

# Petrochemical Industry

## Distillation

### Introduction

*Distillation is method of separation of components from a liquid mixture which depends on the differences in boiling points of the individual components and the distributions of the components between a liquid and gas phase in the mixture.*

The liquid mixture may have different boiling point characteristics depending on the concentrations of the components present in it. Therefore, distillation processes depends on the vapor pressure characteristics of liquid mixtures. The vapor pressure is created by supplying heat as separating agent.

The distillation is a most important operations processes in petroleum and chemical industries ,and it is widely use of in refinery to separate the crude oil into petroleum products

### Principles concepts

**Mixture:** it is a homogeneous solution that contains several components in different concentrations.

Hydrocarbon mixtures can be classified :

1. According to the components:

- Two material in the mixture.
- More than two.

2. According to the boiling point of the mixture:

- **Real mixture:** It is the mixture that have a initial and final boiling point and the vapor formed as a result of evaporation of the liquid mixture highly concentrated with lighter components , the real mixture is separated by normal distillation, like crude oil .
- **Isotropic mixture:** a mixture that has a constant boiling point and vapor formed as a result of evaporation of the liquid mixture contains same boiling concentrations of the components in the liquid.

Isotropic mixture cannot be separated by normal distillation.

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**Evaporation:** *The phenomenon conversion liquid phase to the vapor phase by heating at same temperture of boiling under certion pressure it is the process of remove a quantity of the solvent from the solution , such as salt from sea water*  
**latent heat of evaporation ( $\lambda$ ):** *the amount of heat required to change unit mass of the liquid phase to the vapor phase without a change temperature. Measured in units of KJ / Kmol*

**Condensation:** *The phenomenon conversion vapor phase to the liquid phase by cooling.*

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**The vapour pressure of pure liquids  $p_o$ :** it is the pressure exerted by the vapour released from any material at a given temperature when enclosed in a container.

Vapour pressure depends only on the temperature and the type of substance, the vapour pressure is calculated from the tables or the equation of a special relationship, such as Antonio equation:

$$\ln p_o = A - B / (T + C)$$

$p_o$  = vapour pressure, mmHg

A, B, C = constants depend on substance.

T = temperature, K

Liquids that evaporate easily and rapidly at normal temperatures are called volatile liquids. They have weak intermolecular attractions. Volatile liquids release more particles above the liquid surface than nonvolatile liquids. Therefore, the vapour pressure of a volatile liquid is higher than that for a nonvolatile liquid when both liquids are at the same temperature.

**Boiling point:** it is temperature at which the vapour pressure of a liquid equal the pressure of the atmosphere above the liquid boiling point is directly proportional with the pressure, when the pressure on a liquid is increased, the Boiling point is increased.

## Explanation of boiling phenomena

When the liquid is heated to a high enough temperature, Bubbles of vapor is form and rise to the surface. (the heating process will increase the kinetic energy of the particles within the vapor bubble inside the bubble), This leads to increased vapor pressure inside the bubble formed to be equal with the pressure off the (atmospheric pressure + pressure liquid) begins to rise to bubble to escape from the liquid surface and explode This process is called boiling, and the temperature at which it occurs is defined as the liquid's boiling point.

For example, in an open container at sea level, the normal boiling point of water is 100° C If a liquid ( water) contained or keep in closed container in the close tank , Some particles will escape from the liquid to the space above the liquid surface as a result of the kinetic energy of particles (evaporation).

That the particles will be force on the walls of the tank and on the surface of the liquid and the force is a vapor pressure of the liquid....

That molecules which is evaporated from liquid will be condensed and the process continues to be a balance between the molecules vaporized and condensed, and this is called (equilibrium ).

Note 1: in the binary mixture, Lighter components have a higher partial pressure (low boiling point ) and thus are concentrated in the vapor, but heavier volatile components have a smaller partial pressure ( high boiling point ).

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Note 2: When the vapor pressure becomes equal to the total pressure the liquid starts boiling.

**Bubble point:** is the temperature at which the first bubble of vapour will formed

When heating the liquid and it is property for liquids

$$T_m = T_A X_A + T_B X_B + T_C X_C + \dots$$

$T_m$  = the boiling point of the mixture

$T_A, T_B, T_C$  = boiling point of the components

$X_A, X_B, X_C$  = mole fraction in the liquid phase of the components of the mixture.

