CHAPTER V
DISTILLATION OPTIMIZATION

5.1 Introduction

One of the most important tasks in the chemical industry is the separation of multi-component liquid mixtures into one or more high-purity products. Several technologies are feasible for this task, either alone or in combination, such as distillation, extraction, crystallization, and so on. Among these, distillation is by far the most widespread and has a long history in chemical technology.

Distillation separates, or fractionates, chemically different species by exploiting the fact that the compositions of coexisting vapor and liquid phases are generally different. The liquid and vapor mixtures that coexist in distillation are at or very near the boiling temperature. In many mixtures, the coexisting vapor and liquid phases rapidly approach equilibrium, and thermodynamics provides a framework for describing the composition differences.

Contact between the vapor and liquid phases can be achieved in many ways. One of the most common is the interconnection of successive stages in an arrangement like the one shown schematically in Figure 5.1 for distillation. Vapor is generated in the reboiler and press up through the stages of the column. The bottoms stream, enriched in one or more of the components, is removed from the reboiler. A condenser at the top of the column is used to provide the liquid that flows down through the stages. A second product stream called distillate is removed at the top of the column.

The first designs of a distillation system are usually developed assuming that vapor-liquid equilibrium (VLE) is achieved on the stages in the column. So, before we implement the case of distillation, we will review the VLE models and the concept of distillation column.
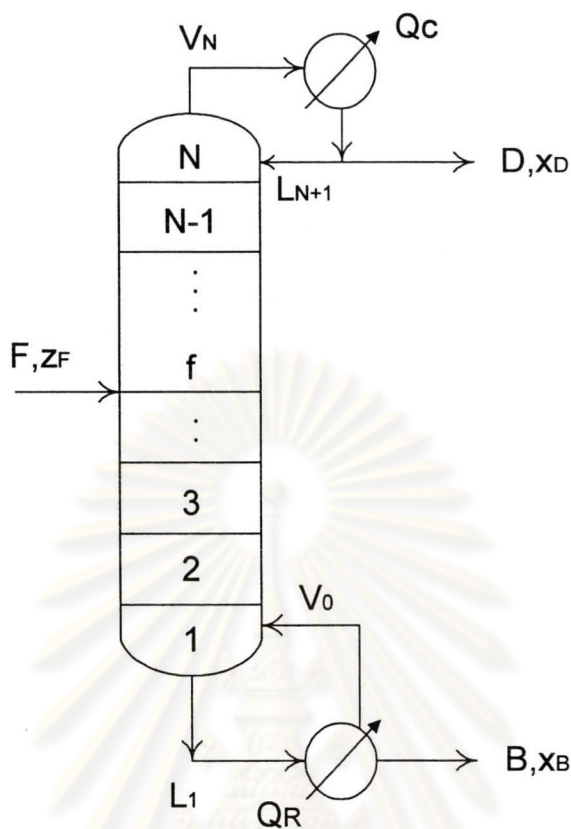
Figure 5.1 A distillation column

5.2 Fundamentals

Many separation devices including distillation column exploit the fact that the equilibrium compositions of chemical species across coexisting phases are not equal. Before beginning the model development for distillation column, we review the essential parts of phase equilibrium thermodynamics, since this plays a central role in the models.

5.2.1 The Equilibrium-Stage Concept

The equilibrium (theoretical)-stage concept (Figure 5.2) is central in distillation. Here we assume vapor-liquid equilibrium (VLE) on each stage and that the liquid is sent to the stage below and the vapor to the stage above. For some trayed columns this may be a reasonable description of the actual physics, but it is certainly

not for a packed column. Nevertheless, it is established that calculations based on the equilibrium-stage concept (with the number of stages adjusted appropriately) fits data from most real columns very well, even packed columns.

One many refine the equilibrium stage concept, e.g. by introducing back-mixing or a Murphee efficiency factor for the equilibrium, but these 'fixes' often have relatively little theoretical justification, and are not used in this work.

For practical calculations, the critical step is usually not the modeling of the stages, but to obtain a good description of the VLE. In this area there has been significant advances in the last 25 years, especially after the introduction of equations of state for VLE prediction. However, here we will use simpler VLE models (constant relative volatility) which apply to relatively ideal mixtures.
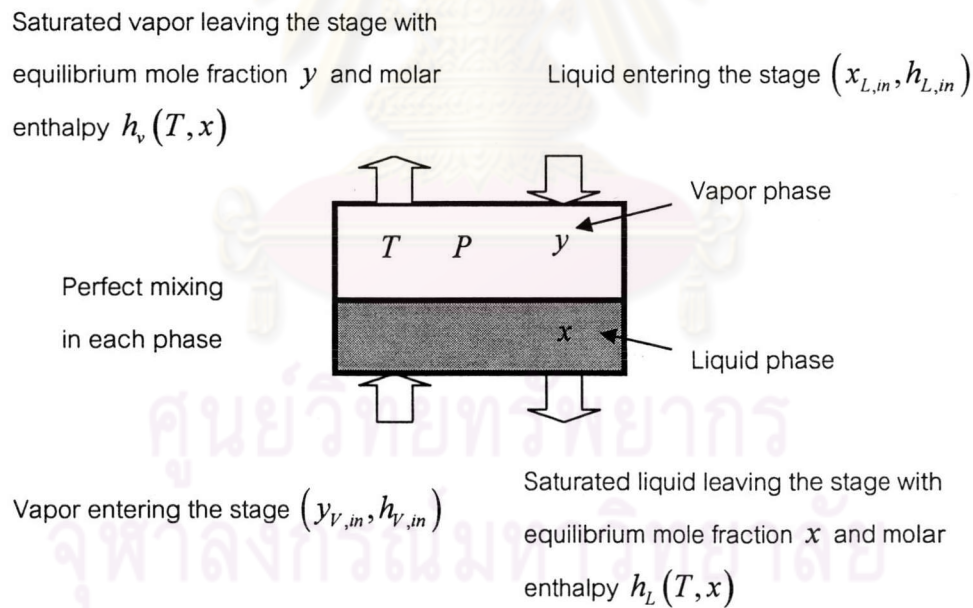
Saturated vapor leaving the stage with equilibrium mole fraction y and molar enthalpy $h_v(T,x)$

Liquid entering the stage $\left(x_{L,in}, h_{L,in}\right)$

Vapor phase

$T \quad P \quad y$

Perfect mixing in each phase

x

Liquid phase

Vapor entering the stage $\left(y_{V,in}, h_{V,in}\right)$

Saturated liquid leaving the stage with equilibrium mole fraction x and molar enthalpy $h_L(T,x)$

Figure 5.2 Equilibrium-stage concept

5.2.2 Vapor-liquid Equilibrium

In a two-phase system $(PH = 2)$ with N_C nonreacting components, the state is completely determined by N_C degrees of freedom (f), according to Gibb's phase rule:

$$f = N_C - PH + 2 \tag{5.1}$$

If the pressure (P) and $N_C - 1$ liquid compositions or mole fractions (x) are used as degree of freedom, then the mole fractions (y) in the vapor phase and the temperature (T) are determined, provided that two phases are present. The general VLE relation can then be written:

$$[y_1, y_2, ... y_{Nc-1}, T] = f(P, x_1, x_2, ..., x_{Nc-1})$$

$$[y, T] = f(P, x) \tag{5.2}$$

Here we have introduced the mole fractions x and y in the liquid and vapor phases respectively, and we trivially have $\sum_{i=1}^{n} x_i = 1$ and $\sum_{i=1}^{n} y_i = 1$.

