CHAPTER 4

FRACTIONAL DISTILLATION
4.1 Introduction

Generally the process for obtaining essential oil is carried out in two steps. In first step the biomass is harvested and left on field for a period of 24 hours for loss of water. The semidried biomass is steam distilled or hydro distilled to obtain essential oil. The second step is known as rectification. In this process the crude essential oil is subjected to fractional distillation and separated on the basis of the volatile property of different components of the essential oil.

The mint oil consists of many components like α-pinene, β-pinene, l-limonene, menthone, l-menthol, etc (table –5.2). The individual fraction of mint crop in pure form costs many times higher than crude essential oil. So various distillation technique were developed and also in the process of development to separate the different fraction of essential oil in maximum purity and quantity.

Separation of liquid mixtures present in natural product into their components is one of the major processes confronted by the chemical engineer. Distillation is the most widely used method for achieving the objective. At present, demand of obtaining components in high purity and maximum yield has necessitated research to develop better distillation technique on the basis of simple method for design calculations.

Generally, the distillation columns are having 0.15 to 10m in diameter and 3 to more than 75m in height. The main aim of the designer is to get product of desire quality and quantity at minimum budget.

The basic principle of design lies in the fact that when a liquid containing two or more components is heated to its boiling point, the composition of the vapour will normally is different from that of the liquid. The difference in composition of the vapour in equilibrium with the liquid can be determined experimentally by using equilibrium still. The results are generally expressed by temperature composition diagram Fig 4.1

Here the curve ABCJ which shows the composition of the liquid that boils at any given temperature is called the boiling point curve and the ADEJ which gives the corresponding composition of the vapour at the temperature is the dew point curve.

Now if a mixture of composition $X_2$ is at a temperature below its boiling point $T_3$ as shown by point G on the diagram, then on heating at constant pressure the following changes will occur:
1. At temperature $T_2$, the liquid will boil and have composition given by point B, the vapour formed will have composition $Y_2$, given by point E.

2. On the heating to temperature $T'$, some more volatile components are lost and the liquid composition is given by point L. The corresponding vapour composition is given by point N. Since no material is lost, the change in the ratio of liquid to vapour is given by

$$\frac{\text{Liquid}}{\text{Vapour}} = \frac{MN}{ML}$$

3. On further heating to temperature $T_1$, all the liquid is vaporised to give vapour D of the same composition $Y_1$ as the original liquid $X_2$.

Fig-4.1 Effect of partial vaporization and condensation at the boiling point
This shows that partial vaporisation of the liquid gives a
vapour richer in the more volatile component than the liquid. Thus
if the vapour of component at E is removed at once by condensation,
then liquid of composition X₃, represented by point C is obtained.
The step BEC may therefore be regarded as representing an ideal
stage, since we pass from a liquid of composition X₂ to that of
composition X₃, which is richer in the more volatile component than,
can be obtained by another degree of vaporisation. Similarly if
superheated vapour of composition H is cooled to D, condensation will
commence, and the first drop of liquid will have a composition K.
Further cooling to T, will give liquid L and vapour N. Thus partial
condensation brings about enrichment of the vapour in the more volatile
component (MVC) in the same manner as partial vaporisation. The
industrial distillation column is in essence a series of units in which
the partial vaporisation and condensation take place simultaneously.

4.2 Methods of Distillation
For two component mixtures:

As seen in the Y,X diagram Fig 4.1, the
vapour formed is always richer in the MVC than the liquid in
equilibrium. Based on this fact, three main methods have been developed
for distillation namely:
4.2.1 Differential distillation
4.2.2 Flash or equilibrium distillation and
4.2.3 Rectification

4.2.1 Differential distillation
This is a simple case of straight
batch distillation. In this the mixture charged in the distillation still
is heated at a constant rate. The vapour formed by boiling is removed
at once. Since the vapour formed is richer in the MVC than the liquid
left in the still, the liquid in the still progressively gets weaker in the
MVC. Thus the composition of the distillate continuously keep on
changing. The vapour formed in the still is in equilibrium with the
liquid only for a short period, where as the total vapour formed is
not in equilibrium with the residual liquid in the still. At the end the
residual liquid is removed as bottom product.

4.2.2 Flash or equilibrium distillation
It is a continuous process
wherein feed is pumped at a constant rate. It is preheated and flashed
in a separator through a valve where the pressure is reduced. An
intimate mixture of vapour and liquid get sufficient time to reach
equilibrium and separate. The vapour is removed from the top of the
separator and condensed. The liquid leaves from the bottom. This system is widely used in the pipe stills of the petroleum industry where for instance a crude oil enters a pipe still at 170°C and about 115 lbs/sq in and leaves at 245°C and a pressure of only 431 lbs/sq in some 15% being vaporised.

4.2.3 Rectification

In differential as well as flash distillation processes described above, the vapour produced at any time is in equilibrium with the liquid, which gives only a small increase in the concentration of MVC. In rectification successive vaporisation and condensation achieve a very high enrichment of the MVC in an arrangement known as fractionation column.

The principle of such an arrangement can be shown by considering 3 vessels arranged as shown in Fig 4.2. Here liquid in vessel I is heated by passing steam in a cooled coil. The vapour $Y_1$ produced at temperature $T_1$ enters liquid $X_2$ at temperature $T_2$ in vessel 12. The vapour $Y_1$ being at higher temperature than liquid $X_2$ partially condense to give vapour $Y_2$. Similarly vapour $Y_2$ condense in liquid $X_3$ in vessel-3 producing vapour $Y_3$. If the starting liquid considered be a mixture of benzene and toluene then vapour $Y_3$ will be richer in benzene than the liquid $X_3$ which will be progressively weakened in benzene, and hence $Y_3$ will steadily fall. If now some of the condensate is returned to vessel-3, it will help to maintain the concentration of benzene in vessel-3.

A material balance will show that in order to keep the concentration of benzene up to the value of $X_3$, it will require to return all the condensate. Thus in all the vessels, the vapour is partly condensed and a new vapour stream is produced giving conditions equivalent to partial condensation and vaporisation. In this way each vessel can be considered as giving enrichment corresponding to an equilibrium stage BEC, shown in Fig 4.1. The heat required is supplied by steam coil in vessel-1. The subsequent vessels being heated by the rising vapour only. All the vessels and lines are well insulated to avoid any heat loss.

4.3 Fractionating Column

The conditions prevailing in these can be better obtained in a fractionating column as shown in Fig 4.3. It comprises of a vertical cylindrical column divided into a number of sections by a series of perforated trays, which permit the upward flow of vapour. The liquid reflux can run over a weir on each tray. At the top of the column is provided a condenser and a reboiler usually heated by steam are provided at the bottom of the column.
Fig-4.3 A simple batch fractionating column
Fig-4.4 A continuous fractionating column
In this the steam condensing in the bunch of heating coil, boil the liquid $X_s$ in the reboiler, giving vapour $Y_s$, which enter the liquid $X_1$, on the first plate. Each of the section or the perforated trays thus form a stage between the vapour bubbles and the liquid on each tray and the system tends to reach equilibrium because,
a) Some of the less volatile component condenses from the rising vapour into the liquid, thus increasing the concentration of the more volatile component (MVC) in the vapour.
b) Some of the MVC is vaporised from the liquid on the tray thus decreasing the concentration of the MVC in the liquid.

The number of molecules passing the each direction from vapour to liquid and in reverse will be approximately the same, since the heat given out by one mole of the vapour on condensing is a approximately equal to the heat required to vaporise one mole of the liquid.

The process of fractionation in an ideal case involves equimolecular counter diffusion. In practice complete equilibrium is not attained between the rising vapour and the liquid on the plate and the enrichment between two plates is less than the ideal stage represented by the step BEC in Fig 4.1. Again whenever any product is withdrawn from the top of the column the enrichment per plate will fall, as insufficient of MVC is then returned from each stage to the one below. Invariably all of the vapour is condensed and the fraction returned to the column is known as reflux. The ratio of the amount returned to that removed as product is known as reflux ratio, denoted by $R$. A fractionating column could be made for batch or continuous operation. For batch operation the column is mounted on a large reboiler or still which holds the charge, and the column is called a rectifying column. The plates in the column increase the concentration of the MVC in the vapour and hence in the product, and the liquid in the still gets richer in the less volatile component. In case of continuous type column the feed is continuously fed and admitted over some intermediate plate in the column. The portion above the feed point is called the rectifying section and that below, the stripping section. In stripping section the plate strips out the MVC, so that the liquid withdrawn from the bottom of the column has a minimum concentration of this component and better recovery is obtained. Such a fractionating column is shown in Fig 4.4.

4.3.1 Equilibrium Curve or Relative Volatility ($\alpha$)

According to Dalton's Law of partial pressure, the total pressure $P$ of a mixture is equal to sum of the partial pressure of its components i.e.

$$ P = \sum P_A $$

For a ideal mixture the partial pressure is proportional to the mole fraction of the component in vapour phase.
i.e. \[ P_A = Y_A P \] ————4.1

Henry's Law states that the partial pressure developed by liquid solute A in a solvent liquid B is proportional to its mole fraction in the solvent

\[ P_A = H X_A \] ———— 4.2

According to Roult's Law partial pressure \( P_A \) of a solute is related to its concentration in the liquid phase and is given by

\[ P_A = P_{A\text{*}} X_A \] ———— 4.3

\( P_{A\text{*}} \) is a vapour pressure of pure A at same temperature if A is regarded as solute and B as solvent.

Volutality of a component in a liquid mixture is defined as the ratio of its partial pressure to its mole fraction i.e.

- Volatility of A = \( P_A / X_A \) ———— 4.4
- Volatility of B = \( P_B / X_B \) ———— 4.5

The relative volatility (\( \alpha \)) is ratio of these two volatility

\[ \alpha = P_A \cdot X_B / P_B \cdot X_A \] ———— 4.6

Substituting \( Y_A P \) for \( P_A \) and \( Y_B P \) for \( P_B \)

\[ \alpha = Y_A \cdot X_B / Y_B \cdot X_A \] ———— 4.7

or \[ Y_A / Y_B = \alpha X_A / X_B \] ———— 4.8

For binary mixture

\[ Y_B = 1 - Y_A \text{ and } X_B = 1 - X_A \]

By substituting we have

\[ Y_A = \alpha X_A / 1 + (\alpha-1) X_A \] ———— 4.9

This is known as equilibrium equation.

Again substituting eq.4.3 in eq.4.6 give

\[ \alpha = P_{A\text{*}} \cdot X_A X_B / P_{B\text{*}} X_B \]

so relative volatility is ratio of the vapour pressure of two components.

4.3.2 Number of Plates required in a distillation column

For getting desired separation it is necessary to develop an analytical approach for calculating the number of plate required.

If we took a plate in the column four streams are involved in transfer of heat and material across a plate as shown in fig-4.5.
Plate’s ‘n’ receive liquid $L_{n+1}$ from plate n+1 above and vapour $V_{n-1}$ from plate n-1 below. Plate ‘n’ supplies liquid $L_n$ to plate n-1 and vapour $V_n$ to plate n+1. So plate ‘n’ acts to bring about mixing so that the vapour $V_n$ of composition $Y_n$ reaches equilibrium with the liquid $L_n$ of composition $X_n$.

The streams $L_{n+1}$ and $V_{n-1}$ approaching plate ‘n’, can not be in equilibrium during the interchange process on plate ‘n’. But $L_{n+1}$ loose some of more volatile component through vaporization, decreasing its concentration to $X_n$ and $V_{n-1}$ loose some of its less volatile component through condensation increasing its vapour concentration to $Y_n$. The heat required to vaporize more volatile component from the liquid is supplied by the partial condensation of the vapour $V_{n-1}$. In this way the more volatile component passes from the liquid running down the
column to the vapour rising up, while the less volatile is transferred in the opposite direction.