**Dew point** is the temperature at which the first drop of liquid will formed when cooling the vapour and it is property for vapours

## The laws of partial pressures:

**Dalton's Law:** *the total pressure of a mixture equal to the sum of partial pressures of the components in the mixture.*

$$P_T = \sum P_i$$

Or partial pressure of the one component equal to total pressure of the mixture multiplied by its mole fraction of that component in vapour phase

$$P_A = P_T \cdot y_A$$

Where:

$P_A$  = partial pressure

$P_T$  = total pressure

$y_A$  = mole fraction of component A

**Raoult law:** *partial pressure of one component in mixture equals to its mole fraction of component in liquid phase multiplied by its pure at same temperature vapor pressure.*

$$P_A = P_A^0 \cdot x_A$$

Where:

$P_A^0$  = vapor pressure of pure

$x_A$  = mole fraction in the liquid phase

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**Henry's Law:** *the partial pressure of one component in a mixture proportion to its mole fraction*

$$P_A = \chi \cdot x_A$$

Where:

$\chi$  = Henri constant from table depend on substance

Note 1: mole fraction in the liquid phase can be calculated by the following law:

$$X_A = \frac{P_T - P_B^O}{P_A^O - P_B^O}$$

**Example 1** / heptane and toluene at a temperature of 373 K and under the pressure of 101.3 KN / m<sup>3</sup>. Calculate the concentration of vapor and liquid components, if the vapor pressure of pure heptanes and toluene is 106 KN / m<sup>3</sup> and 73.7 KN / m<sup>3</sup> respectively.

**Example 2** /of a mixture of methane and ethane at a total pressure 750 mmHg. The weight fraction of methane, 0.4. Calculate the partial pressure of methane and ethane? If you knowing the molecular weight of methane and ethane is 16 , 30 respectively

## Example No.1

heptane A , B = toluene

$$X_A = \frac{P_T - P_B^O}{P_A^O - P_B^O} = \frac{101.3 - 73.7}{106 - 73.7} = .856$$

$$Y_A = \frac{P_A^O X_A}{P_T} = \frac{106(.856)}{101.3} = .896$$

$$X_A + X_B = 1 \Rightarrow 0.856 + X_B = 1 \Rightarrow X_B = 0.144$$

$$Y_A + Y_B = 1 \Rightarrow 0.896 + Y_B = 1 \Rightarrow Y_B = 0.104$$

## Example No. 2

A =methane, B = Ethane

convert weight fraction to the mole fraction

$$Y_A = \frac{0.4/16}{0.4/16 + 0.6/30} = 0.55$$

$$Y_A + Y_B = 1 \Rightarrow 0.55 + Y_B = 1 \Rightarrow Y_B = 0.45$$

$$P_A = P_T Y_A \Rightarrow P_A = 750 * 0.55 = 412.5$$

$$P_B = 750 * 0.45 = 337.5$$

**Example 3** / liquid mixture consists of (methanol and water).Total vapor pressure of the mixture is 760 mm Hg. If you knowing the vapor pressure of pure water is 350 mmHg and for pure methanol is 1300 mmHg, Calculate:

1 - mole fraction of water and methanol in the liquid phase .

2 - partial pressure of methanol and water

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## Volatility ( $\alpha$ ):

In a binary mixture, the component that has a high vapor pressure (low boiling point), called the higher volatile component, and the component with a low vapor pressure (high boiling point) is called the low volatile component.

Volatility: Ratio of partial vapor pressure of the component to the mole fraction of the component in the liquid phase

$$\alpha_A = P_A / X_A$$

The relative volatility = volatility of the component A / volatility of the component B

$$\alpha_{AB} = (P_A / X_A) / (P_B / X_B)$$

$$\alpha_{AB} = (P^{\circ}_A) / (P^{\circ}_B)$$

Note:

If  $\alpha_{AB} > 1$  means that the component A more volatility

If  $\alpha_{AB} < 1$  means that the component B the more volatility

If  $\alpha_{AB} = 1$  means that the volatility of component A is equal to the volatility of component B, and then the mixture cannot be separated using normal distillation

## The principle of the distillation process

When heating a liquid mixture to its boiling point, the vapour will be liberated, containing the light component (more volatile) of the low boiling point and higher vapor pressure while the liquid containing heavier component (less volatile) of boiling point and low vapor pressure, the figure (1) show a simple distillation of water

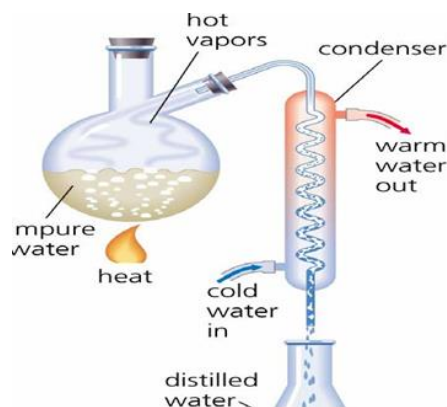


Figure 1 simple distillation of water

When heating the impure water and reach to the boiling, the vapor is rises and enter the condenser and contact with cold surface and then condensation to the liquid

## Classification of distillation

Distillation is classified according to :

### 1 - Number of system components:

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- **Binary distillation:** it is separating process of a mixture containing only two components, such as separation of ethanol from water.
- **Multi component distillation:** it is separating process of a mixture containing three or more components such as the separation of crude oil.

