Distillation.

* Introduction :-

Distillation is a unit operation in which the constituents of liquid mixture (solution) are separated using thermal energy. Basically, the diff. in vapour pressures (volatilities) of diff. constituents at the same tempreture is responsible for such a separation. this unit operation is known as fractional distillation or Fractionation. with this technique it is possible ~~the~~ to sepa the liquid mixture in to it's components in almost pure form and this fact has made distillation perhaps the most important of all the mass transfer operations.

In ~~this~~ distillation, the phases are involved ie liquid and vapour or gas (the vapour phase is created by supplying heat to the liquid) and mass is transfered from both the phases to one another by vapourisat from the liquid phase and by condensatio from the vapour phase. the net effect is

an increase in composition of the more volatile component in the liquid. the basic requirement for a separation of components by distillation. is that the composition of vapour be different from the composition of the liquid with which it is in equilibrium the vapour is richer in the more volatile component than the liquid from which it is formed. If the vapour composition is same as the liquid composition, distillation technique is not effect a separation.

Distillation is commonly encountered in chemical and petrochemical industries or petroleum industry as a means of separating the liquid mixture in to it's components parts.

<u>for example</u> :- separation of ethanol and water mixture, production of absolute alcohol from 95% ethanol using benzene, separation of petroleum crude in to gasoline, kerosene, fuel oils etc. are the typical example of distillation.

Evaporation is concerned with the separation of solution containing a non volatile solute & volatile solvent, where as distillation is concerned with the separation of solution where all the components are appreciably volatile. thus, the separation of a brine in to salt and water is a evaporation where the separation of a mixture of alcohol and water in to components is a distillation.

* flash distillation OR (Equilibrium distillation)

flash distillation is normally carried out in a continious manner. In this method, a liquid mixture is partially vapourised, the vapour & liquid are allowed at an equlibrium and finally withdrawn separately.

feed is heated in tubular heat exchanger the hot liquid mixture is then fed to a separator via pressure redusing valve where by pressure is reduced & the vapour is formed at the expense of liquid is withdrawn from the bottom of separator and the equilibrium vapour leaves the separator from the top which is then liquified in a condenser. Flash distillation is commonly used in petroleum Industry, handling multicomponents distillation is concerned with the separation of solution where all the components are appreciably volatile. thus, the separation of a brine in to salt and water is a evaporation where the separation of a mixture of alcohol and water in to components is a distillation.

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Systems in pipe stills.

* Diagram :-

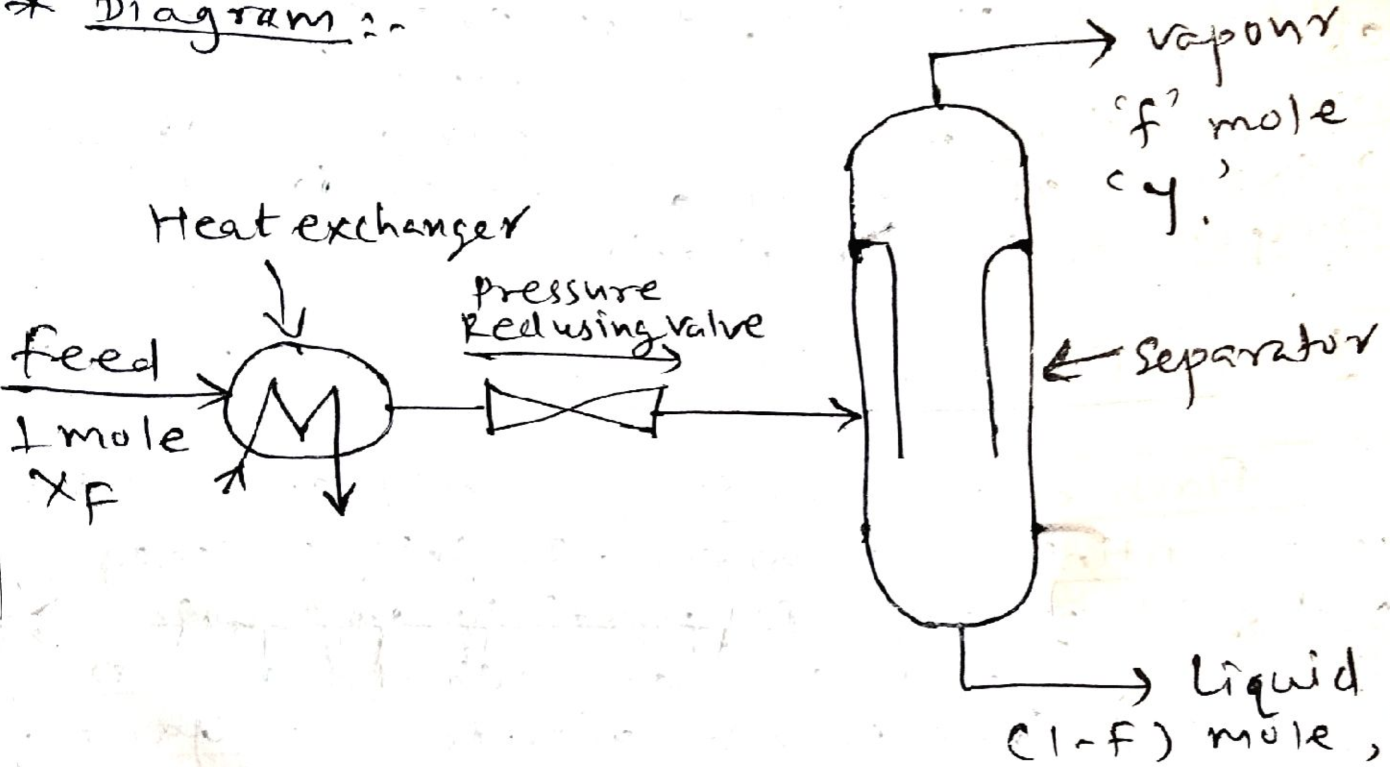


fig:- Flash /equilibrium distillation.