4.3.3 Heat Balance over a plate

Heat balance across a plate

\[ \dot{L}_{n+1} \cdot H_{L,n+1} + \dot{V}_{n-1} \cdot H_{V,n-1} = \dot{V}_n \cdot H_{V,n} + \dot{L}_n \cdot H_{L,n} + \text{losses} + \text{Heat of mixing} \]

where

- \( H_{L,n} \) is enthalpy per mole of liquid on plate \( n \)
- \( V_{L,n} \) is enthalpy per mole of vapour rising from plate \( n \)

In an ideal system the heat of mixing is zero. According to Trouton's rule, at constant temperature the molar heat of vaporization can be taken as constant and independent of the composition. It follows that heat released by condensing one mole of \( V_{n-1} \) is sufficient to vaporise one mole of vapour \( V_n \).

This \( V_n = V_{n-1} \)

So the molar flow of vapour in the column is constant unless introduced or withdrawn from the section. The temperature change from one plate to another will be small, so that

\[ H_{L,n} = H_{L,n+1} \]

Similarly, \( L_n = L_{n+1} \)

So \( V_n \) and \( L_n \) will be constant over the rectifying zone and \( V_n \) and \( L_n \) over the stripping section.

4.3.4 Methods for Calculating the Number of Plates

4.3.4a Lewis and Sorel (1909) Method for calculating number of Plates

Suppose a column is operating as in Fig-4.6 and a binary feed \( F \) is distilled to get a top product \( D \) and a bottom product \( W \), with \( X_f, X_d, \) and \( X_w \) as the corresponding mole fractions of the MVC. The vapour \( V_t \) rising from the top plate is condensed. Part of the condensate is taken as product \( D \) and the rest is sent back into the column at its boiling point as reflux \( R \).

Material Balance over plate \( n \) as shown in loop '1' in Fig-4.6

\[ V_n = L_{n+1} + D \] \hspace{1cm} 4.11

In term of MVC

\[ Y_n V_n = L_{n+1} X_{n+1} + X_d \] \hspace{1cm} 4.12

\[ Y_n = L_{n+1} / V_n, X_{n+1} + D / V_n + X_d \] \hspace{1cm} 4.13

Since molar liquid overflow is constant then

\[ L_n = L_{n+1} \]
\[ Y_n = \frac{L_n}{V_n} X_{n+1} + \frac{D}{V_n} X_d \] \hspace{1cm} 4.14

This gives a relation between the composition of the vapour rising to the plate and the composition of the liquid on any plate above the feed plate.

Fig-4.6 Material balances at top and bottom of column

Material balance over plate ‘m’ and also in term of MVC as in loop- II. Fig-4.6 and putting

\[ L_m = L_{m+1} \]

we have
This is similar to eq. 4.14. It gives relation between composition of the vapour rising to plate and liquid below the feed plate. Their two equations are the equation of the operating lines. For calculating change in composition from one plate to next. The equilibrium data is used to find the composition of the vapour above the liquid and the enrichment line to calculate the composition of the liquid on the next plate. Using equation 4.17 for plates below the feed point and equation 4.14 for plates above the feed point can repeatedly use the Method.

4.3.4b Mc Cabe & Thiele (1925) Method

Graphical method for calculating the number of plates. They made use of the enrichment equations, assuming that constant molar heat of vaporization

\[
Y_n = \frac{L_n}{V_n} X_{n+1} + \frac{D}{V_n} X_d
\]

\[
Y_m = \frac{L_m}{V_m} X_{m+1} - \frac{W}{V_m} X_w
\]

No heat loss and no heat of mixing which also lead to constant molar vapour flow and a constant molar reflux flow in any section of the column i.e.

\[
V_n = V_{n+1}
\]

\[
L_n = L_{n+1}
\]

They suggested that since these equations represent straight line connecting \(Y_n\) with \(X_{n+1}\) and \(Y_m\) with \(X_{m+1}\). These when drawn on same diagram as the equilibrium curve, give simple graphical solution for the number of plate require. By putting \(X_{n+1} = X_d\) in equation (4.14) we give

\[
Y_n = \frac{L_n}{V_n} X_d + \frac{D}{V_n} X_d
\]

\[
= (L_n + D) \frac{V_m}{V_n} X_d = X_d
\]

This represent a line passing through \(Y_n = X_{n+1} = X_d\). Then \(Y_n = DX_d / V_n\) Which gives another easily determined point. The top operating line can therefore be drawn through the points \(A(X_d, X_d)\) and \(B(O, DX_d / V_n)\). Similarly in equation 4.17 if we put \(X_m = X_w\) we get

\[
Y_m = \frac{L_m}{V_m} X_{w} - \frac{W}{V_m} X_w
\]

\[
= L_m - \frac{W}{V_m} X_w
\]

Now, \(V_m = L_m - W\)

\[
Y_m = X_w
\]

The bottom operating line passes through \((X_w, X_w)\) and has the slope \(L_m / V_m\). When the operating lines are drawn with the equilibrium
curve as shown in fig 4.7. The number of stage required can be found by drawing step between operating line and equilibrium curve start from point A.

Assuming that two operating line in fig-4.7 intersect at point having coordinate \((x_q, y_q)\). Then the equation 4.14 and 4.17 becomes

\[
V_n y_q = L_n x_q + D x_{d} \tag{4.19}
\]

\[
V_m y_q = L_m x_q - W x_{w} \tag{4.20}
\]

Subtraction gives

\[
y_q (V_m - V_n) = x_q (L_m - L_n) - (D x_{d}) \tag{4.21}
\]

A material balance over feed plate gives

\[
F + L_n + V_m = L_m + V_m \\
V_m - V_n = L_m - L_n - F \tag{4.22}
\]

To obtain a relation between \(L_n\) and \(L_m\) it is necessary to make an enthalpy balance over the feed plate and to consider what happen when feed
enter the column if the feed is all in the form of liquid at a boiling point. The reflux $L_m$ over flowing to the plate below will be $L_n + F$.

If however, the feed is a liquid at a temperature $T_f$, less than the boiling point, some vapour rising from the plate below will condense to provide sufficient heat to bring the feed liquor to the boiling point.

If the enthalpy per mole feed $H_f$ and has feed at it's boiling point $H_{fs}$. Then the heat to be supplied to bring the feed to its boiling point is $F(H_{fs} - H_f)$ and number of mole of vapour to be condensed to provide that heat is $(H_{fs} - H_f)\lambda$, where $\lambda$ is the molar latent heat of the vapour.

Then reflux liqueur

\[
L_m = L_n + F + \frac{F(H_{fs} - H_f)}{\lambda}
\]

\[
= L_n + F \left(\frac{\lambda + H_{fs} - H_f}{\lambda}\right)
\]

\[
= L_n + q F........................................4.23
\]

or $L_m - L_n = q F$

where, $q =$ heat to vaporize one mole of feed

Molar latent heat of the feed

Thus from eq. 4.22

\[
V_m - V_n = q F - F = F(q - 1) .........................4.24
\]

A material balance of the more volatile component over the total column gives: -

\[
F x_f = D x_d + W x_w
\]

Substituting in eq. 4.21

\[
F(q - 1) y_q = q F x_q - F x_f
\]

\[
y_q = q / q - 1 . x_q - x_f / q - 1
\]

This equation is commonly known as equation of the $q$ - line. This shows that the point of intersection of the two operating lines lies on the straight line of slope $q / (q - 1)$. On putting $x_q = x_f$; we see that $y_q = x_f$, and the $q$ - line cuts the diagonal at $y = x_f$. If $y_q = 0$ then $x_q = x_f / q$ and the line can be drawn through two points. It is thus clear that the slope of the $q$ - line is governed by the nature of the feed. i.e. for

a) cold feed as liquor $= q > 1$, q line /

b) feed at boiling point $q = 1$, q line |

c) feed partly vapour $= 0 < q < 1$, q line \

d) feed saturated vapour $q = 0$, q line –

e) feed super heated vapour $q < 0$, q line

The various condition are indicated in Fig-4.8
Alternation in the slope of $q$–line will change the liquid concentration at which the two operating line cut each other for a given reflux ratio. This will mean a slight alternation in number of plate required for the given separation, which the change in the number of plates will usually be rather small, if the feed is cold. There will be an increase in reflux flow below the feed plate, and hence an increased heat consumption from the boiler per mole of distillate. This would mean slight alternation in the number of plate required in the rectification, stripping as well as the total number of plates.

4.3.4c Effect of reflux ratio on the number of plate required

'\(R\)' denotes the ratio of $\ln/D$ of the top over flow to the quantity of the product. This introducing $R$ in equation 4.15 gives

\[
Y_n = \frac{L_n}{L_{n+D}} X_{n+1} + \frac{D}{L_{n+D}} X_d \quad \text{..................................4.25}
\]

\[
Y_n = \frac{R}{R+1} X_{n+1} + \frac{X_d}{R+1} \quad \text{..................................4.26}
\]

Any change in '\(R\)' will therefore modify the slope of the operating line and will alter the number of plate required for a given separation.
By knowing 'R' the top line can be drawn with the co-ordinate A \((x_d, x_d)\) & B \((0, \frac{x_d}{R+1})\), if \(D = 0\) the column is said to be under total reflux substituting \(D = 0\) in equation – 4.26
\[ Y = x_n + 1 \]

This shows that operating line coincides with the line \(Y = x\) and hence minimum number of plates are required. If the reflux ratio is reduced the slope of the operating line is reduced and more stages are required to pass from \(x_f\) to the slope of the operating line is reduced and more stages are required to pass from \(x_f\) to \(x_d\) as shown by line AK in Fig-4.9. Further reduction in ‘R’ will eventually bring the operating line AE where an infinite number of stages are needed to pass from \(x_f\) to \(x_d\).

This arises from the fact that under these conditions the step becomes very close together at liquid composition near \(x_f\) and no enrichment occur from the feed plate to the plate above. This conditions are known as minimum reflux and reflux ratio is denoted by \(R_m\). Any small increase in R beyond \(R_m\) will give a workable system, though number of plates required will be large if reflux ratio is below \(R_m\) as denoted by AG, which will give an important deduction may be made first. That maximum number of plates are required for a given separation at condition of total reflux and secondly that there is a minimum reflux ratio below which it is impossible to obtain the desired enrichment, however many plats are used.

4.3.4d Calculation of Minimum Reflux Ratio \(R_m\)

In Fig-4.9 AE is given by
\[ \frac{R_m}{R_m+1} = \frac{x_d - y_f}{x_d - x_f} \]

or, \(R_m = \frac{x_d - y_f}{y_f - x_f}\) ..........................4.27

If q – line is horizontal as Fig-4.10 AC gives the enrichment line for minimum reflux, where C has co-ordinate \((x_c, y_c)\). Then
\[ \frac{R_m}{R_m+1} = \frac{x_d - y_c}{x_d - x_c} \]

Or \(y_c = x_f\)

\[ R_m = \frac{x_d - y_c}{y_c - x_c} \]

\[ R_m = \frac{x_d - y_f}{x_f - x_c} \] ..........................4.28
Fig-4.9 Influence of reflux ratio on the number of plates required for a given separation

Fig-4.10 Minimum reflux ratio with feed as saturated vapour
4.3.4e Underwood (1946) and Fenske (1932) Equations

That for ideal mixtures the relative volatility ($\alpha$) can be taken as constant, $R_m$ can be obtained analytically from the physical proportion of system. This if $x_{nA} < x_{nB}$ are mole fraction of two component A and B in the liquid of any plate number. Then a material balance over the top portion of the column above the plate n gives.

\[ V_n Y_{nA} = L_n x_{(n+1)A} + D x_{dA} \] ......................................4.29

\[ V_n Y_{nB} = L_n x_{(n+1)B} + D x_{dB} \] ......................................4.30

Now under maximum reflux condition a column will have infinite number of plate, so that the composition of plate ‘n’ will be the same as a plate ‘n+1’. Dividing equation-4.29 by equation-4.30 taking $x_{(n+1)A} = x_{nA}$ and $x_{(n+1)B} = x_{nB}$ we get

\[ \frac{Y_{nA}}{Y_{nB}} = \frac{\alpha}{x_{nA}}/x_{nB} = L_n x_{nA} + D x_{dA}/L_n x_{nB} + D x_{dB} \]

\[ = 1/\alpha - 1 \{ (x_{dA}/x_{nA}) - (\alpha x_{dA}/x_{nA}) \} \] ......................................4.31

