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Department of Energy and Process Engineering

Unit Operations 1
(Distillation, Solid-Liquid Extraction, Mixing)

Master 1: Chemical Engineering

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Preface

This Unit Operations 1 course handout is intended for 1st year Masters students in Process Engineering, specialising in Chemical Engineering. The chapters are arranged in such a way as to correspond to the Chemical Engineering programme.

The first chapter, entitled Distillation, introduces the fundamental concepts of liquid-vapour equilibrium, the principle of flash distillation, bubble point and dew point. The McCabe and Thiele and Ponchon Savarit methods for distilling binary mixtures are also developed in detail.

The second chapter, entitled Liquid-Solid Extraction (Leaching), introduces the fundamental concepts of solid-liquid equilibrium, the Janecke diagram and the equations for determining the theoretical number of stages in liquid-solid extraction.

The third chapter is devoted to the mixing operation. This final chapter presents applications (mixing and dispersion), the different types of agitator, calculation of the Reynolds number, the power number, the Froude number and the sizing of an agitation system.

This handout is the result of reading numerous books and documents, some of which are cited in the bibliography.

Summary

Chapter 1: Distillation

Chapter 2: Solid-Liquid Extraction

Chapter 3: Mixture operation

Introduction

The unit operations of separation hold a prominent place at the core of process engineering, representing fundamental processes essential for the transformation and purification of raw materials. These operations play a crucial role in various industries, serving as key processes in the production of chemicals, pharmaceuticals, food, and many others. The essence of process engineering lies in the ability to master these operations to obtain high-quality end products. The effective separation of components in a complex mixture is a major challenge, whether it involves isolating pure products, removing impurities, or recovering specific substances. Thus, this general overview aims to highlight the indispensable nature of unit operations of separation in the design and optimization of industrial processes, emphasizing their decisive role in achieving operational efficiency, economic profitability, and enhanced environmental performance.

Unit operations of separation hold a central and versatile position that transcends many industries. In the chemical industry, they are essential for isolating and purifying specific chemical compounds, while in petrochemicals, they play a role in separating different fractions of crude oil for the production of plastics and fuels. In the food industry, unit operations of separation are used to extract specific flavors, oils, or nutrients, while in the pharmaceutical industry, they are crucial for isolating pure active ingredients.

Thus, regardless of the sector, these operations are of paramount importance to ensure the quality of end products, meet safety standards, and comply with environmental regulations. Explaining their central role in these various industries emphasizes their universality and relevance across the spectrum of process engineering.

1.1 Introduction

Distillation is one of the most important separation methods available to chemical engineering. This operation enables the separation of one or more constituents from a homogeneous liquid mixture, taking advantage of the difference in volatility of the constituents. Distillation is a double operation: after heating to boiling point, the vapor phase above the boiling liquid and in equilibrium with it does not have the same composition.

Condensation of the vapor phase produces a liquid called distillate or extract (also known as overhead product), whose composition differs from that of the initial mixture. The non-evaporated liquid phase constitutes the residue or raffinate (also known as the bottom product).

With very few exceptions, the distillate is enriched in light constituents with a lower boiling point, while the residue is formed by heavy constituents with a higher boiling point. Distillation can be carried out at different pressures, depending on the feedstock to be treated.

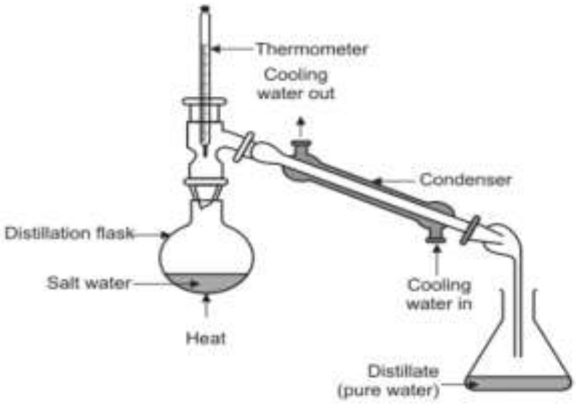


Figure 1.1 Basic Principle and methodology of simple distillation process.

Rectification is a technique that uses repeated distillation in a column to create exchanges between the vapor phase rising and the liquid phase flowing back through the column. Rectification involves an exchange of matter between a liquid phase and a vapor phase circulating in counter-current in a column designed to bring the two phases into intimate contact. Separation and the conditions required to achieve it depend on the liquid-vapor system and, consequently, on the liquid-vapor equilibrium of the mixture to be distilled.

