



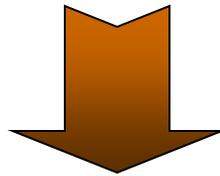
**UNIT OPERATIONS (CHE 347/ 251)**  
**DISTILLATION**

**FACULTY OF CHEMICAL ENGINEERING**  
**UiTM PULAU PINANG**



## OBJECTIVE

- i. To **understand** fundamental concepts of distillation that underlie unit operations processes.

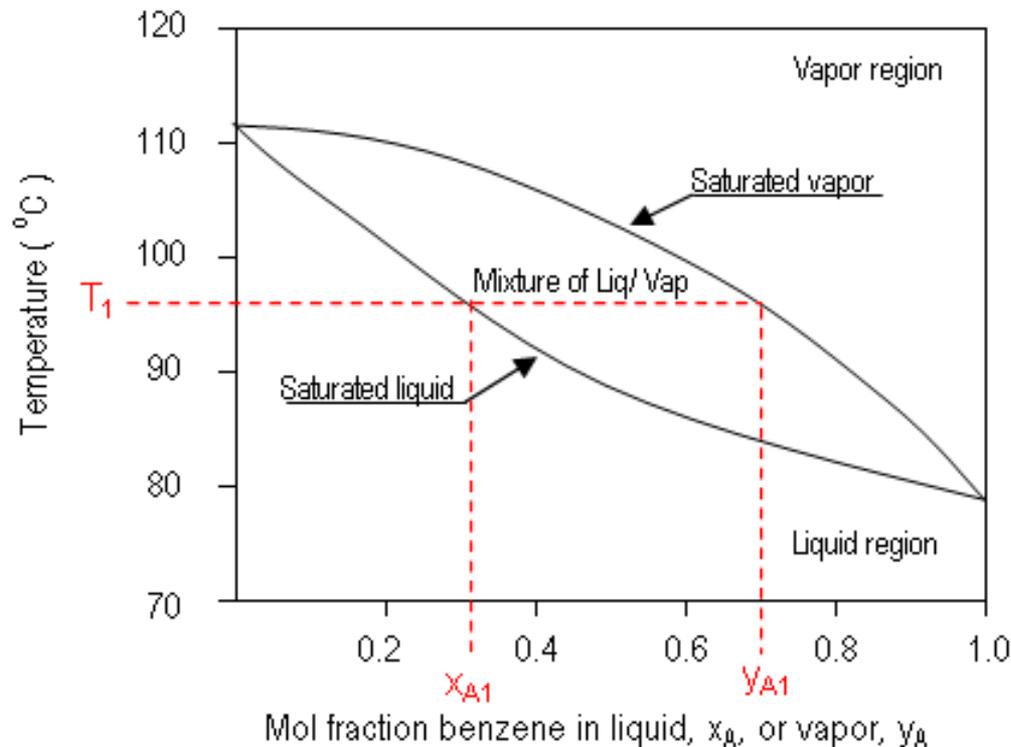


## LEARNING OUTCOMES

- i. **Acquire** fundamental concepts of VLE & distillation.
- ii. Ability to **identify, formulate** and **solve** engineering problems

# 1. VAPOR-LIQUID EQUILIBRIUM (VLE)

- Fundamentally govern by evaporation and condensation process.
  - Open system
  - Closed system
- Factor derived by volatility of component (  $\alpha$  )



$$x_A + x_B = 1 ; y_A + y_B = 1$$

$$P_T = p_A + p_B$$

Raoult's law:-

$$p_A = x_A P_A^0$$

Where:

$p_A$  = partial pressure of A in vapor phase

$x_A$  = mol fraction of A in liquid phase

$P_A^0$  = vapor pressure of pure A at certain Temp

**Figure 1: Boiling point diagram for benzene (A) – toluene (B) at 101.3 kPa (1 atm) total pressure**

# 1.1 VLE COMPOSITIN FOR BINARY MIXTURE

## 1.1.1 Raoult's law

$$p_A = x_A P_A^0$$

Where:

$p_A$  = partial pressure of A in vapor phase

$x_A$  = mol fraction of A in liquid phase

$P_A^0$  = vapor pressure of pure A at certain Temp

## 1.1.2 Dalton's law

$$p_A = y_A P_T \quad ; \quad P_T = p_A + p_B$$

Where:

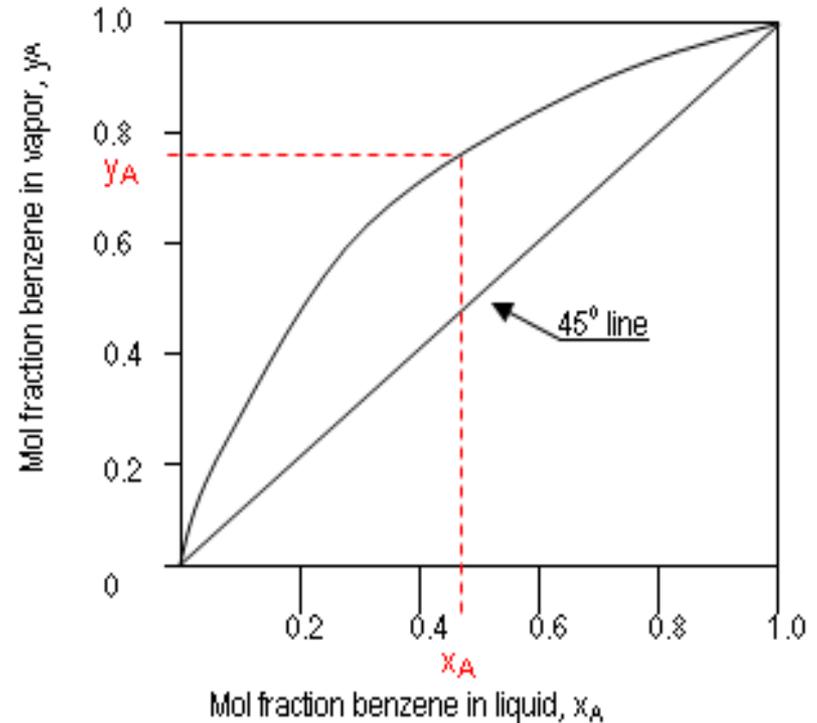
$y_A$  = mol fraction of A in liquid phase