Where $\alpha$ is volatility of A relative to B. there is therefore in general a different value to $R_m$ for each plate. In order to produce any separation of the feed. The maximum relevant value to $R_m$ is therefore the feed plates. So that the minimum reflux ratio for a binary system becomes:

\[ R_m = 1/\alpha - 1 [(x_{dA}/x_{fA}) - \alpha(1- x_{dA}/1-x_{fA})] \] ......................................4.32

The number of plates at total Reflux

Fenske’s (1932) Method

Assuming that relative volatility is constant, Fenske derived an equation for calculating the required number of plates for a desired separation. Since no product is with drawn. The equation of the two operating lines becomes:

\[ Y_n = x_{n+1} \text{ and } Y_m = x_{m+1} \] ......................................4.33

For binary mixture A & B conc of which of the still are $x_{SA}$ and $x_{SB}$. Thus the composition as first plate is obtained by

\[ (x_A/x_B)_A = (Y_A/Y_B)_5 = \alpha_5 (x_A/x_B)_5 \]

The subscript outside the bracket indicate the plate and 5th still:

For plate 2:

\[ (x_A/x_B)_2 = (Y_A/Y_B)_1 = \alpha_1 (x_A/x_B)_1 = \alpha_1 \alpha_5 (x_A/x_B)_5 \]

For the plate n:

\[ (x_A/x_B)_n = (Y_A/Y_B)_{n-1} = \alpha_1 \alpha_2 \alpha_3 \ldots \ldots \alpha_{n-1} \alpha_5 (x_A/x_B)_5 \]
If an average value of $\alpha$ is used

$$(xA / xB)_n = \alpha_{AV} (xA/ xB)_5$$

In most cases total condensation occurs in the condenser.

$$(xA / xB)_d = (Y_A / y_B)_n = \alpha_n (xA/ xB)_n = \alpha_{h+1} AV (xA/ xB)_5$$

$$\log \left[ \frac{((xA/ xB)_d) ((xA/ xB)_5)}{\log \alpha_{AV}} \right] = \frac{n + 1}{4.34}$$

$n$ is required number of theoretical plate in column.

### 4.3.4d In Multi-component System

The number of plate desired can be found by applying the Fenske’s equation to the two key components. Underwood (1946) also developed a method for minimum reflux ratio $R_m$ in cases where relative volatility remains constant. He developed the following two equations where $R_m$ may be calculated.

$$\alpha_A x_{fA}/\alpha_{A-0} + \alpha_B x_{fB}/\alpha_{B-0} + \alpha_C x_{fC}/\alpha_{C-0} + \cdots = 1 - q \quad \ldots \ldots \ldots \ldots 4.35$$

$$\alpha_A x_{dA}/\alpha_{A-0} + \alpha_B x_{dB}/\alpha_{B-0} + \alpha_C x_{dC}/\alpha_{C-0} + \cdots = R_{m+1} \quad \ldots \ldots \ldots \ldots 4.36$$

where, $X_{fA}, x_{fB}, x_{fC}, x_{dA}, x_{dB}, x_{dC}$ are mole fraction of component A, B, C etc in the feed distillation

- $A$ is light & $B$ is heavy key components
- $q$ is ratio heat required to vaporize one mole of feed to the molar latent heat of the feed.
- $\alpha_A, \alpha_B, \alpha_C$ are volatility.
- $\theta$ is the root of equation – 4.35 which lies between the value of $\alpha_A$ & $\alpha_B$.

### 4.3.4e Gilliland (1940) Method

Developed in empirical relation between the reflux ratio $R$ and the number of plate ‘n’ in which any the minimum reflux ratio $R_m$ and the number of the plate at total reflux $N_m$ are required.

### 4.4 Batch Distillation

In a continuous fractionating column there is a continuous flow of feed into the column at some point along its height. There is continuous withdrawal of the product too, from the top as well as from the bottom of the column. The concentration of the top and bottom products depends on the feed composition, the number of plates present in the column and the reflux ratio used. Their composition remain constant, so long as there is no change in the feed composition, flow rates, reflux ratio and the other parameters like temperature pressure difference.
across the column etc. In batch distillation column, the feed is charged in the reboiler at the bottom of the column, all at a time and the product is taken out from the top. A general set up is shown in Fig-4.11. In this case the product composition go on changing continuously with the passage of time. The top product is relatively richer in more volatile component, leaving the still weaker in the same. Thus their component go on changing. There are two ways of operating the batch column.

![Fig-4.11 Column for batch distillation](image)

### 4.5 Packed Column

Variety of packing one used more popular one the bubble cap, sieve plates, value plate etc. In all cases efforts one made to give large interfacial area between the rising vapour and the reflux by causing, the vapour to bubble through the liquid. In these column the height of a plate is high. An alternative design is packed column in which the cylindrical shell of the column is filled with some type of packing, which also provides the necessary large interfacial area for diffusion. In these the vapour flows steadily up and return steadily down giving a true column current system.

### 4.6 Column Packing

Column Packing can be divided into three classes: -

1. Random Packing: - These have specific geometric shape and are dumped into column shell. The Random packing has under gone three generation of evolution.
First generation from 1907 to 1950 produced two basic shapes, Rasching ring & Best saddle. The second generation (late 1950 to early 1970s) produced the popular pall rings evolved from Rasching ring and Intalax saddle from berl saddle. Third generation (1970 to update) produced a number of popular geometries mostly evolved from pall ring and intalax saddle.

2. Structural packing: These are the forms of crimped layer of wire mesh. These are slacked in the form of sections in the column.

3. Grids: These are also systematically arranged open lattice structure packing (Fig-5.12).

4.7 Material & Methods

4.7.1 Materials

4.7.1a Crude Mint Oil

Crude mint oil obtained after steam distillation was used for rectification. The general composition of mint oil is as 70-80% is 1-menthol, 9-12% menthone and 5-8% isomenthone and 6-7% terpene (Fig-5.2).

4.7.1b Batch Fractionating Column

The main column and still were designed on the basis of composition of mint terpene. Stainless steel (316) batch fractionating column packed with structured packing (crimped layer of wire mesh) was fabricated by M/s Food Bio-Tech Pvt. Ltd. Faridabad (HR) with own specific instructions. It is shown in Fig-4.13

The column has still capacity of 100 liters. It has four sections of 1200 mm each with diameter 100 mm. The packing height of column was 3600 mm (Photo-4.1). Each section was provided with reflux distributor at the top. The column is provided with a vertical condenser at top, a solenoid value for reflux distribution, one receiver of 5 liter capacity was joined before the two vertical back condensers to minimize the loss due to vacuum (Photo-4.2). A vacuum pump with vapour trap, and chilled by circulating cold water was attached to the condenser unit.

4.7.1c Gas Liquid Chromatography

GLC of Nucon-5700 series was used for getting composition of feed and product samples.

- Amount of sample injected = 2 µl.
- Injector temperature = 120° C
- Detector temperature = 120° C
- Oven temperature = 60° C
- Programming = 4° C/min.

The identification on the basis of standards purchased from Sigma & Aldrich.
Fig. 4.12 Types of packing (Norton Co.). (a) Raschig rings (b) Pall rings
(c) Berl saddle ceramic (d) Intalox saddle ceramic (e) Metal Hypac
(f) Ceramic, super Intalox
A: 50 Lit Heating kettle  
B: Column 4" dia x 2.5 mtr x 4 section  
C: Liquid distribution System  
D: S.S. packing  
E: Condenser (primary) 19mm OD Tube x 9NO  
F: Condenser (Secondary) - do- 
G: Condenser (Tertiary) - do- 
H: 1st stage ejector  
I: 2nd - do-  
J: Vacuum pump optional  
H: Collector pot

Fig-4.13 Fractionating Column  
(Capacity 50 lit.)
Photo 4.1 Pilot scale column having still capacity of 100 liters

Photo 4.2 The vertical condenser system of fraction distillation unit
4.7.1d Vapour Pressure Data

Vapour pressure data of various components was obtained from:
2. The essential Oils by E. Guenther Vol.-1

The vapour pressure data of different components involved is given in Fig-4.12 and table-4.1.

Fig-4.12 Vapour pressure of terpene hydrocarbons
Table 4.1 The Boiling point of different constituents of mint terpenes at different atmospheric pressure.

4.7.2 Methods

The method adopted is same as adopted by M.V. Winkle and W.G. Todd except few addition steps have been introduced in case of multicomponent batch fractionation.

They made use of the following equations:

4.7.2a Minimum Plates – Fenske (1932) method

\[ N_m = \frac{\log \left( \frac{X_{Lk}}{X_{HKD}} \right)}{\log \left( \frac{\alpha_{Lk/HK}}{\text{Avg.}} \right)} \] ................. 4.37

4.7.2b Minimum Reflux – Underwood (1946) equation

For- \( \theta \)

\[ \alpha_A X_{FA}/\alpha_{A-0} + \alpha_B X_{FB}/\alpha_{B-0} + \alpha_C X_{FC}/\alpha_{C-0} + \ldots = 1 - q \] ............. 4.38

where

\[ X_{FA}, X_{FB}, X_{FC}, X_{dA}, X_{dB}, X_{dC}, \ldots \] etc are the mole fraction of the component A, B, C etc in the feed and distillates.

'A' being light key component.

'B' being heavy key component.

'q' is the ratio of the heat required to vaporize 1 mole of the feed to
the molar latent heat of the feed. 
\( \alpha_A, \alpha_B, \alpha_C \) etc are the volatility with respect to the least volatile component and \( \theta \) is the root of equation 4.38. 
where \( \alpha_{LK} > \theta > \alpha_{HK} \)

4.7.2c \( R, R_m, N, N_m \) - Gilliland (1940) Method

For \( 0.0078 < x < 0.125 \)
\[ Y = 0.5039 - 0.5968x - 0.0908 \log x \]
\[ y = 0.6257 - 0.9868x + 0.5160x^2 - 0.1738 x^3 \]

Where 
\[ x = \frac{R - R_m}{R + 1} \]
\[ y = \frac{N - N_m}{N + 1} \]

4.7.2d Component Distribution – Geddes (1958) method

\[ \log \left( \frac{i_D}{i_B} \right) = C + M \log \alpha_{ir} \] 4.39

The constant \( C \) and \( M \) are formed by solving equation –4.39
for \( f_n \) split of \( f_u \) heavy key \( (i_D/i_B)_{HK} \) and light key \( (i_D/i_B)_{LK} \) in distillate and bottoms. After determine \( C \) and \( M \) \( f_u \) distribution of other component may also be calculated.

4.7.2e To use these equations following correlation was to be calculated

1) Feed composition, composition of the products and calculate the distribution of the components in the distillate and bottoms.
2) Calculate the dew point and bubble point of the liquid.
3) Calculate \( \alpha_{LK}/\alpha_{HK} \) at the average column temperature.
4) Determine \( N_{Opt}/N_m \) from Fig-4.14 and calculate \( N_{Opt} \).
5) Calculate the value of \( \log \left( \frac{[X_{LK}/X_{HK}]_D}{(X_{HK}/X_{LK})_B} \right) \) and using \( \alpha_{Avg} \) determine ratio \( R_{Opt}/R_m \) from Fig-4.15
6) Calculate \( R_m \) using \( R_{Opt}/R_m \) determine from Fig-4.16
7) Relation between the reflux ratio \( R \) and the number of plate ‘n’ in which only the minimum reflux ratio \( R_m \) and the number of plate at total reflux \( N_m \) are required.

In this \( R - R_m / R + 1 \) is plotted against \( (n+1) - (n+1)_m / n+2 \) in Fig-4.16
Fig-4.14 Relation between optimum- to-minimum and Fenske separation factor of $\alpha_{avg}$ values.

