25

DISTILLATION

Keywords: Phase Equilibrium, Isothermal Flash, Adiabatic Flash, Batch Distillation

Distillation refers to the physical separation of a mixture into two or more fractions that have different boiling points. The general objective is to separate substances having different vapor pressures at any given temperature. If a liquid mixture of two volatile materials is heated, the vapor that comes out with a higher concentration of the lower boiling material than the liquid from which it was evolved. Conversely, if a warm vapor is cooled, the higher boiling material has a tendency to condense in a greater proportion than the lower boiling material. The early distillers of alcohol for beverages applied these fundamental ideas.

A distillation column consists of a series of plates (or trays). In normal operation, there is a certain amount of liquid on each plate, and some arrangement is made for ascending vapors to pass through the liquid and make contact with it. The descending liquid flows down from the plate above through a downcomer, across the next plate, and then over a weir and into another downcomer to the next lower plate as shown in fig 1. Earlier on, bubble caps were used on the trays for the purpose of vapor and liquid contacting. Recent developments include the use of sieve tarys, valve trays, perforated or ballast trays.

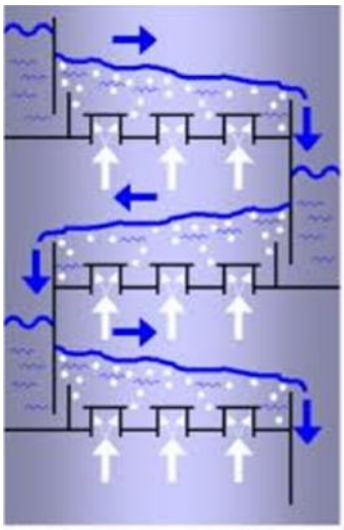

Fig. 25.1: Section of Distillation Column

Distillation columns can be as high as 200ft. Diameters as large as 44ft have been used; operates at a pressure ranging from 15mm to 500psia. As indicated in fig 25.2, the overhead vapor V_1 , upon leaving the top plate enters the condenser where it is either partially or totally condensed. The liquid formed is collected in an accumulator from which the liquid stream L_0 (reflux) and the top product stream D (distillate) are withdrawn. When the overhead vapor, V_1 is totally condensed to the liquid state to produce L_0 and D is withdrawn as a liquid, the condenser is called **total condenser**. If V_1 is partially condensed to the liquid state to produce L_0 and D is withdrawn as a vapor, the condenser is **called partial condenser**. The amount of reflux is generally expressed in terms of reflux ratio, L_0/D. The liquid that leaves the bottom plate of the column enters the reboiler, where it is partially vaporized. The vapor produced is allowed to flow back up through the column, and the liquid is withdrawn from the reboiler known as bottom product, B.

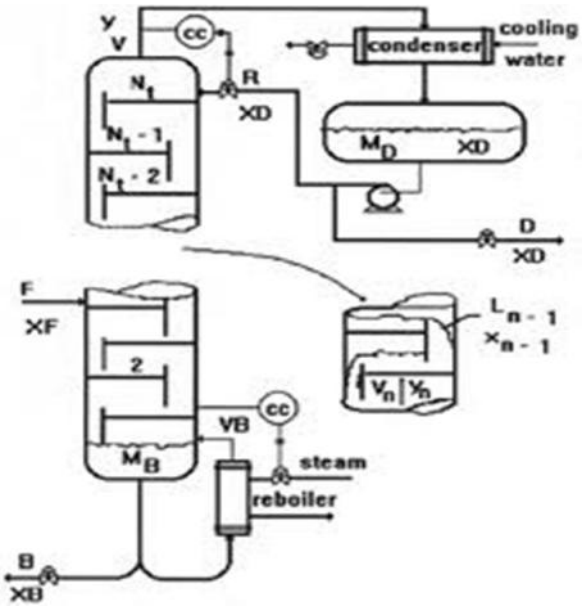

Fig. 25.2: Continuous Distillation Column

Fundamental Principles involved in distillation

In order to compute top product, D and bottom product, B ; it is necessary to obtain a solution of equilibrium relationships, component material balances, total material balances and energy balances respectively.

Consider first equilibrium relationships.

