

CHAPTER 11

Distillation

11.1. INTRODUCTION

The separation of liquid mixtures into their various components is one of the major operations in the process industries, and distillation, the most widely used method of achieving this end, is the key operation in any oil refinery. In processing, the demand for purer products, coupled with the need for greater efficiency, has promoted continued research into the techniques of distillation. In engineering terms, distillation columns have to be designed with a larger range in capacity than any other types of processing equipment, with single columns 0.3–10 m in diameter and 3–75 m in height. Designers are required to achieve the desired product quality at minimum cost and also to provide constant purity of product even though there may be variations in feed composition. A distillation unit should be considered together with its associated control system, and it is often operated in association with several other separate units.

The vertical cylindrical column provides, in a compact form and with the minimum of ground requirements, a large number of separate stages of vaporisation and condensation. In this chapter the basic problems of design are considered and it may be seen that not only the physical and chemical properties, but also the fluid dynamics inside the unit, determine the number of stages required and the overall layout of the unit.

The separation of benzene from a mixture with toluene, for example, requires only a simple single unit as shown in Figure 11.1, and virtually pure products may be obtained. A more complex arrangement is shown in Figure 11.2 where the columns for the purification of crude styrene formed by the dehydrogenation of ethyl benzene are shown. It may be seen that, in this case, several columns are required and that it is necessary to recycle some of the streams to the reactor.

In this chapter consideration is given to the theory of the process, methods of distillation and calculation of the number of stages required for both binary and multicomponent systems, and discussion on design methods is included for plate and packed columns incorporating a variety of column internals.

11.2. VAPOUR–LIQUID EQUILIBRIUM

The composition of the vapour in equilibrium with a liquid of given composition is determined experimentally using an equilibrium still. The results are conveniently shown on a temperature–composition diagram as shown in Figure 11.3. In the normal case shown in Figure 11.3*a*, the curve ABC shows the composition of the liquid which boils at any

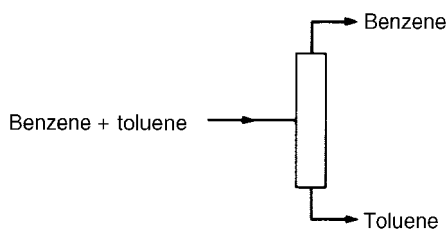


Figure 11.1. Separation of a binary mixture

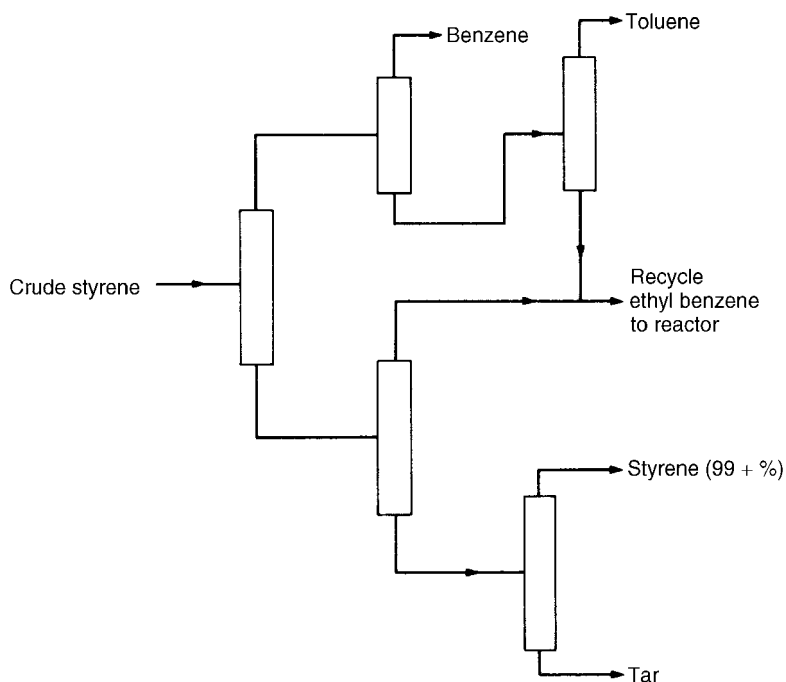


Figure 11.2. Multicomponent separation

given temperature, and the curve ADC the corresponding composition of the vapour at that temperature. Thus, a liquid of composition x_1 will boil at temperature T_1 , and the vapour in equilibrium is indicated by point D of composition y_1 . It is seen that for any liquid composition x the vapour formed will be richer in the more volatile component, where x is the mole fraction of the more volatile component in the liquid, and y in the vapour. Examples of mixtures giving this type of curve are benzene–toluene, *n*-heptane–toluene, and carbon disulphide–carbon tetrachloride.