In ideal mixtures, the VLE can be derived from Raoult's law which states that the partial pressure p_i of a component (i) in the vapor phase is proportional to the vapor pressure (p_i^o) of the pure component (which is a function of temperature only: $p_i^o = p_i^o(T)$) and the liquid mole fraction (x_i):

$$p_i = x_i P_i^o(T) \tag{5.3}$$

For an ideal gas, according to Dalton's law, the partial pressure of a component is proportional to the mole fraction $p_i = y_i P$ and since the total pressure $P = p_1 + p_2 + ... + p_{Nc} = \sum_i P_i = \sum_i x_i P_i^o(T)$ we derive:

$$y_i = x_i \frac{P_i^o}{P} = \frac{x_i p_i^o(T)}{\sum_i x_i p_i^o(T)} \tag{5.4}$$

The following empirical formula is frequently used to compute the pure component vapor pressure:

$$\ln p^o(T) \approx a + \frac{b}{c+T} + d \ln(T) + e T^f \tag{5.5}$$

The coefficients are listed in component property databases. The case with $d = e = 0$ is called the Antonie equation.

5.2.3 K-values and Relative Volatility

The K-value for a component i is defined as: $K_i = y_i / k_i$. The K-value is sometimes called the equilibrium constant, but this is misleading as it depends strongly on temperature and pressure (or composition).

The relative volatility between component I and j is defined as:

$$\alpha_{ij} = \frac{y_i / x_i}{y_j / x_j} = \frac{K_i}{K_j} \tag{5.6}$$

For ideal mixtures that satisfy Raoult's law we have:

$$\alpha_{ij} = \frac{y_i / x_i}{y_j / x_j} = \frac{K_i}{K_j} = \frac{p_i^o(T)}{p_j^o(T)} \tag{5.7}$$

Here $p_i^o(T)$ depends on temperature so the K-values will actually be constant only close to the column ends where the temperature is relatively constant. On the other hand, the ratio $\dfrac{p_i^o(T)}{p_j^o(T)}$ is much less dependent on temperature, which makes the relative volatility vary attractive for computations. For ideal mixtures, a geometric average of the relative volatilities for the highest and lowest temperature in the column usually gives sufficient accuracy in the computations: $\alpha_{ij} = \sqrt{\alpha_{ij,top} \times \alpha_{ij,bottom}}$.

We usually select a common reference component r (usually the least volatile or heavy component), and define:

Table 5.1 Antoine coefficients for selected substances

Substance	A	B	C	Temperature Range, °C
Acetone	7.63132	1566.69	273.419	57 to 205
Water	8.01767	1715.70	234.268	100 to 265
Benzene	6.87987	1196.76	219.161	8 to 80
Toluene	6.95087	1342.31	219.187	-27 to 111
Ethylene glycol	8.09083	2088.936	203.454	50 to 150
Hexane	6.91058	1189.64	226.280	-30 to 170
p-Xylene	6.99053	1453.430	215.310	27 to 166
Ethanol	8.11220	1592.864	226.184	20 to 93
Acetic acid	8.02100	1936.010	258.451	18 to 118
Acetaldehyde	7.20812	1099.810	233.945	-83 to 20
Methanol	8.08097	1582.271	239.726	15 to 84
Methyl ethyl ketone	7.06356	1261.340	221.969	43 to 88
Chloroform	6.95465	1170.966	226.232	-10 to 60
Ethylenediamine	8.09831	1893.720	245.676	11 to 117
4-Methyl-2-pentanol	8.46706	2174.869	257.780	25 to 133
Dichloromethane	7.08030	1138.910	231.450	-44 to 59
1,3-Butadiene	6.85364	933.586	239.511	-75 to -2
Styrene	7.50233	1819.810	248.662	-7 to 145
Ethyl acetate	7.10179	1244.950	217.881	16 to 76
Vinylacetylene	7.02515	999.110	235.817	-93 to 5
Acetic anhydride	7.69301	1781.29	230.395	2 to 140
Dichlorosilane	7.18600	1224.50	273.16	-45 to 121
Trichlorosilane	6.95524	1102.900	238.865	-81 to 32
Silicon tetrachloride	7.02404	1212.890	235.910	-63 to 57
Hydrogen chloride	7.44899	868.358	274.904	-85 to 36

$$\alpha_i = \alpha_{ir} = \frac{p_i^o(T)}{p_r^o(T)} \qquad (5.8)$$

The VLE relationship (equation 5.4) becomes:

$$y_i = \frac{\alpha_i x_i}{\sum_i \alpha_i x_i} \qquad (5.9)$$

For the binary mixture we usually omit the component index for the light component, i.e. we write $x = x_1$ (light component) and $x_2 = 1 - x$ (heavy component). Then the VLE relationship becomes:

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \qquad (5.10)$$

This equilibrium curve is illustrated in Figure 5.3.

The difference $y - x$ determines the amount of separation that can be achieved on a stage. Large relative volatilities imply large differences in boiling points and easy separation. Close boiling points imply relative volatility closer to unity, as shown below quantitatively.

5.2.4 Estimating the Relative Volatility from Boiling Point Data

The Clapeyron equation relates the vapor pressure temperature dependency to the specific heat of vaporization (ΔH^{vap}) and the volume change between liquid and vapor phase (ΔV^{vap}):

$$\frac{dp^o(T)}{dT} = \frac{\Delta H^{vap}(T)}{T \Delta V^{vap}(T)} \qquad (5.11)$$

If we assume an ideal gas phase, and that the gas volume is much larger than the liquid volume, then $\Delta V^{vap} \approx RT / P$, and integration of Clapeyron's equation from temperature T_{bi} (boiling point at pressure P_{ref}) to temperature T (at pressure p_i^o) gives, when ΔH_i^{vap} is assumed constant:

$$\ln p_i^o \approx \left(\frac{\Delta H_i^{vap}}{R} \left(\frac{1}{T_{bi}} \right) + \ln P_{ref} \right) + \frac{\left(-\frac{\Delta H_i^{vap}}{R} \right)}{T} \tag{5.12}$$

This gives us the Antonie coefficients:

$$a_i = \frac{\Delta H_i^{vap}}{R} \left(\frac{1}{T_{bi}} \right) + \ln P_{ref} \, ,$$