Fig-4.15 Optimum reflux ratio relationship to the column's feed, distillate and bottom composition.
4.7.2f Distribution of Non-Key components

For non-key components.

The equation for components material balance

\[ F_i = d_i + b_i \] ..........................4.40

The form of the Fenske equation in the term of an arbitrary component ‘i’ and ‘a’ reference component ‘r’ is

\[ \frac{(d/b)_i}{(d/b)_r} = \left(\frac{\alpha_{\text{av}}}{\alpha_{\text{raw}}}\right)^{NM} \frac{(d/p)_r}{(d/p)_a} \] ..........................4.41

A mean value of \( \alpha \) from equation-4.42 is used to know the degree of volatility of a component

\[ \alpha_{\text{mean,av}} = \frac{\alpha_{\text{LK,av}} + \alpha_{\text{HK,av}}}{2} \] ..........................4.42

The following equation are used to revise the estimate of the distillate and bottom products.

Light component \((d_i > b_i)\): \( \alpha_{\text{av}} > \alpha_{\text{mean,av}} \)

Reflux component \( r \) is the heavy key (HK)

\[ b_i = \frac{f_i}{1 + (d/b)_{HK} \left(\frac{\alpha_{\text{av}}}{\alpha_{\text{HK,av}}}\right)^{N_{\text{min}}}} \] ..........................4.43

\[ d_i = f_i - b_i \] ..............................4.44

Heavy component \((b_i > d_i)\)

\[ \alpha_{\text{av}} < \alpha_{\text{mean,av}} \]
Reflux component \( r \) is the light key (LK)

\[
d_i = \frac{f_i}{1 + (b/d)_{LK} \left( \frac{\alpha_{L,Kav}}{\alpha_{L,AV}} \right)^{N(min)}}
\]

\[
b_i = f_i - d_i
\]

In this by using the required product distillation the appropriate specification can be verified.

### 4.8 Design of pilot scale plant

For experimental purpose a pilot scale stainless steel column having 100mm diameter with a jacketed having capacity of 100 liter was designed & fabricated (Photo-4.3). The total height of column was 40 feet. The column was operated at 100mm of Hg. Seventy-liter synthetic mixture containing 75% \( \alpha \)-pinene and 25% \( \beta \)-pinene was taken trial for standardizing the functioning of column. The heating to the re-boiler was carried out by circulating high themic oil (600-700° C). The thermopac and vacuum pump were provided with automatic temperature and vacuum controller respectively. To attain 100mm Hg the column used to take about 15-20 minutes at the top.

The column was operated to find the number of plates present in it at total reflux, HETP (Height of packing equivalent to one theoretical plate) of packing, its boiling up rate, pressure across the height of the column, column hold up etc.

The boiling point of the component at 100mm Hg is under:

\(\alpha\)-pinene \( \rightarrow \) 89.49° C
\(\beta\)-pinene \( \rightarrow \) 94° C

### 4.8.1 Relative Volatility (\( \alpha \))

The relative volatility was calculated on the basis of vapour pressure data of various components of mint terpenes (Table-4.1).

After running plate, sample was drawn from the top of the column for GLC analysis.

The GLC of the sample drawn at flooding rate was under:

<table>
<thead>
<tr>
<th>Components</th>
<th>Feed (%)</th>
<th>Top product (%)</th>
<th>Bottom product (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-pinene</td>
<td>25%</td>
<td>94.5%</td>
<td>15%</td>
</tr>
<tr>
<td>(\beta)-pinene</td>
<td>75%</td>
<td>5.5%</td>
<td>84.5%</td>
</tr>
</tbody>
</table>
Photo 4.3 A pilot plant of fractional distillation installed for Dayal Agro Hi-Tech Food Products Pvt. Ltd. Rohtak, Haryana
A product sample was drawn at full rate at no reflux from the top of the column for 5 minute. It was found to be 7.10 liter. This gave flooding rate of the column as: -

\[ 7.10 \times 60/5 = 82.5 \text{ liter/hour}. \]

Now the system was closed, heating oil circulation and vacuum was stopped to bring down the pressure difference of ±10mm Hg. The product collected (7.10 liter) was charged back to re-boiler. Again pressure was maintained at 100mm Hg at the top. The system was again run and another sample of product was taken at full rate (with out reflux) for 5.0 minute. Stopping heating and vacuum stopped system.

The volume of sample collected was = 5.0 liters  
This gave the working boiling up rate \( 5 \times 60/5 = 60 \text{ liter/hour} \).

The vapour pressure Vs absolute temperature \( k \) was plotted of different components of mint terpenes. In Fig- 4.14 from table- 4.2

Relative volatility = \( P_{A^o}/P_{B^o} \).
\( P_{A^o} \) is vapour pressure of pure A component
\( P_{B^o} \) is vapour pressure of pure A component.

The average relative volatility \( \alpha_{Avg} \) between \( \alpha \)-pinene and \( \beta \)-pinene given in (Table-4.3).

So, the number of plates given by \( N_m = \)

\[
N_{m+1} = \frac{\log \left[ (x_A/ x_B)_D (x_A/ x_B)_B \right]}{\log (\alpha_{AB})_{AV}}
\]

Substituting the value of Fenske’s equation for number of plates at total reflux.

\[
N_{m+1} = \frac{\log \left[ (94.5/ 5.5) (84.5/ 15.0)\right]}{\log 1.14} = \frac{\log 96.790}{\log 1.14} = \frac{1.9306}{1.14} = 1.7004 \\
N_m = 33 \text{ plates.} 
\]
The vapour pressure of different components at same absolute temperature (1/Tk×10³)

Table -4.2

<table>
<thead>
<tr>
<th>S.N</th>
<th>Absolute temp. (1/Tk×10³)</th>
<th>Vapoure pressure in mm Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α-pinene</td>
<td>β-Pinene</td>
</tr>
<tr>
<td>1</td>
<td>2.823</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>7.724</td>
<td>114</td>
</tr>
<tr>
<td>3</td>
<td>2.700</td>
<td>130</td>
</tr>
<tr>
<td>4</td>
<td>2.583</td>
<td>230</td>
</tr>
<tr>
<td>5</td>
<td>2.444</td>
<td>400</td>
</tr>
</tbody>
</table>

Table -4.3

The relative volatility of different component at different vacuum (mm Hg)

4.8.2 HETP: - To calculate HETP

\[
\text{HETP} = \frac{\text{Total height of packed column}}{\text{Number of plates}} = \frac{6000/33}{181.8 \text{ mm}}.
\]

Column holds up [H]

\[
H = M_0 (1 - y_0/y_1) = 70 \times 0.1124 = 7.86 \text{ liter}.
\]
4.8.3 Experimental problem: -
To fractionate a sample of mint oil in the designed column.
Composition of mint terpene (without menthone and octanol)
\[ \alpha\text{-pinene} = 15\% \]
\[ \beta\text{-pinene} (\text{sabinene, myrcene}) = 25\% \]
\[ 1\text{-limonene} (1,8\text{ cineole, }\gamma\text{-terpinolene}) = 60\% \]
The mint terpen was categorized into three major fractions as above.

Desired composition of fraction: -
\[ \alpha\text{-pinene} = 95\% \]
\[ \beta\text{-pinene} = 5\% \]

4.8.3a Case-I
Assuming a cut of 5% distillate is obtained. The amount of \( \alpha\)-pinene and \( \beta\)-pinene recovered will be: -
\[ \alpha\text{-pinene} = 5 \times 0.95 = 3.325 \text{ liters} \]
\[ \beta\text{-pinene} = 5 \times 0.05 = 0.175 \text{ liters} \]
(sabinene, myrcene)

Balance in still: -

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Amount left</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( \alpha)-pinene</td>
<td>10.5 - 3.325 = 7.175 liter 10.76%</td>
</tr>
<tr>
<td>2. ( \beta)-pinene</td>
<td>17.5 - 0.175 = 17.325 liter 25.98%</td>
</tr>
<tr>
<td>3. ( 1)-limonene</td>
<td>42.0 - 0.0 = 42.0 liter 62.99%</td>
</tr>
</tbody>
</table>

Stream Composition

<table>
<thead>
<tr>
<th>Components</th>
<th>Feed (%)</th>
<th>Top product (%)</th>
<th>Bottom product (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha)-pinene</td>
<td>15</td>
<td>95</td>
<td>10.76</td>
</tr>
<tr>
<td>( \beta)-pinene</td>
<td>25</td>
<td>5</td>
<td>25.99</td>
</tr>
<tr>
<td>( 1)-limonene</td>
<td>60</td>
<td></td>
<td>63.00</td>
</tr>
</tbody>
</table>

So, the number of plates can be calculated by: -
\[ N_{m+1} = \frac{\log [(95/5) (25.99/10.76)]}{\log 1.14} \]
\[ = \frac{1.6641}{0.0569} \]
\[ = 29.24 \]
\[ N_{m} = 28 \text{ plates.} \]
From Fig 4.14: -

\[ \frac{N_{\text{opt}}}{N_m} = 1.72 \]

\[ N_{\text{opt}} = 28 \times 1.72 = 48.16 \]

\[
\log \left[ \frac{(X_{L_L}/X_{H_K})_D}{(X_{H_K}/X_{L_L})_B} \right] \left( \frac{(X_{L_L}/X_{H_K})^{0.55}}{X_{L_L}/X_{H_K}} \right)^{0.55} \\
= 1.5226
\]

From fig 4.15: -

\[ \frac{R_{\text{opt}}}{R_m} = 1.442 \]

To calculate the \( \theta \) from Underwood equation

\[
\frac{\alpha_A \times F_A}{\alpha_A - \theta} + \frac{\alpha_B \times F_B}{\alpha_B - \theta} + \frac{\alpha_C \times F_C}{\alpha_C - \theta} = 0
\]

\[
\frac{1.14 \times 0.15}{1.14 - \theta} + \frac{1.0 \times 0.25}{1.0 - \theta} + \frac{0.67 \times 0.60}{0.65 - \theta} = 0
\]

\[ 0.821 \theta^2 - 0.8560 \theta + 0.7614 = 0 \]

\[ \theta = 0.982 \]

To calculate the minimum reflux (\( R_m \))

Component | Distillate (%) | \( \alpha_i \) | \( \alpha_i \times \frac{iD}{\alpha_i - \theta} \)
---|---|---|---
\( \alpha \)-pinene | 94.5 | 1.14 | 6.818
\( \beta \)-pinene | 5.5 | 1.0 | 3.00

\[ R_{m+1} = 9.8 \]

\[ R_m = 8.8 \]

\[ R_{\text{opt}} = 8.8 \times 1.442 = 12.6 \]

So,

\[
\frac{(N + 1) - (N + 1)_m}{n + 2} = \frac{(33 + 1) - (29 + 1)}{33 + 2}
\]

\[ = 0.1143 \]
From Fig- 4.16
\[
\frac{R - R_m}{R + 1} = 0.6 \\
R - 8.8 = 0.6R + 0.6 \\
0.4R = 9.4 \\
R = 23.5 \\
R_{opt} = 23
\]

So here reflux = 23.5

Here the reflux ratio required for a column 33 plate is 27.5 which is quite high for a commercial column hence it is impracticable. So, it is very difficult to get 95% purity of $\alpha$-pinene in a commercial column because the quantity of $\alpha$-pinene is much less in mint terpene than other key components. So, assuming l-limonene as heavy key component, $\beta$-pinene as light key component and $\alpha$-pinene as non-key component.

The relative volatility of a non-key ($\alpha$-pinene), light key ($\beta$-pinene) and heavy key component (l-limonene) will be

<table>
<thead>
<tr>
<th>$\alpha_{AX}$</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.69</td>
<td>$\alpha$-pinene (LK +1)</td>
</tr>
<tr>
<td>1.49</td>
<td>$\beta$-pinene (LK)</td>
</tr>
<tr>
<td>1.0</td>
<td>l- limonene (HK)</td>
</tr>
</tbody>
</table>

It is desired to have maximum distillate of average composition

$\alpha$-pinene = 55%  
$\beta$-pinene = 40%  
l-limonene = 5%

mixture 95%

at reasonable reflux ratio.