$P_T$  = total pressure of the system

$p_{A/B}$  = partial pressure of A/B in vapor phase

by manipulating above equations,  
composition of each component can be obtain as follows:

$$x_A = \frac{(P_T - P_B^0)}{(P_A^0 - P_B^0)} \quad \dots\dots\dots (1) \quad ; \quad y_A = \frac{x_A P_A^0}{P_T} \quad \dots\dots\dots (2)$$



**Figure 2: Equilibrium diagram for benzene (A) - toluene (B) at 101.3 kPa (1atm) total pressure**

## 1.2 RELATIVE VOLATILITY OF MIXTURE

- Separations of components for distillation process depend on the differences in volatilities of that leads to solution to be distilled.
- $\alpha \uparrow$  : **good separation**; while  $\alpha \downarrow$  : **poor separation**
- Relative volatility of A to B ( $\alpha_{AB}$ ) – indication of how much A volatile than B

$$\alpha_{AB} = \frac{y_A / x_A}{y_B / x_B} = \frac{y_A x_B}{y_B x_A} \dots\dots\dots(3)$$

- Note:
  - $\alpha_{AB}$  (*ideal solution*) = constant vs temp.
  - $\alpha_{AB}$  (*non-ideal solution*) = varies vs temp.

## Exercise 1

A liquid mixture is formed by mixing n-heptane (A) & n-octane (B) in a closed container at constant pressure of 1 atm (101.3kPa).

- i. Calculate the equilibrium compositions of vapor & liquid
- ii. Plot a boiling point diagram for the system
- iii. Plot an equilibrium curve for the system
- iv. Calculate the  $\alpha_{AB}$
- v. What is the condition of the mixture?

Use the following list if vapor pressure for pure n-heptane & n-octane at various temperature.

T (K)	Vapor pressure (kPa) of pure component	
	n-heptane	n-octane
371.6	101.3	-
374.0	110.8	56.9
377.0	122.6	62.3
380.0	134.4	67.6
383.0	146.2	73
386.0	158	78.4
389.0	169.8	83.8
392.0	181.6	89.1
395.0	193.5	94.5
398.8	-	101.3

**(ANSWER)**

## 1.3 DISTILLATION

- Is known as a method for separating various components of a liquid solution which depends upon the distribution of these components between a vapor phase and a liquid phase.
- Classified into 2 main methods in practice i.e:-
  1. Involves the production of a vapor by boiling the liquid mixture to be separated in a single stage and condensing the vapors. No liquid is allowed to return to the single-stage still to contact the rising vapors.



**i.e. : FLASH; SIMPLE BATCH; SIMPLE STEAM DISTILLATIONS**

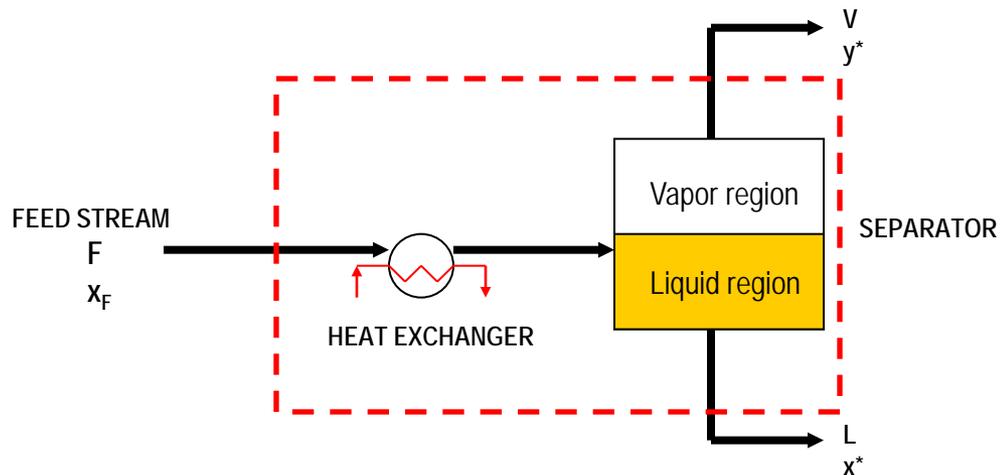
2. Involves the returning of a portion of the condensate to the still. The vapor rise through a series of stages/ trays , and part of the condensate flow downward through the series of stages/ trays countercurrent to the vapors.



**i.e. : FRACTIONAL/ CONTINUOUS DISTILLATION; RECTIFICATION**

## 1.3.1 FLASH/ EQUILIBRIUM DISTILLATION

- Occurs in single stage , where a liquid mixture is partially vaporized.
- The vapor is allowed to come to equilibrium with the liquid , and then the vapor and liquid phases are separated.
- It can be done either by batch or continuous.



Where;

$F$  = feed (mol/h)

$x_F$  = initial mol fraction of A in feed

$V$  = equilibrium vapor (mol/h)

$y^*$  = equilibrium mol fraction of A in the vapor

$L$  = equilibrium residual liquid (mol/h)

$x^*$  = equilibrium mol fraction of A in the residual liquid

— = diagram's boundary

Figure 3: Schematic diagram of flash/ equilibrium distillation.