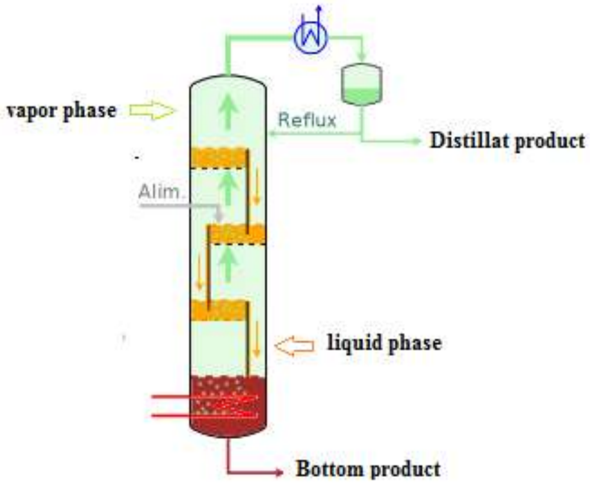


Figure 1.2 Continuous rectification column design.

1.2 Liquid-vapor equilibrium of a binary mixture

A binary mixture is defined as a mixture composed of two entities in the liquid or gas phase. Consider a system composed of two entities A and B (A is the more volatile compound), x_A and x_B the molar fractions of components A and B in the liquid phase; also y_A and y_B the molar fractions in the vapor phase.

$$x_A = \frac{n_A}{n_A + n_B} \quad x_B = \frac{n_B}{n_A + n_B} \quad y_A = \frac{n'_A}{n'_A + n'_B} \quad y_B = \frac{n'_B}{n'_A + n'_B} \qquad (1.1)$$

With

n_i: the number of moles of entity i in the liquid phase.

n'_i: the number of moles of entity i in the vapor phase.

$$x_A + x_B = 1 \quad et \quad y_A + y_B = 1 \qquad (1.2)$$

A solution of molar titre **z1**, when heated to the temperature of point **T1**, is partially vaporized, giving two phases **L1** (liquid) and **V1** (vapor), with the abscissae of points **x1** and **y1** as fractions (see Figure 1.3)

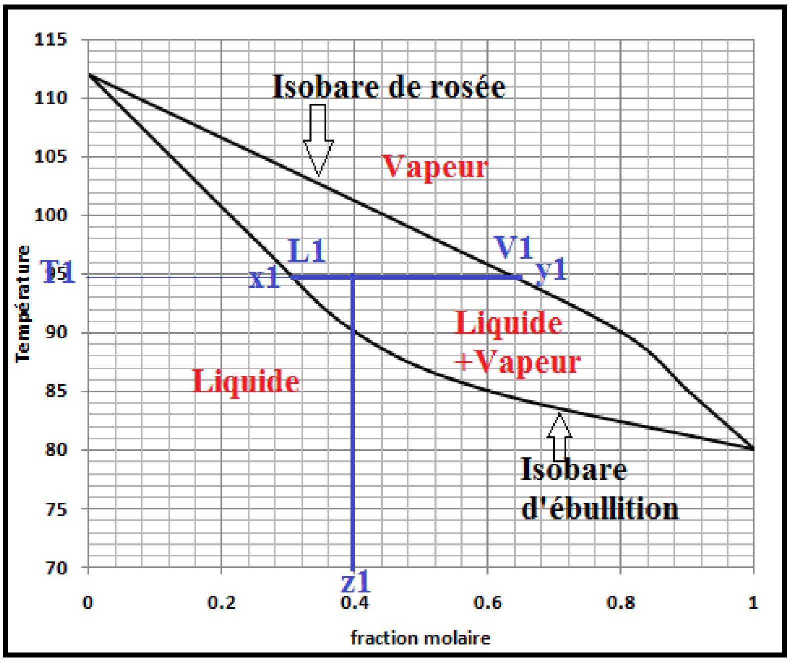


Figure 1.3 Liquid-vapor equilibrium curve for the ideal mixture.

- For a given temperature, the total pressure is, according to Dalton's law of perfect gases :

$$P = P_A + P_B \tag{1.3}$$

With P_A et P_B, the partial pressures of components A and B.