Physical equilibrium

A two phase multicomponent mixture is said to be in equilibrium if

- The temperature T^v of the vapor phase is equal to T^l of the liquid phase.
- The total pressure P^v throughout the vapor phase is equal to the total pressure P^l throughout the liquid phase.
- The tendency of each component to escape from the liquid phase to the vapor phase is exactly equal to its tendency to escape from the vapor phase to the liquid phase.

In the following analysis it is assumed that $T^v = T^l = T$, $P^v = P^l = P$ and the escaping tendencies are equal. A special case of the third condition for equilibrium is represented by Raoult's law.

$$P\, y_i = P_i\, x_i \qquad \ldots 25.1$$

Where x_i and y_i are liquid and vapor mole fractions of component i at temperature T of the system.

The separation of a binary mixture is represented by a 2D space. The graphical method by McCabe and Thiele for solution of problems involving binary mixtures is shown in subsequent section. This method makes use of an equilibrium curve that may be obtained from the "boiling point diagram"(BPD).

Construction and interpretation of BPD for binary mixtures

For a binary system having components A and B; the equilibrium relationships are given as follows : $P\, y_A = P_A\, x_A$, $P\, y_B = P_A\, x_B$, $y_A + y_B = 1$, $x_A + x_B = 1$. …25.2

Following Gibbs phase rule , the degree of freedom for the above set of equations (2),is 2 and thus two variables must be fixed in order to get the solution of the equation (2). For construction of BPD , the total pressure P must be fixed and a solution is obtained for each of several temperatures lying between the temperatures at which the respective vapor pressures P_A and P_B are equal to the total pressure P. The solution of eqation (3.2) for x_A in terms of P_A and P_B and P is effected as follows $P = P_A x_A + P_B x_B$ …25.3

$$\text{Or, } x_A = (P-P_B)/(P_A - P_B) \qquad \ldots 25.4$$

From the definition of a mole fraction , equation (4) has a meaningful solution at a given P for any T lying between the boiling point temperatures T_A and T_B of pure A and pure B. Using the first expression of equation (2) y_A can also be calculated. By plotting T vs x_A and T vs y_A we get the lower and upper curves respectively , fig 1.3 are typical of those obtained when when component A is more volatile than B. If for the close interval $T_A \leq T \leq T_B$, $P_A > P_B$, the parallel lines such as CE that join the equilibrium pairs (x,y) , computed at a given values of T and P by the earlier quations is called **Tie lines**.

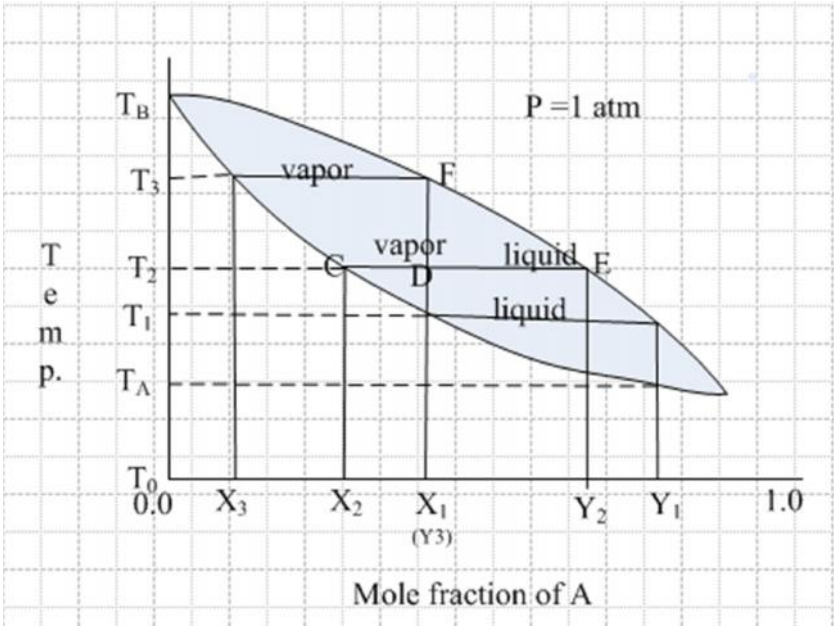

Fig. 25.3: The boiling point Diagram

Determination of bubble point and dew point temperatures of multi-component mixtures (BPT, DPT)

The state of equilibrium for a two phase system is described by the following equations in which any number of components 'c' are distributed between the two phases

$$y_i = K_i x_i \ , \quad \sum_{i=1}^{c} y_i = 1 \ , \ \sum_{i=1}^{c} x_i = 1 \text{ where } (1 \leq i \leq c) \qquad \ldots 25.5$$

where K_i is ratio of the fugacities of i^{th} component at liquid to vapor phases respectively for an ideal solution. From this equation it is evident that number of equations is 'c+2' and number of variables is '2c+2'. Thus, to obtain a solution to these equations , 'c' variables must be fixed.