# 1.3.1.1 PREDICTION OF AN EQUILIBRIUM COMPOSITION FOR BINARY MIXTURE

- Consider a binary mixture to be separated by a flash distillation as shown in Fig. 3.
- When the system has attained its equilibrium, the material balance for the diagram's boundary can be written as:-

Overall mass balance :  $F = V + L$

Mass balance on more volatile comp. i.e A :  $Fx_F = Vy^* + Lx^*$

$$x_F = y^* \frac{V}{F} + x^* \frac{L}{F} \quad \dots\dots(4)$$

Remarks: \* denote at the state of equilibrium

Assumption: f denote to the fraction of feed which has been vaporized where  $f = V/F$

Substitute f into overall m/balance :  $1 = V/F + L/F$

$$\therefore L/F = 1 - f \quad \dots\dots(5)$$

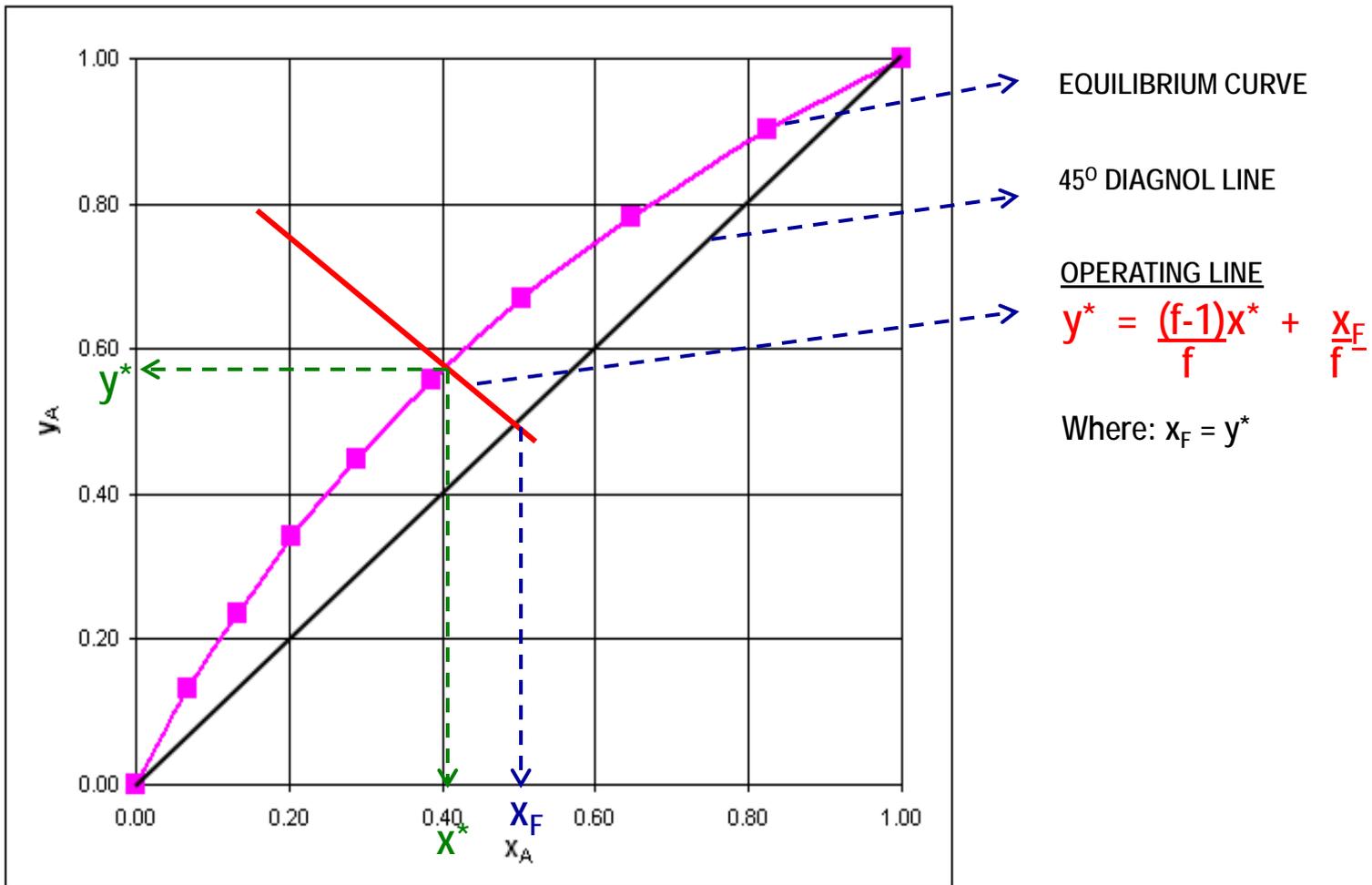
Substitute (5) into (4) :

$$x_F = y^*f + x^*(1-f)$$

$$y^* = \frac{(f-1)x^*}{f} + \frac{x_F}{f} \quad \dots\dots(6)$$



$$y = m x + c$$



**Figure 4: Determination of equilibrium composition in flash distillation by graphical method**

## Exercise 2

A liquid mixture containing 70 mol% n-heptane (A) and 30 mol % n-octane at 30°C is to be continuously flash at the standard atmospheric pressure vaporized 60 mol% of the feed. What will be the compositions of vapor and liquid and the temperature of the separator for an equilibrium stage?

\* Use the previous table of the vapor pressure for pure n-heptane & n-octane at various temperature.