4.8.3b Case II

Assuming a cut of 25% of the distillate is obtained.

Then the amount of $\alpha$, $\beta$-pinene mixture & l-limonene recovered will be

$\alpha$-pinene $\_L\_K +1$ $\rightarrow$ 9.625 liter  
$\beta$-pinene $\_L\_K$ $\rightarrow$ 7.0 liter  
l-limonene $\rightarrow$ 0.875 liter

Total recovery will be = 17.5 liter.

Balance lift in the re-boiler:

$\alpha$-pinene $\_L\_K +1$ = 10.5 – 9.625 = 0.875 liter  
$\beta$-pinene $\_L\_K$ = 17.5 – 7.0 = 10.5 liter  
l-limonene = 42 – 0.875 = 41.125 liter
Stream Composition:

<table>
<thead>
<tr>
<th>Components</th>
<th>Feed (%)</th>
<th>Distillate (%)</th>
<th>Bottom (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loading amount in re-boiler (70 liter)</td>
<td>17.5 liter</td>
<td>(52.5 liter)</td>
<td></td>
</tr>
<tr>
<td>α-pinene</td>
<td>15</td>
<td>55</td>
<td>1.66</td>
</tr>
<tr>
<td>β-pinene</td>
<td>25</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>l-limonene</td>
<td>60</td>
<td>5</td>
<td>78.33</td>
</tr>
</tbody>
</table>

Relative Volatility:

\[ \alpha_{LK} = 1.69, \quad \alpha_{HK} = 1.00 \]

\[
N_{m+1} = \frac{\log \left( \frac{x_{LK}}{x_{HK}} \right)_D \left( \frac{x_{HK}}{x_{LK}} \right)_B}{\log \alpha_{AV}}
\]

\[
N_{m+1} = \frac{\log \left[ \left( \frac{40}{5} \right) \left( \frac{78.33}{20} \right) \right]}{\log 1.49}
\]

\[ N_{m+1} = 14.4 \]

\[ N_m = 13.4 \]

From fig 4.14

\[
\frac{N_{opt}}{N_m} = 1.90
\]

\[ N_{opt} = 1.90 \times 13.4 = 25.46 \]

\[ \log \left[ \left( \frac{X_{LK}}{X_{HK}} \right)_D \left( \frac{X_{HK}}{X_{LK}} \right)_B \left( \frac{X_{LK}}{X_{HK}} \right)^{0.55\alpha_F} \right] \]

\[ \log \left[ \left( \frac{40}{5} \right) \left( \frac{78.33}{20} \right) \left( \frac{25}{60} \right)^{0.55 \times 1.49} \right] = 1.184 \]

From fig 4.15

\[ \frac{R_{opt}}{R_m} = 1.230 \]

To calculate the θ from Underwood equation

\[
\frac{\alpha_A \times F_A}{\alpha_A - \theta} + \frac{\alpha_B \times F_B}{\alpha_B - \theta} + \frac{\alpha_C \times F_C}{\alpha_C - \theta} = 0
\]

\[
\frac{1.69 \times 0.15}{1.69 - \theta} + \frac{1.49 \times 0.25}{1.49 - \theta} + \frac{1.0 \times 0.60}{1.0 - \theta} = 0
\]

\[ 1.226 \theta^2 - 3.5412 \theta + 2.5172 = 0 \]

\[ \theta = 1.62 \]
For \((R_{m+1})\)

<table>
<thead>
<tr>
<th>Components</th>
<th>(\alpha_i)</th>
<th>(\alpha_i - \theta/\alpha_i)</th>
<th>(\alpha_i \times D_i/\alpha_i - \theta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-pinene</td>
<td>1.69</td>
<td>0.0414</td>
<td>13.27</td>
</tr>
<tr>
<td>(\beta)-pinene</td>
<td>1.49</td>
<td>-0.0872</td>
<td>-4.58</td>
</tr>
<tr>
<td>1- limonene</td>
<td>1.00</td>
<td>-0.62</td>
<td>-0.0806</td>
</tr>
</tbody>
</table>

\[R_{m+1} = 8.61\]
\[R_m = 7.61\]
\[R_{opt} = 7.61 \times 1.230 = 9.360\]

So,
\[
\frac{(n + 1) - (n + 1)_m}{n + 2} = \frac{(33 + 1) - (14.4)}{33 + 2}
\]

= 0.560

From Fig. 4.16
\[R - \frac{R_m}{R + 1} = 0.240\]
\[R - 7.61 = 0.24 R + 0.24\]
\[0.760 R = 7.85\]
\[R = 10.32\]

4.8.3c Case III

Assuming a cut of 30% distillate is obtained then the amount of \(\alpha\) & \(\beta\) mixture recovered will be:

Total obtained will be = 21.0 liter
\(\alpha\)-pinene & \(\beta\)-pinene mixture = 19.95 liter
\(\alpha\)-pinene = 10.5 liter
\(\beta\)-pinene = 9.45 liter
1- limonene = 0.2625 liter

Balance left in the re-boiler

\(\alpha\)-pinene = 10.5 - 10.5 = 0.0
\(\beta\)-pinene = 17.5 - 9.45 = 8.05
1- limonene = 42 - 1.05 = 40.95

Stream Composition:

<table>
<thead>
<tr>
<th>Components</th>
<th>Feed (%)</th>
<th>Distillate (%)</th>
<th>Bottom (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loading amount in re-boiler (70 liter)</td>
<td></td>
<td>21 liter</td>
<td>(49 liter)</td>
</tr>
<tr>
<td>(\alpha)-pinene</td>
<td>15</td>
<td>50.00</td>
<td>00</td>
</tr>
<tr>
<td>(\beta)-pinene</td>
<td>25</td>
<td>45.00</td>
<td>-16.428</td>
</tr>
<tr>
<td>1- limonene</td>
<td>60</td>
<td>5</td>
<td>-83.57</td>
</tr>
</tbody>
</table>
Relative Volatility:

\[ N_{m+1} = \frac{\log \left[ \frac{X_{LK}}{X_{HK}} \right] \left( \frac{X_{HK}}{X_{LK}} \right)}{\log \alpha_{AV}} \]

\[ N_{m+1} = \frac{\log \left[ \frac{40}{5} \left( \frac{83.57}{16.42} \right) \right]}{\log 1.49} \]

\[ N_{m+1} = 9.595 \]

\[ N_m = 8.5 \]

From fig 4.14

\[ \frac{N_{opt}}{N_m} = 1.70 \]

\[ N_{opt} = 1.70 \times 8.5 = 14.45 \]

\[ \log \left[ \frac{X_{LK}}{X_{HK}} \right] \left( \frac{X_{HK}}{X_{LK}} \right) \left( \frac{X_{LK}}{X_{HK}} \right)^{0.55\alpha_F} \]

\[ = \log \left[ \frac{40}{5} \left( \frac{83.57}{16.42} \right) \left( \frac{25}{60} \right)^{0.55 \times 1.49} \right] \]

\[ = 1.348 \]

From fig 4.15

\[ \frac{R_{opt}}{R_m} = 1.255 \]

Now from case II \( \theta = 1.62 \)

To calculate \( R_{m+1} \)

<table>
<thead>
<tr>
<th>Components</th>
<th>Distillate (%)</th>
<th>( \alpha_i )</th>
<th>( \alpha_i - \theta/\alpha_i )</th>
<th>( \alpha_i \times D_i/\alpha_i - \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-pinene</td>
<td>50</td>
<td>1.69</td>
<td>0.0414</td>
<td>12.07</td>
</tr>
<tr>
<td>( \beta )-pinene</td>
<td>40</td>
<td>1.49</td>
<td>-0.0872</td>
<td>-4.584</td>
</tr>
<tr>
<td>( \lambda )-limonene</td>
<td>5.0</td>
<td>1.00</td>
<td>-0.62</td>
<td>-0.13</td>
</tr>
</tbody>
</table>

\[ R_{m+1} = 7.7.4 \]

\[ R_m = 6.4 \]

\[ R_{opt} = 6.4 \times 1.255 = 8.032 \]

\[ \frac{(n + 1) - (n + 1)_m}{n + 2} = \frac{(33 + 1) - (9.7)}{33 + 2} \]

\[ = 0.694 \]
From Fig - 4.16
\[ \frac{R - R_m}{R + 1} = 0.155 \]
\[ R - 6.4 = 0.155 R + 0.155 \]
\[ 0.845 R = 6.555 \]
\[ R = 7.75 \]

**4.8.3d Case IV**

Assuming a cut of 40% distillate is obtained then the amount of \( \alpha \) & \( \beta \) mixture recovered will be:

Total obtained will be = 28.0 liter
\( \alpha \)-pinene & \( \beta \)-pinene mixture = 26.6 liter

\( \alpha \)-pinene = 10.5 liter
\( \beta \)-pinene = 16.1 liter
\( \lambda \)-limonene = 1.4 liter

Balance left in the re-boiler

\( \alpha \)-pinene = 10.5 – 10.5 = 0.0
\( \beta \)-pinene = 17.5 – 16.1 = 1.4 liter
\( \lambda \)-limonene = 42 – 1.4 = 40.6 liter

**Stream Composition:**

<table>
<thead>
<tr>
<th>Components</th>
<th>Feed (%)</th>
<th>Distillate (%)</th>
<th>Bottom (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loading amount in re-boiler</td>
<td>Feed (70 liter)</td>
<td>28 liter</td>
<td>(42 liter)</td>
</tr>
<tr>
<td>( \alpha )-pinene</td>
<td>15</td>
<td>37.5</td>
<td>0.00</td>
</tr>
<tr>
<td>( \beta )-pinene</td>
<td>25</td>
<td>57.5</td>
<td>-3.33</td>
</tr>
<tr>
<td>( \lambda )-limonene</td>
<td>60</td>
<td>5</td>
<td>-96.66</td>
</tr>
</tbody>
</table>

**Relative Volatility:**

\[
N_{m+1} = \frac{\log \left( \frac{x_{HK}}{x_{LK}} \right)_{D} \left( \frac{x_{HK}}{x_{LK}} \right)_{B}}{\log \alpha_{AV}}
\]

\[
N_{m+1} = \frac{\log \left( \frac{57.5}{5} \right) \left( \frac{96.66}{3.33} \right)}{\log 1.49}
\]

\[N_{m+1} = 14.57\]
\[N_{m} = 13.57\]
From fig 4.14

\[ \frac{N_{\text{opt}}}{N_m} = 1.88 \]

\[ N_{\text{opt}} = 1.88 \times 13.57 = 25.51 \]

\[ \log \left[ \left( \frac{X_{LK}}{X_{HK}} \right)_D \left( \frac{X_{HK}}{X_{LK}} \right)_B \left( \frac{X_{LK}}{X_{HK}} \right)^{0.55} \right] \]

\[ \log \left[ \left( \frac{57.5}{5} \right) \left( \frac{96.66}{3.33} \right) \left( \frac{25}{60} \right)^{0.55 \times 1.49} \right] \]

\[ = 2.211 \]

From fig 4.15

\[ \frac{R_{\text{opt}}}{R} = 2.25 \]

Now from case I \( \theta = 1.62 \)

**To calculate \( R_m \)**

<table>
<thead>
<tr>
<th>Components</th>
<th>Distillate (%)</th>
<th>( \alpha_i )</th>
<th>( \alpha_i-\theta/\alpha_i )</th>
<th>( \alpha_i \times D_i/\alpha_i-\theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-pinene</td>
<td>37.5</td>
<td>1.69</td>
<td>0.0414</td>
<td>9.053</td>
</tr>
<tr>
<td>( \beta )-pinene</td>
<td>57.5</td>
<td>1.49</td>
<td>-0.0872</td>
<td>-6.59</td>
</tr>
<tr>
<td>l- limonene</td>
<td>5.0</td>
<td>1.00</td>
<td>-0.62</td>
<td>-0.0806</td>
</tr>
</tbody>
</table>

\[ R_{m+1} = 1.66 \]

\[ R_m = 0.66 \]

\[ R_{\text{opt}} = 0.66 \times 2.25 = 1.485 \]

So,

\[ \frac{(n + 1) - (n + 1)_m}{n + 2} = \frac{(33 + 1) - (14.57)}{33 + 2} \]

\[ = 0.555 \]

where 'n' is number of plates.

