

From the enthalpy data and the reflux ratio, the upper pole point M may be located as shown in Figure 11.32. Points F and S' are located on the liquid line, and the position of the effective feed, such that  $F'S'/F'F = 10$ . NF' is joined and extended to cut  $x = x_w$  at M, the lower pole point.

MF is joined and extended to cut NS' at O, the immediate pole point. The number of stages required is then obtained from the figure and

13 theoretical stages are required.

## 11.6. BATCH DISTILLATION

### 11.6.1. The process

In the previous sections conditions have been considered in which there has been a continuous feed to the still and a continuous withdrawal of products from the top and bottom. In many instances processes are carried out in batches, and it is more convenient to distil each batch separately. In these cases the whole of a batch is run into the boiler of the still and, on heating, the vapour is passed into a fractionation column, as shown in Figure 11.33. As with continuous distillation, the composition of the top product depends on the still composition, the number of plates in the column and on the reflux ratio used. When the still is operating, since the top product will be relatively rich in the more volatile component, the liquid remaining in the still will become steadily weaker in this component. As a result, the purity of the top product will steadily fall. Thus, the still may be charged with  $S_1$  mols of a mixture containing a mole fraction  $x_{s1}$  of the more volatile component. Initially, with a reflux ratio  $R_1$ , the top product has a composition

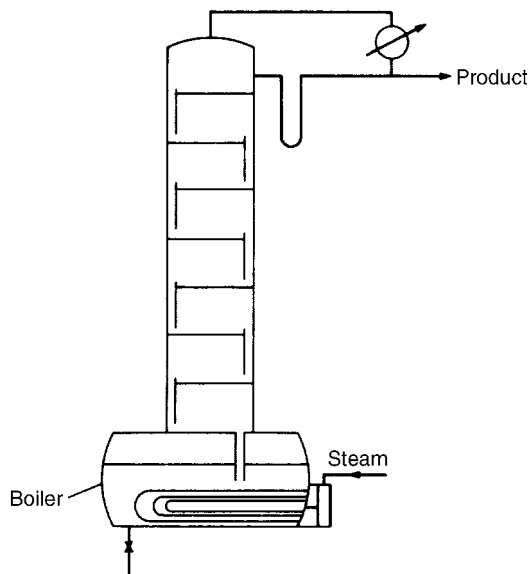


Figure 11.33. Column for batch distillation

$x_{d1}$ . If after a certain interval of time the composition of the top product starts to fall, then, if the reflux ratio is increased to a new value  $R_2$ , it will be possible to obtain the same composition at the top as before, although the composition in the still is weakened to  $x_{s2}$ . This method of operating a batch still requires a continuous increase in the reflux ratio to maintain a constant quality of the top product.

An alternative method of operation is to work with a constant reflux ratio and allow the composition of the top product to fall. For example, if a product of composition 0.9 with respect to the more volatile component is required, the composition initially obtained may be 0.95, and distillation is allowed to continue until the composition has fallen to some value below 0.9, say 0.82. The total product obtained will then have the required composition, provided the amounts of a given purity are correctly chosen.

One of the added merits of batch distillation is that more than one product may be obtained. Thus, a binary mixture of alcohol and water may be distilled to obtain initially a high quality alcohol. As the composition in the still weakens with respect to alcohol, a second product may be removed from the top with a reduced concentration of alcohol. In this way it is possible to obtain not only two different quality products, but also to reduce the alcohol in the still to a minimum value. This method of operation is particularly useful for handling small quantities of multi-component organic mixtures, since it is possible to obtain the different components at reasonable degrees of purity, in turn. To obtain the maximum recovery of a valuable component, the charge remaining in the still after the first distillation may be added to the next batch.