1.2.1 Dalton's equation

In the binary case, in vapor phase, the partial pressures represent the fractions of these multiplied by the system pressure.

$$P_A = y_A\, P \quad \text{and} \quad P_B = y_B\, P \tag{1.4}$$

1.2.2 Raoult's equation

For an ideal liquid, the partial pressure of component A in the vapour in equilibrium with the liquid having the molar titre x_A, at constant temperature, is given by Raoult's law:

$$P_A = x_A P_A^{\circ} \quad \text{et} \quad P_B = x_B P_B^{\circ} \tag{1.5}$$

With P_A° et P_B° the saturation vapor pressures of components A (pure) and B at the mixture's boiling temperature.

1.2.3 Antoine's equation

Saturation vapour pressure: noted **$P_A°$** can be calculated from Antoine's equation shown below.

$$\log_{10}(P_A°) = A - \frac{B}{C+T} \quad \text{with } P_A° \text{ in mmHg and T in °C} \qquad (1.6)$$

A, *B* and *C* parameters are available for a large number of components in the literature.

Table 1.1 Antoine's parameters for selected components

Constituant	*A*	*B*	*C*
Acetic acid	7.18807	1416.7	211
Acetone	7.02447	1161.0	224
Aniline	7.24179	1675.3	200
Benzene	6.90565	1211.033	220.79
i-butane	6.74808	882.8	240.0
n-butane	6.83029	945.9	240.0
ethanol	8.04494	1554.3	222.65
diethyl ether	6.78574	994.195	220.0
ethyl benzene	6.95719	1424.255	213.206
ethylene glycol	7.8808	1957.0	193.8
n-heptane	6.9024	1268.115	216.9
n-hexane	6.8777	1171.53	222.366
n-octane	6.9237	1355.126	209.517
i-pentane	6.78967	1020.012	233.097
n-pentane	6.8522	1064.63	232.00
styrene	6.92409	1420.0	206.0
toluene	6.95464	1344.800	219.482
water	7.9668	1668.21	228.0

From the liquid-vapour equilibrium and combining equations (1.4) and (1.5), we obtain :

$$y_A = x_A\,(P_A^{\circ}/P) \qquad (1.6)$$

$$y_A = x_B\,(P_B^{\circ}/P) \qquad (1.7)$$

Combining equations (1.6) and (1.7), we obtain:

$$y_A = x_A\,(P_A^{\circ}/P) \rightarrow (1 - y_B) = x_A\,(P_A^{\circ}/P) \qquad (1.9)$$

$$\Longrightarrow \quad 1-(x_B\,(P_B^{\circ}/P))=x_A\,(P_A^{\circ}/P) \tag{1.10}$$

$$\Longrightarrow \quad \mathrm{P}-(x_B\,P_B^{\circ})=x_A\,P_A^{\circ} \tag{1.11}$$

$$\Longrightarrow \quad \mathrm{P}-(x_B\,P_B^{\circ})=P_A^{\circ}(1-x_B) \tag{1.12}$$

$$\Longrightarrow \quad P-P_A^{\circ}=x_B(P_B^{\circ}-P_A^{\circ}) \tag{1.13}$$

$$\Longrightarrow \quad x_B=\frac{P-P_A^{\circ}}{P_B^{\circ}-P_A^{\circ}} \tag{1.14}$$

1.2.4 Relative volatility

The relative volatility (α) of a compound of a compound A with reference to a compound B is defined by the ratio:

$$\alpha=\frac{K_A}{K_B} \tag{1.15}$$

With **K_A** and **K_B** are equilibrium coefficients or absolute volatility.

$$K_A=\frac{y_A}{x_A}=\frac{P_A^{\circ}}{P} \tag{1.16}$$

$$K_B=\frac{y_B}{x_B}=\frac{P_B^{\circ}}{P} \tag{1.17}$$

Combining equations (1.15) to (1.17), we obtain:

$$\alpha=\frac{\mathrm{y_A/x_A}}{\mathrm{y_B/x_B}}=\frac{P_A^{\circ}}{P_B^{\circ}} \tag{1.18}$$

Relative volatility expresses the possibility of separating a component A from a mixture A-B; the greater the α, the more easily it can be separated by distillation.