From Fig- 4.16

\[ R - R_m / R + 1 = 0.223 \]

\[ R = 0.66 = 0.223 R + 0.233 \]

\[ 0.777 R = 0.883 \]

\[ R = 1.136 \]
4.8.4 Reloading of first cut of case -IV

The distillate obtained from different cases, when 1-limonene was taken as key component contains a mixture of α & β-pinene. For getting high purity of α & β-pinene it is necessary to subject the distillate of different cases (Cases II, III and IV) as feed for second operation.

Case A- By assuming that distillate case IV was taken as feed having composition as under:

- α-pinene --------- 37.5%
- β-pinene --------- 57.5%
- 1- limonene ------ 5%

It is desired to have maximum distillate of average composition:

- α-pinene ------- 95%
- β-pinene ------- 5%

Solutions

Calculations by applying the simple graphical methods:

Case I- Assuming a art 20% of the distillate is obtained, then the amount of α & β-pinene recovered will be:

Total recovered will be = 14 litres
- α-pinene -------- 13.3 litres
- β-pinene -------- 0.7 litre

Balance left in the reboiler
- α-pinene = 26.25 - 13.3 = 12.95 litres
- β-pinene = 40.25 - 0.7 = 39.55 litres
- 1- limonene = 3.5 - 0 = 3.5 litres

Total = 56 litres

Stream compositions will be:

<table>
<thead>
<tr>
<th>Components</th>
<th>Feed (%)</th>
<th>Distillate (%)</th>
<th>Bottom (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-pinene (LK)</td>
<td>37.5</td>
<td>95.0</td>
<td>23.12</td>
</tr>
<tr>
<td>β-pinene (HK)</td>
<td>57.5</td>
<td>5.0</td>
<td>70.62</td>
</tr>
<tr>
<td>1- limonene (HK+1)</td>
<td>5.0</td>
<td>0</td>
<td>6.25</td>
</tr>
</tbody>
</table>

Relative volatilities of different constituent when β-pinene was used as key component (heavy key component):

- α_{LK} = 1.14
- α_{HK} = 1.00
- α_{HK+1} = 0.67

Then

\[ N_{m+1} = \frac{\log \left( \frac{(x_{LK}/x_{HK})_D}{(x_{HK}/x_{L,K})_B} \right)}{\log \alpha_{AV}} \]
$$N_{m+1} = \frac{\log \left[ \frac{95}{5} \left( \frac{70.62}{23.12} \right) \right]}{\log 1.14}$$

$$N_{m+1} = 30.99 \approx 31$$
$$N_m = 30$$

From fig 4.14
$$\frac{N_{opt}}{N_m} = 1.69$$
$$N_{opt} = 30 \times 1.69 = 50.7$$

$$\log \left[ \frac{X_{L_K}/X_{H_F}}{D} \left( X_{H_F}/X_{L_K} \right)_B \left( X_{L_K}/X_{H_F} \right)^{0.55\alpha} \right]$$

$$\log \left[ \frac{(58.03)(37.50/57.50)0.627}{1.6472} \right] = 1.6472$$

From fig 4.15
$$\frac{R_{opt}}{R_m} = 1.446$$

To calculate the $\theta$ from Underwood equation

$$\frac{\alpha_A \times F_A}{\alpha_A - \theta} + \frac{\alpha_B \times F_B}{\alpha_B - \theta} + \frac{\alpha_C \times F_C}{\alpha_C - \theta} = 0$$

$$\frac{1.14 \times 0.375}{1.14 - \theta} + \frac{1.00 \times 0.575}{1.00 - \theta} + \frac{0.67 \times 0.05}{0.67 - \theta} = 0$$

$$\theta = 1.62$$

To calculate $(R_{m+1})$

<table>
<thead>
<tr>
<th>Components</th>
<th>Distillate (%)</th>
<th>$\alpha_i$</th>
<th>$\alpha_i-\theta/\alpha_i$</th>
<th>$\alpha_i \times D_i/\alpha_i-\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-pinene</td>
<td>95</td>
<td>1.14</td>
<td>0.0614</td>
<td>15.47</td>
</tr>
<tr>
<td>$\beta$-pinene</td>
<td>5</td>
<td>1.00</td>
<td>-0.07</td>
<td>-0.714</td>
</tr>
</tbody>
</table>

$$R_{m+1} = 14.756$$
$$R_m = 13.756$$
$$R_{opt} = 13.756 \times 1.446 = 19.89$$
\[
\frac{(n +1) - (n +1)m}{n +2} = \frac{(33 +1) - 31}{33 +2} \]

\[
= 0.0857
\]

From Fig - 4.16
\[
R - R_m / R + 1 = 0.510
\]
\[
R - 13,756 = 0.510 R + 0.510
\]
\[
0.490 R = 14.266
\]
\[
R = 29.114
\]
The reflux ratio is very high and impractical for a commercial column.

4.8.5 Reloading of the first cut of case- III

Case B – Now it is desired to take the distillate of case III as feed for second operating having composition as under:

\[\alpha\text{-pinene} \quad 50\%
\]
\[\beta\text{-pinene} \quad 45\%
\]
\[l\text{-limonene} \quad 5\%
\]

It is desired to have maximum distillate of average composition:

\[\alpha\text{-pinene} \quad 95\%
\]
\[\beta\text{-pinene} \quad 5\%
\]

Solutions

Calculations by applying the simple graphical methods:

Case IIIa

Assuming a art 20\% of the distillate is obtained, then the amount of \(\alpha\) & \(\beta\)-pinene recovered will be:

Total loading 70 litres
Total distillate 14 litres

\[\alpha\text{-pinene} \quad 13.3 \text{ litres}
\]
\[\beta\text{-pinene} \quad 0.07 \text{ litre}
\]

Balance left in the reboiler

\[\alpha\text{-pinene} = 35.00 - 13.3 = 21.70 \text{ litres}
\]
\[\beta\text{-pinene} = 31.5 - 0.07 = 30.8 \text{ litres}
\]
\[l\text{-limonene} = 3.5 - 0 = 3.5 \text{ litres}
\]

Stream compositions

<table>
<thead>
<tr>
<th>Components</th>
<th>Feed (%)</th>
<th>Distillate (%)</th>
<th>Bottom (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha\text{-pinene})</td>
<td>50</td>
<td>95.0</td>
<td>38.75</td>
</tr>
<tr>
<td>(\beta\text{-pinene})</td>
<td>45</td>
<td>5.0</td>
<td>55.0</td>
</tr>
<tr>
<td>(l\text{-limonene})</td>
<td>5</td>
<td>0</td>
<td>6.25</td>
</tr>
</tbody>
</table>
Relative volatilities of different constituent when \( \beta \)-pinene was used as key component (heavy key component): -

\[
\begin{align*}
\alpha_{\alpha \text{- pinene}} &= 1.14 \\
\alpha_{\beta \text{- pinene}} &= 1.00 \\
\alpha_{\alpha \text{- limonene}} &= 0.67
\end{align*}
\]

Then

\[
N_{m+1} = \frac{\log \left( \frac{x_{LK}}{x_{HK}} \right) \left( x_{HK} \right) \left( x_{LK} \right)_{B}}{\log \alpha_{AV}}
\]

\[
N_{m+1} = \frac{\log \left( \frac{95}{5} \right) \left( 55 \right) \left( 38.75 \right)}{\log 1.14}
\]

\[
N_{m+1} = 25.14 \\
N_{m} = 24.14
\]

From fig 4.14

\[
N_{opt}/N_{m} = 1.72 \\
N_{opt} = 24.14 \times 1.72 = 41.52
\]

\[
\log \left( \frac{X_{LK}/X_{HK}}{X_{HK}/X_{LK}} \right)_{B} \left( X_{HK}/X_{LK} \right)^{0.55\alpha_{F}} \]

\[
\log \left( \frac{26.967 \times 55 \times 38.75^{0.627}}{38.75} \right) = 1.527
\]

From fig 4.15

\[
R_{opt}/R_{m} = 1.430
\]

To calculate the \( \theta \) from Underwood equation

\[
\frac{\alpha_{A} \times F_{A}}{\alpha_{A} - \theta} + \frac{\alpha_{B} \times F_{B}}{\alpha_{B} - \theta} + \frac{\alpha_{C} \times F_{C}}{\alpha_{C} - \theta} = 0
\]

\[
\frac{1.14 \times 0.053}{1.14 - \theta} + \frac{1.00 \times 0.3875}{1.00 - \theta} + \frac{0.67 \times 0.05}{0.67 - \theta} = 0
\]

\[
\theta = 1.058
\]
To calculate \((R_{m+1})\)

<table>
<thead>
<tr>
<th>Components</th>
<th>Distillate (%)</th>
<th>(\alpha_i)</th>
<th>(\alpha_i/\alpha_j)</th>
<th>(\alpha_i \times D_i/\alpha_j)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-pinene</td>
<td>95</td>
<td>1.14</td>
<td>0.0719</td>
<td>13.20</td>
</tr>
<tr>
<td>(\beta)-pinene</td>
<td>5</td>
<td>1.00</td>
<td>0.058</td>
<td>-0.862</td>
</tr>
</tbody>
</table>

\[R_{m+1} = 12.33\]
\[R_m = 11.33\]
\[R_{opt} = 11.33 \times 1.440 = 16.31\]

\[
\frac{(n + 1) - (n + 1)_m}{n + 2} = \frac{(33 + 1) - 31}{33 + 2} = 0.282
\]

From Fig - 4.16
\[R - R_m / R + 1 = 0.380\]
\[R - 11.33 = 0.380 \times R + 0.380\]
\[0.620 \times R = 11.71\]
\[R = 18.88\]

4.8.6 **Reloading of first cut of case-II**

By using distillate of case II as feed in reboiler with loading of 70 litre per batch.

Composition of feed as under

- \(\alpha\)-pinene ---------- 55%
- \(\beta\)-pinene ---------- 40%
- \(\alpha\)-limonene ------ 5%

It is desired to have maximum distillate purity of:

- \(\alpha\)-pinene -------- 95%
- \(\beta\)-pinene -------- 5%

at reasonable reflex.