### 11.6.2. Operation at constant product composition

The case of a column with four ideal plates used to separate a mixture of ethyl alcohol and water may be considered. Initially there are  $S_1$  moles of liquor of mole fraction  $x_{s1}$  with respect to the more volatile component, alcohol, in the still. The top product is to contain a mole fraction  $x_d$ , and this necessitates a reflux ratio  $R_1$ . If the distillation is to be continued until there are  $S_2$  moles in the still, of mole fraction  $x_{s2}$ , then, for the same number of plates the reflux ratio will have been increased to  $R_2$ . If the amount of product obtained is  $D_b$  moles, then a material balance gives:

$$S_1 x_{s1} - S_2 x_{s2} = D_b x_d \quad (11.96)$$

and: 
$$S_1 - S_2 = D_b \quad (11.97)$$

Thus: 
$$S_1 x_{s1} - (S_1 - D_b) x_{s2} = D_b x_d$$

and: 
$$S_1 x_{s1} - S_1 x_{s2} = D_b x_d - D_b x_{s2}$$

and: 
$$D_b = S_1 \left[ \frac{x_{s1} - x_{s2}}{x_d - x_{s2}} \right] = \left( \frac{a}{b} \right) S_1 \quad (11.98)$$

where  $a$  and  $b$  are as shown in Figure 11.34. If  $\phi$  is the intercept on the  $Y$ -axis for any operating line, equation 11.48, then:

$$\frac{x_d}{R + 1} = \phi, \quad \text{or} \quad R = \frac{x_d}{\phi} - 1 \quad (11.99)$$

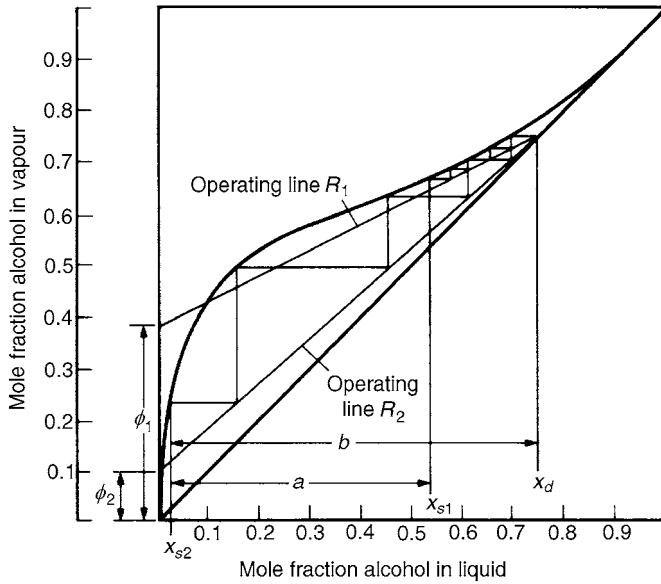


Figure 11.34. Graphical representation of batch distillation

These equations enable the final reflux ratio to be determined for any desired end concentration in the still, and they also give the total quantity of distillate obtained. What is important, in comparing the operation at constant reflux ratio with that at constant product composition, is the difference in the total amount of steam used in the distillation, for a given quantity of product,  $D_b$ .

If the reflux ratio  $R$  is assumed to be adjusted continuously to keep the top product at constant quality, then at any moment the reflux ratio is given by  $R = dL_b/dD_b$ . During the course of the distillation, the total reflux liquor flowing down the column is given by:

$$\int_0^{L_b} dL_b = \int_{R=R_1}^{R=R_2} R dD_b \quad (11.100)$$

To provide the reflux  $dL_b$  the removal of a quantity of heat equal to  $\lambda dL_b$  in the condenser is required, where  $\lambda$  is the latent heat per mole. Thus, the heat to be supplied in the boiler to provide this reflux during the total distillation  $Q_R$  is given by:

$$Q_R = \lambda \int_0^{L_b} dL_b = \lambda \int_{R=R_1}^{R=R_2} R dD_b \quad (11.101)$$

This equation may be integrated graphically if the relation between  $R$  and  $D_b$  is known. For any desired value of  $R$ ,  $x_s$  may be obtained by drawing the operating line, and marking off the steps corresponding to the given number of stages. The amount of product  $D_b$  is then obtained from equation 11.88 and, if the corresponding values of  $R$  and  $D_b$  are plotted, graphical integration will give the value of  $\int R dD_b$ .

The minimum reflux ratio  $R_m$  may be found for any given still concentration  $x_s$  from equation 11.56.