For an ideal binary mixture, we can write :

$$y_A=\frac{\alpha\,x_A}{x_A(\alpha-1)+1} \tag{1.19}$$

More often than not, the liquid cannot be assimilated to an ideal solution, so we retain the form of the preceding expressions and include corrective terms, known as activity coefficients γ, which are usually determined by means of experimental information. The result is:

$$k_A=\gamma_A P_A^{\circ}/P \tag{1.20}$$

$$\alpha = \left(\frac{\gamma_A}{\gamma_B}\right)\left(\frac{P_A^{\circ}}{P_B^{\circ}}\right) \tag{1.21}$$

1.2.5 Correlations for Liquid-Phase Activity Coefficients

The liquid-phase activity coefficient, γ_A, is a function of pressure, temperature, and liquid composition. At conditions remote from the critical conditions, it is virtually independent of pressure and, in the range of temperature normally encountered in distillation, can be taken as independent of temperature. Several equations have been developed to represent the dependence of activity coefficients on liquid composition. Only those of most use in the design of separation processes be given.

Wilson Equation [1]

The Wilson equation for determining liquid-phase activity coefficients was proposed by Wilson in 1964. The Wilson equation is particularly useful for predicting vapor-liquid equilibrium (VLE) behavior in non-ideal liquid mixtures. The equation is expressed as follows:

$$ln\left(\frac{\gamma_1}{x_1}\right) = \frac{-ln\left(\frac{\gamma_2}{X_2}\right)+\ln(\emptyset_2)+A_{21}}{A_{12}+A_{21}} \tag{1.22}$$

$$ln\left(\frac{\gamma_2}{x_2}\right) = \frac{-ln\left(\frac{\gamma_1}{X_1}\right)+\ln(\emptyset_1)+A_{12}}{A_{12}+A_{21}} \tag{1.23}$$

where:

γ_1 and γ_2 are the activity coefficients of components 1 and 2, respectively;

x_1 and x_2 are the mole fractions of components 1 and 2, respectively;

ϕ_1 and ϕ_2 are the fugacity coefficients of components 1 and 2, respectively;

A_{12} and A_{21} are dimensionless binary interaction parameters, are determined through regression against experimental VLE data.

Nonrandom Two Liquid (NRTL) Equation [2]

The Non-Random Two Liquid (NRTL) equation is a thermodynamic model used for predicting liquid-phase activity coefficients in non-ideal liquid mixtures, especially in the context of vapor-liquid equilibrium (VLE) calculations. The NRTL equation was proposed by Renon and Prausnitz in 1968.

Universal Quasi-Chemical (UNIQUAC) Equation

The UNIQUAC equation developed by Abrams and Prausnitz is usually preferred to the NRTL equation in the computer-aided design of separation processes.

It is suitable for miscible and immiscible systems, and so can be used for vapor-liquid and liquid-liquid systems. As with the Wilson and NRTL equations, the equilibrium compositions for a multicomponent mixture can be predicted from experimental data for the binary pairs that comprise the mixture. Also, in the absence of experimental data for the binary pairs, the coefficients for use in the UNIQUAC equation can be predicted by a group contribution method: UNIFAC. The best source of data for the UNIQUAC constants for binary pairs is the DECHEMA vapor-liquid and liquid-liquid data collection [3].

Estimation of Activity Coefficients from Azeotropic Data

If a binary system forms an azeotrope, the activity coefficients can be calculated from knowledge of the composition of the azeotrope and the azeotropic temperature.

$$\boldsymbol{\gamma_i = \frac{P}{P_i^{\circ}}} \tag{1.24}$$

where:

$\boldsymbol{P_i^{\circ}}$: is determined at the azeotropic temperature.

$\boldsymbol{\gamma_i}$ **:**The values of the activity coefficients determined at the azeotropic composition can be used to calculate the coefficients in the Wilson equation.

Activity Coefficients at Infinite Dilution

The constants in any of the activity coefficient equations can be readily calculated from experimental values of the activity coefficients at infinite dilution. For the Wilson equation.

$$\boldsymbol{ln\gamma_1^{\infty} = -lnA_{12} - A_{21} + 1} \tag{1.25}$$

$$\boldsymbol{ln\gamma_2^{\infty} = -lnA_{21} - A_{12} + 1} \tag{1.26}$$

where:

$\boldsymbol{\gamma_1^{\infty}, \gamma_2^{\infty}}$: the activity coefficients at infinite dilution for components 1 and 2, respectively;

$\boldsymbol{A_{12}}$: the Wilson A-value for component 1 in component 2;

$\boldsymbol{A_{21}}$: the Wilson A-value for component 2 in component 1.

Group Contribution Methods [4-6].

Group contribution methods have been developed for the prediction of liquid-phase activity coefficients. The objective has been to enable the prediction of phase equilibrium data for the tens of thousands of possible mixtures of interest to the process designer to be made from the contributions of the relatively few functional groups that made up the compounds. The UNIFAC method is probably the most useful for process design, it is the preferred equation for use in design, and it is included in all the commercial simulation and design programs.

