

## CHAPTER VI

### The synthesis of phenol recovery process

#### 6.1 Introduction

Phenol compounds are priority pollutants that enter water bodies through discharge from pharmaceutical, petrochemical and other chemical manufacturing processes. They are harmful to organisms even at low concentrations. Moreover, many of them have been classified as hazardous pollutants because of their potential to harm human health. Given their toxicity, phenols have been included in the US Environmental Protection Agency (USA EPA, 1987) list of priority pollutants. Phenol waste water accumulates in many areas of plastic and resin production. The phenol content, which depends on the process, is normally 2-12%.

Industrial waste water often contains phenol. Thus, it cannot be discharged into a sewage treatment plant without reprocessing and cleaning. Since destruction through burning is not only a bad alternative ecologically but also too costly due to the high water content, the preferred way is phenol recovery with simultaneous cleaning of the waste water until it can be discharged into the sewage treatment plant.

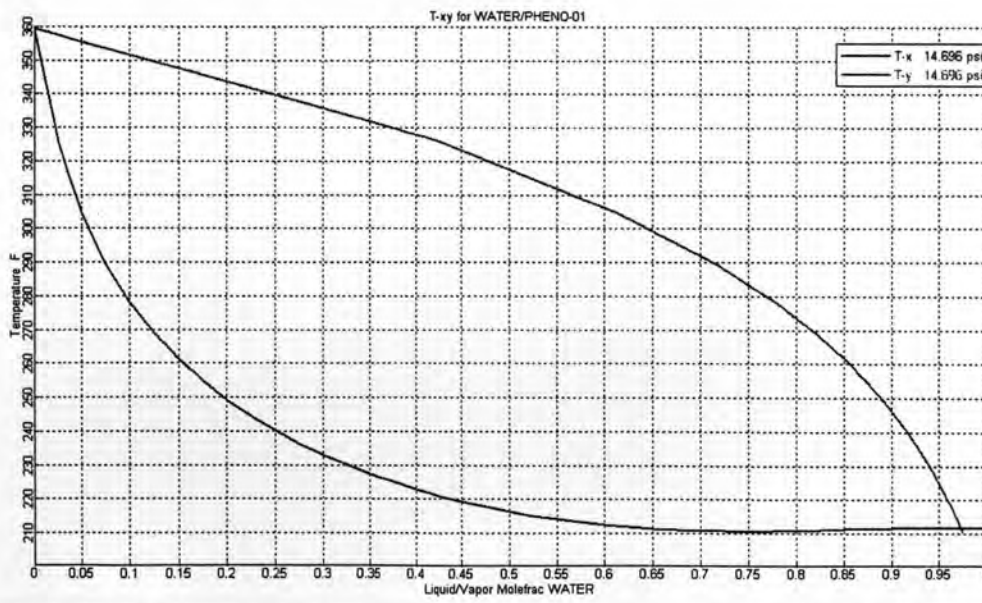
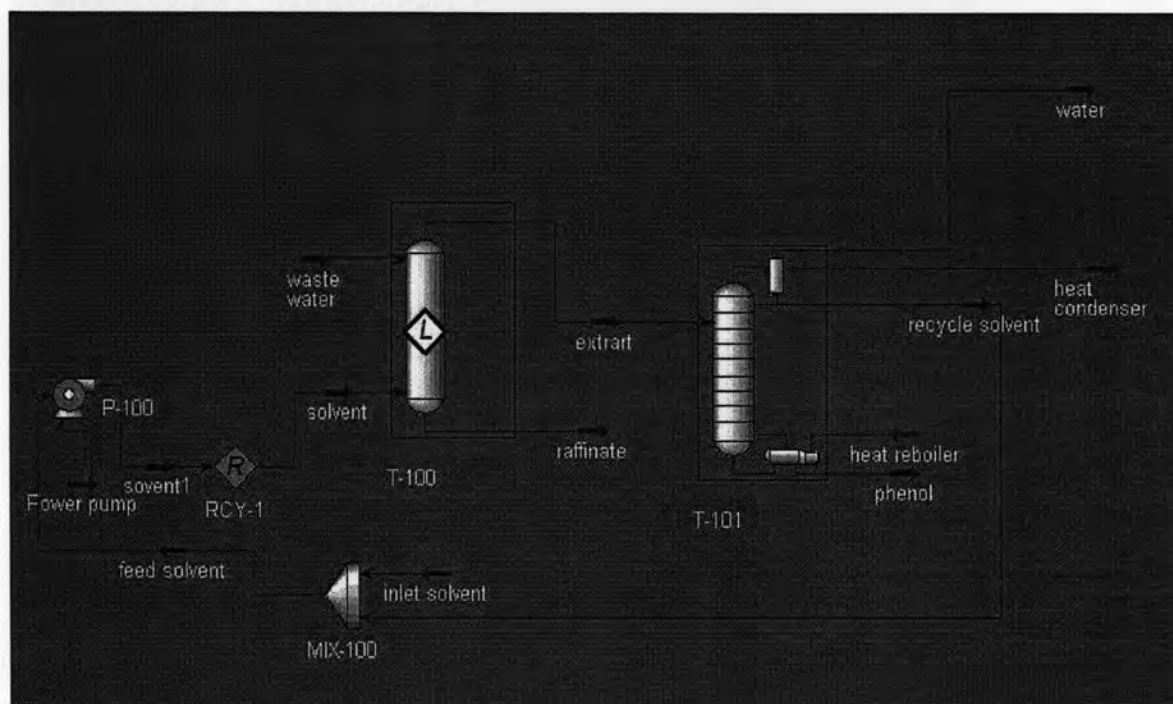


Figure 6.1: The azeotrope point of phenol-water system.

In this work, we investigated a phenol recovery process for phenolic-resin manufacturing. The wastewater stream containing 2 %mol of phenol is fed to the recovery process. In the phenol recovery process, the mixture forms an azeotrope at 9.2 mol % of phenol. Thus, a distillation may not be efficiently. Therefore, a mass-separating agent-based technique is necessary for a separation. The system shows liquid/liquid (L/L) equilibrium. Thus, a liquid-liquid extraction is employed in this case. The mass-separating agent is removed immediately after liquid-liquid extraction operation. A distillation column is also required in order to remove the mass-separating agent.