### 11.6.3. Operation at constant reflux ratio

If the same column is operated at a constant reflux ratio  $R$ , the concentration of the more volatile component in the top product will continuously fall. Over a small interval of time  $dt$ , the top-product composition with respect to the more volatile component will change from  $x_d$  to  $x_d + dx_d$ , where  $dx_d$  is negative for the more volatile component. If in this time the amount of product obtained is  $dD_b$ , then a material balance on the more volatile component gives:

$$\text{More volatile component removed in product} = dD_b \left[ x_d + \frac{dx_d}{2} \right]$$

$$\text{which, neglecting second-order terms, gives:} = x_d dD_b \quad (11.102)$$

$$\text{and:} \quad x_d dD_b = -d(Sx_s)$$

$$\text{But } dD_b = -dS,$$

$$\text{and hence:} \quad -x_d dS = -S dx_s - x_s dS$$

$$\text{and:} \quad S dx_s = dS(x_d - x_s)$$

$$\begin{aligned} \text{Thus:} \quad \int_{S_1}^{S_2} \frac{dS}{S} &= \int_{x_{s1}}^{x_{s2}} \frac{dx_s}{x_d - x_s} \\ \ln \frac{S_1}{S_2} &= \int_{x_{s2}}^{x_{s1}} \frac{dx_s}{x_d - x_s} \end{aligned} \quad (11.103)$$

The right-hand side of this equation may be integrated by plotting  $1/(x_d - x_s)$  against  $x_s$ . This enables the ratio of the initial to final quantity in the still to be found for any desired change in  $x_s$ , and hence the amount of distillate  $D_b$ . The heat to be supplied to provide the reflux is  $Q_R = \lambda R D_b$  and hence the reboil heat required per mole of product may be compared with that from the first method.

### Example 11.12

A mixture of ethyl alcohol and water with 0.55 mole fraction of alcohol is distilled to give a top product of 0.75 mole fraction of alcohol. The column has four ideal plates and the distillation is stopped when the reflux ratio has to be increased beyond 4.0.

What is the amount of distillate obtained, and the heat required per kmol of product?

### Solution

For various values of  $R$  the corresponding values of the intercept  $\phi$  and the concentration in the still  $x_s$  are calculated. Values of  $x_s$  are found as shown in Figure 11.35 for the two values of  $R$  of 0.85 and 4. The amount of product is then found from equation 11.98. Thus, for  $R = 4$ :

$$D_b = 100 \left[ \frac{0.55 - 0.05}{0.75 - 0.05} \right] = 100 \left( \frac{0.5}{0.7} \right) = \underline{\underline{71.4 \text{ kmol}}}$$

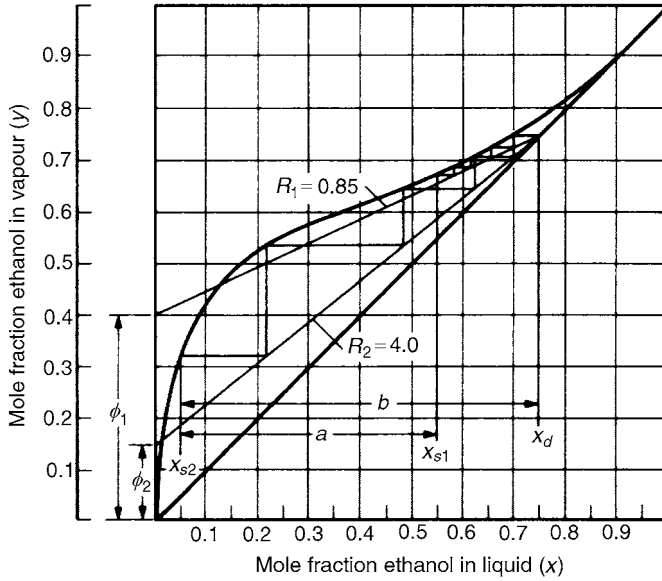


Figure 11.35. Batch distillation—constant product composition

Values of  $D_b$  found in this way are:

$R$	$\phi$	$x_s$	$D_b$
0.85	0.405	0.55	0
1.0	0.375	0.50	20.0
1.5	0.3	0.37	47.4
2.0	0.25	0.20	63.8
3.0	0.187	0.075	70.5
4.0	0.15	0.05	71.4

The relation between  $D_b$  and  $R$  is shown in Figure 11.36 and the  $\int_{R=0.85}^{R=4.0} R dD_b$  is given by area OABC as 96 kmol.