Consider one mole of liquid mix. having X_F mole fraction of more volatile component is fed to a flash distillation unit. Let 'f' be the fraction of feed that is vapourised and is of composition 'y' then (1-f) will be moles of residual liquid obtained. Let 'x' be the mole fraction of more volatile component in liquid

Then, a material balance of more volatile component gives,

$$x_F = F.y + (1-f).x \quad \text{— ①}$$

$$\therefore F.y = -(1-f)x + x_F \quad \text{— ②}$$

$$\therefore y = -\frac{(1-f)x}{f} + \frac{x_f}{f} \quad \text{— ③}$$

eqn-③ is material balance / operating line for flash distillation with slope equal to $-(1-f)/f$ and intersept equal to x_f/f.

The point of intersection of the operating line of diagonal $(x=y)$ is,

$$y = -\frac{(1-f)x}{f} + \frac{x_F}{F}$$

$$X = Y$$

$$x = -\frac{(1-f)}{f}.x + \frac{x_F}{F}$$

$x_f = -x' + x.F + x_F$

$\therefore$ ~~x_F~~ $\boxed{x = x_F}$

$\therefore$ $\boxed{y = x_F}$

for $f = 1$, feed totally vapourised (feed 100 mole percent vapourised)

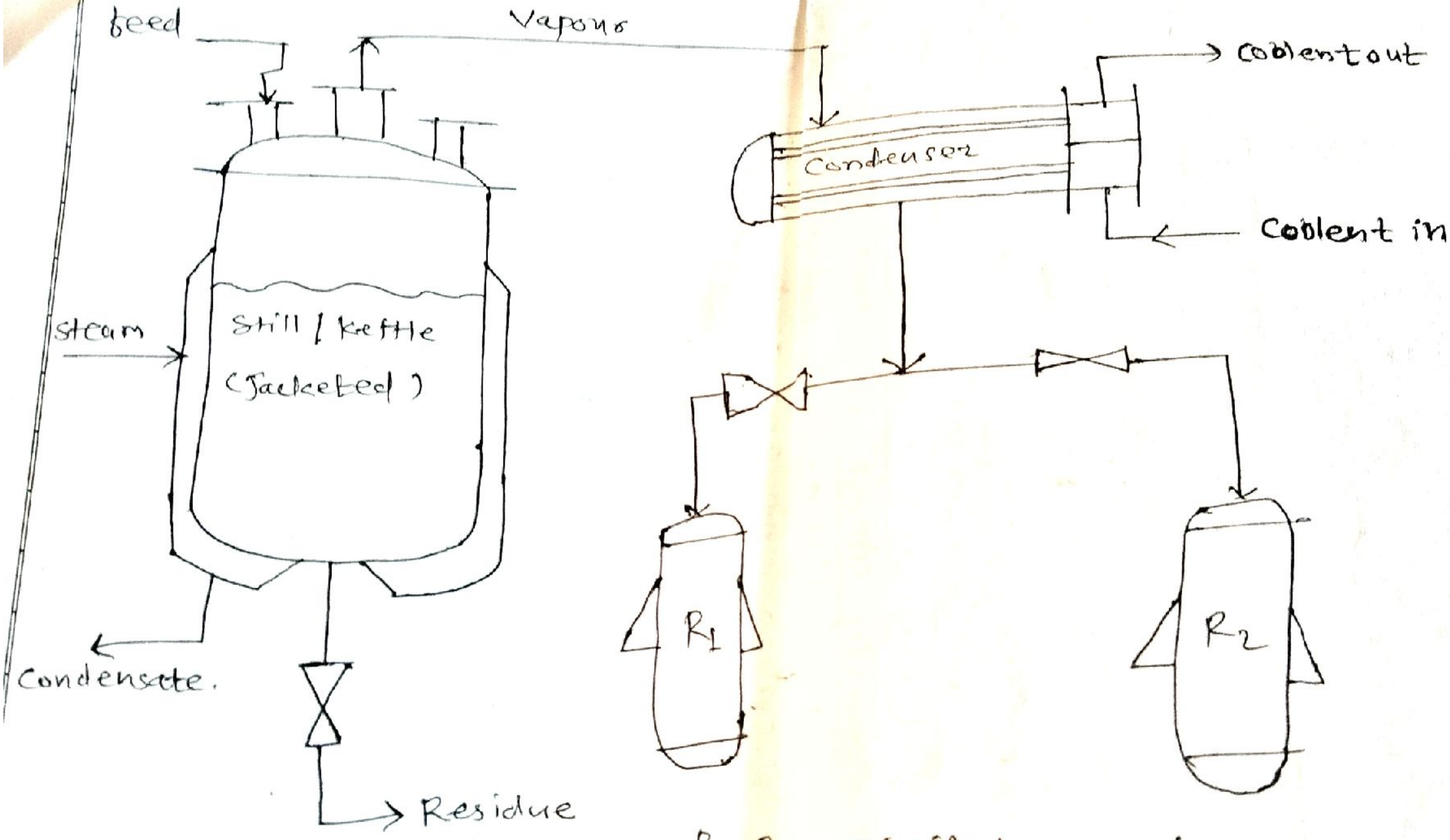
$$\boxed{\text{Slope} = -\frac{(1-f)}{f} = 0}$$