In Figures 11.3*b* and *c*, there is a critical composition x_g where the vapour has the same composition as the liquid, so that no change occurs on boiling. Such critical mixtures are called azeotropes. Special methods which are necessary to effect separation of these are discussed in Section 11.8. For compositions other than x_g , the vapour formed has a

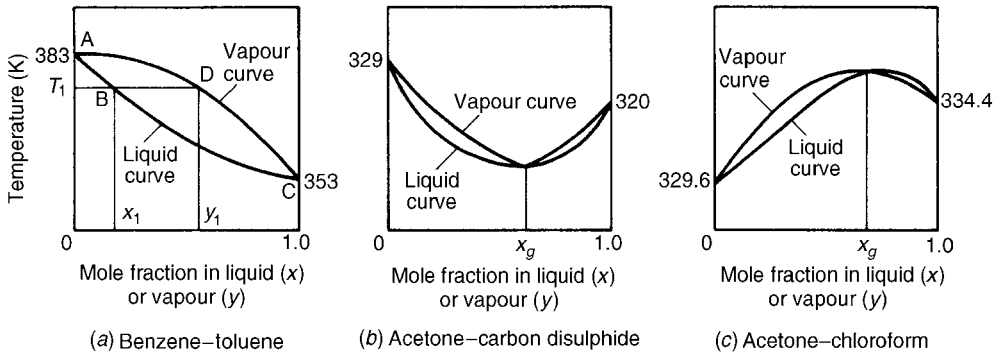


Figure 11.3. Temperature composition diagrams

different composition from that of the liquid. It is important to note that these diagrams are for constant pressure conditions, and that the composition of the vapour in equilibrium with a given liquid will change with pressure.

For distillation purposes it is more convenient to plot y against x at a constant pressure, since the majority of industrial distillations take place at substantially constant pressure. This is shown in Figure 11.4 where it should be noted that the temperature varies along each of the curves.

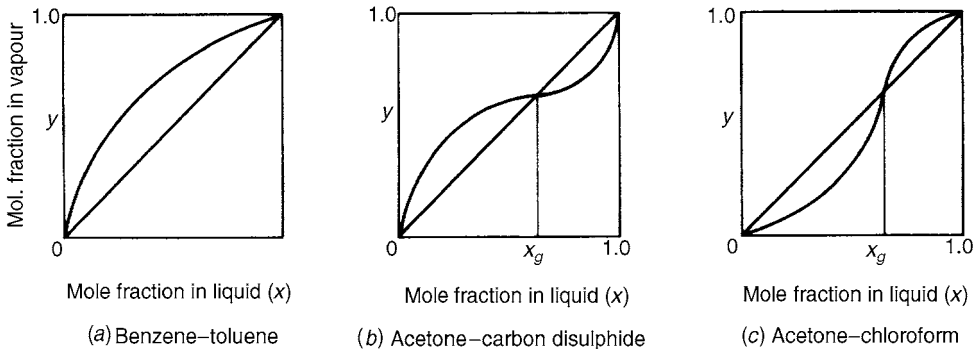


Figure 11.4. Vapour composition as a function of liquid composition at constant pressure

11.2.1. Partial vaporisation and partial condensation

If a mixture of benzene and toluene is heated in a vessel, closed in such a way that the pressure remains atmospheric and no material can escape and the mole fraction of the more volatile component in the liquid, that is benzene, is plotted as abscissa, and the temperature at which the mixture boils as ordinate, then the boiling curve is obtained as shown by ABCJ in Figure 11.5. The corresponding dew point curve ADEJ shows the temperature at which a vapour of composition y starts to condense.