Assuming an average latent heat for the alcohol–water mixtures of 4000 kJ/kmol, the heat to be supplied to provide the reflux,  $Q_R$  is  $(96 \times 4000)/1000$  or approximately 380 MJ.

The heat to be supplied to provide the reflux per kmol of product is then  $(380/71.4) = 5.32$  MJ and the total heat is  $(5.32 + 4.0) = \underline{\underline{9.32}}$  MJ/kmol product.

### Example 11.13

If the same batch as in Example 11.12 is distilled with a constant reflux ratio of  $R = 2.1$ , what will be the heat required and the average composition of the distillate if the distillation is stopped when the composition in the still has fallen to 0.105 mole fraction of ethanol?

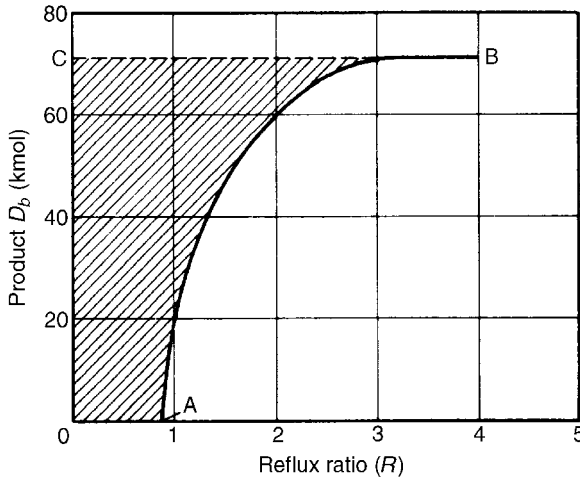


Figure 11.36. Graphical integration for Example 11.12

**Solution**

The initial composition of the top product will be 0.78, as shown in Figure 11.37, and the final composition will be 0.74. Values of  $x_d$ ,  $x_s$ ,  $x_d - x_s$  and of  $1/(x_d - x_s)$  for various values of  $x_s$  and a constant reflux ratio are:

$x_s$	$x_d$	$x_d - x_s$	$1/(x_d - x_s)$
0.550	0.780	0.230	4.35
0.500	0.775	0.275	3.65
0.425	0.770	0.345	2.90
0.310	0.760	0.450	2.22
0.225	0.750	0.525	1.91
0.105	0.740	0.635	1.58

Values of  $x_s$  and  $1/(x_d - x_s)$  are plotted in Figure 11.38 from which  $\int_{0.105}^{0.55} (dx_s/(x_d - x_s)) = 1.1$ .

From equation 11.103:  $\ln(S_1/S_2) = 1.1$  and  $(S_1/S_2) = 3.0$ .

Product obtained,  $D_b = S_1 - S_2 = (100 - 100/3) = 66.7$  kmol.

Amount of ethanol in product =  $x_1S_1 - x_2S_2$   
 $= (0.55 \times 100) - (0.105 \times 33.3) = 51.5$  kmol

Thus: average composition of product =  $(51.5/66.7) = \underline{\underline{0.77}}$  mole fraction ethanol.

The heat required to provide the reflux =  $(4000 \times 2.1 \times 66.7) = 560,380$  kJ.

Heat required to provide reflux per kmol of product =  $(560,380/66.7) = \underline{\underline{8400}}$  kJ.

Thus in Example 11.12 the total heat required per kmol of product is  $(5320 + 4000) = 9320$  kJ and at constant reflux ratio (Example 11.13) it is  $(8400 + 4000) = 12,400$  kJ, although the average quality of product is 0.77 for the second case and only 0.75 for the first.