∴ hence operating line is parallel to x-axis through a point (x_f, x_F) on the diagonal. for $f = 0$, – no feed is vapourised ∴ slope = ∞ (Infinity) and operating line will be parallel to y-axis through point. (x_F, x_F) on the diagonal.

* Simple distillation :- OR Differential distillation :-

In this distillation technique, a known quantity of a liquid mixture, is charged in to a jacketed kettle or still. The jacket is provided for heating the liquid mass in the still with the help of heating media such as steam. The charge is boiled slowly, vapours formed are withdrawn and fed to a condenser where they are liquified and collected in a receiver as distillate. In the early stage of distillation, vapours leaving the still are richest in the more volitile component and as the distillation proceeds the liquid in the still becomes lean with respect to the more volitile compone The composition of the less volitile component thereby increases and hence the boiling point increases. the product (distillate) from such units can be collected in several receivers, called cuts, to give products of various purities over the length of distillation period. the distillation is continued till the boiling point of liquid reaches a predetermined vallue and the content of the still is finally removed as residua liquid containing majority of less volitile component.

diagram :-



101325 Pa

(less volatile components) R_1, R_2 – Distillate receivers.

fig :- Simple distillation unit

Steam distillation :-

steam distillation (It is a distillation process ~~open~~ with open steam) is used :

(i) for separating a high boiling ~~point~~ component from the non-volitile impurities,

(ii) for separating a high mixture in to different fraction's where in the decomposition of material might be occur if direct distillation were employed.

(iii) In cases where vapourisation tempreture cannot be reached by steam heat.

Steam distillation is specially adopted in cases where substances involved cannot withstan temprature of distillation and decompose (i'e, heat sensitive materials). substances of this kind can be separated by redusing the partial pressure of volitile component. this can be done by making use of an inert vapour that decreases the temp. of distillation. The inert vapour used should be practically immiscible with components to be distilled. steam is generally used for this perpose and operation is called as steam distillation. Steam is widely used as : it is immiscible with many organic compounds, it provides requireds heat for vapourisation and it is ready available at low cost.

In steam distillation, steam is directly admitted into the liquid in the still. (steam directly admitted ~~to~~ in a pool of liquid is called as live or open steam). The mixed vapour containing a desired component is taken as an overhead, condensed and desired is separated from the water phase by gravity while the non-volitile material remains behind in the still. The necessary condition for employing steam distillation is that the solubility of steam in the liquid must be very low. ie product must be practically immiscible with water.

The process of steam distillation may make use of superheated steam which provide sufficient heat to vapourise the desired component without self condensing or it make use of saturated steam which provide sufficient heat ~~to~~ to vapourise the desired component by partly condensing. In the later case, the liquid (water) phase is produced in the still. In either case, when the sum of the partial pressure of steam and desired component reaches the total pressure, both substances pass over ~~the~~ (as a vapour) in the molecular ratio of their partial pressures. the mass relationship is;

$$\frac{\frac{m_A}{M_A}}{\frac{m_B}{M_B}} = \frac{P_A}{P_B}$$

$$= \frac{P_A}{P - P_A} \quad \Big| \quad \because P = P_A + P_B \quad \therefore P_B = P - P_A$$

$$\frac{m_A}{m_B} = \frac{P_A \cdot M_A}{P_B \cdot M_B} \quad \Big| \quad \because P_B = P - P_A$$

$$\boxed{\frac{m_A}{m_B} = \frac{P_A \cdot M_A}{(P - P_A) M_B}.}$$

Where,

M_A, M_B are molecular weights of desired component and steam respectively. P_A, P_B and P are the partial pressure of desired component, steam (called as carrier) and total pressure respectively.

m_A, m_B are the masses of desired component and steam in the vapour respectively. when water phase is present and effect on a non-volitile ~~component~~ material on vapourisation is neglected them for the system under consideration there will be two componts and three phase. According to phase rule, F = C − P + 2, there is a on one variable that can be varied independantly and setting the tempreture adjust itself, so tha the sum of partial pressures of two components equal to one atmosphere. the tempreture so reached is less than the boiling points of pure components. thus if the pressure is atmospheric & then it is possible to steam distill the material at a temp. lower than 100°c thus blocking / avoiding the destructive tempretures.

* Continious Rectification – (Binary systems)

Rectification is commonly encountered in industrial practice as it is possible to get almost pure product by this method.

The enrichment of the vapour steam as it passe through the collumns in contact with reflux is termed as rectification.