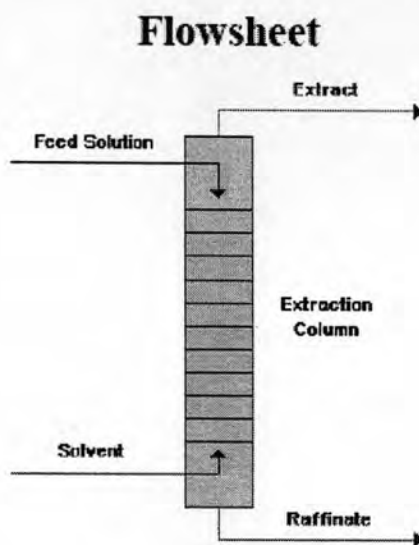
**Figure 6.2:** The phenol recovery process

## 6.2 Fundamentals

### 6.2.1 Liquid-liquid Extraction

Extraction is a process that separates components based upon chemical differences rather than differences in physical properties. The basic principle behind extraction involves the contacting of a solution with another solvent that is immiscible with the original. The solvent is also soluble with a specific solute contained in the solution. Two phases are formed after the addition of the solvent, due to the differences in densities. The solvent is chosen so that the

solute in the solution has more affinity toward the added solvent. Therefore mass transfer of the solute from the solution to the solvent occurs. Further separation of the extracted solute and the solvent will be necessary. However, these separation costs may be desirable in contrast to distillation and other separation processes for situations where extraction is applicable.



**Figure 6.3:** Extraction flowsheet for an Extractor Column

A general extraction column has two input stream and two output streams. The input streams consist of a solution feed at the top containing the solute to be extracted and a solvent feed at the bottom which extracts the solute from the solution. The solvent containing the extracted solute leaves the top of the column and is referred to as the extract stream. The solution exits the bottom of the column containing only small amounts of solute and is known as the raffinate. Further separation of the output streams may be required through other separation processes.

#### 6.2.1.1 Process Operation

There are certain design variables that must be assigned in an extraction process.

-Operating Temperature

-Operating Pressure

-Feed Flow Rate

Composition

Temperature of entering stream

Pressure of entering stream

As in many separation processes, the pressure and temperature conditions play a large role in the effectiveness of the separation. In order for a good split of the feed the pressure and temperature must be such so as to ensure that all components remain in the liquid phase. The process will be adversely affected if one or more of the components are allowed to become a vapor, or the extraction may not occur at all if a large enough portion of a component is allowed to vaporize. In addition, the temperature should be high enough that the components are all soluble with one another. If extremes in temperature are present, finding a suitable solvent for extraction can be problematic. This is however generally not the case since one of the biggest benefits in the extraction process is that it can be done at ambient pressures and temperatures. In many applications, a separation process is desired where an extreme temperature will destroy the desired product such as the pharmaceutical industry. For these applications, extraction is ideally suited, since the only temperature requirement is that dictated by the solubility. At this point the biggest challenge would be finding a suitable solvent for the extraction. We can also use the pharmaceutical industry in another example for the benefits of extraction and this has to do with the volumes involved for effective extraction. The extraction process can become very expensive if the solvent needed to be used is costly these expenses can be contained if a batch process is being used and this is often the case with medicines. In a non-batch process the solvent would need to be constantly supplied and this would involve either a huge amount of solvent or another separation process in order to recycle the solvent.

#### **Reasons to use liquid-liquid Extraction**

- Separation not feasible by distillation
- Break azeotropes
- Energy requirements of distillation are prohibitive
- A complex distillation sequence is required
- The material is heat sensitive
- The material is non-volatile

The general rule: If a separation can be made economically by distillation, there is no reason to consider extraction. However, in situations where distillation is not feasible for reasons such as a complex process sequence, high investment or operating costs, heat sensitive materials, or low volatility, extraction is often the best technology to use.

Extraction frequently involves additional steps to recover and recycle the solvent. Since most investment and operating costs are associated with the solvent recovery steps, it is very important to consider and study this aspect when designing the entire process.

In a typical extraction process about 3% of the operating cost is in the extractor, with the remaining 97% in solvent recovery. Therefore, it is extremely important to consider the solvent recovery aspects early in the project since they play such an important role in overall process economics.

#### 6.2.1.2 Liquid-liquid equilibrium

When talking about liquid-liquid extraction, liquid-liquid equilibrium must be considered. This is best represented by equating the chemical potential of both liquid phases:

$$u_i = u_i^* \quad (6.1)$$

This relationship reduces to an expression, which is dependent only on the liquid mole fractions and activity coefficients:

$$\gamma_i x_i = \gamma_i^* x_i^* \quad (6.2)$$

We can use activity coefficient models, such as UNIFAC (UNIQuac Functional-group Activity Coefficient), UNIQUAC (universal quasichemical), and NRTL (nonrandom two-liquid) to determine the mole fractions. All three models above apply for liquid-liquid equilibrium, it rolls down to which is easier to use and what properties we have available. For a multi-component system, the UNIQUAC equation for the liquid-phase activity coefficient is represented as follows:

$$\ln \gamma_i = \ln \gamma_i (\text{combinatorial}) + \ln \gamma_i (\text{residual}) \quad (6.3)$$

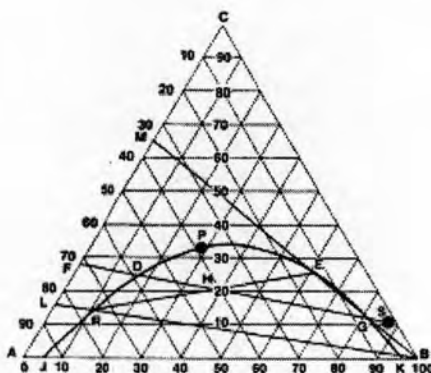
The combinatorial and residual activities are based on the statistical mechanical theory and allowed the local compositions to result from the size and energy differences between the

molecules in the mixture. The relationships for these two activities are made available to us through.

### 6.2.1.3 Ternary Phase Diagram

We then are able to relate this data from the activity into a ternary phase diagram. Ternary phase diagrams are unique in that they show all three components of a reactor system on one plot. There are general principles that govern ternary phase diagrams, and those are the following:

- Sum of the perpendicular distances from any point within the triangle to the three sides equals the altitude of the triangle.
- Each apex of the triangle represents one of the pure components.
- Any point of a side of the triangle represents a binary mixture.
- Lines may be drawn parallel to the sides of the equilateral triangle for the plotting of the compositions.