## 1.3.2 SIMPLE BATCH DISTILLATION

- Also known as differential distillation which only one vaporization stage involved.
- It is done by boiling a liquid mixture in a steam jacketed kettle/ pot and the vapor generated is withdrawn and condensed as fast as it formed so that the vapor and liquid do not have sufficient time to reach its equilibrium.

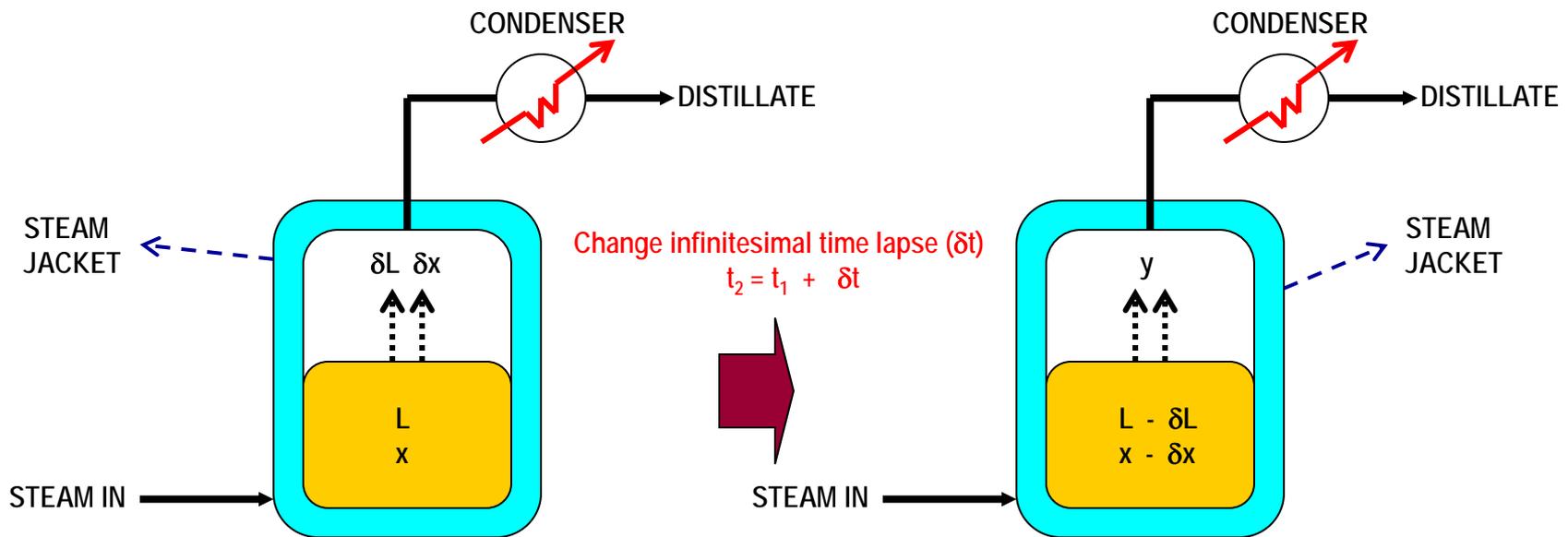


Figure 5: Schematic diagram of simple batch distillation.

Where,

$L$  = number of moles of liquid mixture in the pot

$x$  = mol fraction of more volatile component i.e. A

$\delta L$  = infinitesimal change number of moles in liquid mixture

$\delta x$  = infinitesimal change of mol fraction A

# 1.3.2.1 RALEIGH EQUATION FOR IDEAL/ NON IDEAL BINARY MIXTURE

- Consider a binary mixture to be separated by a flash distillation as shown in Fig. 5.
- A material balance on A can be made, where:-

$$\text{ORIGINAL AMOUNT} = \text{AMOUNT OF RESIDUAL LIQUID} + \text{AMOUNT OF VAPOR}$$

Mass balance on more volatile comp. i.e A will yeild:-

$$xL = (x - \delta x)(L - \delta L) + y(\delta L)$$

$$\cancel{xL} = \cancel{xL} - x\delta L - L\delta x + \cancel{\delta x\delta L} + y\delta L$$

$$L\delta x = -x\delta L + y\delta L$$

$$L\delta x = (y - x)\delta L$$

$$\frac{\delta L}{L} = \frac{\delta x}{(y - x)}$$

Where:

$L_1$  = number of moles of liquid at  $t_1$

$L_2$  = number of moles of liquid at  $t_2$

$x_1$  = mol fraction of A in liquid at  $t_1$

$x_2$  = mol fraction of A in liquid at  $t_2$

Integrating both sides within limits initial ( $t_1$ ) to final ( $t_2$ ):-

$$\int_{L_2}^{L_1} \frac{\delta L}{L} = \ln \frac{L_1}{L_2} = \int_{x_2}^{x_1} \frac{1}{(y - x)} \delta x \quad \dots\dots(7)$$

**RALEIGH EQUATION**

- The term  $\int_{x_2}^{x_1} \frac{1}{(y - x)} \delta x$  must be evaluated graphically by determining an area under the graph of  $\frac{1}{(y - x)}$  vs  $x$  between the limit  $x_1$  and  $x_2$ .

## Exercise 3

A liquid mixture of acetone-water containing 50 mol% acetone is distilled under differential batch condition at atmospheric pressure, until 10 mol% of acetone remained in the still-pot. The vapor-liquid equilibrium data for the acetone-water mixture is given below :

Mol fraction of acetone in liquid phase ( $x_A$ )	0.05	0.10	0.15	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	0.95
Mol fraction of acetone in vapor phase ( $y_A$ )	0.64	0.73	0.77	0.79	0.81	0.83	0.84	0.85	0.87	0.89	0.93	0.96

Determine:

- The fraction of acetone in the distillate
- Composition of the distillate

## 1.3.3 FRACTIONAL/ CONTINUOUS DISTILLATION

- In a multi stage fractional distillation process, the vapor and liquid are brought into continuous and counter-current contact inside the a column as shown in Figure 6.