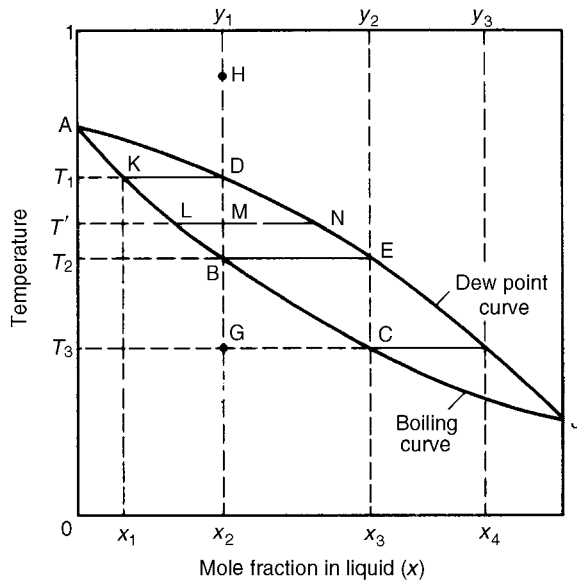


Figure 11.5. Effect of partial vaporisation and condensation at the boiling point

If a mixture of composition x_2 is at a temperature T_3 below its boiling point, T_2 , as shown by point G on the diagram, then on heating at constant pressure the following changes will occur:

- When the temperature reaches T_2 , the liquid will boil, as shown by point B, and some vapour of composition y_2 , shown by point E, is formed.
- On further heating the composition of the liquid will change because of the loss of the more volatile component to the vapour and the boiling point will therefore rise to some temperature T' . At this temperature the liquid will have a composition represented by point L, and the vapour a composition represented by point N. Since no material is lost from the system, there will be a change in the proportion of liquid to vapour, where the ratio is:

$$\frac{\text{Liquid}}{\text{Vapour}} = \frac{MN}{ML}$$

- On further heating to a temperature T_1 , all of the liquid is vaporised to give vapour D of the same composition y_1 as the original liquid.

It may be seen that partial vaporisation of the liquid gives a vapour richer in the more volatile component than the liquid. If the vapour initially formed, as for instance at point E, is at once removed by condensation, then a liquid of composition x_3 is obtained, represented by point C. The step BEC may be regarded as representing an ideal stage, since the liquid passes from composition x_2 to a liquid of composition x_3 , which represents a greater enrichment in the more volatile component than can be obtained by any other single stage of vaporisation.

Starting with superheated vapour represented by point H, on cooling to D condensation commences, and the first drop of liquid has a composition K. Further cooling to T' gives liquid L and vapour N. Thus, partial condensation brings about enrichment of the vapour in the more volatile component in the same manner as partial vaporisation. The industrial distillation column is, in essence, a series of units in which these two processes of partial vaporisation and partial condensation are effected simultaneously.

11.2.2. Partial pressures, and Dalton's, Raoult's and Henry's laws

The partial pressure P_A of component **A** in a mixture of vapours is the pressure that would be exerted by component **A** at the same temperature, if present in the same volumetric concentration as in the mixture.

By Dalton's law of partial pressures, $P = \Sigma P_A$, that is the total pressure is equal to the summation of the partial pressures. Since in an ideal gas or vapour the partial pressure is proportional to the mole fraction of the constituent, then:

$$P_A = y_A P \quad (11.1)$$

For an *ideal mixture*, the partial pressure is related to the concentration in the liquid phase by Raoult's law which may be written as:

$$P_A = P_A^\circ x_A \quad (11.2)$$

where P_A° is the vapour pressure of pure **A** at the same temperature. This relation is usually found to be true only for high values of x_A , or correspondingly low values of x_B , although mixtures of organic isomers and some hydrocarbons follow the law closely.

For low values of x_A , a linear relation between P_A and x_A again exists, although the proportionality factor is Henry's constant \mathcal{H} , and not the vapour pressure P_A° of the pure material.

For a liquid solute **A** in a solvent liquid **B**, Henry's law takes the form:

$$P_A = \mathcal{H} x_A \quad (11.3)$$

If the mixture follows Raoult's law, then the vapour pressure of a mixture may be obtained graphically from a knowledge of the vapour pressure of the two components. Thus, in Figure 11.6. OA represents the partial pressure P_A of **A** in a mixture, and CB the partial pressure of **B**, with the total pressure being shown by the line BA. In a mixture of composition D, the partial pressure P_A is given by DE, P_B by DF, and the total pressure P by DG, from the geometry of Figure 11.6.