**Figure 6.4:** Phase diagram for a three component system.

The ternary phase diagram may be constructed directly from experimental data. The saturation curve (miscibility boundary), represented by JDPEK in Fig. 6.4, can be obtained experimentally by a cloud point titration. For example, a solution containing components A & C with some composition is made, and then component B is added until the onset of cloudiness due to the formation of a second phase occurs. Then the composition is known for the mixture of the three components and can be plotted onto the ternary phase diagram. Tie lines are lines that connect points on the miscibility boundary. The tie lines may also be presented onto the ternary

phase diagram from an experiment. A mixture may be prepared with composition that of point H (40% A, 40% C, 20% B) from Fig. 6.4. If we allow it to equilibrate, then we can chemically analyze the final extract (E) phase and the raffinate (R) phase. Point F is a feed composition into the extractor while point S is the solvent feed to the extractor. Point H represents the composition of the two feeds at equilibrium. This point is determined by summing the feed (F) and solvent (S) compositions for each component. Points R and E are the compositions of the raffinate and extract from the unit, respectively, and the line between them forms the tie line. The tie lines move above and below this line based on the relationship between the raffinate and the extract. Point P represents the plait point. At this point, only one liquid phase exists and the compositions of the two effluents are equal. The curve represented by JRDPEK is the equilibrium between all three components. The area under the curve is the region where two liquid phases will exist. Above the curve, there will only be one liquid phase. If a line is drawn from F to E or from S to R, this will represent the operating line. Although this diagram is not the basic theory behind liquid-liquid extraction, it is helpful to review this procedure before continuing with an in-depth discussion.

In addition to the above-mentioned considerations, equilibrium constraints must be satisfied. This implies that

$$\gamma_{i,AE} = \gamma_{i,AR}^* \quad (6.4)$$

Where  $\gamma_{i,AE}$  is the activity coefficient for the solute A in the extract and  $\gamma_{i,AR}^*$  is the activity coefficient of A in the raffinate. This condition is one of the most important aspects of liquid-liquid extraction since it allows for calculations and assumptions that based on equilibrium systems (e.g. the ternary phase diagram).

One consideration to be made is for the separation factor. We want this factor to as far away from unity as possible. This leads to a better separation in the extraction process. The separation factor is represented as follows:

$$\beta = \frac{y_E^*}{x_R} \quad (6.5)$$

One of the last essential points to the theory behind liquid-liquid extraction is mass transfer. The driving force for this mass transfer arises from the concentration difference of the

solute in each of the solvents. In general, it is assumed that the system is at an equilibrium state when mass transfer is occurring. Solute fluxes in the raffinate and extract can be expressed as

$$N = K_E A (x_E^i - x_E) \quad (6.6)$$

$$N = K_R A (x_R^i - x_R) \quad (6.7)$$

Where  $K_E$  and  $K_R$  are the overall mass transfer coefficients,  $A$  is the cross-sectional area,  $x_E$  and  $x_R$  are the concentrations of solute in the extract and raffinate respectively, and  $x_E^i$  and  $x_R^i$  are the concentrations of solute in each phase at the liquid-liquid interface.

### 6.2.2 Distillation

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.

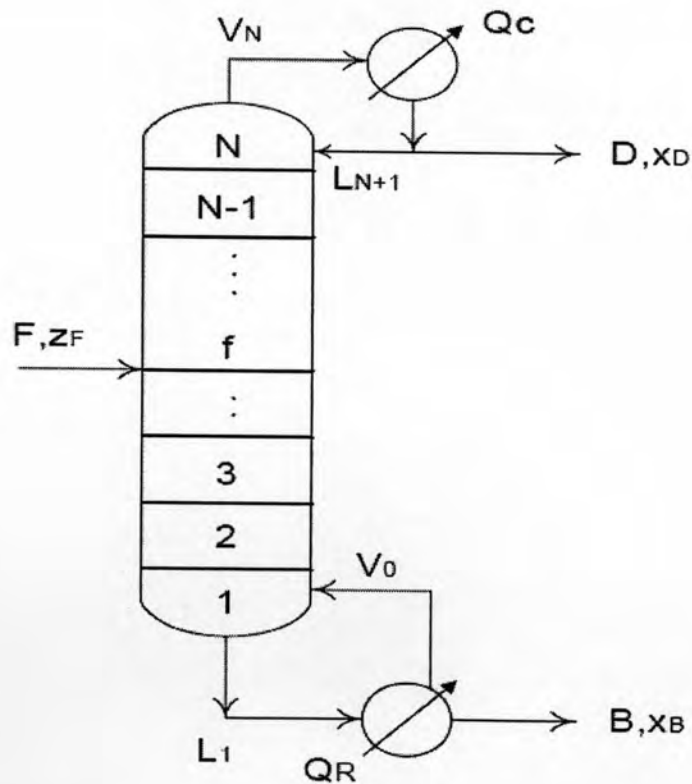


Figure 6.5: A distillation column



### 6.2.2.1 The Equilibrium-Stage Concept

The equilibrium (theoretical)-stage concept (Fig. 6.6) 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 tray 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 may 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 have 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.

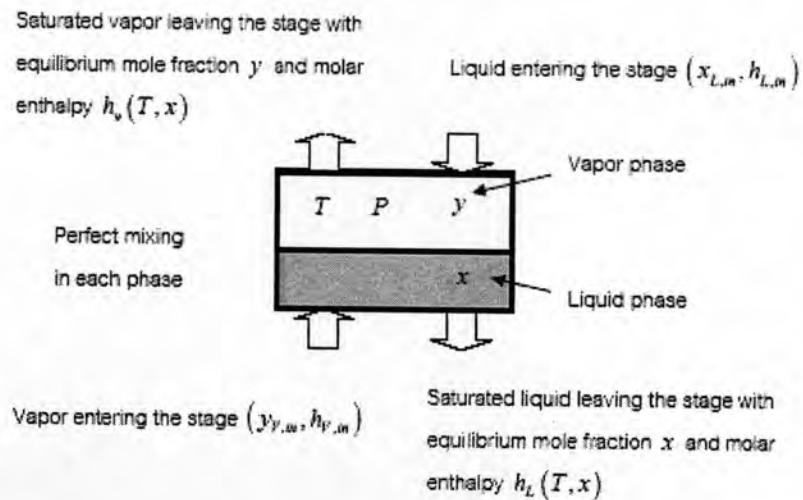


Figure 6.6: Equilibrium-stage concept

### 6.2.2.2 Vapor-liquid Equilibrium

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

$$f = N_c - PH + 2 \quad (6.8)$$

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:

$$\begin{aligned} [y_1, y_2, \dots, y_{N_c-1}, T] &= f(P, x_1, x_2, \dots, x_{N_c-1}) \\ (y, T) &= f(P, x) \end{aligned} \quad (6.9)$$