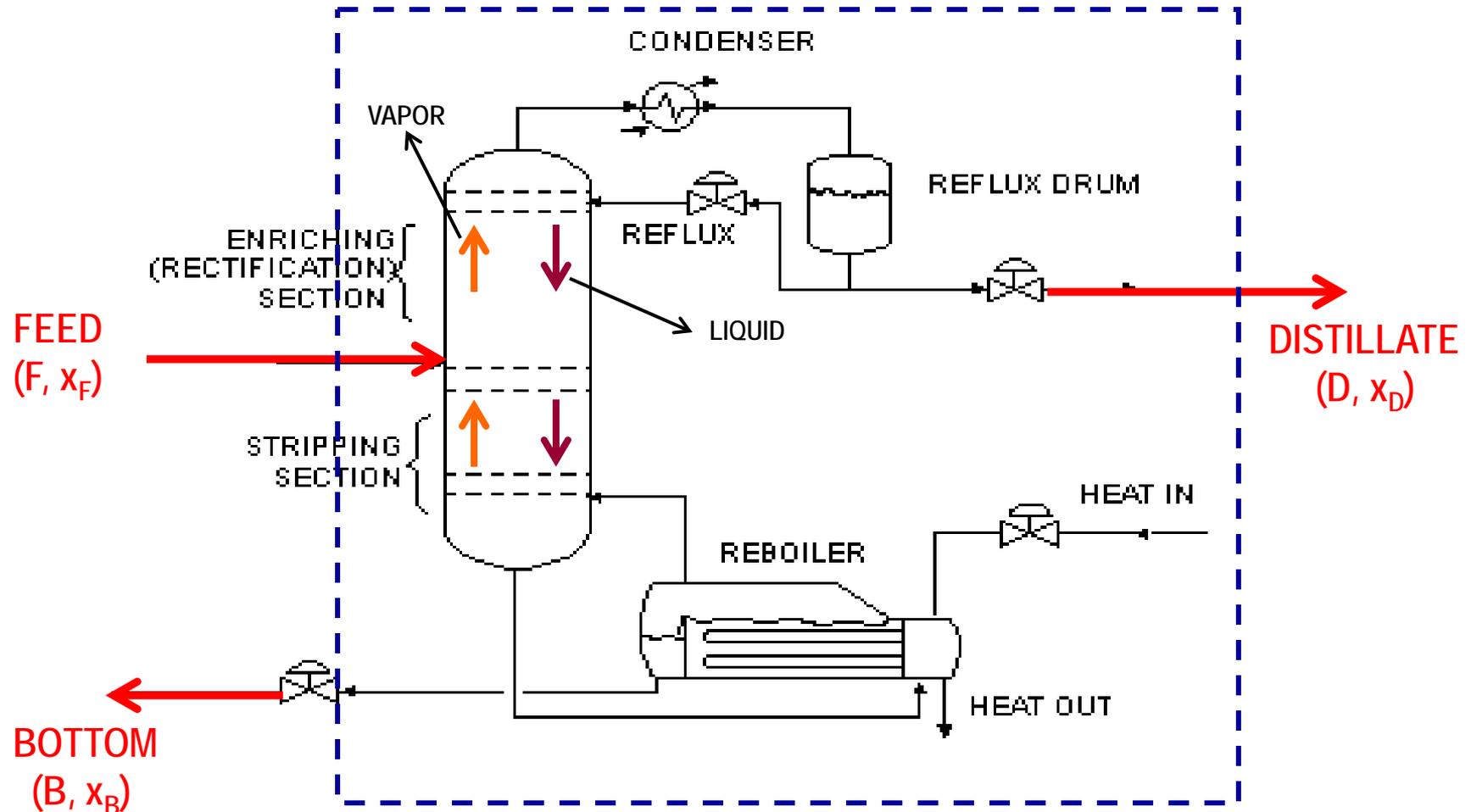


Figure 6: Schematic diagram of a fractionating distillation.

- The feed enters somewhere in the middle of the column (Fig. 6). The portion above the feed stream is known as enriching section, while the bottom is known as stripping section.
- If the feed is liquid, it flows down to a stage/tray. Vapor enters the tray and bubbles through the liquid on this tray as the entering liquid flows across.
- The vapor and liquid leaving the tray are essentially in equilibrium.
- The vapors continues up to the next tray, where it is again contacted with the down-flowing liquid. In this case the concentration of more volatile component i.e A is being increased in the vapor from each stage going upward and decreased in the liquid from each tray going downward.
- The final vapor product coming overhead is condensed in a condenser and a portion of the liquid product (distillate) is removed, which contains a high concentration of A. The remaining liquid from the condenser is refluxed (returned) as a liquid to the top tray.
- The liquid leaving the bottom tray enters the reboiler, where it is partially vaporized and the remaining liquid, which is rich in B is withdrawn as bottom liquid product. The vapor from the reboiler is sent back to the bottom tray.