**Solutions**

Calculations by applying the simple graphical methods:

Assuming a cut 20% of the distillate is obtained, then the amount of \(\alpha\) & \(\beta\)-pinene recovered will be:

Total loading 70 litres
Total distillate 14 litres

\(\alpha\)-pinene ------ 13.3 litres
\(\beta\)-pinene ------ 0.07 litre

Balance left in the reboiler

\(\alpha\)-pinene = 38.5 - 13.5 = 25.00 litres
\(\beta\)-pinene = 28.07 - 0.07 = 27.3 litres
\(\alpha\)-limonene = 3.5 - 0 = 3.5 litres
Stream compositions

<table>
<thead>
<tr>
<th>Components</th>
<th>Feed (%)</th>
<th>Distillate (%)</th>
<th>Bottom (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-pinene</td>
<td>55</td>
<td>95.0</td>
<td>44.64</td>
</tr>
<tr>
<td>β-pinene</td>
<td>40</td>
<td>5.0</td>
<td>48.75</td>
</tr>
<tr>
<td>1-limonene</td>
<td>5</td>
<td>0</td>
<td>6.25</td>
</tr>
</tbody>
</table>

Relative volatilities

- $\alpha_{\alpha\text{-pinene}} = 1.14$
- $\alpha_{\beta\text{-pinene}} = 1.00$
- $\alpha_{1\text{-limonene}} = 0.67$

Then

$$N_{m+1} = \frac{\log \left[ \frac{x_{LK}}{x_{HK}} \right]_{D} \left( \frac{x_{HK}}{x_{LK}} \right)_{B}}{\log \alpha_{AV}}$$

$$N_{m+1} = \frac{\log [(95/5) (48/44.64)]}{\log 1.14}$$

$$N_{m+1} = 23.14$$

$$N_{m} = 22.14$$

From fig 4.14

$$\frac{N_{opt}}{N_{m}} = 1.74$$

$$N_{opt} = 24.14 \times 1.72 = 38.52$$

$$\log \left[ \frac{x_{LK}}{x_{HK}} \right]_{D} \left( \frac{x_{HK}}{x_{LK}} \right)_{B} \left( \frac{x_{LK}}{x_{HK}} \right)^{0.55\alpha_{F}}$$

$$\log [(26.967) (55/38.75) a^{0.627}]$$

$$= 1.4037$$

From fig 4.15

$$\frac{R_{opt}}{R_{m}} = 1.430$$

To calculate the $\theta$ from Underwood equation

$$\frac{\alpha_{A} \times F_{A}}{\alpha_{A}-\theta} + \frac{\alpha_{B} \times F_{B}}{\alpha_{B}-\theta} + \frac{\alpha_{C} \times F_{C}}{\alpha_{C}-\theta} = 0$$

$$\frac{1.14 \times 0.55}{1.14 - \theta} + \frac{1.00 \times 0.44}{1.00 - \theta} + \frac{0.67 \times 0.05}{0.67 - \theta} = 0$$

$$\theta = 1.054$$
To calculate \((R_{m+1})\)

<table>
<thead>
<tr>
<th>Components</th>
<th>Distillate (%)</th>
<th>(\alpha_i)</th>
<th>(\alpha_i \theta / \alpha_i)</th>
<th>(\alpha_i \times D_i / \alpha_i \theta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-pinene</td>
<td>95</td>
<td>1.14</td>
<td>0.075</td>
<td>12.59</td>
</tr>
<tr>
<td>(\beta)-pinene</td>
<td>5</td>
<td>1.00</td>
<td>-0.054</td>
<td>-0.925</td>
</tr>
</tbody>
</table>

\[ R_{m+1} = 11.66 \]
\[ R_m = 10.66 \]
\[ R_{opt} = 10.66 \times 1.430 = 15.24 \]

\[ \frac{(n+1) - (n+1)_m}{n+2} = \frac{(33+1) - 23.14}{33+2} = 0.310 \]

From Fig - 4.16
\[ R - R_m / R + 1 = 0.370 \]
\[ R - 10.66 = 0.370 R + 0.370 \]
\[ 0.630 R = 11.03 \]
\[ R = 17.50 \]

### 4.8.7 Theoretical Results

Table 4.4 shows, theoretical data for fractional of terpenes by assuming different key components. When \(\beta\)-pinene was assuming as heavy key component for getting 95% \(\alpha\)-pinene. The reflux ratio was too high (23.5) that is impractical for a column having 33 plates designing. Besides this when 1-limonene was taken as heavy key component (HK), the distillate will be the mixture of \(\alpha\) & \(\beta\) pinene. The amount of \(\alpha\) & \(\beta\) pinene in mixture depend up the % cut of distillate from feed. The reflux ratio obtained during these assumptions was practically possible.

Table 4.5 shows the theoretical column data, when distillate of first loading was recharged to get \(\alpha\)-pinene of 95% purity. The \(\beta\)-pinene was assumed to be heavy key component (HK). The distillate of case III & IV showed high reflux ratio \(R\), 29.11 and 23.5 respectively, while the distillate of case II showed 95% purity of \(\alpha\)-pinene at the reflux ratio of 17.50 that is possible for a commercial scale fractionating column.
### Table-4.4 The different theoretical fractional data obtained with different amount of distillate

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Column parameters</th>
<th>Product parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_m$</td>
<td>$N_{opt}$</td>
</tr>
<tr>
<td>Case I</td>
<td>28</td>
<td>48.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case II</td>
<td>13.4</td>
<td>25.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case III</td>
<td>8.7</td>
<td>14.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case IV</td>
<td>13.3</td>
<td>25.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: The table above lists various assumptions, column parameters, and product parameters along with the key component assumed, % cut of distillate, total distillate obtained (liter), product rate liter/hr, time taken by distillate (hr), purity of distillate (%), and composition of bottom (%).
Table-4.5 The different theoretical data obtained by reloading of fraction from first loading.

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Column parameters (Total loading 70 liter)</th>
<th>Product parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N_m</td>
<td>N_opt</td>
</tr>
<tr>
<td>Case IV</td>
<td>30</td>
<td>50.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case III</td>
<td>23.1</td>
<td>40.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case II</td>
<td>22.1</td>
<td>38.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.8.8 Practical result from column

Experiment-I A. 1st cycle:-

Seventy litre of mint terpene oil having composition as under: -

- α-pinene -------- 15%
- β-pinene -------- 25%
- l- limonene ------ 60%

was charged in the reboiler of the pilot state column packed with hyflux packing with total packed height of 6000mn. The column was found to have 33 plates, flooding rate 72 litre/hr at 100mm hg, 7.86 litre of column hold up, working boil up rate of 60 litre/hr.

The column was operated at 100mm hg at the top.

The pressure difference across the column was found to be 15mm hg which was maintained at

15± 1mm hg

4.8.8a First operation

During operation the column was operated so as to have the product rate of 5.3 litre/hr which correspond to a reflux ration of 10:32:1.

The total cut of 17.5 litre was found to have a average composition as under: -

- α-pinene -------- 54%
- β-pinene -------- 41%
- l- limonene ------ 5%

Bottom composition

- α-pinene -------- 2.0%
- β-pinene -------- 19.66%
- l- limonene ------ 78.3%

which correspond to well with the assumptions.

4.8.8b Second operation

The distillate was to be contained with aim to recover both α & β pinene having l-limonene in the still with about 1.00% α-pinene and 2% β-pinene. The top product may also contain some limonene (6%). The probable composition of the top and bottom product will come as under

<table>
<thead>
<tr>
<th>Component</th>
<th>feed (litres)</th>
<th>%</th>
<th>Top (litre)</th>
<th>%</th>
<th>Bottom (litre)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-pinene (LK+1)</td>
<td>1.05</td>
<td>2.0</td>
<td>0.63</td>
<td>5.81</td>
<td>0.420</td>
<td>1.010</td>
</tr>
<tr>
<td>β-pinene (LK)</td>
<td>10.325</td>
<td>19.66</td>
<td>9.4885</td>
<td>87.48</td>
<td>0.833</td>
<td>2.0</td>
</tr>
<tr>
<td>l-limonene (HK)</td>
<td>41.125</td>
<td>78.3</td>
<td>0.727</td>
<td>6.70</td>
<td>40.40</td>
<td>96.99</td>
</tr>
<tr>
<td>Total (100)</td>
<td>52.5</td>
<td>100</td>
<td>10.846</td>
<td>100</td>
<td>41.654</td>
<td>100</td>
</tr>
</tbody>
</table>

\[ N_{m+1} = \frac{\log \left( \frac{x_{LK}}{x_{HK}} \right)_D \left( \frac{x_{HK}}{x_{LK}} \right)_B }{\log \alpha_{AV}} \]
\[ N_{m+1} = \frac{\log \left( \frac{87.48}{6.70} \cdot \frac{96.99}{2} \right)}{\log 1.49} \]
\[ N_{m+1} = 16.18 \]
\[ N_m = 15.18 \]

Checking the distribution of non-key components:

Here,

\[ N_m = 15.18 \]

\[ f_{\alpha\text{-pinene}} = 1.05 \]
\[ b_i = \frac{f_i}{1 + (d/b)HK \left( \alpha_{iAV} / \alpha_{HKAV} \right)^{N_{\text{min}}}} \]
\[ b_{\alpha\text{-pinene}} = \frac{1.05}{1 + (0.727/40.40) (1.69/1.00)^{15.8}} = 0.014 \]

So, \[ d_i = f_i - b_i \]
\[ d_i = 1.05 - 0.014 = 1.036 \]

Hence the final composition of the entire stream will become

<table>
<thead>
<tr>
<th>Component</th>
<th>feed (litres)</th>
<th>% Top</th>
<th>% Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha\text{-pinene} ) ((LK+1))</td>
<td>1.05</td>
<td>2.0</td>
<td>9.2</td>
</tr>
<tr>
<td>( \beta\text{-pinene} ) ((LK))</td>
<td>10.325</td>
<td>19.66</td>
<td>84.34</td>
</tr>
<tr>
<td>( l\text{-limonene} ) ((HK))</td>
<td>41.125</td>
<td>78.3</td>
<td>6.46</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>52.5</strong></td>
<td><strong>100</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

From fig-4.14

\[ N_{\text{opt}}/N_m = 1.825 \]
\[ N_{\text{opt}} = 15.18 \times 1.825 = 27.70 \]

\[ \log \left[ \frac{X_{L,K}}{X_{HK}}D \left( \frac{X_{HK}}{X_{L,K}} \right)_B \left( \frac{X_{L,K}}{X_{HK}} \right)^{0.55F} \right] \]
\[ \log \left[ \frac{(84.34/6.46) (97.94/2.0) (19.66/78.3)^{0.627}}{2.547} \right] \]

From fig 4.15

\[ R_{\text{opt}}/R_m = 1.36 \]
To calculate the $\theta$ from Underwood equation

$$\frac{\alpha_A \times F_A}{\alpha_A - \theta} + \frac{\alpha_B \times F_B}{\alpha_B - \theta} + \frac{\alpha_C \times F_C}{\alpha_C - \theta} = 0$$

$$\frac{1.69 \times 0.02}{1.69 - \theta} + \frac{1.49 \times 0.196}{1.49 - \theta} + \frac{1.00 \times 0.783}{1.00 - \theta} = 0$$

$$\theta = 1.40$$

To calculate $(R_{m+1})$

<table>
<thead>
<tr>
<th>Components</th>
<th>Distillate (%)</th>
<th>$\alpha_i$</th>
<th>$\alpha_i - \theta / \alpha_i$</th>
<th>$\alpha_i \times D_i / \alpha_i - \theta$</th>
<th>$14.365$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-pinene</td>
<td>9.2</td>
<td>1.69</td>
<td>0.1715</td>
<td>0.536</td>
<td></td>
</tr>
<tr>
<td>$\beta$-pinene</td>
<td>84.34</td>
<td>1.49</td>
<td>0.06</td>
<td>13.96</td>
<td></td>
</tr>
<tr>
<td>l-limonene</td>
<td>6.46</td>
<td>1.00</td>
<td>-0.49</td>
<td>-0.131</td>
<td></td>
</tr>
</tbody>
</table>

$R_{m+1} = 14.365$

$R_m = 13.36$

$R_{opt} = 13.36 \times 1.36 = 18.16$

$$\frac{(n+1) - (n+1)_m}{n+2} = \frac{(33+1) - 16.18}{33+2}$$

$$= 0.509$$

From Fig - 4.16

$R - R_m / R + 1 = 0.250$

$R - 13.36 = 0.250 R + 0.250$

$0.750 R = 13.61$

$R = 18.14$
<table>
<thead>
<tr>
<th>Operation</th>
<th>Column parameters (Total loading 70 liter)</th>
<th>Product parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N_m</td>
<td>N_opt</td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>13.4</td>
<td>25.4</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>15.1</td>
<td>27.7</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>22.1</td>
<td>38.5</td>
</tr>
</tbody>
</table>

Table-4.6 Practical data obtained from fractionating column.
4.8.9 Summary

Calculated

\[ N_m = 15.18 \]
\[ N_{opt} = 27.70 \]
\[ R_m = 13.36 \]
\[ R_{opt} = 18.16 \]
\[ R = 18.14 \]

Designed

\[ N_m = 15.1 \]
\[ N_{opt} = 33 \]
\[ R_m = 13.3 \]
\[ R_{opt} = 18.16 \]
\[ R = 18.0 \]

The column was further operated at \( R = 18.14 \); with product ratio of \( 3.134 \pm 0.2 \) litre/hr. The 11.25 litre of product was collected and composition found as under:

- \( \alpha \)-pinene – 54%
- \( \beta \)-pinene (Sabinene, myrcene) – 84.04%
- \( \delta \)-limonene (1,8 cinole, \( \gamma \)-terpene) – 6.76%

which match approximately with the assumed composition.