Here we have introduced the mole fractions  $x$  and  $y$  in the liquid and vapor phases respectively,

and we trivially have  $\sum_{i=1}^n x = 1$  and  $\sum_{i=1}^n y = 1$

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  $p_i^\circ$  of the pure component (which is a function of temperature only:  $p_i^\circ = p_i^\circ(T)$ ) and the liquid mole fraction ( $x_i$ )

$$p_i = x_i p_i^\circ(T) \quad (6.10)$$

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  $P = p_1 + p_2 + \dots + p_{N_c} = \sum_i P_i = \sum_i x_i p_i^\circ(T)$  we derive:

$$y_i = x_i \frac{p_i^\circ}{P} = \frac{x_i p_i^\circ(T)}{\sum_i x_i p_i^\circ(T)} \quad (6.11)$$

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

$$\ln p^\circ(T) \approx a + \frac{b}{c+T} + d \ln(T) + eT^f \quad (6.12)$$

### 6.2.2.3 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:

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} = \frac{K_i}{K_j} \quad (6.13)$$

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

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} = \frac{K_i}{K_j} = \frac{p_i^\circ(T)}{p_j^\circ(T)} \quad (6.14)$$

Here  $p_i^\circ(T)$  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  $\frac{p_i^\circ(T)}{p_j^\circ(T)}$  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:

$$\alpha_i = \alpha_r = \frac{p_i^\circ(T)}{p_r^\circ(T)} \quad (6.15)$$

The VLE relationship (equation 6.11) becomes:

$$y_i = \frac{\alpha_i x_i}{\sum \alpha_i x_i} \quad (6.16)$$

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.

#### 6.2.3.4 Non-ideal Mixtures

For non-ideal 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

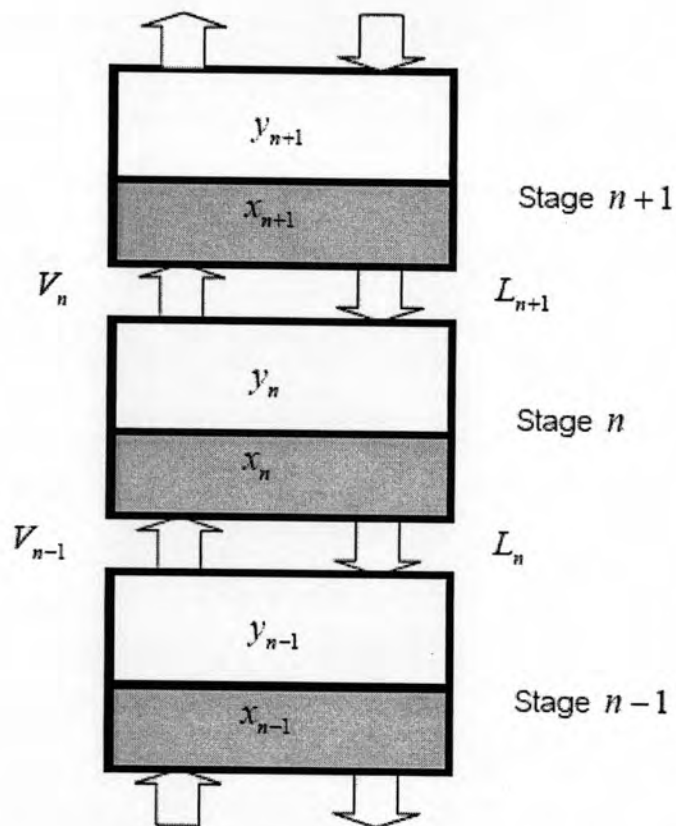
$$Py_i = \gamma_i x_i P^{sat} \quad (6.17)$$

Activity coefficients can be calculated from experimental data by methods described in Denbigh (1971), and Smith and VanNess (1996.). If  $P, T, y, x$  data are available together with an accurate saturated vapor pressure for each component, then one way to calculate activity

coefficients is to rearrange equation (6.17) explicitly for  $\gamma_i$ . Many models are proposed in order to represent the experimental data.

### 6.2.3.5 Material Balance on a Distillation Stage

Based on the equilibrium-stage concept, a distillation column section is modeled as shown in Fig. 6.7.



**Figure 6.7:** Distillation column section modeled as a set of connected equilibrium stages.

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<sup>-1</sup>):

$$\frac{dN_{i,n}}{dt} = (L_{n+1}x_{i,n+1} - V_n y_{i,n}) - (L_n x_{i,n} - V_{n-1} y_{i,n-1}) \quad (6.18)$$

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

It is convenient to define the net material flow ( $w_i$ ) of component  $i$  upwards from stage  $n$  to  $n+1$  (mol s<sup>-1</sup>):

$$w_{i,n} = (V_n y_{i,n} - L_{n+1} x_{i,n+1}) \quad (6.19)$$

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 ( $x_{n+1}$ ):

$$y_{i,n} = \frac{L_{n+1}}{V_n} x_{i,n+1} + \frac{1}{V_n} w_i \quad (6.20)$$

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 know the flows in the system. This is illustrated in Fig. 6.8, and forms the basis of McCabe-Thiele approach.

#### 6.2.3.6 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<sup>-1</sup>) and  $V_{n-1} = V_n = V$  (mol s<sup>-1</sup>). 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.,

$y_{i,n} = \frac{L}{V} x_{i,n+1} + \frac{1}{V} w_i$ . This makes computations much simpler since the internal flows ( $L$  and  $V$ ) do not depend on compositions.