## 2- Processing mode

- **Continuous distillation**

Liquid mixture is continuously fed into the process and separated fractions are drawn continuously as output streams. Continuous distillation produces at least two output products, including top product (volatile distillate fraction), which has boiled and separately as a vapor and then condensed to a liquid. And bottom product (residue fraction), some of liquid distillate is often returned to the column where it flows back to the bottom which called reflux.

Figure ( 2) show the continuous distillation.

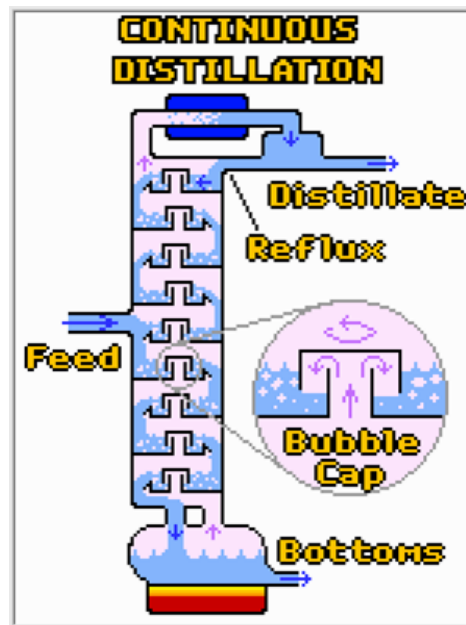


Figure 2 Continuous distillation.

This type is used in oil refineries and large industrial projects where it is producing large quantities and with high specifications and quality.

This unit use integrated control system to control about the operating variables (pressure, temperature, level, flow rate).

- **batch distillation**

In this process the amount of feed in the tank is heating and the mixture is boiling producing vapour above the liquid, The vapour (low boiling point component) goes through the condenser and is removed from the system and the liquid which remain in the still contain high boiling point component ,this type is used in small industrial units,

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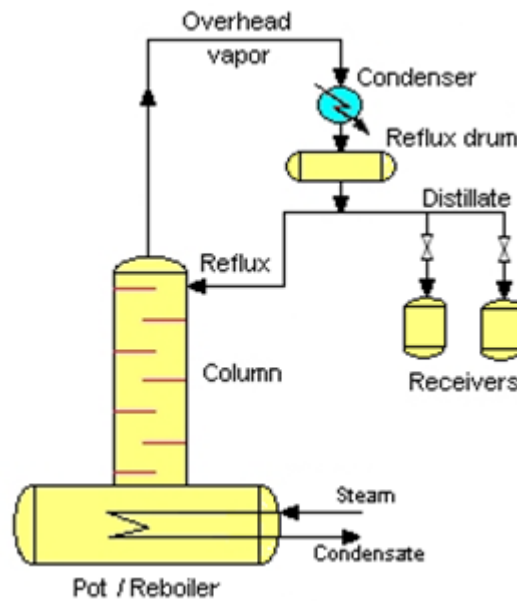


Figure 3

## 3 - Operation pressure

### A / atmospheric distillation

It is a distillation process is performed under normal atmospheric pressure, such as distillation of crude oil in refinery.

### B / vacuum distillation

Distillation process is carried out using vacuum pressure (pressure less than atmospheric pressure), the reduce in pressure cause to reduce in boiling point of components therefore the vacuum distillation is used to separate the heavy components such as atmospheric distillation residues (RC) to avoid decomposed their molecules , the vacuum pressure is generate by using ejector or vacuum pumps.

## 4 - The type and nature of the mixture:

### A / distillation of a real mixture:

The mixture is called real mixture when have initial and final boiling point, this mixture is distilled by normal distillation.

### B / distillation of azeotropic mixture

Some liquid mixture cannot be separated by distillation because the volatility of components are approaches (relative volatility of mixture normal is equal to one) . This type of mixture is called azeotropic mixture like, ethyl alcohol and water form an azeotrope of 95.6% at 78.1 °C. So to distillate this type we change the rate of volatilization of the mixture by adding benzene  $C_6H_6$  to make mixture rate volatility is greater than one compared to alcohol.

Immiscible liquids, such as water and benzene, easily form azeotropes. Commonly, these azeotropes are referred to as a low boiling azeotrope because the boiling point of the

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azeotrope is lower than the boiling point of either pure component (ethyl alcohol). The new azeotropes (water and benzene ) is separated from the top of the tower either alcohol will be withdrawn from the bottom of the tower.