In this separation method, a part of the condensed liq. is return back as reflux and a max. enrichment the more volitile component in the vapour steam is obta-ed by successive partial vaporisation & condensation a multistagestage contact of the ~~liq.~~ vapour & liq.
(multistage)
this is achieved ~~by~~ in a single unit called as fractionating column.

* fractionating collumn :-

A fractionating column or fractionator Consists of (i) cylindrical shell devided in to sections by a series of a perforated trays, (ii) a reboiler, and (iii) a condenser. A liquid mixture to be ~~prepared~~ separated is introduced in the cylindrical collumn more or less centrally. The collumn itself is devided in to two sections.- rectifying and stripping section. The section above the feed plate or tray is called the rectifying section, where in vapour is washed to remove the less volitile component with liq. returned to the collumn from top (known as reflux). The portion below the feed plate including feed plate is called as stripping section where in liq. is stripped off more volitile component by rising vapour. Perforated trays are nothing but gas liq. contacting devices on which gas/vapour and liq. are brought in to intimate contact for mass transfer to ~~occur~~. occur.

Vapour's are generated in a reboiler (generally steam heated) and are fed to the bottom of the collumn. The liquid removed from the fractionator. rich in less volitile component is called the ~~bottoms~~ bottoms or bottom product. The vapour issuing from the top of collumn is fed to a condenser where the latent heat is removed with the help of circulated coolent through the condenser.

* fractionating column :-

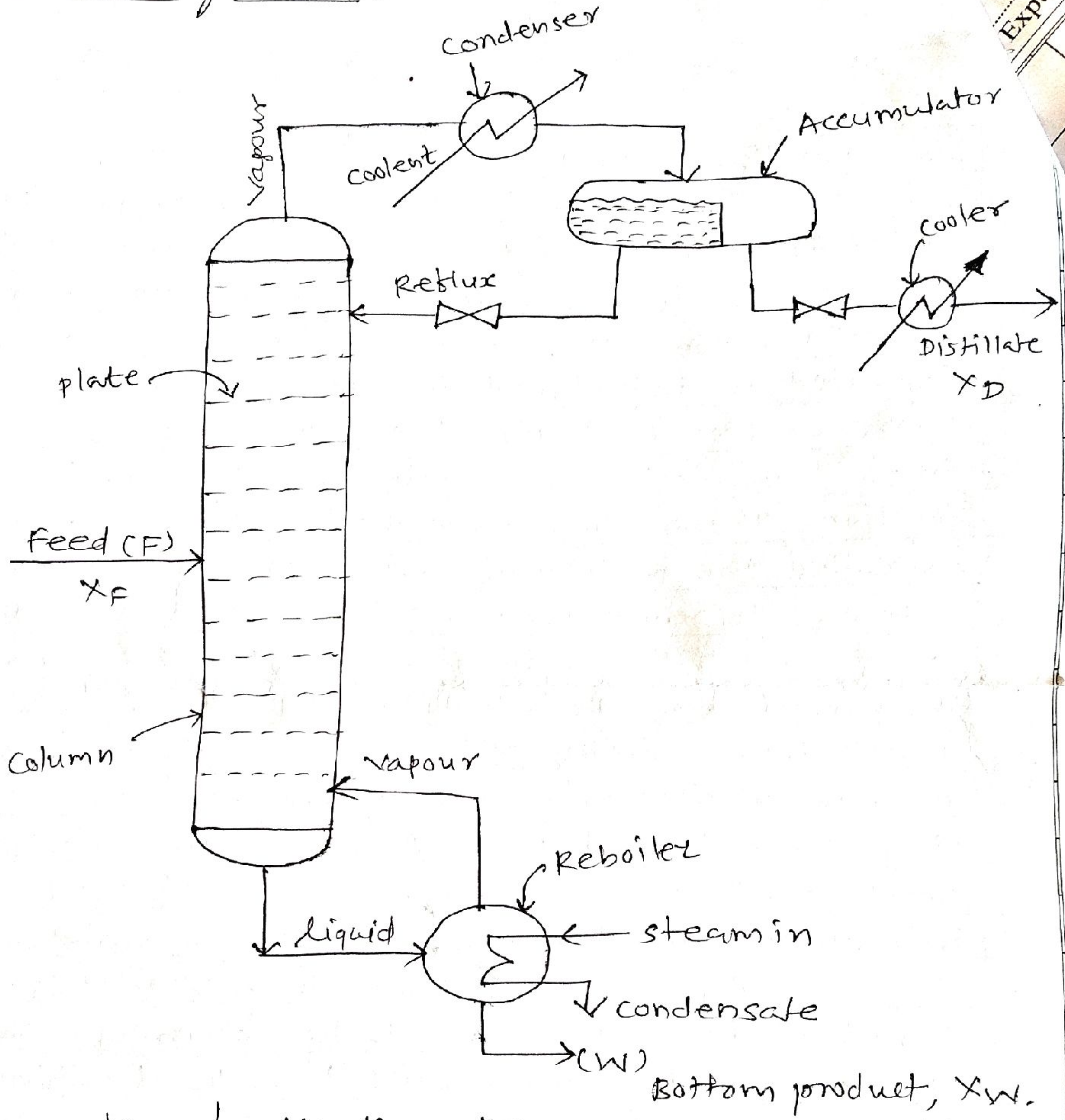


fig:- fractionating collumn

A part of condensed liq. is returned to the column (reflux) and the remaining part is withdrawn. as top product. or distillate which is rich in more volitile component. As the liq. is at it's bubble point