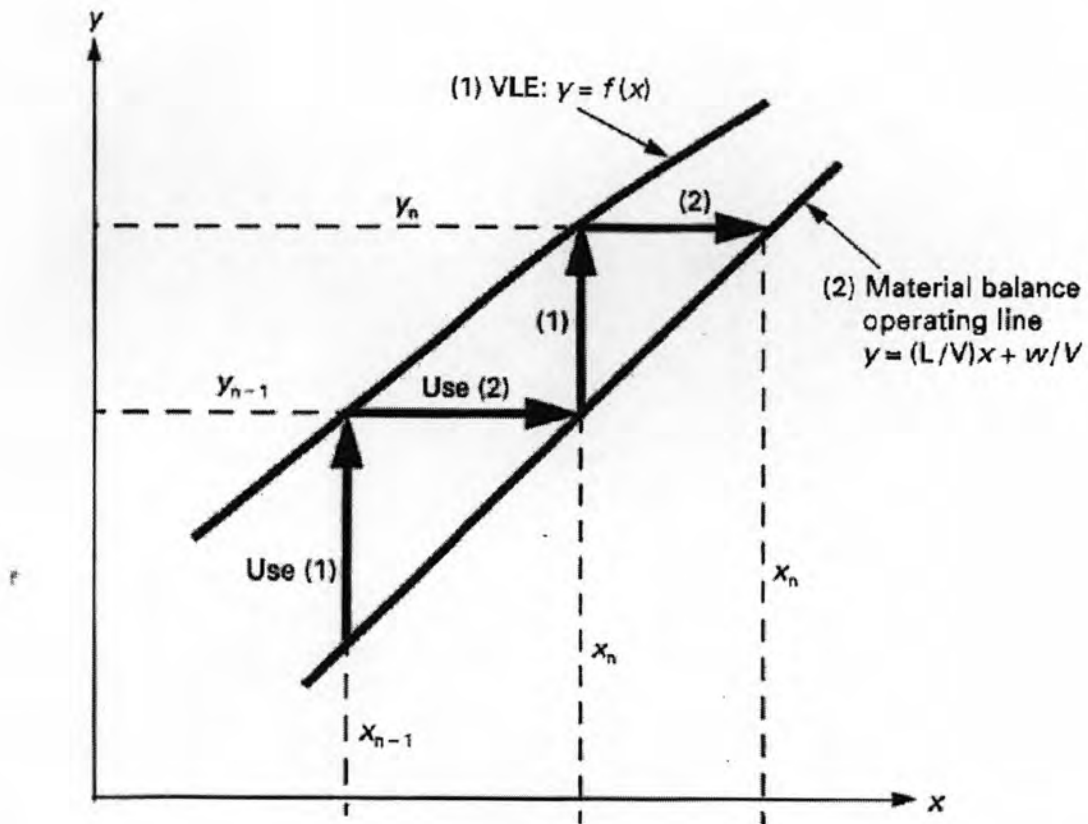


Figure 6.8: Combining the VLE and the operating line to compute mole fractions in a section of equilibrium stages

### 6.2.3 The Continuous Distillation Column

#### 6.2.3.1 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 Fig. 6.5, an overall balance.

$$F = D + B \quad (6.21)$$

And a balance for the light component

$$F_{zF} = D_{zD} + B_{zB} \quad (6.22)$$

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

$$\frac{D}{F} = \frac{Z_F - Z_B}{Z_D - Z_B} \quad (6.23)$$

$$\frac{B}{F} = \frac{Z_D - Z_F}{Z_D - Z_B} \quad (6.24)$$

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

$$\frac{D}{B} = \frac{Z_F - Z_B}{Z_D - Z_F} \quad (6.25)$$

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  $f_l = \frac{D z_D}{F z_F}$ . Similarly, the fractional recovery of the heavy component is  $f_h = \frac{B(1 - Z_B)}{F(1 - Z_F)}$ . The fractional recoveries can be related to the feed and product compositions by material balances. For example,  $(f_h = \frac{Z_D(Z_F - Z_B)}{Z_F(Z_D - Z_F)})$  and there is a similar expression for  $f_l$ . We will use compositions, fractional recoveries, or a combination of both as convenient.

The primary task in the design of a column is to relate the size and energy requirements to the specifications on the feed and product streams. The related performance calculation seeks to determine the flow rates 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.

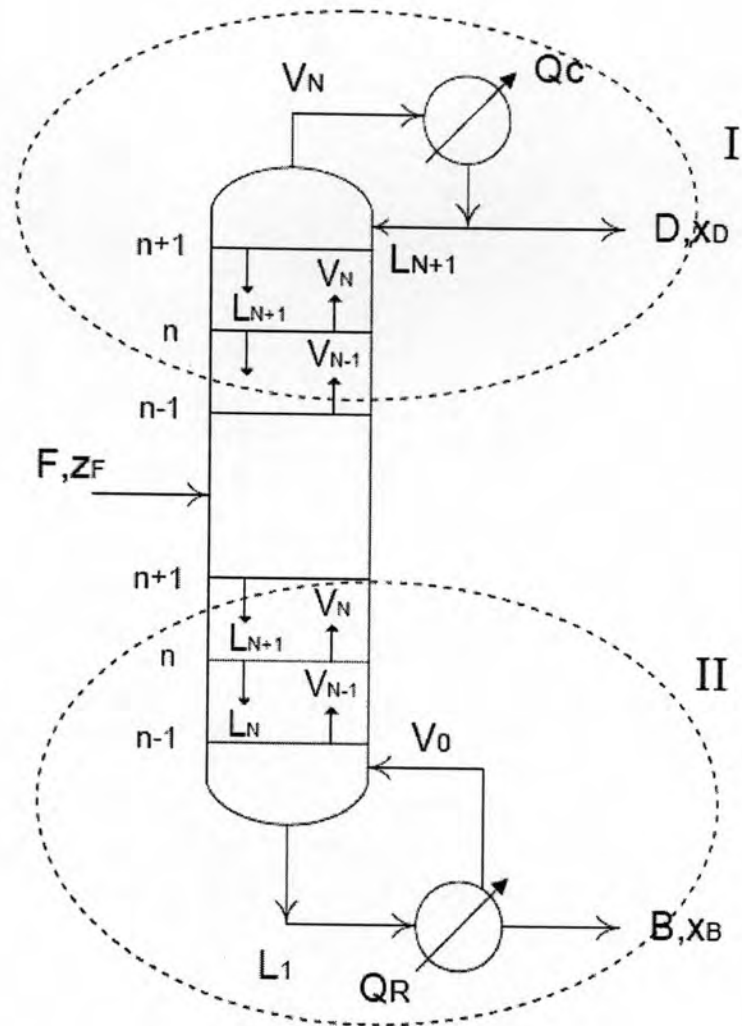


Figure 6.9: Stream labels and material balance envelopes for a simple column

Figure 6.9 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 Fig. 6.9).

$$V_{n-1} = L_n + D \quad (6.26)$$

$$V_{n-1}y_{n-1} = L_nx_n + Dz_D \quad (6.27)$$

$$y_{n-1} = \frac{L_n}{V_{n-1}}x_n + \frac{D}{V_{n-1}}z_D \quad (6.28)$$



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

$$L_{n+1} = V_n + B \quad (6.29)$$

$$L_{n+1}y_{n+1} = V_n y_n + Bz_B \quad (6.30)$$

$$y_n = \frac{L_{n+1}}{V_n} x_{n+1} + \frac{B}{V_n} z_B \quad (6.31)$$

For  $n=0, 1, 2, \dots, f-1$

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 6.5 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 flow rate  $L_{N+1}$  and is referred to as the reflux. The external reflux ratio  $r$  is

$$r = \frac{L_{N+1}}{D} \quad (6.32)$$

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

$$\frac{L_{N+1}}{V_N} = \frac{r}{r+1} \quad (6.33)$$

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

The reboiler 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 flow rate of the vapor generated in the reboiler is related to the bottoms and the internal flows by the external reboil ratio  $s$ , defined as

$$s = \frac{V_0}{B} \quad (6.34)$$

The relationship analogous to equation 6.33 is

$$\frac{L_1}{V_0} = \frac{s+1}{s} \quad (6.35)$$

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

$$V_N = (r+1)D \quad (6.36)$$

Similarly, for the reboiler,

$$L_1 = (s+1)D \quad (6.37)$$

### 6.2.3.2 Energy Balances

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

$$Fh_F + Q_R = Dh_D + Bh_B + Q_C \quad (6.38)$$

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 6.38 with the mass balances in equation 6.23 and equation 6.24 to find

$$Q_R - Q_C = \frac{(z_F - z_B)(h_D - h_F) + (z_D - z_F)(h_B - h_F)}{z_D - z_B} F \quad (6.39)$$