Figure 11.7 shows the partial pressure of one component **A** plotted against the mole fraction for a mixture that is not ideal. It is found that over the range OC the mixture follows Henry's law, and over BA it follows Raoult's law. Although most mixtures show wide divergences from ideality, one of the laws is usually followed at very high and very low concentrations.

If the mixture follows Raoult's law, then the values of y_A for various values of x_A may be calculated from a knowledge of the vapour pressures of the two components at

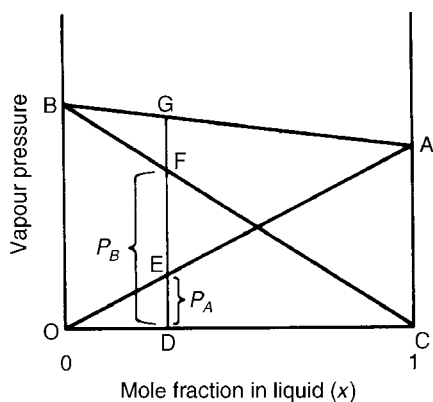


Figure 11.6. Partial pressures of ideal mixtures

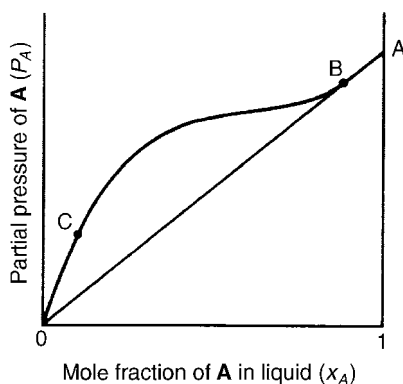


Figure 11.7. Partial pressures of non-ideal mixtures

various temperatures.

Thus:

$$P_A = P_A^\circ x_A$$

and:

$$P_A = P y_A$$

so that:

$$y_A = \frac{P_A^\circ x_A}{P}, \quad \text{and} \quad y_B = \frac{P_B^\circ x_B}{P} \tag{11.4}$$

But:

$$y_A + y_B = 1$$

$$\frac{P_A^\circ x_A}{P} + \frac{P_B^\circ (1 - x_A)}{P} = 1$$

giving:

$$x_A = \frac{P - P_B^\circ}{P_A^\circ - P_B^\circ} \tag{11.5}$$

Example 11.1

The vapour pressures of *n*-heptane and toluene at 373 K are 106 and 73.7 kN/m² respectively. What are the mole fractions of *n*-heptane in the vapour and in the liquid phase at 373 K if the total pressure is 101.3 kN/m²?

Solution

$$\text{At 373 K, } P_A^\circ = 106 \text{ kN/m}^2 \text{ and } P_B^\circ = 73.7 \text{ kN/m}^2$$

Thus, in equation 11.5:

$$x_A = (P - P_B^\circ)/(P_A^\circ P_B^\circ) = \frac{(101.3 - 73.7)}{(106 - 73.7)} = \underline{\underline{0.856}}$$

and, in equation 11.4:

$$y_A = P_B^\circ x_B / P = \frac{(106 \times 0.856)}{101.3} = \underline{\underline{0.896}}$$

Equilibrium data usually have to be determined by tedious laboratory methods. Proposals have been made which enable the complete diagram to be deduced with reasonable accuracy from a relatively small number of experimental values. Some of these methods are discussed by ROBINSON and GILLIAND⁽¹⁾ and by THORNTON and GARNER⁽²⁾.