Batch distillation operation may be carried by varying with Reflux ratio so as to get a constant overhead composition. In this case, Initially column is operated under total Reflux and then some value of the Reflux ratio is adjusted. But as the distillation proceeds, the top product quality may fall. Thus, to keep the top product quality to be constant, the Reflux ratio is increased. Reflux ratio is continuesly incresed till it reaches a max. value and then it is reduced and the cut is taken in to a separate receiver. It may be charged in a next batch.

Another method of operating batch distillation unit is to operate column under a const. reflux ratio. collumn is operated under total Reflux Initially and then reflux is set to a predetermined value. As the distillation proceeds quality will steadily fall but distillate is collected in the same receiver until the average distillate composition is riched at the desired value & then overhead product is collected in the second receiver till the termination of operation and the same may be charged in the next batch.

Still Another way to operate the unit is to be adopt a practice of cycling procedure wherein the Collumn is operated at total reflux till the desired top temp. is achieved where is Indication of product purity) and then all the overhead prod is withdrawn at once distillate removal valve is closed and again column is operated under total Reflux.

* Plate Efficiencies :- The Relationship between the performance of theoretical / ideal and actual plates is expressed in terms of plate efficiency. The types of plate efficiency are ;

① Overall plate Efficiency / overall column efficiency :-

② Murphree plate efficiency

③ Point / local efficiency.

* ① Overall plate efficiency is the ratio of no. of ideal or theoretical plates (stages) required to produce a given separation in entire column to the no. of actual plates.

If overall efficiency is 60 % & 12 Ideal plates are called for, then the actual plates needed are $^{12}/_{0.60} = 20$

*② Murphree plate efficiency :- It applies to a Individual plate in a collumn and is deffined as the actual change in average composition accomplis by a given plate devided by the change in average composition if vapour leaving the plate were in equil with the liquid leaving the plate.

*③ Point efficiency :- (Local efficiency)

Point efficiency is defined as same manner as the murphree plate efficiency but it applies to single location on a given plate.

* Constant molal overflow :-

For most distillations, the molar flow rates of vapour and liquids are nearly constant in each section of the column, and the operating lines are almost straight. This results nearly from ~~equally~~ equal molar heats of vapourisation, so that each mole of high boiler that condenses as the vapour moves up the collumn provides energy to vapourise about 1 mole of low boiler. For example, the molar heats of vapourisation of Toulene and benzene are, 7960 and 7,360 cal/mol, respectively, so that 0.92 mol of toluene corresponds to 1.0 mol of benzene. The changes in enthalpy ~~and~~ of liquid and vapour streams & heat losses from the collumn require slightly more vapour to be formed at the bottom, so the molar ratio of vapour flow at the bottom of a collumn section to that the top is even closer to 1.0 In ~~decreasing the collumn~~ designing collumns or ~~designing~~ Interpreting plant performance the concept of constant molal overflow is often used.

* Reflux ratio :-

The Analysis of fractionating collumn is facilitated by the use of a quantity called the Reflux Ratio. Two such qualities are used.

one is the Ratio of Reflux to the overhead product and other is Ratio of Reflux to the vapour. Both ratios refer to quantities in rectifying section. The eqns for these ratios are;

$$\therefore R_D = \frac{L}{D} = \frac{V-D}{D} \quad \& \quad R_V = \frac{L}{V} = \frac{L}{L+D}$$

*Minimum Reflux Ratio - Rm :-

At total reflux, operating lines coinside with diagonal and to effect a desire ~~product~~ separations, no. of stages required to minimum. As the reflux ratio is reduced, operating line move towords the equlm curve along the feed line and the no. of stages increases. Ultimately, further reduction of reflux ratio results in to a condition wherein top of operating ~~lines~~ line touches the equlm curve as shown in fig.