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 flow rate.

$$Q_C = [r(h_N^V - h_{N+1}^L) + (h_N^V - h_D)]D \quad (6.40)$$

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

$$Q_R = [s(h_0^V - h_1^L) + (h_B - h_1^L)]B \quad (6.41)$$

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 6.25, 6.32, and 6.34 to relate the external reflux and reboil ratios to the product specifications and the enthalpy of the feed.

$$\frac{D}{B} = \frac{z_F - z_B}{z_D - z_F} = \frac{s(h_0^V - h_1^L) - (h_1^L - h_F)}{r(h_N^V - h_{N+1}^L) + (h_N^V - h_F)} \quad (6.42)$$

Equation 6.42 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

$$V_{N-1}h_{N-1}^V = L_N h_N^L + D h_D + Q_C \quad (6.43)$$

And for the stripping section,

$$L_{N+1}h_{N+1}^L = V_N h_N^V + B h_B - Q_R \quad (6.44)$$

These energy balances must be solved simultaneously with the material balances and the phase equilibrium relationship to determine the variation of compositions and flow rates 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 flow rates in the top or rectifying section as  $L_T$  and  $V_T$ , and in the bottom or stripping section as  $V_B$  and  $L_B$ . In this case, equation 6.26 to 6.30 become

$$V_T = L_T + D \quad (6.45)$$

$$V_T y_{N-1} = L_T x_N + Dz_D \quad (6.46)$$

For  $n=N+1, N, N-1, \dots, f+1$  and

$$V_B = L_B - B \quad (6.47)$$

$$V_B y_N = L_B x_{N+1} - Bz_B \quad (6.48)$$

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

$$y_{N-1} = \frac{r}{r+1} x_N + \frac{z_D}{r+1} \quad (6.49)$$

And the bottom operating line

$$y_{N-1} = \frac{s+1}{s} x_N - \frac{z_B}{s} \quad (6.50)$$

Where  $r = \frac{L_T}{D}$  and  $s = \frac{V_B}{B}$ . These relationships demonstrate that the vapor composition at any point in the rectifying or stripping section is a linear function of the liquid-phase composition on the stage above. It is also convenient to rewrite the enthalpy of the feed as a linear combination of the enthalpies of a saturated vapor and a saturated liquid mixture, each at the overall composition of the feed.

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

$$q = \frac{h_F^{V,sat} - h_F}{h_F^{V,sat} - h_F} = \frac{h_F^{V,sat} - h_F}{\lambda_F} \quad (6.51)$$

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

$$q = \frac{\lambda - h_F}{\lambda} \quad (6.52)$$

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

$$Q_C = (\lambda(r+1) - h_D)D \quad (6.53)$$

$$Q_R = (\lambda s + h_B)B \quad (6.54)$$

The relationship between the external reflux and reboil ratios in equation 6.42 becomes

$$\frac{D}{B} = \frac{z_F - z_B}{z_D - z_F} = \frac{s+1-q}{r+q} \quad (6.55)$$

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

$$F + V_B + L_T = V_T + L_B \quad (6.56)$$

And energy balance is

$$Fh_F + V_B h^V + L_T h^L = V_T h^V + L_B h^L \quad (6.57)$$

These two equations, along with the definition of  $q$  in equation 6.52, can be combined to related the liquid flows in the two column sections

$$L_B - L_T = qF \quad (6.58)$$

As well as the two vapor flows

$$V_B - V_T = (q-1)F \quad (6.59)$$

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

The locus of points  $\hat{x}$  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 6.46) from a similar balance in the bottom section (equation 6.48) and replacing the differences between the vapor rates and the liquid rates using equation 6.58 and equation 6.59 to find

$$\hat{y} = \frac{q}{q-1} \hat{x} - \frac{z_F}{q-1} \quad (6.60)$$

### 6.3 Formulated problem

#### 6.3.1 Solvent selection

The size of liquid-liquid extraction unit and the amount of extraction solvent required are inversely proportional to the value of solute distribution coefficient. In addition, High solvent selectivity is necessary to reduce the cost of solute recovery. Thus, an attractive solvent should have a high value of the solute distribution coefficient, solvent selectivity and solvent power and a low solvent loss.

**Table 6.1** Partial lists of properties used to construct the trade-off set and MOS

Property	Estimation method
Solute distribution	$\frac{\gamma_{A,B}^{\infty} MW_B}{\gamma_{A,M}^{\infty} MW_M}$
Solvent loss	$\frac{1}{\gamma_{M,B}^{\infty}} \frac{MW_M}{MW_B}$
Solvent selectivity	$\frac{\gamma_{B,M}^{\infty} MW_A}{\gamma_{A,M}^{\infty} MW_B}$
Solvent power	$\frac{1}{\gamma_{A,M}^{\infty}} \frac{MW_A}{MW_M}$

\*MW, molecular weight; A, phenol solvent; B, water solvent; M, designing solvent

UNIFAC vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) parameter sets are used to predict thermodynamic properties of the system. Pretel, E.J (1994) presented solvent application for extractive phenol from water, there are toluene, n-butyl acetate, iso-butyl

acetate, methyl isobutyl ketone and benzene, but when we used all solvent that Pretel, E.J has previously identified. The result shows that Methyl isobutyl ketone form azeotrope with water. In the synthesis of phenol recovery process, we selected toluene, benzene, n-butyl acetate and iso-butyl acetate as potential for problem formulation.