Care must be exercised in applying the UNIFAC method. The specific limitations of the method are:

1. Pressure not greater than a few bar (say, limit to 5 bar);

2. Temperature below 1508C;

3. No noncondensable components or electrolytes;

4. Components must not contain more than 10 functional groups

K-values for Hydrocarbons

A useful source of K-values for light hydrocarbons is the well-known ‘‘De Priester charts’’, which are reproduced as Figures 1.4a and b. These charts give the K-values over a wide range of temperature and pressure.

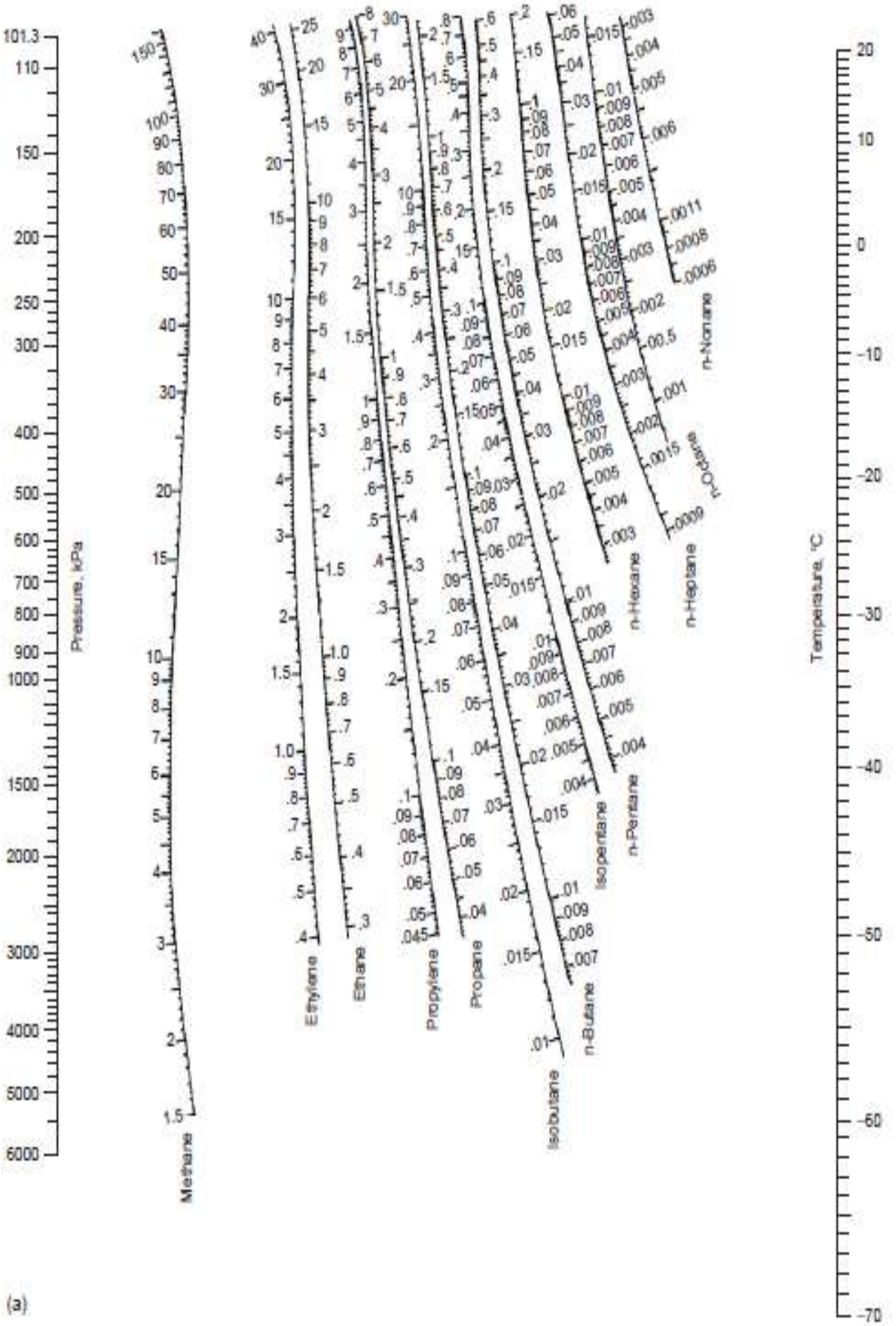


Figure 1.4 (a) De Priester chart—K-values for hydrocarbons, low temperature.