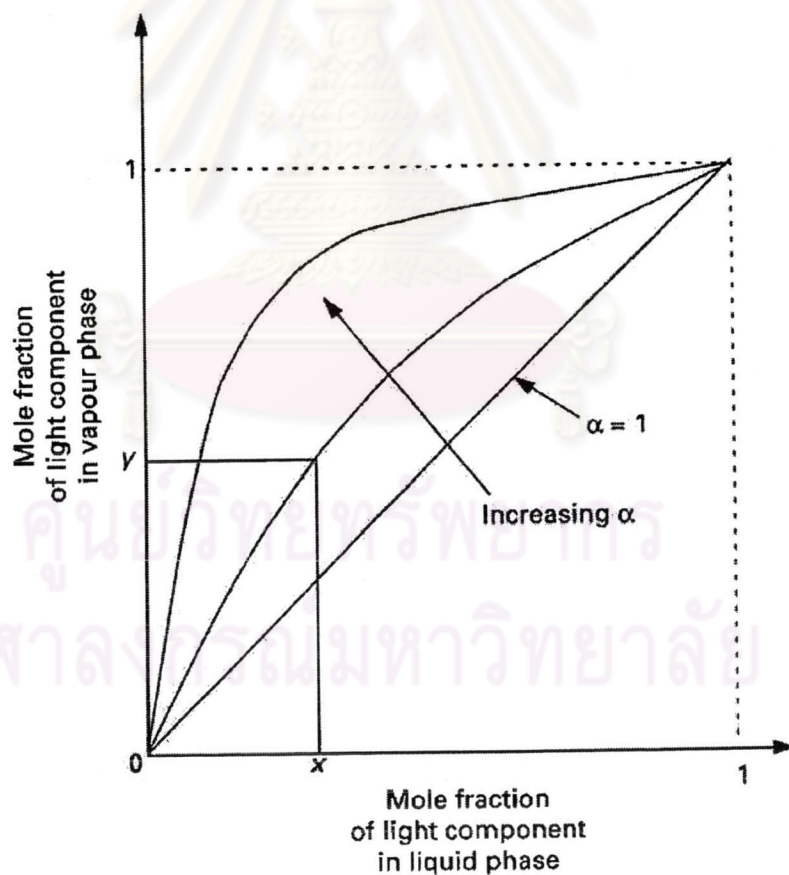$$b_i = -\frac{\Delta H_i^{vap}}{R} \, , \text{ and}$$

$$c_i = 0$$

Figure 5.3 VLE for ideal binary mixture: $y = \alpha x / 1 + (\alpha - 1) x$

In most cases P_{ref} equal to 1 atm. For an ideal mixture that satisfies Raoult's law we have $\alpha_{ij} = \dfrac{p_i^o(T)}{p_j^o(T)}$ and we derive:

$$\ln \alpha_{ij} = \frac{\Delta H_i^{vap}}{R}\frac{1}{T_{bi}} - \frac{\Delta H_i^{vap}}{R}\frac{1}{T_{bj}} + \frac{\Delta H_j^{vap} - \Delta H_i^{vap}}{RT} \tag{5.13}$$

We see that the temperature dependency of the relative volatility arises from different specific heats of vaporization. For the similar values $(\Delta H_i^{vap} \approx \Delta H_j^{vap})$, the expression simplifies to:

$$\ln \alpha_{ij} = \frac{\Delta H_i^{vap}}{R\overline{T}_b}\frac{T_{bj} - T_{bi}}{\overline{T}_b} \tag{5.14}$$

where: $\overline{T}_b = \sqrt{T_{bi}T_{bj}}$

Here we may use the geometric average also for the heat of vaporization:

$$\Delta \overline{H}^{vap} = \sqrt{\Delta H_i^{vap}(T_{bi}) \times \Delta H_j^{vap}(T_{bj})} \tag{5.15}$$

This results in a rough estimate of the relative volatility α_{ij}, based on the boiling points only:

$$\alpha_{ij} \approx e^{\beta(T_{bj} - T_{bi})/\overline{T}b} \tag{5.16}$$

where: $\beta = \dfrac{\Delta \overline{H}^{vap}}{R\overline{T}_b}$

If we do not know $\Delta \overline{H}^{vap}$, a typical value $\beta \approx 13$ can be used for many cases.

5.2.5 Nonideal Mixtures

For nonideal mixtures, pressure cannot calculate from Raoult's law as shown in equation 5.3. The correction factor called activity coefficient is added in the equation. So, the equilibrium relation becomes

$$Py_i = \gamma_i P_i^{sat} x_i \qquad (5.17)$$

Activity coefficients can be calculated from experimental data by methods described in Denbign (1971, Chapter 9), and Smith and VanNess (1996, Chapter 11). If P, T, y_i, x_i data are available together with an accurate saturated vapor pressure for each component, then one way to calculate activity coefficients is to rearrange equation (5.17) explicitly for γ_i. Many models are proposed in order to represent the experimental data. A widely used model is the Wilson equation, which has the following from for binary mixtures:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \qquad (5.18)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) + x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \qquad (5.19)$$

Where: $\Lambda_{12} = \dfrac{v_2^L}{v_1^L} \exp(-A_{12} / RT)$

$\Lambda_{21} = \dfrac{v_1^L}{v_2^L} \exp(-A_{21} / RT)$

γ = Activity coefficient

A = Wilson equation parameter

v^L = pure component liquid molar volume

R = Universal gas constant = 1.98721 (cal/kmol*K)

Table 5.2 Wilson equation parameters for selecting binary mixtures under isobaric conditions at 1 atm pressure

Mixture		A_{12}	A_{21}
Component 1	Component 2	(cal/gmol)	(cal/gmol)
Acetone	Water	489.3727	1422.849
Hexane	p-Xylene	-164.7038	390.7738
Benzene	Toluene	377.976	-354.9859
Ethanol	Ethylene glycol	-129.2043	1539.4142
Ethanol	Water	464.2336	926.2759
Water	Ethylene glycol	-297.2946	16553.5350
Methyl ethyl ketone	Water	892.6557	2013.7175
Acetone	Methyl ethyl ketone	-232.9286	476.8721
Benzene	Ethylenediamine	490.0693	560.0207
Acetaldehyde	Water	285.5863	1045.5669
Methanol	Water	19.2547	554.0494
Acetone	Chloroform	116.117	-506.8519
Chloroform	Ethanol	-268.7676	1270.3897
Benzene	4-Methyl-2-pentanol	214.3044	363.9183
Dichloromethane	Ethyl acetate	-174.5487	-212.1071
1,3-Butadiene	Styrene	1100.1231	-417.8319

Table 5.3 Pure component liquid molar volumes

Substance	v^L (cm^3/gmol)
Acetone	74.05
Water	18.07
Benzene	89.41
Toluene	106.85
Ethylene glycol	55.92
Ethylenediamine	67.84
Hexane	131.61
p-Xylene	123.93
Ethanol	58.68
Acetic acid	57.54
Acetaldehyde	56.62
Methanol	40.73
Methyl ethyl ketone	90.17
Chloroform	80.67
4-Methyl-2-pentanol	127.33
Dichloromrthane	64.5
Ethyl acetate	98.49
1,3-Butadiene	87.09
Styrene	115.57

5.2.6 Material Balance on a Distillation Stage

Based on the equilibrium-stage concept, a distillation column section is modeled as shown in Figure 5.4.

Note that we choose to number the stages starting from the bottom of the column. We denote L_n and V_n as the total liquid and vapor molar flow rates leaving stage n (and entering stages $n-1$ and $n+1$, respectively). We assume perfect mixing in both phases inside a stage. The mole fraction of species i in the vapor leaving the stage with V_n is $y_{i,n}$, and the mole fraction in L_n is $x_{i,n}$.

The material balance for component i at stage then becomes (in mol s^{-1}):

$$\frac{dN_{i,n}}{dt} = \left(L_{n+1}x_{i,n+1} - V_n y_{i,n}\right) - \left(L_n x_{i,n} - V_{n-1} y_{i,n-1}\right) \tag{5.20}$$

Where $N_{i,n}$ is the number of moles of component i on stage n. In the following we will consider steady-stage operation, i.e: $\dfrac{dN_{i,n}}{dt} = 0$.