### 6.3.2 Liquid-liquid extraction Model formulation

For liquid-liquid extraction column model, mathematical models are used where the material balances, liquid-liquid equilibrium are included. The assumptions of this problem are:

- 1) Binary phase
- 2) Immiscible between solvent and water
- 3) Liquid activity coefficient modeled using UNIFAC-LLE

Material balance:

$$0 = (x_i)_{n-1} R_{n-1} + (y_i)_{n+1} E_{n+1} - (x_i)_n R_n - (y_i)_n E_n \quad (6.61)$$

LLE equation:

$$y_i = \frac{\gamma_x}{\gamma_y} x_i \quad (6.62)$$

Unifac equation:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (6.63)$$

### 6.3.3 Distillation Model Formulation

The formulation of an optimization problem as well as the selection of the numerical optimization method and its computer implementation can have a great effect on the success in solving the problem. The formulation of distillation column is described below. For column model, mathematical models are used where the material and energy balances, Vapor-liquid equilibrium are included. The assumptions are made as following:

- 1) Ternary separation,

- 2) Constant molar overflow,
- 3) Saturated vapor pressure calculated from Antoine equation,
- 4) Liquid activity coefficient modeled using UNIFAC-VLE, and
- 5) Liquid and vapor hold-up in each tray are neglected.

Material balance:

Column

$$0 = (x_i)_{n-1}L_{n-1} + (y_i)_{n+1}V_{n+1} - (x_i)_nL_n - (y_i)_nV_{nD} \quad (6.64)$$

Feed stage

$$0 = (x_i)_{n-1}L_{n-1} + (y_i)_{n+1}V_{n+1} - (x_i)_nL_n - (y_i)_nV + F_Z \quad (6.65)$$

Condenser

$$0 = (y_i)_2V_2 - (x_i)_1L_1 - (y_i)_1V_1 \quad (6.66)$$

$$L_1 = \text{reflux} + \text{distillate} \quad (6.67)$$

Reboiler

$$0 = (x_i)_{nD-1}L_{nD-1} - (x_i)_{nD}L_{nD} - (y_i)_{nD}V_{nD} \quad (6.68)$$

Energy balance:

Enthalpy of vapor

$$H_v = a + bT + cT^2 + dT^3 + eT^4 + fT^5 \quad (6.69)$$

Enthalpy of vaporization

$$H_{vap} = A(1 - T/T_c)^n \quad (6.70)$$

Enthalpy of liquid

$$H_l = H_v - H_{vap} \quad (6.71)$$

Column

$$0 = \sum_{i=1}^c (x_i)_{n-1}L_{n-1}Hl_{n-1} + \sum_{i=1}^c (y_i)_{n+1}V_{n+1}Hv_{n+1} - \sum_{i=1}^c (x_i)_nL_nHl_n - \sum_{i=1}^c (y_i)_nV_nHv_n \quad (6.72)$$

Feed stage

$$0 = \sum_{i=1}^c (x_i)_{n-1}L_{n-1}Hl_{n-1} + \sum_{i=1}^c (y_i)_{n+1}V_{n+1}Hv_{n+1} - \sum_{i=1}^c (x_i)_nL_nHl_n - \sum_{i=1}^c (y_i)_nV_nHv_n + Q_{feed} \quad (6.73)$$



Condensator

$$0 = \sum_{i=1}^c (y_i)_{n+1} V_{n+1} H_{v_{n+1}} - \sum_{i=1}^c (x_i)_n L_n H_{l_n} - \sum_{i=1}^c (y_i)_n V_n H_{v_n} - Q_{Con} \quad (6.74)$$

Reboiler

$$0 = \sum_{i=1}^c (x_i)_{n-1} L_{n-1} H_{l_{n-1}} - \sum_{i=1}^c (x_i)_n L_n H_{l_n} - \sum_{i=1}^c (y_i)_n V_n H_{v_n} + Q_{Reboiler} \quad (6.75)$$

VLE equation

$$y = \frac{x \gamma^D^{Sat}}{P} \quad (6.76)$$

Antoine equation

$$\ln P^{sat} = a + \frac{b}{T+c} + d \ln(T) + eT^f \quad (6.77)$$

#### 6.3.4 Objective functions formulation

**Table 6.2** Process data

Flow of waste water	1000 kmol/hr
Waste water composition	2%mol phenol 98%mol water
Feed liquid fraction for distillation	$q_F = 1$
Pressure in distillation	$P_{top}=1 \text{ atm}, P_{bottom}=1.2 \text{ atm}$
Extraction operation temperature	$30^\circ \text{ C}$

This problem has several variables to be optimized. These are

1. The number of stage of liquid-liquid extractor.
2. The number of stage of distillation column.
3. Flow rate of solvent stream.
4. Feed location of distillation column,
5. Reflux ratio of distillation column
6. Type of solvent

The formulated problem is mixed-integer multi-objective optimization problem. Two most important objectives in the problem are economic and environmental performances.

The economic performance (objective1) is evaluated based on a summation of fixed costs and operating costs and the subtraction of product revenues. The evaluation procedure is to map alternatives into flow rates and process equipment specifications. The flow rates can be changed into revenues and operating costs. Fixed costs can be evaluated from process equipment specifications through the use of cost correlations (Gerrard, 2000). The economic objective is represented by the total annualized (TAC).

The environmental performance (objective2) is quantified by the toxicity of each species,  $LC_{50}$ . The environmental objective is represented by summation of mole solvent or phenol loss to environment and multiplication of toxicity index of each component. Toxicity index of each component is shown in table 6.3

**Table 6.3** Formulate environmental impact

Component	Toxicity index
phenol	434.267
toluene	2.1258
benzene	1.8021
n-butyl acetate	1.0229
iso-butly acetate	1

\* Evaluated from  $LC_{50}$



**Formulate problem**

$$\begin{aligned} \text{Minimize } F_1 &= \sum \text{Capital cost} + \sum \text{Operating cost} \\ \text{Minimize } F_2 &= \sum \text{Environmental impact} \end{aligned} \quad (6.78)$$

s.t.

Purity of waste water  $\geq 99\%$  mol water

Purity of recycled phenol  $\geq 99\%$  mol phenol

Recycled phenol  $\geq 98\%$

$g_1(x, u) = 0$  , model equations

$g_2(x, u) = 0$  , operational constraints

Where:  $x$  = state variables

$u$  = optimization variables

This problem is very hard to optimize because it contains both non-linear constraints (mass balance, energy balance) and discrete variables (the number of stage of extraction and distillation columns). Therefore, calculus-based method cannot efficient to solve this problem without special treatment. Therefore, evolutionary algorithm is the suitable approach to overcome these difficulties.

NSGA-II has been applied in order to find the Pareto optimal front of this case study. Moreover, the performance of NSGA-II with genetic parameters previously determined is compared with NSGA-II with genetic parameters outside the determined ranges. Other genetic operators and parameters were defined as shown in the table 6.4.