To Calculate the Time

Time taken during first operation

Product rate = \( 60/11:32 \)

\[ = 5.3 \text{ litre/hr} \]

Time taken to get 17.5 = \( 17.5/5.3 \)

\[ = 3.30 \text{ hrs.} \]

Time for the second operation

Product rate = \( 60/19:14 \)

\[ = 3.13 \text{ litre/hr} \]

Time taken to get 11.25 litre cut

\[ = 3.59 \text{ hrs.} \]

The rest was taken out at full rate, leaving a residual of about 3 litre in the still, the time taken was 0.75 hrs.

Total time taken

- 1\(^{st}\) operation – 3.30hrs
- 2\(^{nd}\) operation – 3.59 hrs
- Rest material – 0.75 hr

Total time = 7.64 hrs

Time cycle for 70 litre mixture.

- Initial heating & vacuum – 0.50hr
- Stabilization – 0.50hr
- Distillation – 7.64 hrs
- Cooling & discharging – 0.40hr

Total time cycle = 9.04 hrs
B) Reloading of distillate of first loading (first operation)

When the distillate of above cycle in first operation was taken as feed having composition as under:

- α-pinene ------ 55%
- β-pinene ------ 40%
- L- limonene ------ 5%

Seventy litre of feed was charged in the re-boiler of the pilot scale column as stated above. The column was operated at the product rate of 3.02 liter/hr which correspond to a reflux ratio of 18 : 88 :1 to 18: 1

The total cut of 17.5 liter was found to have composition as under:

- α-pinene ------ 94.5%
- β-pinene ------ 4%
- L- limonene ------ 0.5%

which correspond well with assumption.

The composition of re-boiler was

- α-pinene ------ 41.80%
- β-pinene ------ 51.70%
- L- limonene ------ 6.401%

that can be mixed with the distillate of 2nd operation in first loading.

Hence, it may be seen that the method developed is quite sound and the results (Table-4.6) obtained match well with the theoretical calculations. So, it is possible to design a commercial column on this basis of the method developed.
4.9 Designing of a commercial batch-fractionating column based on the developed method

It was desired to design a batch column for M/s Dayal Agro Hitech Food Products Pvt. Ltd., Rohtak, to fractionate the different constituents of mint oil having capacity of 1000 liter in about 24 hours and to have maximum cut of composition:

$$\alpha\text{-pinene} \quad 95\%$$
$$\beta\text{-pinene} \quad 5\%$$

Composition of feed:

$$\alpha\text{-pinene} \quad 15\%$$
$$\beta\text{-pinene} \quad (\text{Sabinene, myrcene}) \quad 25\%$$
$$1\text{-limonene} \quad (1,8 \text{cinole, } \gamma\text{-terpene}) \quad 60\%$$

Let ‘X’ liter/hr be the working boil up rate of the column. So from the practical results we have seen that in the first loading time taken for cut of 25% at ‘R’ is equal to 10.32:1, in first loading of 1000 liter.

Product rate = $X/l 1:32 \text{ hrs}$

Time taken = $250 \times \frac{11.32}{x} \text{ hours}$

Time for the 2nd operation cut of 21.4% at R = 18.14:1

Product rate = $X/l 19.14/x \text{ hrs}$

Time taken = $214 \times \frac{19.14}{x} \text{ hrs}$

Taking the rest 48.6% at R = 1:1, leaving 5% as residue.

Product rate = $X/2 \text{ liter/ hrs}$

Time taken = $486 \times \frac{2}{x} \text{ hours}$

Total time for distillate

Now let the distillate taken 20 hrs leaving rest and hour for heating, equilibrium cooling and discharging of column.

$$250 \times \frac{11.32}{x} + 214 \times \frac{19.14}{x} + 486 \times \frac{2}{x} = 20 \text{ hrs}$$

$$2830 + 4095.96 + 972 = 20x$$

$$x = 394.89$$

which is the approximate working boil up rate.

Taking it 75% of flooding rate.

Therefore flooding rate = $394.89/0.75$

= 526.52 liter/hr

Now from pilot plant trial (earlier discussed)

Flooding rate 100mm Hg operating pressure for 100mm dia. Column = 72 litre/hr

Therefore column dia for flooding rate of 526.52 rate = $D^2/100 \times 100$

= 526.52/72

141
D = 270.42 mm

Rounding up gives a column dia of 300 mm
No. of plates in the packed column
Column diameter = 270 mm
No. of sections = 5 Nos.
Total height of each section = 3000 mm
Packed height of first three sections = 2600 mm each
Packed height of top sections = 2800 mm

Each section of the column should be provided with a distributor at the top, above the packing. The first two distributor of 300 mm height and top one of 100 mm. All the sections should be made up of 55304. The middle four section should be packed with 25 mm 55304 pall rings.

The number of plates were calculated as under

\[
\text{HETP} = K_1 G^{K_2} d^{K_3} h^{1/3} \alpha^{\mu/p}
\]

where \( K_1, K_2, K_3 \) are constants as functions of the packing these values for steel.

Rasching ring are:

a) for 25mm rings \( K_1 = 0.57, K_2 = -10, K_3 = 1.24 \)

\( G = \) superficial mass velocity of vapour lb/hr (sq.ft)
\( d = \) column diameter (inches)
\( h = \) height of packing (ft)
\( \alpha = \) relative volatility (1.14)
\( \mu = \) liquid viscosity centipose (0.55)
\( \rho = \) liquid density, g/c.c (0.86)

\( \text{HETP} = \) height of packing equivalent to one theoretical plate

Substitution of values gives

\[
\text{Column diameter} = \frac{300}{25.4} \times 12
\]

\[
= 0.9842 \text{ ft}
\]

\[
G = \frac{526.52 \times 0.86 \times 2.2 \times 4 \times 0.75}{\pi(0.9842)^2}
\]

\[
= 982.56
\]

\[
G^{K_2} = (982.63)^{-1.10} = 0.5020
\]

\[
d^{K_3} = (300/25.4)^{1.24} = 21.3617
\]

\[
h^{1/3} = (2600/25.4 \times 12)^{1/3} = 2.04
\]

for top column = \((2800/25.4 \times 12)^{1/3} = 2.09\)

From above

1) HETP for the lower 3 sections packed with 25mm SS pall rings. Now

HETP for steel rasching rings: -

\[
= 0.57 \times 0.5020 \times 21.3617 \times 2.04 \times 1.14 \times 0.55
\]

\[
= 0.86
\]

\[
= 9.09 \text{ inches}.
\]

Now efficiency of steel rasching rings is around 70% of steel pall ring.

\[
\text{HETP of steel pall rings} = 9.09 \times 0.7 = 6.36 \text{ inches}
\]
2) HETP for top section with 25mm SS pill rings, packed height = 2800mm

HETP for steel rasching ring
= 0.57 x 0.5020 x 21.3617 x 2.09 x 1.14 x 0.55
= 9.31 inches.

HETP for steel pall ring = 9.31 x 0.7 = 6.52 inches.

Now total number of plates in the column
= (2600/25.4 x 6.63) + (2800/25.4 x 6.52)
= 16.09 + 16.9
≈ 33 plates
Adding one plate constituted by reboiler and condenser therefore total number of plates
= 33 + 1 = 34

4.10 Azeotropic Distillation

Azeotropic distillation is an old process that has widely used since about 1930.

Application of azeotropic distillation has continued to expand because many very close boiling mixtures may be separated economically by use of these techniques. The separation of such mixture by conventional distillation methods is usually uneconomical because of the large number of stages, which would be required to effect such separations.

Because of the tendency toward non-ideal behaviour of mixture, it is generally possible to find some component which when added to a given mixture will increase the difference between the volatilities of the light and heavy key components to be separated. The component or material added to mixture, to be separated is called solvent. When the solvent added to mixture is withdrawn from the column, usually in the distillate, as an azeotrope with one or both of the key components, the separation process is called azeotropic distillation. The term azeotrope is formed and the solvent is withdrawn almost exclusively in the distillate.

When the solvent added to the mixture is withdrawn almost exclusively in the bottom product without forming an azeotrope, the process is called extractive distillation.

4.10.1 Behaviour of Solvents

An effective solvent for an extractive distillation is one, which is attracted to one or more of the components. This attraction of the solvent for these components reduces the volatility of the solvent as well as the volatilities of the components to which it is attracted. It is desirable that the attraction occurs in the natural direction; that is the solvent is
attracted to the relatively heavy components. However, this is not a necessary condition for the behaviour of the solvent. Many separations are carried out in the bottom product with the solvent.

A variety of theories have been advanced for the roles of the solvent in azeotropic and extractive distillation. In the case of extractive distillation, attraction of the solvent for the components of the mixture is commonly attributed to one or more or a combination of the following phenomena: (1) hydrogen bonding, (2) polar characteristic of the solvent and members of the mixture, (3) the formation of weak unstable chemical complex, (4) chemical reactions between the solvent and one or more of the components of the mixture. A more complete statement of theories has been summarized by Berg (1969).

The role of polarity has been elucidated by Hopkins et al. (1955) who described the use of the azeotropic and extractive distillation in the separation of the products by oxidation of selected hydrocarbons. Because of the dissimilarities in molecular structure, the oxidation products can be arranged in the order of increasing polarity (Carlson, C. S. et al., 1954; Hopkins, W. C. and Fritsch, J. J., 1955): namely, ester, oxide aldehydes, ketones, acetals, alcohols. In any class of compounds the polarity is inversely proportional to the molecular weight, the polarity of the straight chain molecules is greater than that of branched chain structures and olefinic compounds are more polar than their corresponding paraffin derivatives.

4.11 Process for separating alpha-pinene from beta-pinene

A process for effecting at least the partial resolution of a pinene mixture containing alpha-pinene and beta-pinene described the sequential steps:

(i) Admixing diethylene glycol with said first pinene mixture of alpha and beta-pinene thus forming a second pinene mixture.

(ii) Subjecting the resulting second pinene mixture of alpha pinene, beta-pinene and diethylene glycol to fractional azeotropic distillation yielding (A) a distillate which is a two liquid phase non-emulsified composition the first phase of which is the lower phase. Which consists essentially of diethylene glycol. The second phase of which is the upper phase and which consists essentially of a third pinene mixture consist of essentially of alpha-pinene and beta-pinene, substantially richer in alpha-pinene than said first pinene mixture and (B) a bottoms mixture, which is a two liquid phase, non-emulsified composition. The first phase of which is the lower phase and which consists essentially of diethylene glycol and the second phase of which is the upper phase and which consists essentially of alpha-pinene and beta-pinene substantially richer in beta-pinene than said first pinene mixture.
(iii) Physically separating said first phase from said second phase by means of decantation.

A preferred manner of carrying out such process comprises the sequential steps of (i) first removing, in the absence of azeotroping agent, by means of distillation a portion of the alpha-pinene from the first pinene mixture where by 80% of the alpha-pinene is removed from the first pinene mixture of alpha-pinene and beta-pinene and where by said first pinene mixture is enriched in concentration of beta-pinene, thereby forming a second pinene mixture of alph-pinene and beta-pinene to form a third pinene mixture of alpha-pinene, beta-pinene and diethylene mixture, (iii) subjecting the resulting third pinene mixture of alpha pinene, beta pinene and diethylene glycol to fractional azeotropic distillation yielding (A) a distillate which is a two liquid phase and which consists essentially of alpha-pinene and beta-pinene substantially richer in alpha-pinene than said second pinene mixture and (B) a bottom’s mixture, which is a two liquid phase, non-emulsified composition, the first phase of which is the lower phase and which consists essentially of diethylene glycol and the second phase of which is the upper phase and which consists essentially of alpha-pinene and beta-pinene substantially richer in beta-pinene than said first pinene mixture.

(iv) Physically separating said first phase from said second phase by decantation.