It is convenient to define the net material flow (w_i) of component i upwards from stage n to $n+1$ (mol s^{-1}):

$$w_{i,n} = \left(V_n y_{i,n} - L_{n+1}x_{i,n+1}\right) \tag{5.21}$$

At steady state, this net flow has to be the same through all stages in a column section, i.e. $w_{i,n} = w_{i,n+1} = w_i$.

The material flow equation is usually rewritten to relate the vapor composition (y_n) on one stage to the liquid composition on the stage above (x_{n+1}):

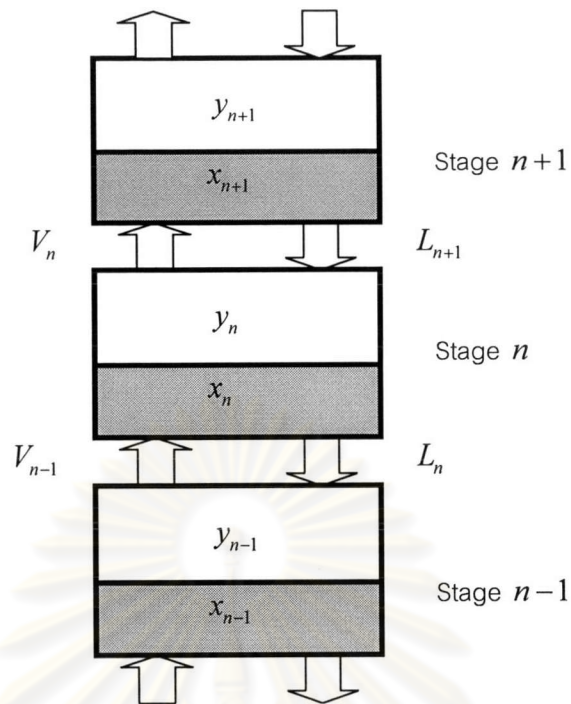$$y_{i,n} = \frac{L_{n+1}}{V_n} x_{i,n+1} + \frac{1}{V_n} w_i \tag{5.22}$$

Figure 5.4 Distillation column section modeled as a set of connected equilibrium stages.

The resulting curve is known as the operating line. Combined with the VLE relationship (equilibrium line), this enables us to compute all stage compositions when we known the flows in the system. This is illustrated in Figure 5.5, and forms the basis of McCabe-Thiele approach.

5.2.7 Assumption about Constant Molar Flows

In a column section, we may very often use the assumption about constant molar flows. That is, we assume $L_n = L_{n+1} = L$ (mol s^{-1}) and $V_{n-1} = V_n = V$ (mol s^{-1}). This assumption is reasonable for ideal mixtures when the components have similar molar heats of vaporization. An important implication is that the operating line is then a straight line for a given section, i.e. $y_{i,n} = \left(\dfrac{L}{V}\right) x_{i,n+1} + \dfrac{w_i}{V}$. This makes computations much simpler since the internal flows (L and V) do not depend on compositions.
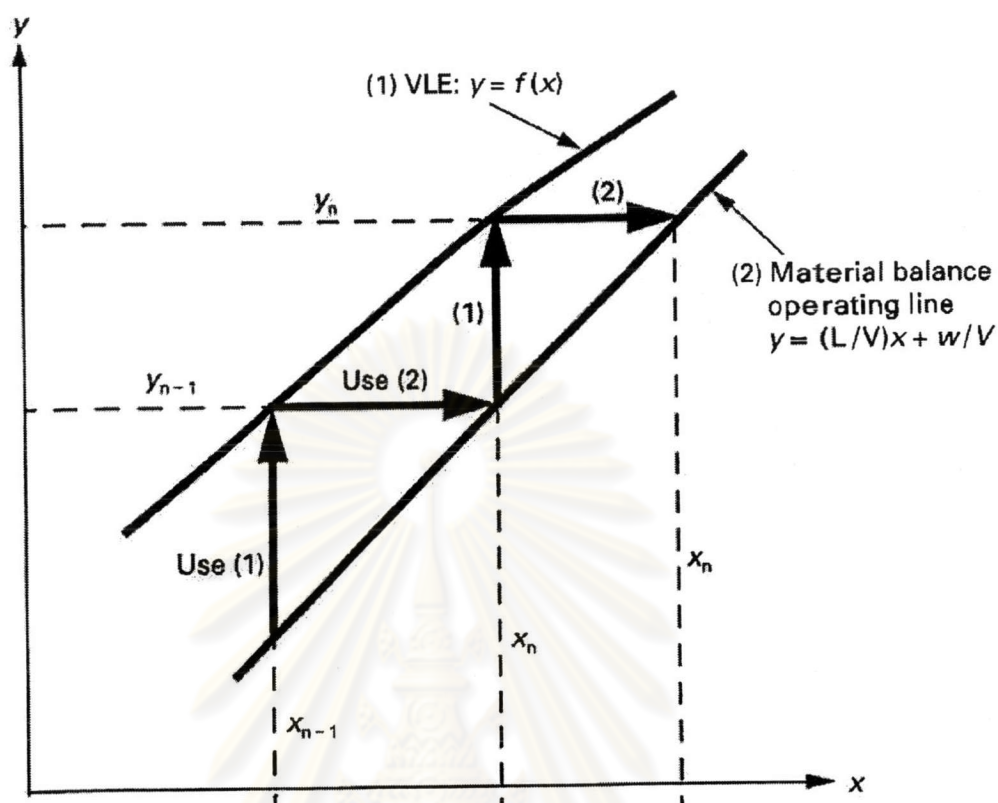
Figure 5.5 Combining the VLE and the operating line to compute mole fractions in a section of equilibrium stages

5.3 The Continuous Distillation Column

5.3.1 Material Balances

In binary mixtures, the composition of each phase can be completely described by one variable, which we choose to be the mole fraction of the component with the lower boiling point, the light component. The mole fractions are denoted as x in the liquid phase and y in the vapor. The mole fraction of the second component is just $1-x$ or $1-y$. When the conditions of a stream can be either vapor or liquid, we denote the mole fraction as z. There are two independent material balances for the column shown in Figure 5.1, an overall balance.

$$F = D + B \tag{5.23}$$

And a balance for the light component

$$F_{zF} = D_{zD} + B_{zB} \tag{5.24}$$

From these material balances it is simple to find expressions for the fraction of the total feed that appears in the distillate and bottoms as

$$\frac{D}{F} = \frac{z_F - z_B}{z_D - z_B} \tag{5.25}$$

$$\frac{B}{F} = \frac{z_D - z_F}{z_D - z_B} \tag{5.26}$$

These simple relationships show that the specification of the feed composition and flowrate along with the product purities is sufficient to determine the flowrate of each product stream. In fact, the ratio of the flowrates of the two products streams is completely determined by a lever rule

$$\frac{D}{B} = \frac{z_F - z_B}{z_D - z_F} \tag{5.27}$$

Although these results may seem intuitive, especially for binary mixtures, their consequences and importance in the analysis of the fractionation of mixtures containing more than two components should not be underestimated.

The use of fractional recoveries is an alternative to the compositions; the fraction of light component in the feed stream that is present in the distillate product is $f_l = \dfrac{D_{zD}}{F_{zF}}$. Similarly, the fractional recovery of the heavy component is $f_h = \dfrac{B(1 - z_B)}{F(1 - z_F)}$. The fractional recoveries can be related to the feed and product compositions by material balances. For example, $f_l = \dfrac{z_D(z_F - z_B)}{z_F(z_D - z_B)}$, and there is a similar expression for f_h. We will use compositions, fractional recoveries, or a combination of both as convenient.