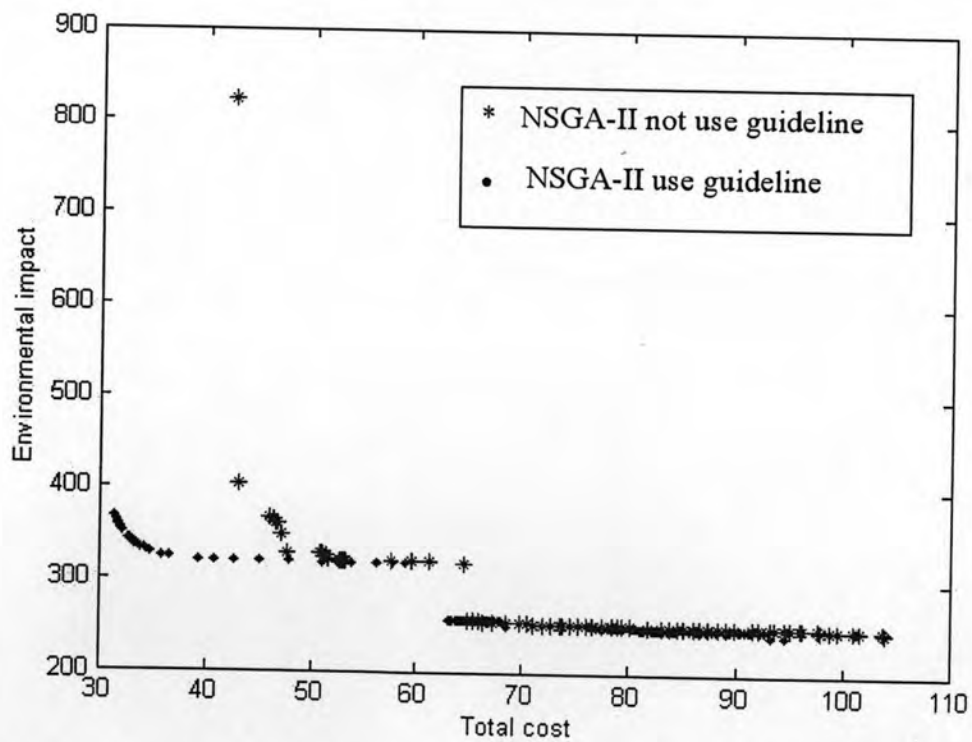
For this problem we was setting crossover probability=1, mutation probability =0.1 and was setting crossover probability=0.45, mutation probability =0.03 for comparison

**Table 6.4** NSGA-II's operators and parameters is used in each step for the case study

Chromosome representation	Real-value chromosome
Selection strategy	Binary tournament selection
Crossover type	Arithmetical crossover
Mutation type	Non-uniform mutation
Maximum number of generation	50
Termination criterion	specified number of generations
Constraint-handing	Penalty function
Population size	200

### 6.3 Optimization Results

The results of optimization are illustrated in the Fig. 6.10. The figure shows the obtained Pareto-optimal solution from NSGA-II.



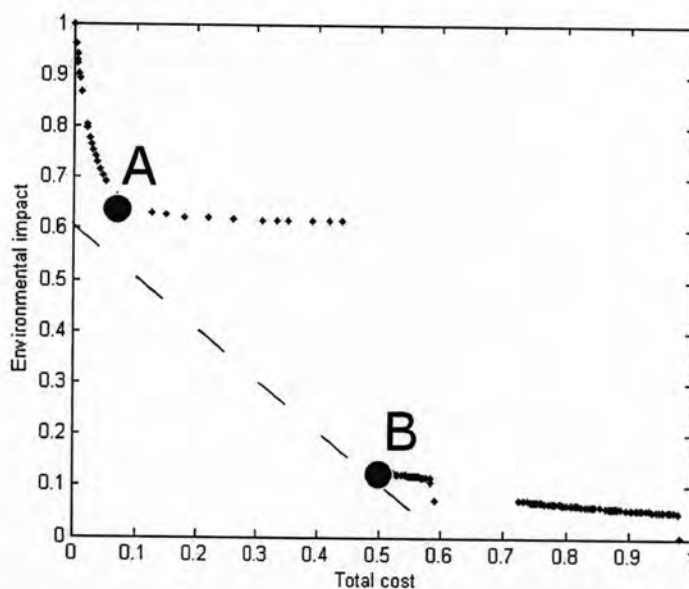
**Figure 6.10:** The obtained Pareto optimal solution of synthesis phenol recovery process problem.

NSGA-II with genetic parameters previously determined can obtain Pareto front better than NSGA-II with genetic parameters outside the determined ranges.

The normalized Pareto optimal solution of total annualized cost ( $F_1$ ) versus normalized environmental impact ( $F_2$ ) is shown in Fig. 6.11. The solutions on Pareto front obtained were used to select the most preferable solution. The solution obtained using described methodology was also compared with the solution obtained using conventional value function. A value function method is to form a value function from all objectives as;

$$F(F_1, F_2, \dots, F_n) = [\sum_{i=1}^n \omega_i F_i^p]^{1/p} \quad (6.79)$$

where  $\omega$  is a weighting factor for each objective which is proportional to the preference factor assigned to that objective, and  $p$  is a dimensional parameter.



**Figure 6.11:** Pareto set of case study problem (normalized economic performance ( $F_1$ ) vs. normalized environmental performance ( $F_2$ ))

It is important to realize that the trade-off solution obtained using the conventional value function strategy is largely sensitive to the weighting factors used in forming the value function. A change in these weighting factors will result in a different solution. Any arbitrary weighting factors need not result in a trade-off optimal solution to all problems. In this case we used  $\omega_1, \omega_2$  equal to 0.5 and  $p$  equal to 1.

Alternative B is selected as the most preferable process due to the positive compromise between economic, environmental. Parameters and objective functions value of alternative B are shown in table 6.5

**Table 6.5** The optimal operating point of case study

<b>The optimal operating point of case study</b>	
Number of liquid-liquid extraction stage	10
Number of distillation stage	22
Flow rate of solvent stream	20,040 kmol/hr
Reflux ratio	1.4466
Feed stage	14( from top)
Type of solvent	n-butyl acetate
Total cost	63.077 \$ /hr
Environmental impact	256.98
Purity of recycle phenol stream	99.544%mol phenol
Phenol recovery	99.544%
Purity of extraction waste water stream	99.975%mol water
Purity of distillation waste water stream	99.991%mol water

#### 6.4 Summary

The generic guideline for selection appropriate genetic parameters is successfully applied to the case study. The NSGA-II with genetic parameters previously determined can create Pareto optimal solution better than algorithm with genetic parameters outside the determined ranges.