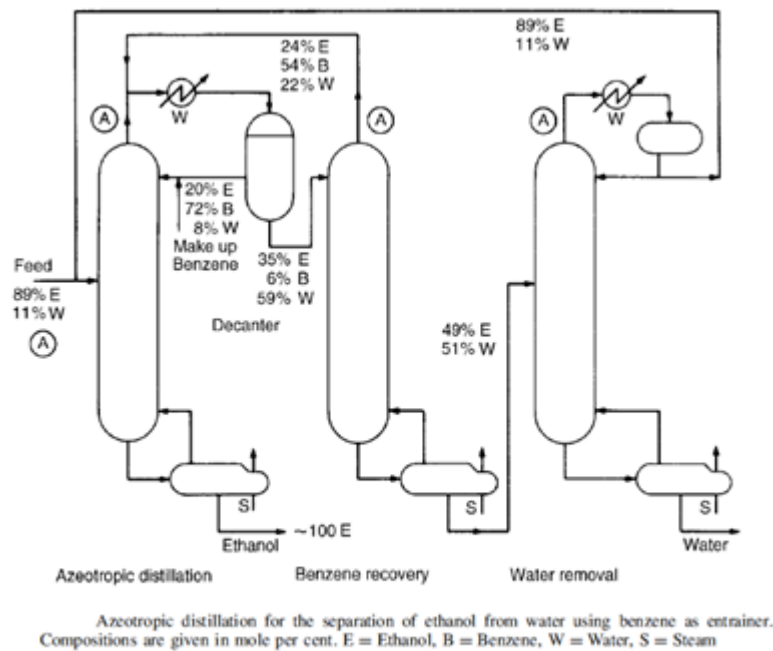
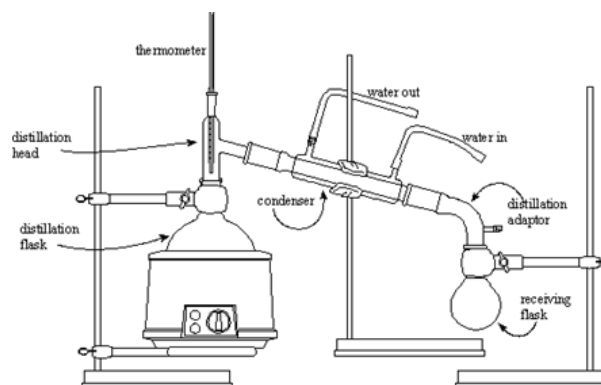


Figure 4

## Distillation methods:

### 1 - Differential distillation:

The device consists of flask ( equipped with steam coil or jacket for heating ) in which the feed material is heated, a condenser in which the heated vapor is cooled back to the liquid state, and a receiver in which the concentrated or purified liquid, called the distillate, the separation of light component is rapidly at the beginning of distillation process , and when the continuation of the distillation the product distillation becomes weaker. Therefore, the distillate concentrations changing with time. This type is usually used for the purposes of laboratory and experimental

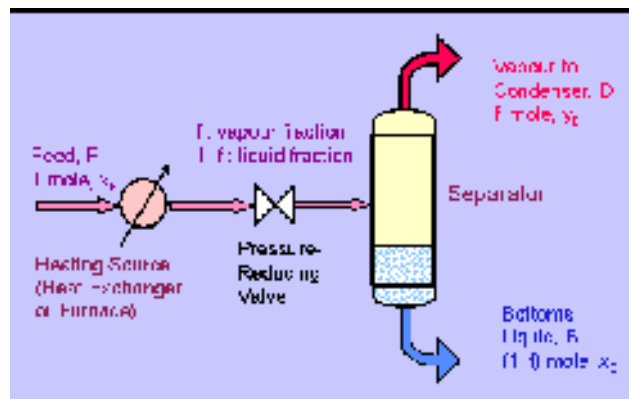




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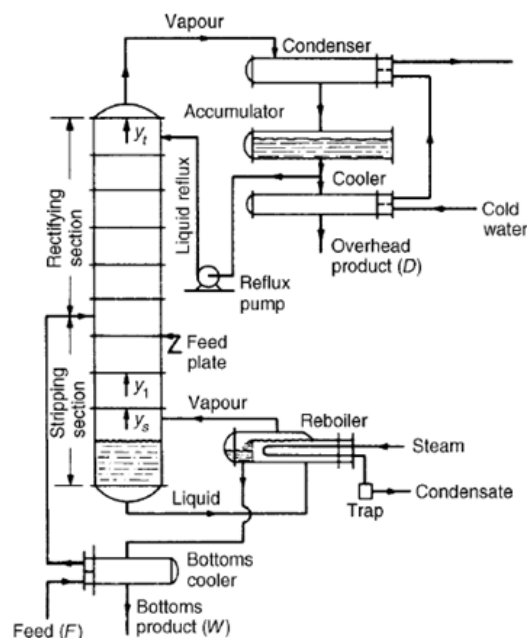
## 2 - Flash distillation:

The distillation unit consists of heat exchanger to heat the mixture and throttle valve and the separation tower. The feed is usually pumped through a fired heater and enters the separator through a valve where the pressure is reduced. The vapor is removed from the top of the separator and usually condensed, while the liquid leaves from the bottom.