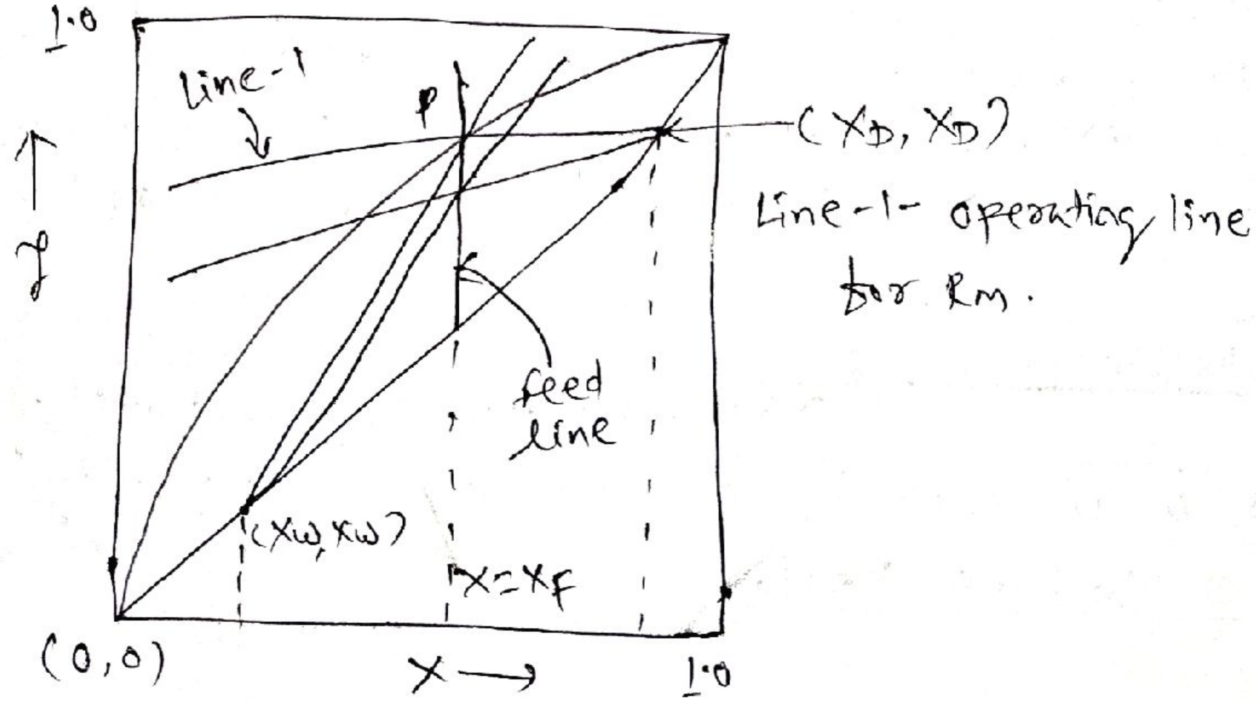


fig:- Minimum Reflux Ratio.

The point of Intersection of operating line ~~[illegible]~~ lies on the equlm curve and at this point step become very close together, so that a zone of nearly constant composition is formed near the feed plate and infinite no. plates are the required this represents a condition of minimum reflux. Thus the minimum reflux ratio is that reflux ratio at which an infinite no. of plates are required for a desired separation. At the min. reflux ratio, required heat supply for a reboiler of constant supply for condenser are minimum.

* Optimum Reflux ratio :-

Any Reflux ratio between infinite reflux ratio requiring a minimum no. of plates & min. reflux ratio requiring an infinite no. of plates is a workable system which requires finite stages ~~o~~for desired degree of separation. At min. reflux ratio as a infinite no. of plates are required, the fixed cost is also infinite while the cost of heat supply to the reboiler & condenser coolent is minimum. As the Reflux ratio is increased, the no. of plates decreases and the fixed cost decreases at the first, passes through a minimum and then increases as ~~a~~ with higher reflux ratio as it is

directly proposnal to the (R+1). At total reflu
through the condens no. of plates are minimum,
cost of heat supply to reboiler and condenser
coolent is max. and also large capacity.

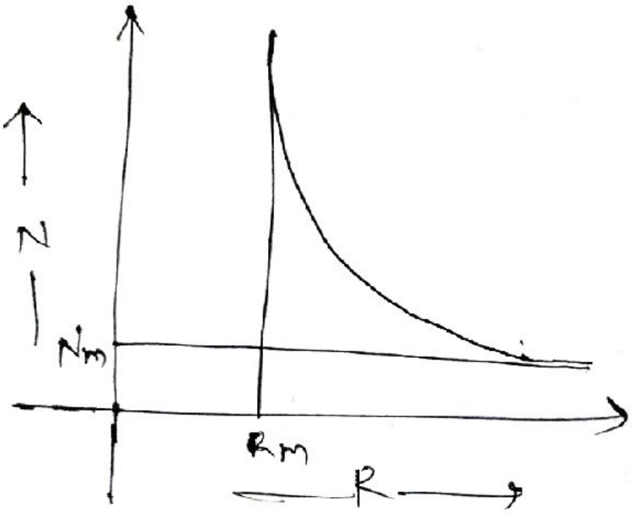


fig:- Relation betn Reflux Ratio & no. of stages for distillation.

Reboiler and condenser are needed. The total cost which is sum of fixed cost and the operating cost also decreases a min. and then increases with reflux ratio, <u>the optimum reflux ratio occurs at a point where the sum of fixed cost and operating cost is minimum.</u> As rough Approximation, the optimum reflux ratio usually lies in the range of 1.1 to 1.5 times the min. reflux ratio.