# 1.3.3.1 McCABE –THIELE METHOD: CALCULATION FOR NO. OF THEORITICAL STAGES/ TRAYS

## 1.3.3.1.1 INTRODUCTION & ASSUMPTION

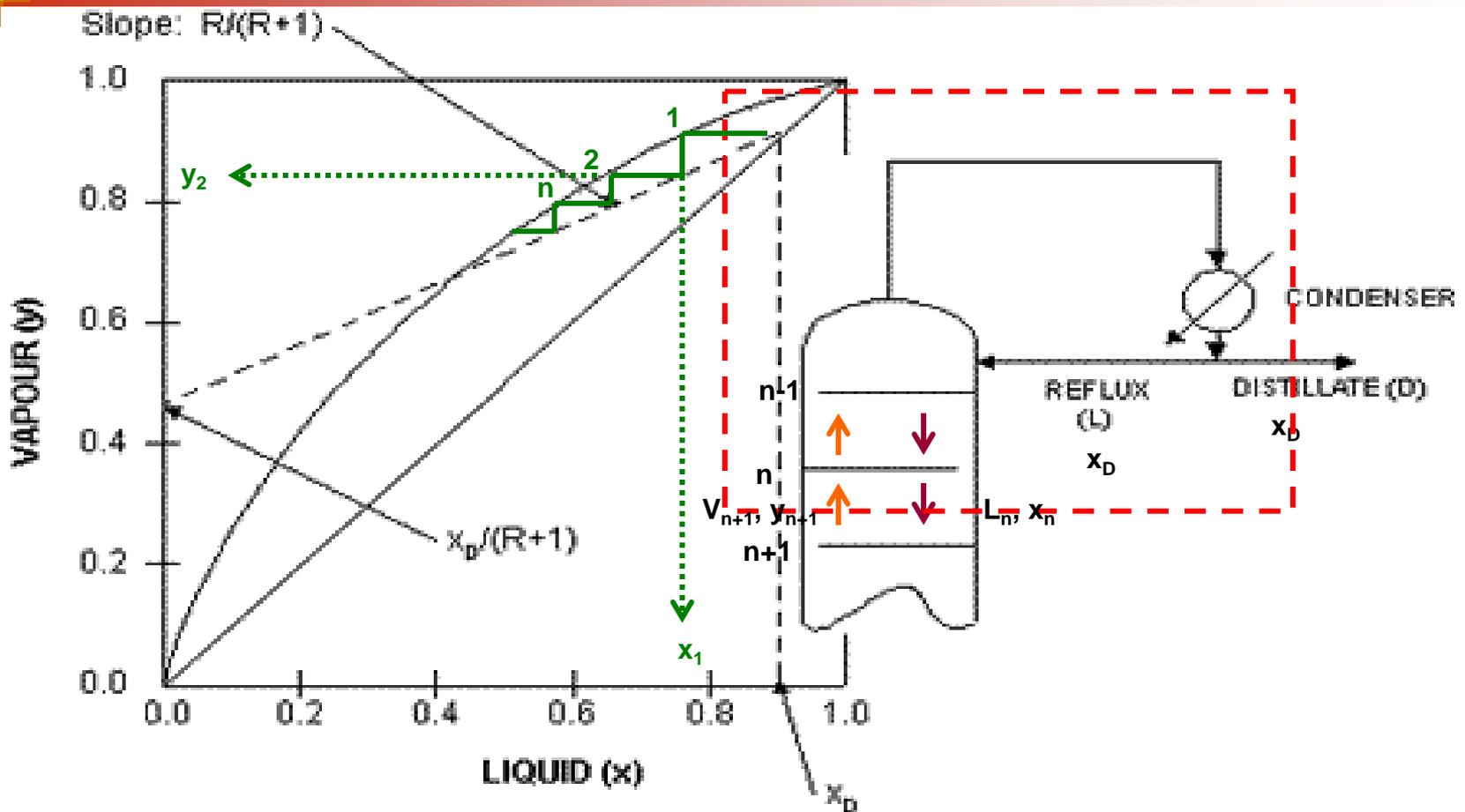
- A mathematical-graphical method for determining the no. of theoretical trays needed for a given separation of a binary mixture of component A and B.
- Assumption: constant molal overflow in the column

## 1.3.3.1.2 EQUATIONS FOR ENRICHING SECTION

- The upper part of the column above the feed entrance is called enriching section. Since the entering feed of binary components A and B is enriched in this section, so that the distillate is richer in A than B.
- Assumption: i. column operates at steady state condition  
ii. constant molal overflow in the column
- The material balance for the diagram's boundary in Fig 6 can be written as:-

$$\text{Overall mass balance} \quad : \quad F = D + B \quad \text{.....(8)}$$

$$\text{Mass balance on comp. A} \quad : \quad Fx_F = Dx_D + Bx_B \quad \text{.....(9)}$$



**Figure 7: Material balance and operating line for enriching section.**

The m/balance over the red dashed line section in Fig 7,

Overall mass balance :  $V_{n+1} = L_n + D$  .....(10)

Mass balance on comp. A :  $V_{n+1}y_{n+1} = L_nx_n + Dx_D$  .....(11)

Solving for  $y_{n+1}$ , the enriching operating line is:-

$$y_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{Dx_D}{V_{n+1}} \quad \dots\dots(12)$$

Since  $V_{n+1} = L_n + D$ ;  $L_n/V_{n+1} = R/(R+1)$  and eq. 12 becomes:-

$$y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1} \quad \dots\dots(13)$$