When the first expression of Eq(25.5) is summed over for all components , we get

$$1= \sum_{i=1}^{c} K_i x_i \qquad \ldots 25.6$$

where K_i is an implicit function of temperature. The solution of the last equation is achieved by Newton's method . In this method ,the Eq (25.6) is restated as shown

$$f(T) = \sum_{i=1}^{c} K_i x_i - 1.$$

The value of T at which $f(T) = 0$, is the bubble point. In this iterative scheme we need to find the first derivative of $f(T)$ and further follow the iterative form

$T_{n+1} = T_n - f(T_n)/f'(T_n)$. where T_n is the assumed value for the first stage of the iteration and T_{n+1} is the modified value after the iteration. The process goes on as long as the values of T are not within a convergence criteria.

When the y_i's and P are fixed rather than x_i's and P, the solution temperature of the Eq (25.5) will give the DBT. Here , just like previous case the governing equation is

$$F(T)= \sum_{i=1}^{c} y_i/K_i - 1.$$

K_b's method of calculating DBT AND BPT

Robinson and Gilliland pointed out that if the relative values of the K_i's are independent of temperature, the Eq (25.5) may be rearranged so that the iterative methods used in previous case may be avoided. Ratio K_i/K_b is called the relative volatility , α_i of component 'i' with respect to component 'b'; where the K values are calculated at same temperature and pressure.

For calculation of BPT, Eq(25.5) is rewritten as

$$y_i= (K_i/K_b)\, K_b\, x_i = \alpha_i K_b x_i \qquad \ldots 25.7$$

Taking summation on both sides , we get on rearranging

$$K_b=1/(\sum_{i=1}^{c} K_i \alpha_i) \qquad \ldots 25.8$$

Since α_i's are independent of temperature , they maybe computed by K_i & K_b evaluated at any arbitrary T and at specified pressure. After K_b has been calculated using eq(25.8) , the

BPT can be found from the known relation between K_b and T. The same procedure is obtained for calculation of DPT.

Separation of Multicomponent Mixtures by use of a Single Equilibrium Stage

Each of the separation processes considered here are special cases of the general separation problem in which a multi-component mixture is to be separated into two or more parts through the use of any number of equilibrium stages.

Flash calculations

The boiling point diagram is useful for visualizing the necessary conditions required for a flash to occur. Suppose the feed to be flashed has the composition x_i , and further suppose that this liquid must be at the temperature T_0 and pressure , P = 1atm, is to be flashed by raising the temperature to the specified flash temperature $T_F = T_2$ at specified flash pressure, P = 1atm . It is observed that the BPT of the feed T_{BPT} = at P = 1atm is T_1. The DPT, T_{DPT} of the feed at the pressure 1 atm is T_3. Then a necessary condition for a flash to occur at the specified pressure is that ; $T_{BPT} < T_F < T_{DPT}$

In practice, the flash process is generally carried out by reducing the pressure on the feed stream rather than heating the feed at constant pressure. To determine whether or not the feed will flash at a given T_F & P, the following two conditions must be satisfied:

1. $f(T_F) > 0$, $F(T_F) > 0$ …25.9

2. $f(T_F) = \sum_{i=1}^{c} K_{Fi} X_i - 1$, $F(T_F) = \sum_{i=1}^{c} X_i / K_{Fi} - 1$ …25.10

There are two types of flash calculations : isothermal flash and adiabatic flash.

Isothermal Flash

In isothermal flash the following specifications are made; T_F, P, $\{X_i\}$ and F. We have to find the unknowns V_F, L_F, $\{y_{Fi}\}$ and $\{x_{Fi}\}$. The following equations are needed:

Equilibrium relations : $y_{Fi} = K_{Fi} x_{Fi}$, , $\sum_{i=1}^{c} y_{Fi} = 1$, $\sum_{i=1}^{c} x_{Fi} = 1$ where $(1 \leq i \leq c)$ …25.11

Material balances: $Fx_i = V_F y_{Fi} + L_F x_{Fi}$.