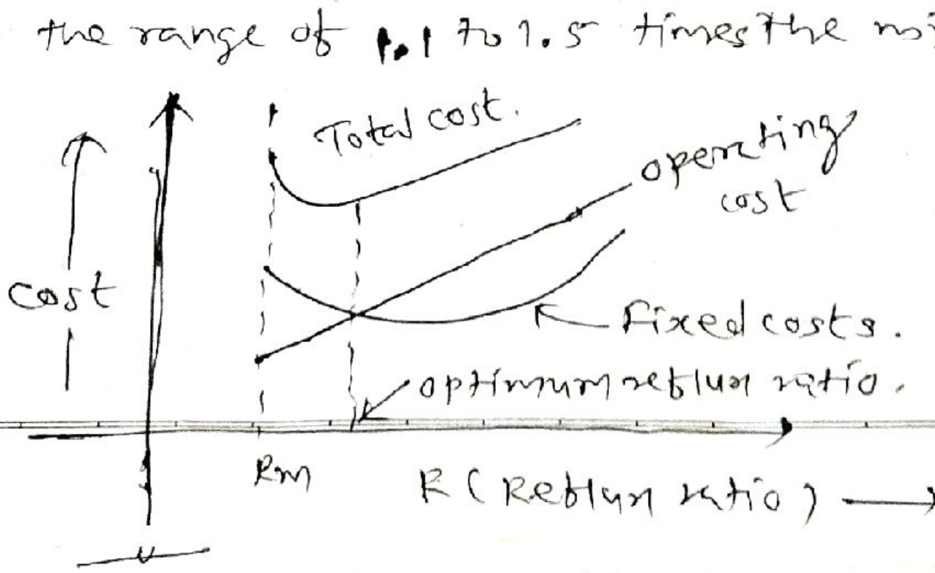


fig:- optimum Reflux ratio for distillation.

Material Balances in Plate columns :-

Overall material balances for two component System's :-

Fig. Represents the material - balance diagram for a typical continious distillation plant the column is fed with F mol/h of concentration 'x_F' and delivers D mol/h of overhead product of concentration 'x_D' and B mol/h of Bottoms product of concentration 'x_B'. Two independent overall material balances can be written.

Total-material balance $F = D + B$ — (1)

Component 'A' balance $F.x_F = Dx_D + Bx_B$ — (2

Eliminating 'B' from these equations gives,

$$\frac{D}{F} = \frac{x_F - x_B}{x_D - x_B} \quad \text{—— (3)}$$

Eliminating 'D' gives

$$\frac{B}{F} = \frac{x_D - x_F}{x_D - x_B} \quad \text{—— (4)}$$

eqⁿs ~~a~~ (3) & (4) are true for all values of flow's of vapour and liquid within the column.