One of the most widely used correlations of saturated vapour pressure is that proposed by ANTOINE⁽³⁾. This takes the form:

$$\ln P^\circ = k_1 - k_2/(T + k_3) \quad (11.6)$$

where the constants, k_1 , k_2 and k_3 must be determined experimentally^(4,5,6) although many values of these constants are available in the literature^(6,7,8,9,10). Equation 11.6 is valid only over limited ranges of both temperature and pressure, although the correlation interval may be extended by using the equation proposed by RIEDEL⁽¹¹⁾. This takes the form:

$$\ln P^\circ = k_4 - k_5/T + k_6 \ln T + k_7 T^6 \quad (11.7)$$

If only two values of the vapour pressure at temperatures T_1 and T_2 are known, then the Clapeyron equation may be used:

$$\ln P^\circ = k_8 - k_9/T \quad (11.8)$$

where: $k_8 = \ln P_1^\circ + k_9/T_1 \quad (11.9)$

and: $k_9 = \ln(P_2/P_1)/[(1/T_1) - (1/T_2)] \quad (11.10)$

Equation 11.8 may be used for the evaluation of vapour pressure over a small range of temperature, although large errors may be introduced over large temperature intervals. If the critical values of temperature and pressure are available along with one other vapour pressure point such as, for example, the normal boiling point, then a reduced form of the Riedel equation may be used; this takes the form:

$$\ln P_r^\circ = k_9 - k_{10}/T_r + k_{11} \ln T_r + k_{12} T_r^6 \quad (11.11)$$

where: P_r = reduced vapour pressure = (P°/P_c) , T_r = reduced temperature = (T/T_c) , $k_9 = -35c_1$, $k_{10} = -36c_1$, $k_{11} = 42c_1 + c_2$, $k_{12} = -c_1$ and $c_1 = 0.0838(3.758 - c_2)$. c_2 is determined by inserting the other known vapour pressure point into equation 11.11 and solving for c_2 . This gives:

$$c_2 = [(0.315c_5 - \ln P_{r1}^\circ)/(0.0838c_5 - \ln T_{r1})] \quad (11.12)$$

where: $c_5 = -35 + 36T_{r1} + 42 \ln T_{r1} - T_{r1}^6$.

Example 11.2

The following data have been reported for acetone by AMBROSE *et al.*⁽¹²⁾: $P_c = 4700 \text{ kN/m}^2$, $T_c = 508.1 \text{ K}$, $P_1^\circ = 100.666 \text{ kN/m}^2$ when $T_1 = 329.026 \text{ K}$. What is P° when $T = 350.874 \text{ K}$?

Solution

$T_{r1} = (329.026/508.1) = 0.64756$, $P_{r1} = (100.666/4700.0) = 0.021418$ and hence, in equation 11.12:

$$c_5 = -35 + (36/0.64756) + 42 \ln 0.64756 - (0.64756)^6 = 2.2687$$

and: $c_2 = [((0.315 \times 2.2687) - \ln 0.021418)/((0.0838 \times 2.2687) - \ln 0.64756)] = 7.2970$

$$c_1 = 0.0838(3.758 - 7.2970) = -0.29657$$

$$k_9 = -35(-0.29657) = 10.380$$

$$k_{10} = -36(-0.29657) = 10.677$$

$$k_{11} = 42(-0.29657) + 7.2970 = -5.1589$$

$$k_{12} = 1(10.29657) = 0.29657$$

Substituting these values into equation 11.11 together with a value of $T_r = (350.874/508.1) = 0.69056$, then:

$$\begin{aligned} \ln P_r^\circ &= 10.380 - (10.677/0.69056) - 5.1589 \ln 0.69056 + \\ &\quad 0.29657(0.69056)^6 = -3.1391 \end{aligned}$$

From which: $P_r^\circ = 0.043322$

and: $P^\circ = (0.043322 \times 4700.0) = \underline{\underline{203.61 \text{ kN/m}^2}}$

This may be compared with an experimental value of 201.571 kN/m^2 .

Example 11.3

The constants in the Antoine equation, Equation 11.6, are:

For benzene:	$k_1 = 6.90565$	$k_2 = 1211.033$	$k_3 = 220.79$
For toluene:	$k_1 = 6.95334$	$k_2 = 1343.943$	$k_3 = 219.377$

where P° is in mm Hg, T is in $^\circ\text{C}$ and \log_{10} is used instead of \log_e .

Determine the vapour phase composition of a mixture in equilibrium with a liquid mixture of 0.5 mole fraction benzene and 0.5 mole fraction of toluene at 338 K. Will the liquid vaporise at a pressure of 101.3 kN/m²?