## 3- Fractional Distillation

The column consists of a cylindrical structure divided into sections by trays which permit the upward flow of vapor. The liquid reflux flows across each tray. The vapor rising from the top tray passes to a condenser and then through an accumulator or reflux drum and a reflux divider, where part is withdrawn as the overhead product D, and the remainder is returned to the top tray as reflux R.



The liquid in the base of the column is frequently heated, by reboiler, where the liquid from the still passes into the reboiler where it flows over the tubes and leaves as the bottom product by way of a bottoms cooler, which preheats the incoming feed. The vapor generated

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in the reboiler is returned to the bottom of the column, and enters the bottom tray where it is partially condensed and then re-vaporised.

## Notes:

1. The partial condensation of the rising vapor and partial vaporization of the reflux liquid is repeated on each tray.
2. The vapor rising from an ideal tray will be in equilibrium with the liquid leaving, .
3. The part of the column above the feed point is known as the rectifying section and the lower portion is known as the stripping section.
4. On each tray the system tends to reach equilibrium because:
  - (a) Some of the less volatile component condenses from the rising vapor into the liquid thus will be increase concentration of the more volatile component (MVC) in the vapor.
  - (b) Some of the MVC is vaporized from the liquid on the tray thus decreasing the concentration of the MVC in the liquid.

## Distillation Equipment:

The distillation tower called fractional tower because of the light component is removed from heavy component and heavy component is removed from light component at the same time.

The tower is divided into two parts.

**1 – Rectifying section:** a section located above the feeding area, a section that gets the removal of heavy material from the light component.

**2 – Stripping section:** a section located below the feeding area, a section that gets the removal of light material from the heavy component.

Notes: -

1 - The highest temperature at the bottom of the tower it must not be exceed the boiling point of the heavy component to prevent vaporization of heavy component .

2 - The lower temperature at the top of the tower, must not be less than the boiling point of the light component to prevent condensation of light component.

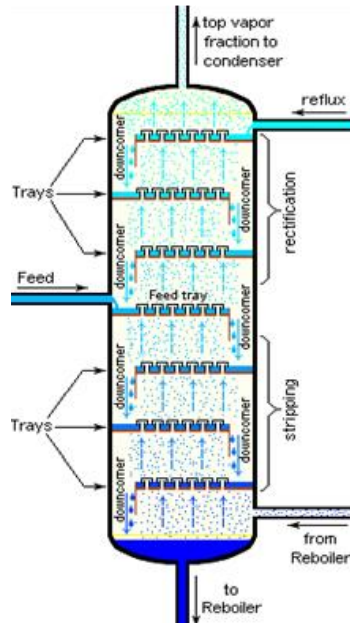
## The tower description:

The tower is a cylindrical column contains a number of trays (plates) or the packets.

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## 1 - Trays tower:

is a cylindrical shape contains a number of trays, placed on a regular basis which are used for providing the largest surface area of contact between the two vapor and liquid.



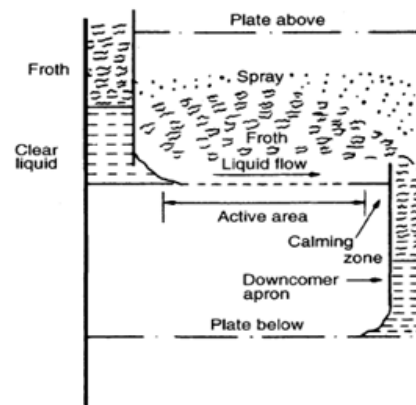
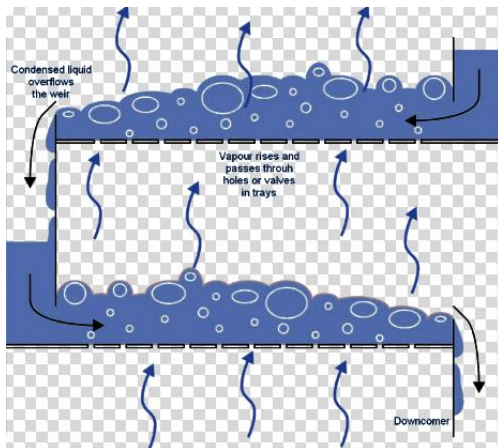
**The main parts of the trays tower:**

### First / plates or trays:

The main purpose of the plates is to make the liquid and vapor touch and direct contact. And providing the largest surface area of contact between the two phases, thus increasing the efficiency of transmission of material between them, thus will increase the efficiency of separation. The plates must be installed well and strong and stable during the operational process and connect in a practical way for easy access and inspection and maintenance. The plates contain the structures attached to them is (downcomer and weir).

### Downcomer :

The flowing liquid is transferred from plate to plate through vertical channels called "downcomers". Liquid is kept on the plate by an outlet weir.