The primary task in the design of a column is to related the size and energy requirements to the specifications on the feed and product streams. The related performance calculation seeks to determine the flowrates and compositions of the product streams for a given feed, from information about the size and operating conditions of the column. In either case, a description of the internal flows and compositions is required.

Figure 5.6 shows a schematic of the column and a numbering scheme for the stages. On each stage, we assume that the compositions in the liquid and vapor phases leaving the stage numbered n are constant, with values given by the mole fraction x_n and y_n, respectively; i.e., the liquid and vapor phases are perfectly mixed. The steady-state material balances for the total molar flows in the top of the column are (see envelope I in figure 5.6).

$$V_{n-1} = L_n + D \tag{5.28}$$

$$V_{n-1}y_{n-1} = L_n x_n + Dz_D \tag{5.29}$$

$$y_{n-1} = \frac{L_n}{V_{n-1}} x_n + \frac{D}{V_{n-1}} z_D \tag{5.30}$$

For $n = N+1, N, N-1, ..., f+1$ and f denotes the feed stage. In the bottom section, a similar balance on envelope II gives

$$L_{n+1} = V_n + B \tag{5.31}$$

$$L_{n+1}x_{n+1} = V_n y_n + Bz_B \tag{5.32}$$

$$y_n = \frac{L_{n+1}}{V_n} x_{n+1} - \frac{B}{V_n} z_B \tag{5.33}$$
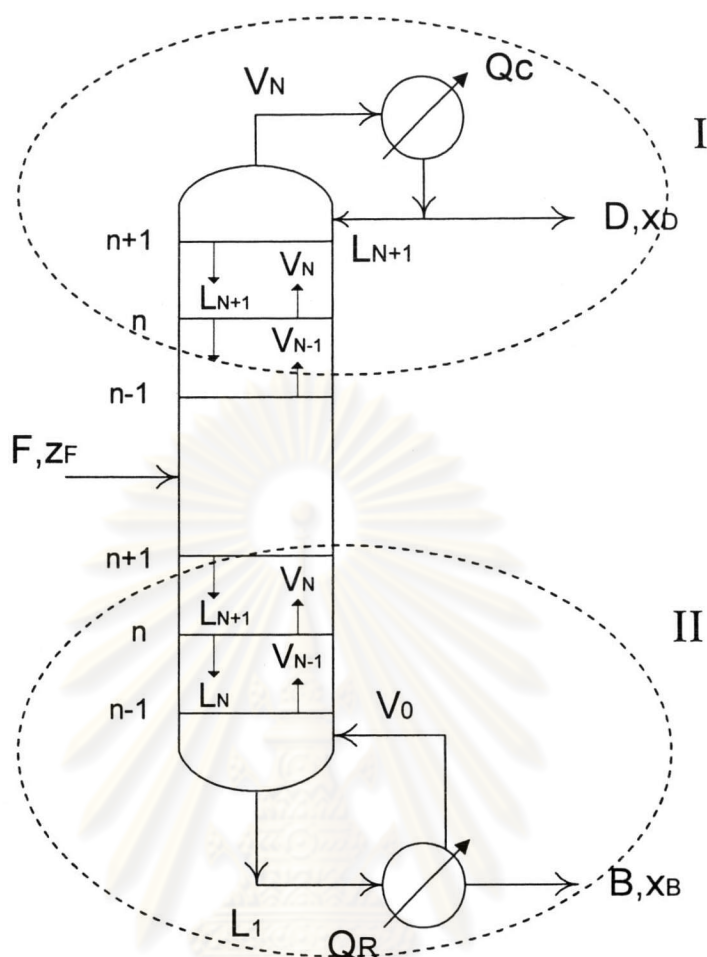
For $n = 0, 1, 2, ..., f-1$.

Figure 5.6 Stream labels and material balance envelopes for a simple column

The material balances for the condenser and reboiler are also needed. A partial condenser provides the equivalent of one additional stage, because the vapors are taken as a product, while a total condenser provides a saturated or subcooled liquid product as the distillate. It is common practice to operate a partial condenser when one of the components has a low boiling point or when the product is desired as a vapor. However, the total condenser is a more common arrangement because it is less expensive to transport liquids than vapors and because a saturated vapor may partially condense in piping runs over any significant distance. In either case, we number the condenser and its product stream as $N+1$. Figure 5.1 shows that part of the liquid condensate is returned to the column to provide liquid on the stages in the rectifying

section; this stream has a molar flowrate L_{N+1} and is referred to as the reflux. The external reflux ratio r is

$$r \equiv \frac{L_{N+1}}{D} \qquad (5.34)$$

This dimensionless number must be positive and the minimum value needed depends on the difficulty of the desired separation. Columns must be designed so that r is somewhat above the minimum. A material balance for a total condenser shows that the internal flows are related to the external reflux ratio by

$$\frac{L_{N+1}}{V_N} = \frac{r}{r+1} \qquad (5.35)$$

A specification of the external reflux ratio fixes the ratio of liquid to vapor flowrates on the top stage of the column. A partial condenser can be described with a similar approach.

The rebolier provides vapor flow at the bottom of the column. The bottoms product is often removed as a liquid but may be taken as a vapor when the purity requirements for the bottom are high. The flowrate of the vapor generated in the reboiler is related to the bottoms and the internal flows by the external reboil ratio s, defined as

$$s \equiv \frac{V_0}{B} \qquad (5.36)$$

The relationship analogous to equation 5.35 is

$$\frac{L_1}{V_0} = \frac{s+1}{s} \qquad (5.37)$$

There is also a minimum and an optimal value for s; r and s are related through an energy balance by the condition of the feed and the separation that that is desired, as discussed in the next section.

The material balance for a total condenser can be combined with the definition of r to show that

$$V_N = (r+1)D \tag{5.38}$$

Similarly, for the reboiler,

$$L_1 = (s+1)B \tag{5.39}$$

5.3.2 Energy Balances

The simplest energy balance for an adiabatic column is the overall balance

$$Fh_F + Q_R = Dh_D + Bh_B + Q_C \tag{5.40}$$

Where h is the specific molar enthalpy, Q_R represents the heat supplied to the reboiler, and Q_C is the heat removed in the condenser. The specific enthalpy of the feed h_F is evaluated at the pressure on the feed stage, excluding heating, cooling, or pressure changes before the column. We have ignored heat gain or loss to the surroundings other than through the condenser and reboiler. We can relate the difference between the condenser and reboiler heat duties to the feed and product specifications by eliminating D and B from equation 5.40 With the mass balances in equation 5.25 and equation 5.26 to find

$$Q_R - Q_C = \frac{(z_F - z_B)(h_D - h_F) + (zD - zF)(h_B - h_F)}{z_D - z_B} F \tag{5.41}$$

This means that a specification of the feed rate, as well as the feed and product compositions, temperatures, and pressures, completely determines the difference between the condenser and reboiler heat duties. It is important to recognize this consequence of the overall balances in solving the model equations; e.g., care is needed in using software for design calculations when the product purities and heat duties are both specified, since these are not all independent.