Solution

The saturation vapour pressure of benzene at 338 K = 65°C is given by:

$$\log_{10} P_B^\circ = 6.90565 - [1211.033/(65 + 220.70)] = 2.668157$$

from which: $P_B^\circ = 465.75$ mm Hg or 62.10 kN/m²

Similarly for toluene at 338 K = 65°C:

$$\log_{10} P_T^\circ = 6.95334 - [1343.943/(65 + 219.377)] = 2.22742$$

and: $P_T^\circ = 168.82$ mm Hg or 22.5 kN/m²

The partial pressures in the mixture are:

$$P_B = (0.50 \times 62.10) = 31.05 \text{ kN/m}^2$$

and: $P_T = (0.50 \times 22.51) = 11.255 \text{ kN/m}^2$ – a total pressure of 42.305 kN/m²

Using equation 11.1, the composition of the vapour phase is:

$$y_B = (31.05/42.305) = \underline{\underline{0.734}}$$

and: $y_T = (11.255/42.305) = \underline{\underline{0.266}}$

Since the total pressure is only 42.305 kN/m², then with a total pressure of 101.3 kN/m², the liquid will not vaporise unless the pressure is decreased.

Example 11.4

What is the boiling point of a equimolar mixture of benzene and toluene at 101.3 kN/m²?

Solution

The saturation vapour pressures are calculated as a function of temperature using the Antoine equation, equation 11.6, and the constants given in Example 11.3, and then, from Raoult's Law, Equation 11.1, the actual vapour pressures are given by:

$$P_B = x_B P_B^\circ \text{ and } P_T = x_T P_T^\circ$$

It then remains, by a process of trial and error, to determine at which temperature: $(P_B + P_T) = 101.3 \text{ kN/m}^2$. The data, with pressures in kN/m², are:

$T(\text{K})$	P_B°	P_T°	P_B	P_T	$(P_B + P_T)$
373	180.006	74.152	90.003	37.076	127.079
353	100.988	38.815	50.494	77.631	128.125
363	136.087	54.213	68.044	27.106	95.150
365	144.125	57.810	72.062	28.905	100.967
365.1	144.534	57.996	72.267	28.998	101.265

101.265 kN/m² is essentially 101.3 kN/m² and hence, at this pressure, the boiling or the bubble point of the equimolar mixture is 365.1 K which lies between the boiling points of pure benzene, 353.3 K, and pure toluene, 383.8 K.

Example 11.5

What is the dew point of a equimolar mixture of benzene and toluene at 101.3 kN/m²?

Solution

From Raoult's Law, equations 11.1 and 11.2:

$$P_B = x_B P_B^0 = y_B P$$

and:

$$P_T = x_T P_T^0 = y_T P$$

Since the total pressure is 101.3 kN/m², $P_B = P_T = 50.65$ kN/m² and hence:

$$x_B = P_B/P_B^0 = 50.65/P_B^0 \text{ and } x_T = 50.65/P_T^0$$

It now remains to estimate the saturation vapour pressures as a function of temperature, using the data of Example 11.3, and then determine, by a process of trial and error, when $(x_B + x_T) = 1.0$. The data, with pressures in kN/m² are:

$T(\text{K})$	P_B^0	x_B	P_T^0	x_T	$(x_B + x_T)$
373.2	180.006	0.2813	74.152	0.6831	0.9644
371.2	170.451	0.2872	69.760	0.7261	1.0233
371.7	172.803	0.2931	70.838	0.7150	1.0081
371.9	173.751	0.2915	71.273	0.7107	1.0021
372.0	174.225	0.2907	71.491	0.7085	0.9992

As 0.9992 is near enough to 1.000, the dew point may be taken as 372.0 K.

11.2.3. Relative volatility

The relationship between the composition of the vapour y_A and of the liquid x_A in equilibrium may also be expressed in a way, which is particularly useful in distillation calculations. If the ratio of the partial pressure to the mole fraction in the liquid is defined as the volatility, then:

$$\text{Volatility of A} = \frac{P_A}{x_A} \text{ and volatility of B} = \frac{P_B}{x_B}$$

The ratio of these two volatilities is known as the relative volatility α given by:

$$\alpha = \frac{P_A x_B}{x_A P_B}$$