Eq(25.10) is seen to represent 2c+2 equations in 2c+2 unknowns. This system of non-linear equations is readily reduced to one equation in one unknown (say V_F) in the following manner. First observe that the total material balance expression may be obtained by summing each member of the last expression of Eq(25.9) over all components to give ,

$$F\sum_{i=1}^{c} X_I = V_F \sum_{i=1}^{c} y_{Fi} + L_F \sum_{i=1}^{c} x_{Fi} \quad \text{or} \quad F = V_F + L_F \qquad \ldots 25.12$$

Elimination of y_{Fi}'s from the last expression of Eq(25.9) by use of the first expression , followed by rearrangement gives :

$$x_{Fi} = X_i / (L_F/F + V_F K_{FV}/F) \qquad \ldots 25.13$$

Elimination of L_F from Eq(25.11) by eq(25.10) yields

$$x_{Fi} = X_i / (1- \psi(1- K_{Fi})) \qquad \ldots 25.14$$

where $\psi = V_F/F$.

when each member of Eq(25.12) is summed over all components and the result so obtained is restated in functional notation , one obtains

$$P(\psi) = \sum_{i=1}^{c} X_i/(1- \psi(1- K_{Fi})) - 1 \qquad \ldots 25.15$$

$$\text{And } P'(\psi) = \sum_{i=1}^{c} X_i(1- K_{Fi})/(1- \psi(1- K_{Fi}))^2 \qquad \ldots 25.16$$

$$h = -P(\psi)/P'(\psi)$$

$$P^{k+1}(\psi) = P^k(\psi) + h$$

The specification of T_F implies that the feed either posses precisely the correct amount of energy for the flash to account at T_F at specified P or , that, energy is to be added or withdrawn at the flash drum.

Enthalpy balance:

$$FH= V_F H_F + L_F h_F \qquad \ldots 25.17$$

$$H_F = \sum_{i=1}^{c} H_{Fi}\, y_{Fi} , \quad h_F = \sum_{i=1}^{c} h_{Fi}\, X_{Fi} \qquad \ldots 25.18$$

Adiabatic Flash

The term adiabatic flash is used to describe the problem wherein the following specifications are made; P,Q = 0 (no heat is added at flash drum) , H, $\{X_i\}$, F. In this case there are 2c+3 unknowns [T_F, V_F,L_F,$\{y_{Fi}\}$,$\{x_{Fi}\}$] and 2c+3 independent equations.

Equilibrium relations, material balances and energy balances are same as in previous case. To solve this problem using N-R method, it is essential that number of independent functions to be equal to number of independent variables.

$f_1 = K_{F1}x_{F1} - y_{F1}$

$f_2 = K_{F2}x_{F2} - y_{F2}$

.....

$f_c = K_{Fc}x_{Fc} - y_{Fc}$

$f_{c+1} = \sum_{i=1}^{c} y_{Fi} - 1$

$f_{c+2} = \sum_{i=1}^{c} x_{Fi} - 1$

$f_{c+3} = V_F y_{F1} + L_F x_{F1} - F X_1$

$f_{c+4} = V_F y_{F2} + L_F x_{F2} - F X_2$

.....

$f_{2c+2} = V_F y_{Fc} + L_F x_{Fc} - F X_c$

$f_{2c+3} = V_F H_F + L_F h_F - FH$

The application of the N-R method to this set of equations may be represented by the following matrix equation : $J\Delta x = -f$

The jacobian matrix ,J and the column vectors Δx are defined as follows:

$$J = \begin{bmatrix} \frac{\partial f1}{\partial yf1} & \cdots & \frac{\partial f1}{\partial yfc} & \frac{\partial f1}{\partial xf1} & \cdots & \frac{\partial f1}{\partial xfc} & \frac{\partial f1}{\partial VF} & \frac{\partial f1}{\partial LF} & \frac{\partial f1}{\partial TF} \\ \vdots & & \ddots & & & & \vdots & & \\ \frac{\partial f2c+3}{\partial yf1} & \cdots & \frac{\partial f2c+3}{\partial yfc} & \frac{\partial f2c+3}{\partial xf1} & \cdots & \frac{\partial f2c+3}{\partial xfc} & \frac{\partial f2c+3}{\partial VF} & \frac{\partial f2c+3}{\partial LF} & \frac{\partial f2c+3}{\partial TF} \end{bmatrix}$$