The individual heat duties can be determined from energy balances around the appropriate units. For example, for a condenser, the energy balance can be combined with equation 5.38 to show the dependence of the condenser heat duty on the reflux ratio and the distillate flowrate.

$$Q_C = \left[r\left(h_N^{\,V} - h_{N+1}^{\,L}\right) + \left(h_N^{\,V} - h_D\right) \right] D \tag{5.42}$$

When the distillate is a saturated liquid, the enthalpy differences are equal to the heat of vaporization at the distillate conditions. The reboiler duty can be found by similar balances as

$$Q_R = \left[s\left(h_0^{\,V} - h_1^{\,L}\right) + \left(h_B - h_1^{\,L}\right) \right] B \tag{5.43}$$

The type of condenser or reboiler influences only the terms h_B and h_D.

An energy balance around the column excluding the condenser and the reboiler can be combined with the overall material balance and equation 5.27, 5.34, and 5.36 to relate the external reflux and reboil ratios to the product specifications and the enthalpy of the feed.

$$\frac{D}{B} = \frac{z_F - z_B}{z_D - z_F} = \frac{s\left(h_0^{\,V} - h_1^{\,L}\right) - \left(h_1^{\,L} - h_F\right)}{r\left(h_N^{\,V} - h_{N+1}^{\,L}\right) + \left(h_N^{\,V} - h_F\right)} \tag{5.44}$$

Equation 5.44 shows that a specification of the product compositions and the condition of the feed (temperature, pressure, and composition) completely determines the relationship between r and s.

The most detailed balances are, as always, at the level of the individual stages; in the rectifying section we have

$$V_{n-1}h_{n-1}^{\,V} = L_n h_n^{\,L} + D h_D + Q_C \tag{5.45}$$

And for the stripping section,

$$L_{n+1}h_{n+1}^{\,L} = V_n h_n^{\,V} + B h_B - Q_R \tag{5.46}$$

These energy balances must be solved simultaneously with the material balances and the phase equilibrium relationship to determine the variation of compositions and flowrates throughout the column. There are many cases, however, where a good approximation to the actual flow can be determined in a simpler manner; this approach is described next.

It is useful (and convenient) to examine cases where the liquid and vapor rates within each column section are constant. This simplification is referred to as the condition of constant molar overflow (CMO). Intuitively, we might expect that a constant molar latent heat of vaporization for the mixture would lead to this condition in an adiabatic column, since identical amounts of energy are required to condense or vaporize a mole of the material.

Accepting the CMO approximation for the moment, we denote the flowrates in the top or rectifying section as L_T and V_T, and in the bottom or stripping section as L_B and V_B. In this case, equation 5.28 to 5.32 become

$$V_T = L_T + D \tag{5.47}$$

$$V_T y_{n-1} = L_T x_n + D z_D \tag{5.48}$$

For $n = N+1, N, N-1, ..., f+1$ and

$$V_B = L_B - B \tag{5.49}$$

$$V_B y_n = L_B x_{n+1} - B z_B \tag{5.50}$$

For $n = 0,1,2,...,f-1$. It is convenient to rewrite these relationship in terms of the reflux and reboil ratios to find equations for the top operating line

$$y_{n-1} = \frac{r}{r+1} x_n + \frac{z_D}{r+1} \tag{5.51}$$

And the bottom operating line

$$y_n = \frac{s+1}{s}x_{n+1} - \frac{z_B}{s} \tag{5.52}$$

Where $r = \dfrac{L_T}{D}$ and $s = \dfrac{V_B}{B}$. These relationships demonstrate that the vapor composition at any point in the rectifying or stripping section is a liner function of the liquid-phase composition on the stage above.

It is also convenient to rewrite the enthalpy of the feed as a liner combination of the enthalpies of a saturated vapor and a saturated liquid mixture, each at the overall composition of the feed.

$$h_F = qh_F^{L,sat} + (1-q)h_F^{V,sat} \tag{5.53}$$

The feed quality q can be computed when the feed composition, temperature, and pressure are specified. For feeds that are mixtures of vapor and liquid, and for mixtures where the constant molar overflow assumption is accurate, q is simply the molar fraction of the feed that is liquid.

Saturated liquid or vapor feeds correspond to q values of 1 and 0, respectively. When the feed is a superheated vapor or a subcooled liquid, q is < 0 or > 1, respectively. Equation 5.53 can be rewritten as

$$q \equiv \frac{h_F^{V,sat} - h_F}{h_F^{V,sat} - h_F} = \frac{h_F^{V,sat} - h_F}{\lambda_F} \tag{5.54}$$

This definition of q is not restricted to constant molar overflow. However, if CMO is accurate and the enthalpy datum is selected as $h_F^{L,sat} = 0$, so that $h_F^{V,sat} = \lambda_F = \lambda$ so q is simply

$$q = \frac{\lambda - h_F}{\lambda} \tag{5.55}$$

The general relationships are much simpler for constant molar overflow. For example, the heat duties become

$$Q_C = \left[\lambda(r+1) - h_D\right]D \tag{5.56}$$

$$Q_R = [\lambda s + h_B] B \tag{5.57}$$

The relationship between the external reflux and reboil ratios in equation 5.44 becomes

$$\frac{D}{B} = \frac{z_F - z_B}{z_D - z_F} = \frac{s+1-q}{r+q} \tag{5.58}$$

Specification of the feed state and the compositions of the distillate and bottoms completely determine the relationship between r and s.

The behavior on the feed stage is slightly different from that on the other stages. At the feed stage, the balance of total mass is

$$F + V_B + L_T = V_T + L_B \tag{5.59}$$

And the energy balance is

$$Fh_F + V_B h^V + L_T h^L = V_T h^V + L_B h^L \tag{5.60}$$

These two equations, along with the definition of q in equation 5.55, can be combined to related the liquid flows in the two column sections

$$L_B - L_T = qF \tag{5.61}$$

As well as the two vapor flows

$$V_B - V_T = (q-1)F \tag{5.62}$$

The thermal condition of the feed determines the difference between the vapor and liquid flowrates in the rectifying and stripping sections of the column. For example, when the feed is a saturated liquid $(q = 1)$ the vapor flowrate is constant throughout the column and the liquid flowrate in the bottom of the column is greater than that in the top by precisely the feed flowrate. The internal flowrate differences that result for other feed conditions are likewise easily found and in agreement with I ntuition.

The locus of pints $\hat{x}$ and $\hat{y}$ where the top and bottom operating lines intersect is called the q-line. This can be found by subtracting the material balance for the light component in the top of the column (equation 5.48) from a similar balance in the bottom section (equation 5.50) and replacing the differences between the vapor rates and the liquid rates using equation 5.61 and equation 5.62 to find

$$\hat{y} = \frac{q}{q-1}\hat{x} - \frac{z_F}{q-1} \qquad (5.63)$$

5.4 Case Study

5.4.1 Problem Description

As mentioned above, distillation is one of the importance tasks in chemical industries. However, distillation is a very energy consuming process. Distillation columns are used for about 95% of liquid separations and the energy used from this process accounts for an estimated 3% of the world energy consumption. With rising energy awareness and growing environmental concerns, there is a need to reduce the energy use in industry. For the distillation process, because it is such a high-energy consumer, any energy savings should have an impact on the overall plant energy consumption.