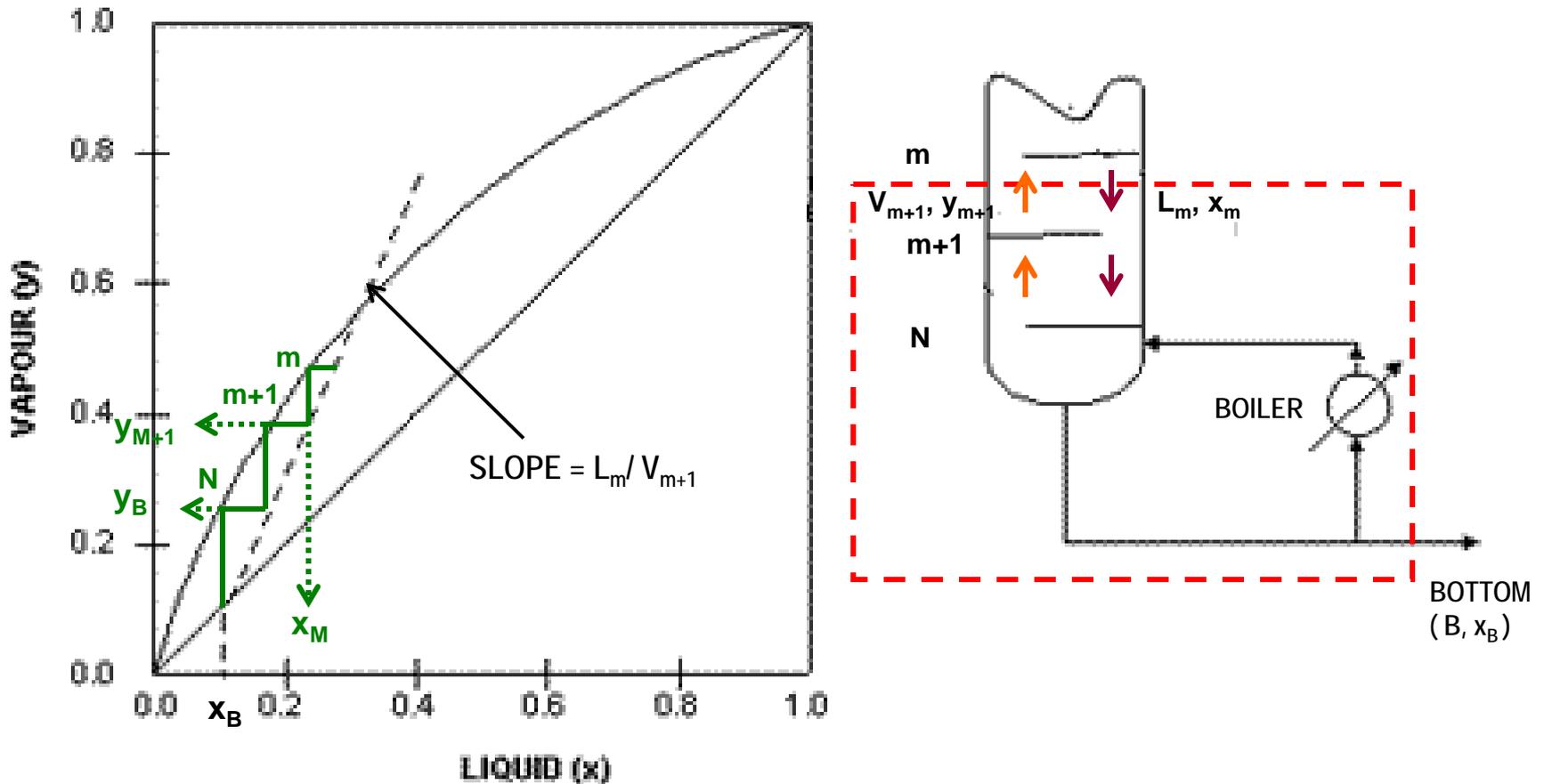


**ENRICHING OPERATING LINE**

Where  $R = L_n/D =$  reflux ratio = constant value

- Eq. 13 is a straight line on a plot of vapor composition (y) vs liquid composition (x) as depicted in Fig. 7.
- It intersects the 45° diagonal line at  $x = x_D$ .
- The interception of the operating line at  $x = 0$  is  $y = x_D/(R+1)$
- The theoretical trays are determined by starting at  $x_D$  and stepping off the first plate to  $x_1$ . Then  $y_2$  is the composition of the vapor passing the liquid  $x_1$ .
- In similar manner, the other theoretical trays are stepped off down the column in the enriching section to the feed tray.

### 1.3.3.1.3 EQUATIONS FOR STRIPPING SECTION



**Figure 8: Material balance and operating line for stripping section.**

The  $m$ /balance over the red dashed line section in Fig 8 for the stripping section of the column below the feed entrance

Overall mass balance :  $V_{m+1} = L_m - B \dots\dots(14)$

Mass balance on comp. A :  $V_{m+1}y_{m+1} = L_mx_m - Bx_B \dots\dots(15)$

Solving for  $y_{m+1}$ , the stripping operating line is:-

$$y_{m+1} = \frac{L_m}{V_{m+1}} x_m - \frac{Bx_B}{V_{m+1}} \quad \dots\dots(16)$$



**STRIPPING OPERATING LINE**

- Since equimolar flow is assumed,  $L_m = L_N = \text{constant}$  &  $V_{m+1} = V_N = \text{constant}$ ; eq. 16 is a straight line when plotted as y vs. x in Fig. 8, with a slope of  $L_m/V_{m+1}$ .
- It intersects the  $y = x$  line at  $x = x_B$ . The intercept at  $x = 0$  is  $y = -Bx_B/V_{m+1}$ .
- Again the theoretical trays for the stripping section are determined by starting at  $x_B$  going up to  $y_B$ , and then across to the operating line and so on.

### 1.3.3.1.4 EFFECT OF FEED CONDITIONS

- The condition of the feed stream (F) entering the column determines the relation between the vapor  $V_m$  in the stripping section and  $V_n$  in the enriching section as well as between  $L_m$  and  $L_n$ .