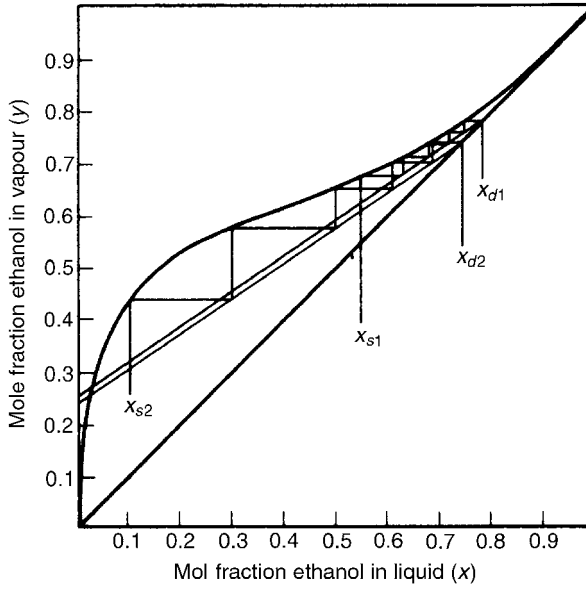


Figure 11.37. Batch distillation—constant reflux ratio (Example 11.13)

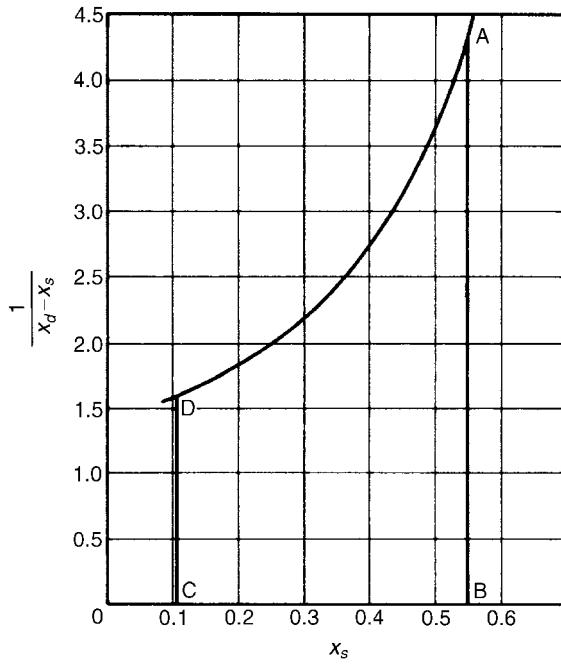


Figure 11.38. Graphical integration for Example 11.13

### 11.6.4. Batch or continuous distillation

A discussion on the relative merits of batch and continuous distillation is given by ELLIS<sup>(36)</sup>, who shows that when a large number of plates is used and the reflux ratio approaches the minimum value, then continuous distillation has the lowest reflux requirement and hence operating costs. If a smaller number of plates is used and high purity product is not required, then batch distillation is probably more attractive.

## 11.7. MULTICOMPONENT MIXTURES

### 11.7.1. Equilibrium data

For a binary mixture under constant pressure conditions the vapour–liquid equilibrium curve for either component is unique so that, if the concentration of either component is known in the liquid phase, the compositions of the liquid and of the vapour are fixed. It is on the basis of this single equilibrium curve that the McCabe–Thiele method was developed for the rapid determination of the number of theoretical plates required for a given separation. With a ternary system the conditions of equilibrium are more complex, for at constant pressure the mole fraction of two of the components in the liquid phase must be given before the composition of the vapour in equilibrium can be determined, even for an ideal system. Thus, the mole fraction  $y_A$  in the vapour depends not only on  $x_A$  in the liquid, but also on the relative proportions of the other two components.

Determining the equilibrium relationships for a multicomponent mixture experimentally requires a considerable quantity of data, and one of two methods of simplification is usually adopted. For many systems, particularly those consisting of chemically similar substances, the relative volatilities of the components remain constant over a wide range of temperature and composition. This is illustrated in Table 11.2 for mixtures of phenol, ortho and meta-cresols, and xyenols, where the volatilities are shown relative to ortho-cresol.

Table 11.2. Volatilities relative to *o*-cresol

	Temperature (K)		
	353	393	453
phenol	1.25	1.25	1.25
<i>o</i> -cresol	1	1	1
<i>m</i> -cresol	0.57	0.62	0.70
xylenols	0.30	0.38	0.42

An alternative method, particularly useful for the separation of multicomponent mixtures of hydrocarbons, is to use the simple relation  $y_A = Kx_A$ .  $K$  values have been measured for a wide range of hydrocarbons at various pressures, and some values are shown in Figure 11.39.

Some progress has been made in presenting methods for calculating ternary data from known data for the binary mixtures, though as yet no entirely satisfactory method is available.