The use of heat integration combined with complex configurations for distillation columns holds a great promise of energy savings up to about 70%. In addition to saving energy, accompanied by reduced environmental impact and site utility costs, there is also a possibility for reduction in capital costs. A number of different methods or designs can be applied to save energy in distillation, such as integration of distillation columns with the background process, heat pumps, multi-effect distillation, and complex arrangements such as prefractionators or thermally coupled columns (Petlyuk columns). Deciding which heat-integrated arrangement to use is not a straightforward task, given that the best arrangement is substantially dependent on the given separation task and the background process.

The study of so-called multi-effect distillation systems is described in this work. Multi-effect integration is achieved for two or more distillation columns by running one of the columns at a higher pressure and integrating the condenser of this high-pressure (HP) column with the reboiler of the low-pressure (LP) column. In general, multi-effect systems have two sequences of integration:

1. forward integration sequence, where the heat integration is in the direction of the mass flow; and

2. backward or reverse integration sequence, where the integration is in the opposite direction of the mass flow.

In this work, we have studied multi-effect distillation of methanol/water system. Our algorithms, LHS-GA, FSS-GA, and HSS-GA, have been applied in order to find the appropriate sequence and to seek the operating condition. Moreover, the performance of our algorithms is compared with SGA. Input arguments of this problem are shown in the table 5.4.

Table 5.4 Feed and column data

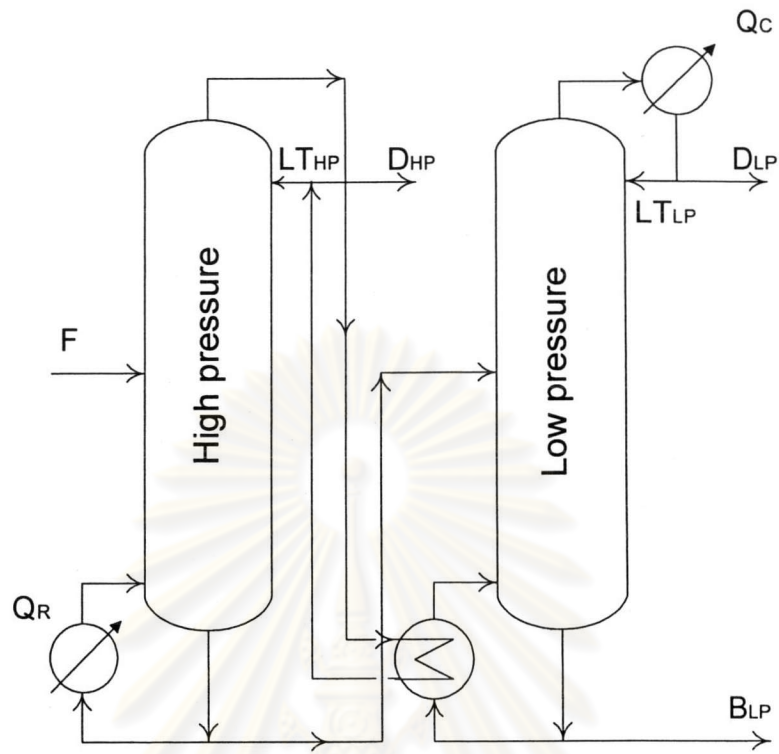| Feed and column data	
Feed rate	4320 (kmol/h)
Feed composition	0.73 mol% methanol (light component)
	0.27 mol% water (heavy component)
Feed liquid fraction	$q_F = 1$
stages of columns	16,26

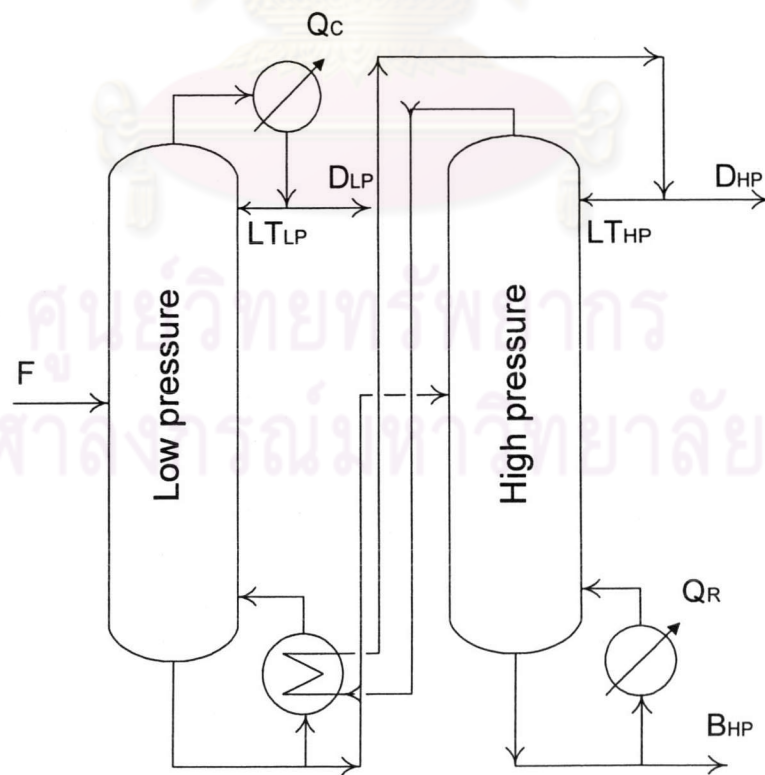Figure 5.7 Multi-effect distillation with forward integration

Figure 5.8 Multi-effect distillation with backward integration

5.4.2 Model Formulation

The formulation of a non-linear model for optimization can have as great (or greater) effect on the success in optimization as the selection of the numerical optimization method and its computer implementation. Model formulation of column model and optimization model are described below.

For column model, mathematical models are used where the material and energy balances are included. Before the models are formulated, the assumptions must be defined. The assumptions of this problem are:

- binary separation,
- ideal gas,
- constant molar overflow,
- vapor pressure calculated from Calusius-Clapeyron equation,
- liquid activity coefficient from Wilson equation, and
- hold-up of vapor is neglected.

<u>Material balance</u>:

- Column

$$0 = \left(V_{i-1} y_{i-1} + L_{i+1} x_{i+1} \right) - \left(V_i y_i + L_i x_i \right) \tag{5.64}$$

- Feed stage

$$0 = \left(V_{i-1} y_{i-1} + L_{i+1} x_{i+1} \right) - \left(V_i y_i + L_i x_i \right) + Fz \tag{5.65}$$

- Partial reboiler

$$0 = L_2 x_2 - \left(V_1 y_1 + B x_1 \right) \tag{5.66}$$

- Total condenser

$$0 = V_{NT-1} y_{NT-1} - \left(L_T + D \right) x_{NT} \tag{5.67}$$

Energy balance:

$$0 = L_2 h_{L,2} - V_1 h_{V,1} + Q_R \tag{5.68}$$

$$0 = V_{NT-1} h_{V,NT-1} - (L_T + D) h_{L,NT} - Q_C \tag{5.69}$$

VLE equation:

$$y = \frac{\gamma x P_i^0}{P} \tag{5.70}$$

Calusius-Clapeyron equation:

$$\ln \frac{P_i^0}{P} = \frac{\Delta h_{vap}}{R} \left(\frac{1}{T_b} - \frac{1}{T} \right) \tag{5.71}$$

Where: T_b = normal boiling point

Wilson equation:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \tag{5.72}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) + x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \tag{5.73}$$

Where: $\Lambda_{12} = \dfrac{v_2^L}{v_1^L} \exp(-A_{12}/RT)$

$$\Lambda_{21} = \frac{v_1^L}{v_2^L} \exp(-A_{21}/RT)$$

For the integrated reboiler/condenser, the heat duty is calculated from:

$$Q = UA(T_{T,HP} - T_{B,LP}) \tag{5.74}$$

Where: $T_{T,HP}$ = the temperature at the top of the HP column

$T_{T,LP}$ = the temperature in the bottom of the LP column

$$U = \text{overall heat transfer coefficient (W/m}^2\text{C})$$

This problem has several variables to optimize. These are

1. sequence of multi-effect distillation (forward or backward sequence),

2. feed location in HP and LP columns,

3. reflux flow in HP and LP columns, and

4. boil-up flow in HP and LP columns.