- The condition of the feed is representing by  $q$ , which defined as:-

$$q = \frac{\text{heat needed to vaporise 1 mol of feed at entering conditions}}{\text{Molar latent heat of vaporization of feed}} \quad \dots\dots(17)$$

$$@ \quad q = \frac{H_V - H_F}{H_V - H_L} \quad \dots\dots(18)$$

Where:

$H_V$  = enthalpy of the feed at dew point

$H_L$  = enthalpy of the feed at the boiling point

$H_F$  = enthalpy of the feed at its entrance conditions

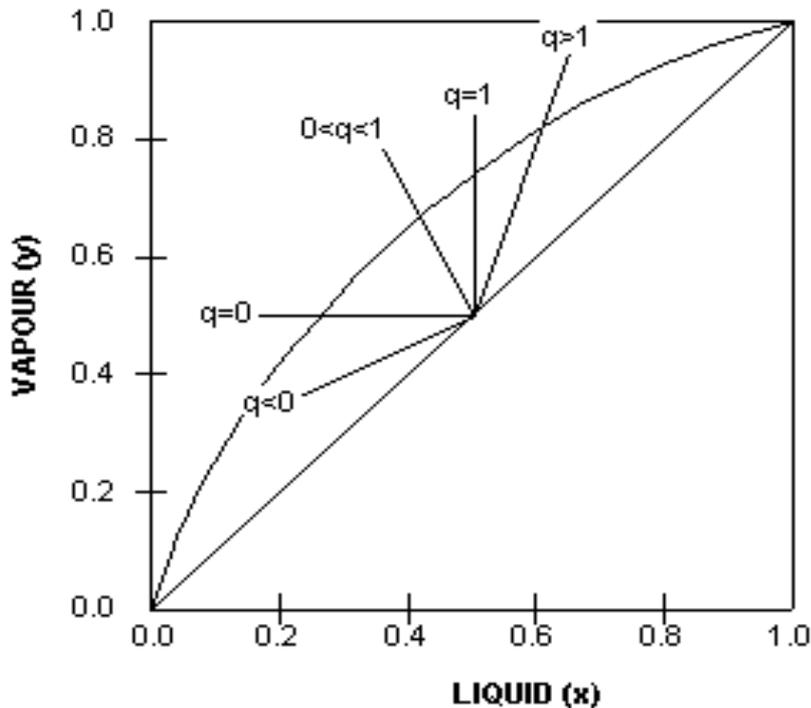
- The q operating line is given by:-

$$y = \frac{q}{q-1} x - \frac{x_F}{q-1} \dots\dots(19)$$



**q OPERATING LINE**

- It is locus of the intersection of the 2 operating lines.
- Setting  $y = x$  in eq. 19, the intersection of the q-line equation with the 45° line is  $y = x = x_F$ , where  $x_F$  is the overall composition of the feed. The q-line is plotted for various feed condition in Fig. 9.



Where:-

- $q < 0$  : superheated vapor
- $q = 0$  : saturated vapor
- $0 < q < 1$  : mixture of liquid + vapor
- $q = 1$  : saturated liquid
- $q > 1$  : cold liquid

Figure 9: Location of the q-line for various feed conditions.

## Exercise 4

A liquid of benzene-toluene mixture is to be distilled in fractionating tower at 101.3 kPa. The feed of 100 kg-mol/h liquid contains of 45 mol% benzene and 55 mol% toluene enters at 327.6 K. A distillate contains 95 mol% benzene and a bottoms containing 10 mol% benzene are to be obtained. The reflux ratio is 4:1. The average heat capacity of the feed is 159 kJ/kg-mol·K and the average latent heat 32099 kJ/kg-mol. The equilibrium data for this mixture is given below.

Mol fraction of benzene in liquid phase ( $x_A$ )	1.00	0.78	0.58	0.41	0.26	0.13	0.00
Mol fraction of benzene in vapor phase ( $y_A$ )	1.00	0.90	0.78	0.63	0.46	0.26	0.00

Determine:

- The distillate and bottom product in kg-mol/h.
- The  $q$  value.
- The number of theoretical tray.
- The position of feed tray.
- The number of actual tray if the overall efficiency is 73%.

# TOTAL REFLUX

- $R = \infty$ ,  $R = L_n/D$ ,  $V_{n+1} = L_n + D$
- Enriching operating line,  
the slope will become 1.0 and both section operating lines coincide with the  $45^\circ$  diagonal line.
- Minimum number of trays
- Required infinite sizes of condenser, reboiler and tower diameter for a given feed rate.
- The minimum number of theoretical steps,  $N_m$  when a total condenser is used:

$$y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1}$$
$$N_m = \frac{\log\left(\frac{x_D}{1-x_D} \frac{1-x_W}{x_W}\right)}{\log \alpha_{av}}$$

$$\alpha_{av} = (\alpha_D \alpha_W)^{1/2}$$

# Minimum Reflux Ratio, $R_m$

- Require an infinite number of trays for the given desired separation.
- Minimum vapor flow in the tower, minimum reboiler and condenser sizes.
- $R$  is decreased, the slope of the enriching operating line is decreased and the intersection of this line and the stripping line with the  $q$  line moves farther from the  $45^\circ$  line and closer to the equilibrium line, a 'pinch point' happens when two operating lines touch the equilibrium line.

$$\frac{R_m}{R_m + 1} = \frac{x_D - y'}{x_D - x'}$$

# Operating & Optimum Reflux Ratio

- Total reflux: minimum number of plates but tower diameter is infinite.
- Minimum reflux: infinite number of trays.
- Actual operating reflux ratio lies between these two limits
- The optimum reflux ratio to use for lowest total cost per year is between  $R_m$  and total reflux.
- Operating reflux ratio between  $1.2 R_m$  and  $1.5 R_m$