$\Delta x = [\Delta y_{F1} \ldots. \Delta y_{Fc} \ \Delta x_{F1} \ldots. \Delta x_{Fc} \ \Delta V_F \ \Delta L_F \ \Delta T_F]^T$

$f = [f_1\ f_2\ .....f_c\ \ f_{c+1}\ .....f_{2c}\ f_{2c+1}\ ..\ f_{2c+3}]^T$

where each element of Δx is equal to the newly predicted values of the variable minus the assumed value; for example , $\Delta y_{F1} = y_{F1,n+1} - y_{F1,n}$. To initiate the calculations , a complete set of values for the variables must be assumed; say ($y_{F1,n}$ …. $y_{Fc,n}$ $x_{F1,n}$ ….$x_{Fc,n}$ $V_{F,n}$ $L_{F,n}$ $T_{F,n}$).

Alternative process for adiabatic flash:

When the pressure of a liquid stream of known composition , flowrate, and temperature is reduced adiabatically across a value an adiabatic flash calculation is made to determine the resulting temperature, compositions and flowrates of equilibrium liquid and vapor streams for a specified pressure downstream of the value. For an adiabatic flash , the isothermal flash calculation procedure can be applied in the iterative way. A guess is made of the flash temperature T_v . Then φ ,V, x,y and L are determined as for an isothermal flash. The guessed value of T_v (equal to T_l) is next checked by an energy balance with Q=0 to give

$$F(T_v) = (\varphi\ h_v + (1- \varphi)\ h_l - h_f) /1000 = 0 \qquad \ldots 25.19$$

Where the division by 1000 is done in order to convert the terms in the order of 1. If the computed value of $F(T_v)$ is not zero, the entire procedure is repeated for two or more T_v. The procedure is tedious as it involves inner loop iteration on φ and outer loop iteration of T_v. outer loop iteration is successful when equation $f(\varphi)= 0=\sum_{i=1}^{c}(z_i)(1 - Ki)/(1+ \varphi(K_i - 1))$

Where $\varphi = \frac{V}{F}$, K_i is a function of $\{T_v,P_v\}$ and $V= \varphi F$

For the closed boiling mixers, the above algorithm dose not work well due to extreme sensitivity T_s in the inner loop. The above problem can be remove by first assume T_v and iterated for external loop and inside loop be iterated for φ.

$$F(T_v) = \sum_{i=1}^{c}(z_i)(1 - Ki)/(1+ \varphi(K_i -1)) \qquad \ldots 25.20$$

Then compute x & y from the following equations:-

$$X_i = z_i/ (1+ \varphi(K_v-1))$$

$$Y_i = z_ik_i/ (1+ \varphi(K_v-1))=x_ik_i$$

Eq(1) is solved directly for φ , from which $\varphi= (h_f - h_l)/ (h_v - h_l)$ …25.21

If φ from Eq(25.21) is not equal to assumed φ then solve Eq(25.20) , the new value of φ is to repeat the outer loop starting with Eq(25.20).

Rachford-Rice Procedure for isothermal flash calculations when K-values are independent of composition follows the algorithm as stated belo

Step 1. Specify variables F, T_F, P_F, X_1,X_2, …,X_c, T_v , P_v

Step 2. $T_L = T_V$, $P_L = P_V$

Step 3. Solve f{ φ } = $\sum_{i=1}^{c}$(Xi)(1 − Ki)/(1+ φ(K_i -1)), Where $\varphi = \frac{V}{F}$, K_i is a function of {T_v,P_v} and V= φF

Step 4. $X_i = z_i/ (1+ \varphi(K_v-1))$, $Y_i = z_ik_i/ (1+ \varphi(K_v-1))=x_ik_i$

Step 5. L= F – V

Step 6. $Q= h_vV + h_LL – h_F F$ is set to 0

Using step 5, and further simplifying , we get $\varphi h_v + (1- \varphi)h_L – h_F = 0$

We may use softwares like Chemcad design II, PRO/II, ASPEN PLUS to solve these equations.