In the formulation of the objective function, there are two conflicting elements: we would like to produce as much valuable product as possible, but using as little energy as possible. For a given feed, the cost function (J) is defined as the amount of distillate (0.99 mol% methanol) multiplied by the price of methanol, minus the cost of energy consumption. As we would like to maximize the profit, we have to minimize (-J). To simplify a relative cost of energy has been used, so the object function to be maximized is:

$$J = D_{HP} + D_{LP} - wQ \tag{5.75}$$

Where: $D_{HP} + D_{LP}$ (mol s^{-1}) are the top products (methanol),

Q (MJ) is the heat load to the column, and

$w = 0.6488$ mol MJ^{-1} is the relative cost of energy.

After defining the objective function, the system constraints are specified. These are the model equations, material and energy balances for the distillation process (equality constraints) and operational constraints (inequalities) that have to be satisfied at the solution. The operational constraints have been defined for the multi-effect system: (1) the product (distillate) from both columns must contain at least 99% methanol, and (2) the bottom stream from the second column should contain at least 99% water.

The optimization problem can then be formulated as:

$$\min_{u}[-J_x(x,u)] \quad \text{objective function} \tag{5.76}$$

s.t.

$$g_1(x,u) = 0 \quad \text{model equations}$$

$$g_2(x,u) = 0 \quad \text{operational constraints}$$

Where: $x =$ state variables

$u =$ optimization variables

5.4.3 Optimization Results

This problem is very hard to optimize because it contains both several non-linear equations (equation 5.70-5.73) and discrete variables (feed location of both columns). Therefore, calculus-based method cannot efficient to solve this problem without special treatment, and genetic algorithm is the suitable approach to optimize this difficulty.

Hence, this objective function (equation 5.76) is optimized by using our algorithms and SGA. Before algorithms start, several genetic operators and its parameters have to define as shown in the table 5.5. Moreover, the number of population must be identified, and it has been set to 300.

Table 5.5 Operators and parameters used in each step for the case study

Step	Operator
Chromosome representation	Real-value chromosome
Selection	Roulette wheel selection
Crossover	Arithmetic crossover, $P_c = 0.6$
Mutation	Uniform Mutation, $P_m = 0.05$

The results of optimization are illustrated in the figure 5.9. The figure plots between generation number and maximum value of J (equation 5.76). The graph show that the solution obtaining form HSS-GA converge to the global optimum point: $J = 853.30$ (mol s^{-1}) at 17th generation, whereas the solution attaining form FSS-GA, LHS-GA, and SGA converge to the others. However, although FSS-GA and LHS-GA not converge to the global optimum, they still provide a better solution than SGA. These mean that all of our algorithms can provide the better solutions than SGA.
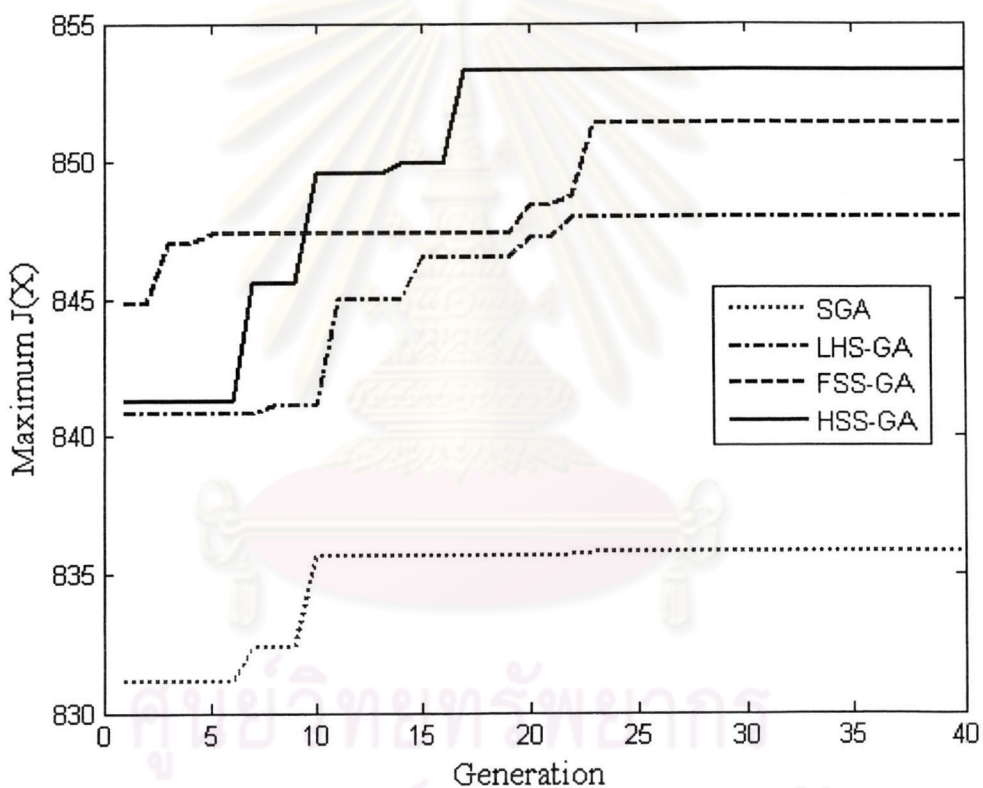

Figure 5.9 Comparison the performance of SGA, LHS-GA, FSS-GA, and HSS-GA: generation number versus maximum value for multi-effect distillation problem

The optimal sequence and operating point providing this global value (form optimized by HSS-GA) are demonstrated in the following table.

Table 5.6 The optimal operating point of case study

Optimal sequence: Forward integration sequence		
Element	High pressure column	Low pressure column
Pressure (bar)	5	1
Number of stage	16	26
Feed stage	5	12
Reflux flow (kmol/hr)	3357.3	1565.2
Boil-up flow (kmol/hr)	4859.9	3420.9
Bottom composition	0.59	0.01
Distillate composition	0.99	0.99

5.5 Summary

Our algorithms, as introduced in the previous chapter, have been applied to the optimization problem of distillation sequence synthesis. From optimization results, our algorithms, especially HSS-GS and FSS-GA, have higher efficiency than SGA in terms of solution quality and speed of convergence to the global optimum. Moreover, even though LHS-GA cannot provide the global solution, it still provides a more acceptable result than SGA. Hence, our algorithms successfully apply to optimization problem of chemical engineering, and our algorithms succeed in enhancing the GA performance.