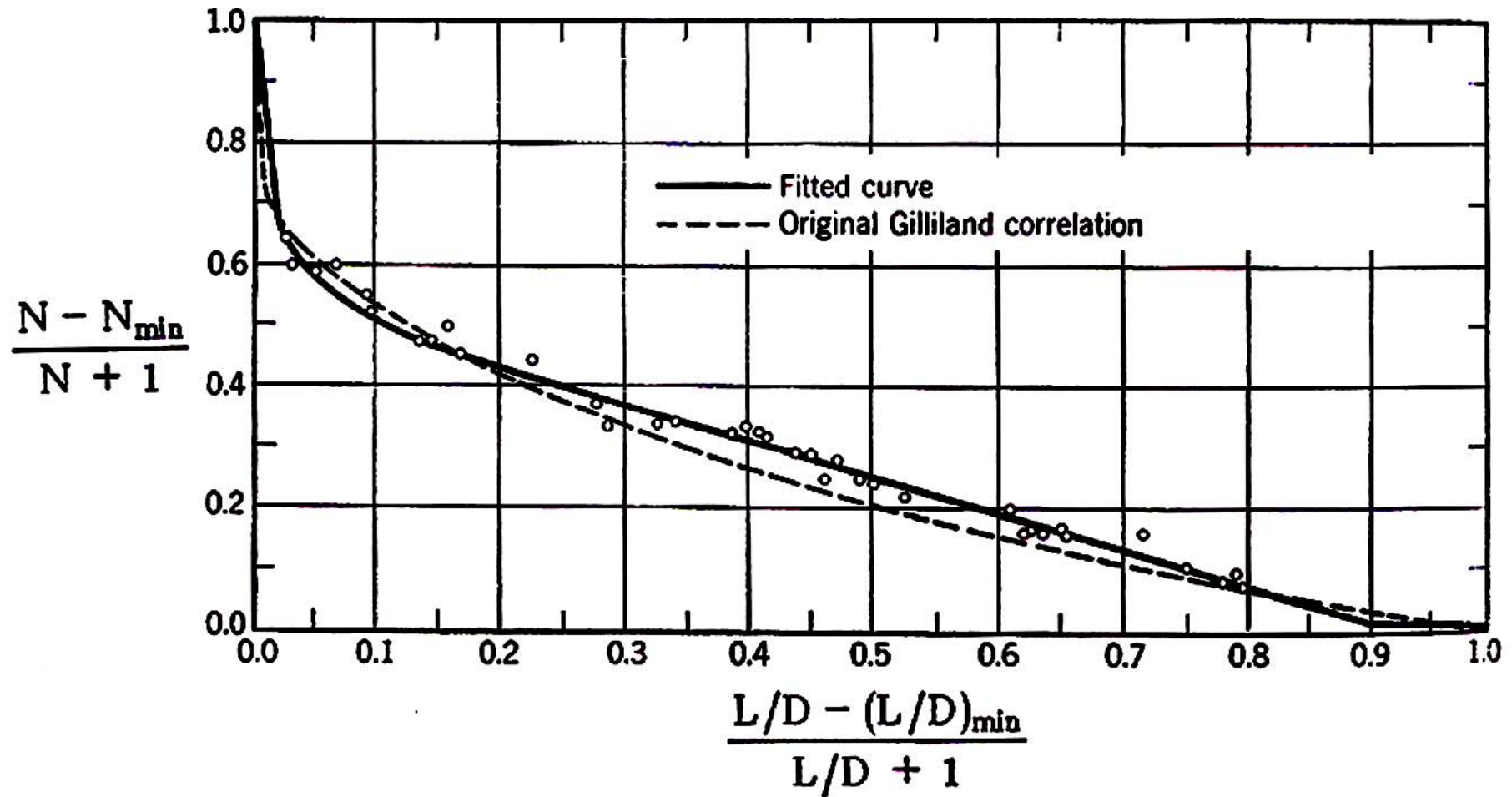
$$N_F = 2.79 \approx 3$$

Figure 6.5: Gilliland's correlation chart (modified by Liddle in 1968)

(from "Separation Process Engineering" by Wankat, 2007)