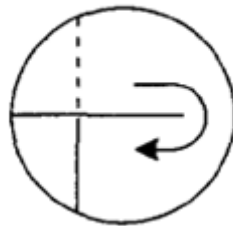


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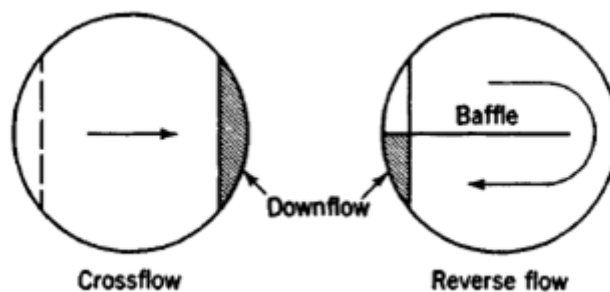
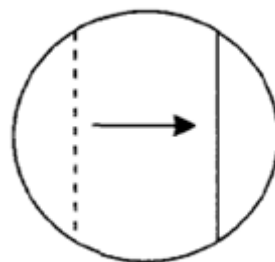
There are two downcomer and two weir equipped for each plate one for enter the liquid, and other for exit the liquid. the efficiency of the separation process on the plate depends on the height of the liquid and the distribution and flow of the liquid on the plate.

Methods of the liquid flowing from plate to other:

**1 - Reverse flow:** the liquid flow down from the slot located on the upper plates and then flow over the next plate and exit from the slot located on it .



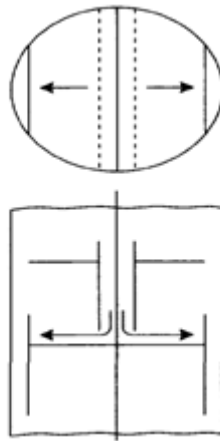
**2 - Cross-flow:** the liquid flow down from the slot located on the left of the upper plate and then flow over the next plate and exit from the slot located on the right of the plate.



### 3- Double pass flow

the liquid down from the slot located on the center of the upper plate and then flow over the next plate and exit from the slot located right and left on the plate .

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## 4 - radial flow:

The liquid down from upper plate through a hole in the center of the plate and then flow over the next plate and exit from surrounding small holes located on it

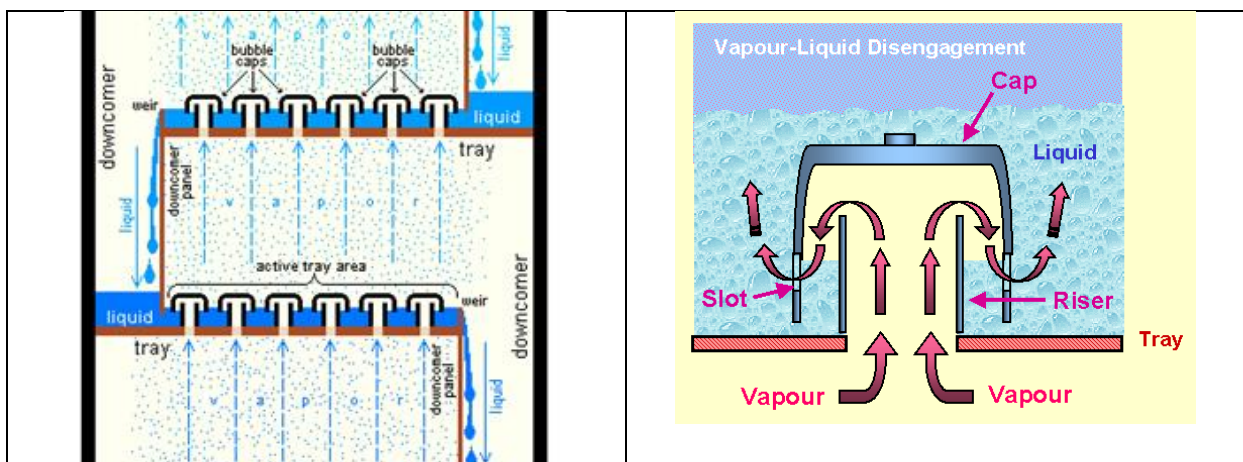
## Types of plates :

### 1 - bubble cup plate:

Plates consists of

- a number of cups or covers ( circular or rectangle) distributed on the plate
- slots arrange on the edge of cup
- The riser (placed under the cup ).

vapor is elevated from the plate to upper plate and passes through the riser and hit with the roof cover and passes through the liquid, causing bubbles and good contact between the liquid and vapor. As shown in the figure below:



### 2 - Sieve plate:

Plate is flat contains a large number of small holes (diameter of the hole 1.3 cm. 0.3 approximately) ,it is simple to install and cheap, easy cleaning and maintenance , vapour

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being vertically passed through the holes to come out in the form of bubbles and contact with liquid.