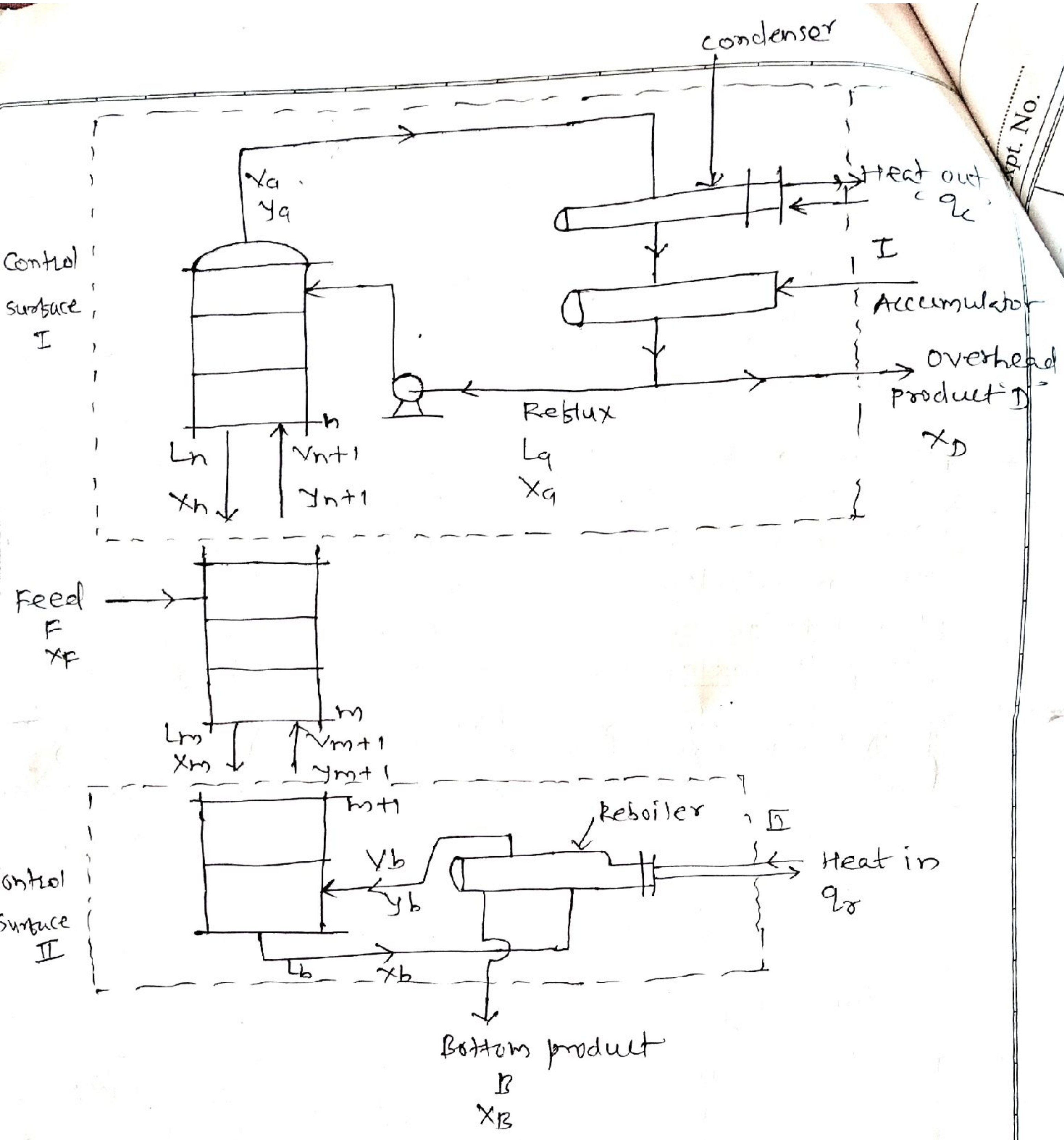


Fig:- Material-balance diagram for Continious fractionating column.

Net flowrates :-

Quantity 'D' is the diff. between the flowrates ~~and~~ of the streams entering and leaving the top of column. A material Balance around the condenser and accumulator in fig. gives -

$$D = V_a - L_a \quad \text{---} \quad ⑤$$

The diff. between the flowrates of vapour & liquid anywhere in the upper section of the Column is also equal to 'D' as shown by considering the part of the plant enclosed by control surface 'I' in fig. this part includes the condenser and all the plates above n+1. A total material balance around this control surface gives.

$$D = V_{n+1} - L_n \quad \text{---} \quad ⑥$$

This quantity 'D' is the net flowrate of material upward in the upper section of the Column. Regardless of changes in V and L, their diff. is constant and equal to 'D'.

Simillar material balances for component 'A' gives the equations -

$$Dx_D = V_a y_a - L_a x_a$$

$$= V_{n+1} y_{n+1} - L_n x_n \quad \text{———} \quad ⑦$$

Quantity Dx_D is the net flowrates of componen 'A' upward in the section of column. It too, is constant throughout this part of ~~this~~ the equipment.

In the lower section of column, the net flowrates are also constant but are in a downwor direction. the net flowrate of the material equals B that of component A is Bx_B. The following eqns apply;

$$B = L_b - V_b = L_m - V_{m+1} \quad \text{———} \quad ⑧$$

$$\therefore Bx_B = L_b x_b - V_b y_b$$

$$= L_m x_m - V_{m+1} y_{m+1} \quad \text{———} \quad ⑨$$

Subscript 'm' is used in place of 'n' to designate a general plate in the stripping section.

* Operating lines :-

Because these are two sections in the column, there are also operating lines, one for the rectifying section and the other for the stripping section. consider first the rectifying section. As shown eq^n. ie

~~$$y_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{V_a y_a - L_a x_a}{V_{n+1}}$$~~

the operating line for this section is ;

$$y_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{V_a y_a - L_a x_a}{V_{n+1}}$$

Substitution for $V_a y_a - L_a x_a$ from eq^n. (

⑦ gives,

$$y_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{D x_D}{V_{n+1}} \quad (1$$

The slope of line defined by eq^n. ~~(11)~~ ⑪ as usual, the ratio of the flow of the li-uid stream to that of vapour stream. further analysis it is convenient to eliminat to V_{n+1} from equation (11) by eq^n -⑥ giving -

from eqn-⑥, ∴ $V_{n+1} = \underline{L_n + D}$

$$y_{n+1} = \frac{L_n}{L_n + D} x_n + \frac{D x_D}{L_n + D} \quad \text{⑫}$$

for the section of column below the feed plate, a material balance over controll surface II in fig. gives,

$$V_{m+1} y_{m+1} = L_m x_m - B x_B \quad \text{⑬}$$

In a different form, this ~~because~~ becomes

$$y_{m+1} = \frac{L_m}{V_{m+1}} x_m - \frac{B x_B}{V_{m+1}} \quad \text{⑭}$$

This eqn. is the operating line in the stripping section. Again the slope is the ratio of the liquid flow to the vapour flow. Eliminating V_{m+1} from eqn-⑭ by eqn-⑧ gives,

$$y_{m+1} = \frac{L_m}{L_m - B} x_m - \frac{B x_B}{L_m - B} \quad \text{⑮}$$

eqn. ⑫ shows that the slope of operating line in the rectifying section is always less than 1.0 ; in the stripping section, as shown by eqn. ⑮ the slope is always greater than 1.0 .

⑫

Number of Ideal plates: McCabe-Thiele method :-

The no. of plates required for a perticular distillation problem can be found by computer design programs such as ASPEN, which usually use ~~to~~ plate to plate calculation's involving material and enthalpy balances. In such programs the no. of plate is specified first; then, for a given overhead composition and reflux ratio, the composition of the buttoms is calculated. If this is not satishfactory, the reflux ratio or the no. of plates is changed until the desired composition is found.

A simplified graphical procedure for calculating no. of plates is the Mc-Cabe-Thiele method. this method can also be adapted for computer calculations.

When the operating lines represented by equations ⑫ & ⑮ are plotted with the equilibrium curve on the xy diagram, the Mc-cabe-Thiele step-by-step construction can be used to compute the no. of ideal plates needed to accomplish a definite concentration difference in either rectifying or stripping section. eqns ⑫ & ⑮, however show that unless L_n & L_m are constant. the operating lines are