The disadvantage of this plate is flow the liquid through the holes ( weeping phenomena ) .. In order to avoid this phenomenon , The flow rate of vapor must be more than the flow rate of the liquid or by decreasing the diameter of hole and increase their numbering.



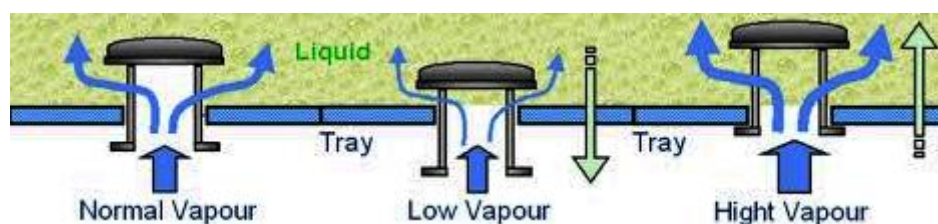
## Comparison of the bubble cup and sieve plate

sieve plate	bubble cup plate
simple structure, cheap and easy to clean	complex and expensive installation
Flow rate of vapor is vertical	Flow rate of vapor is kinky
Speed of vapor is high	Speed of vapor is few
contact between the phases is few	contact between the phases is large
Plate Efficiency is small	Plate Efficiency is high

### 3 – Valves tray:

It is sieve plate with large-diameter holes covered by movable flaps, which lift as the vapor flow increases.

As the area for vapor flow varies with the flow-rate, valve plates can operate efficiently at lower flow-rates than sieve plates: the valves closing at low vapor rates. These plates with high flexibility and inexpensive (costing more than about 20% for plates holes).



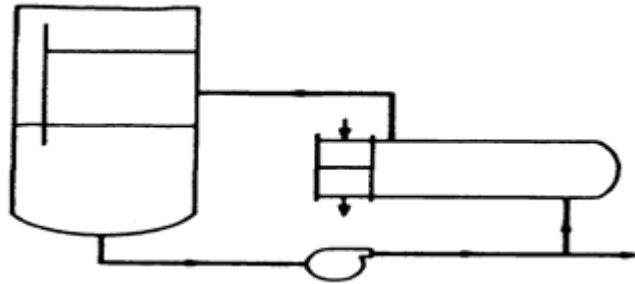
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## Second / Reboiler

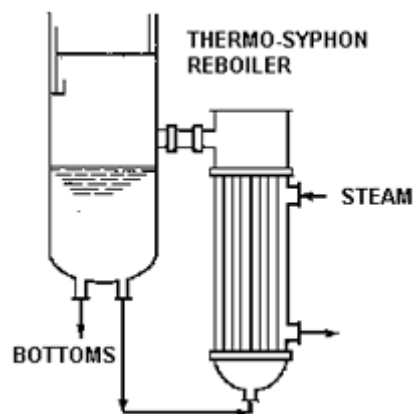
Reboilers are used with distillation columns to vaporise a fraction of the bottom product;

Four principal types of reboiler are used:

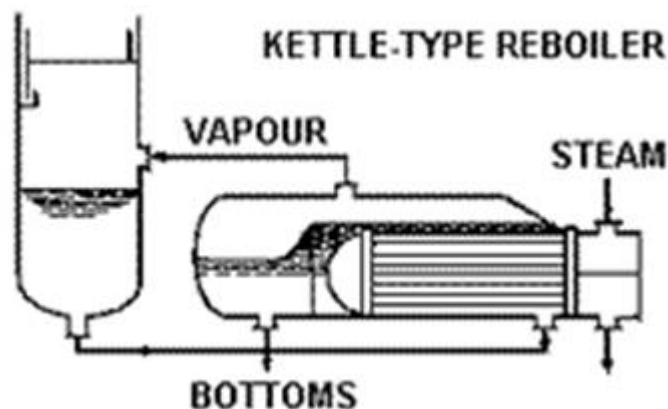
1. **Forced circulation**, : in which the fluid is pumped through the exchanger, and the vapor formed is retrain to the base of the column.



2. **Natural circulation**: The liquid circulation through the exchanger is by the difference in density between the two-phase mixture of vapor and liquid in the n the base of the column.

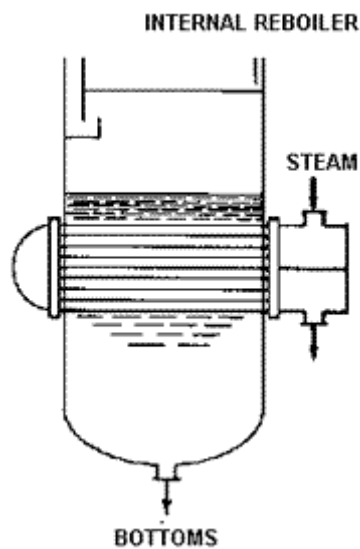


3. **Kettle type**, : in which boiling takes place on tubes immersed in a liquid; there is no circulation of liquid through the exchanger.



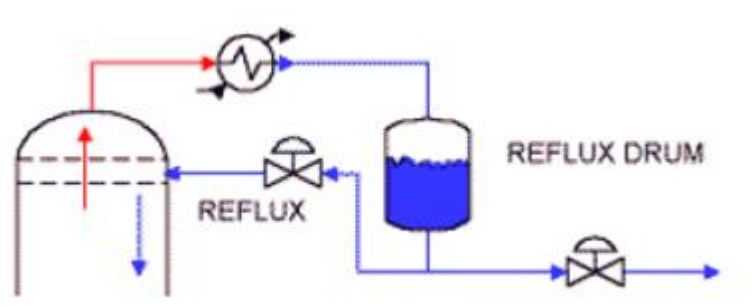
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4. Internal reboiler: it is bundle of tube exchanger in the base of the column.



## Reflux:

Reflux refers to the portion of the condensed overhead liquid product from a distillation or fractionation tower that is returned to the upper part of the tower, the benefit of reflux is control about top tower temperature by cooling it & increase the purity of product.



## Types of reflux:

1 - Cold reflux: it is the reflux which have temperature less than the bubble point of the liquid condensate, and it is used to control the temperature of top tower and prevent the escape of heavy components by condensate it .

2 - Hot reflux: it is the reflux which have temperature at the bubble point of the liquid ( saturated liquid ) also the internal liquid inside the tower called hot reflux.



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## The reflux ratio{R}:

That is the ratio of the top overflow to the quantity of product, is denoted

$$R = LR / D$$

The total cost of the distillation tower depends on the

- 1 – Fixed (capital) cost, which depends on the operating and diameter of the trays
- 2 - Operating costs, which depend on the steam used for heating and water used for cooling

The increase in reflux ratio influences both operating and capital costs.

- 1- If the increase is little the capital cost decrease due to decrease the number of plate
- 2- If the increase is large the capital & operating cost increase because the vapor load becomes greater. The associated condenser and reboiler will also be larger and hence more expensive.

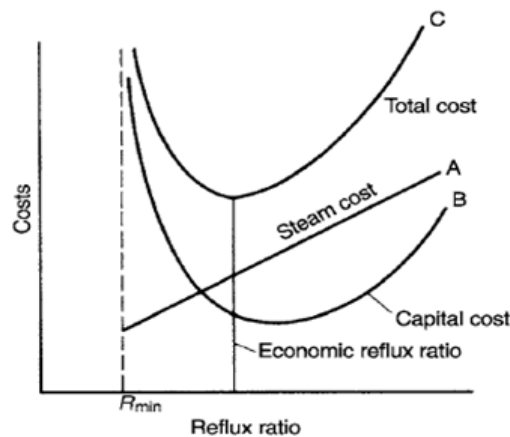


Figure 5 Explain relation between reflux ratio and cost

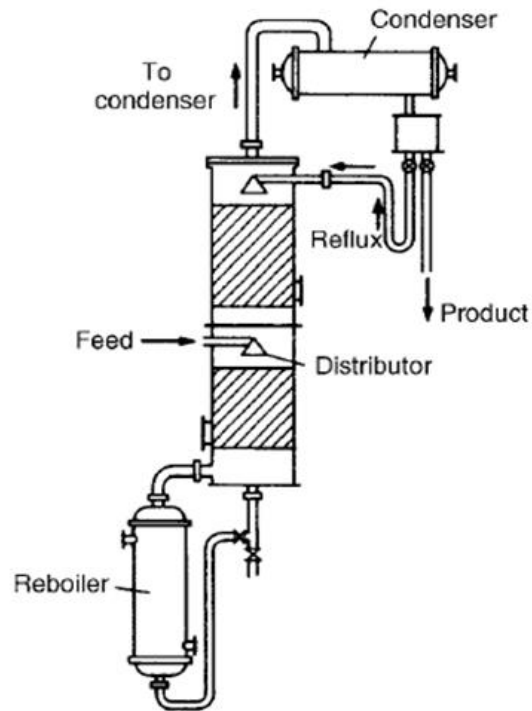
## 2 – Packed tower:

It is the cylindrical column filled with packing which are designed to provide a high interfacial area for transfer.

the vapor - liquid contact in a packed bed column is continuous, not stage-wise, as in a plate column. The liquid flows down the column over the packing surface and the vapor counter-currently up the Packing

The performance of a packed column is very dependent on the good liquid and gas distribution throughout the packed bed.

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## References

1. *Chemical Engineering, Volume (2) By Coulson & Richardson s, Fifth edition, 2002*
2. *Chemical Engineers Handbook. By Robert H.Perry.Don*
3. *Baghdad oil training institute (lectures)*