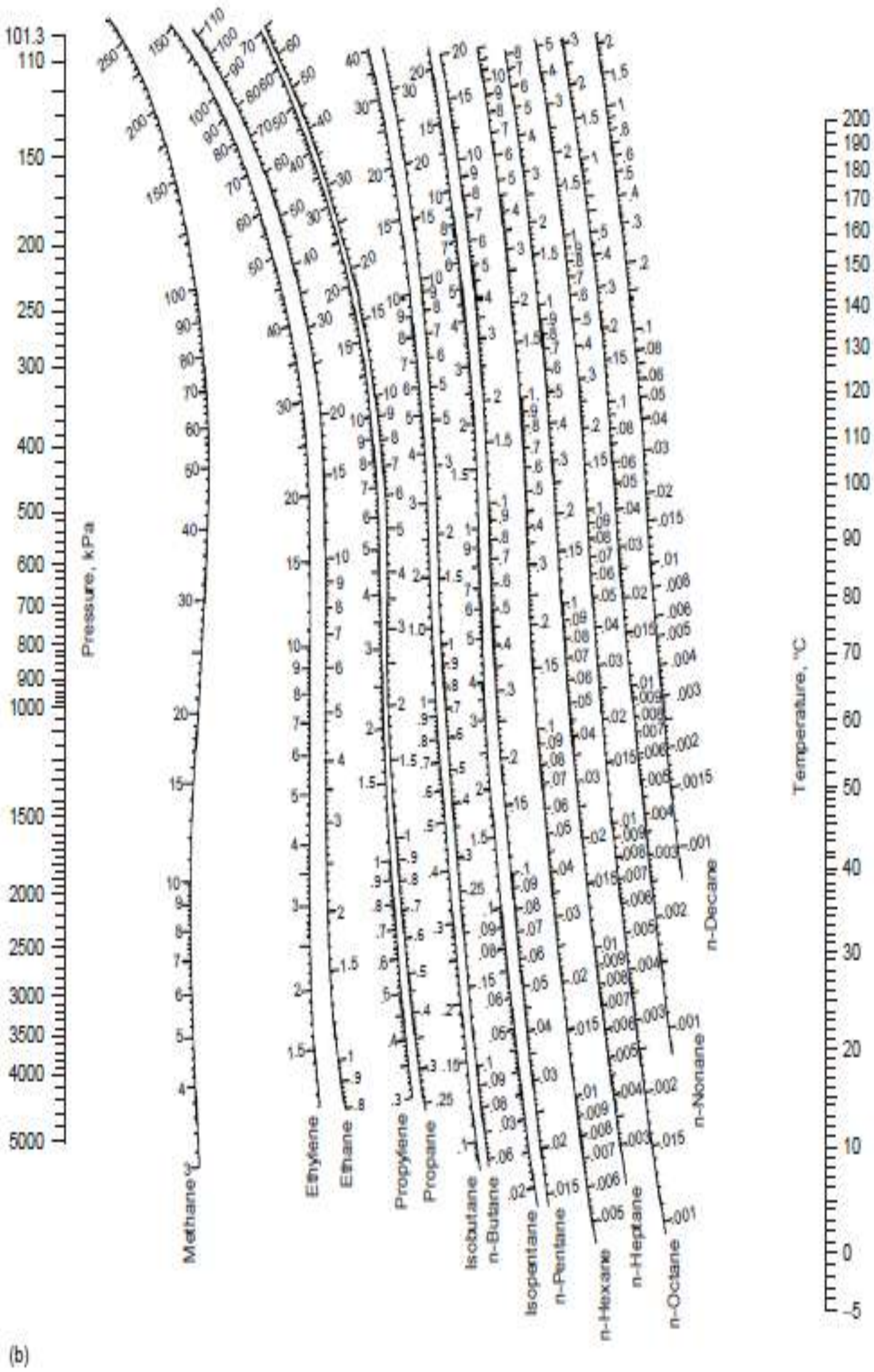


Figure 1.4 (b) De Priester chart—K-values for hydrocarbons, high temperature

1.3 Types of mixtures

1.3.1 Zeotrope mixtures

Zeotropic mixtures are mixtures that have no fixed boiling point, so the composition of the vapor phase is always different from that of the liquid phase.

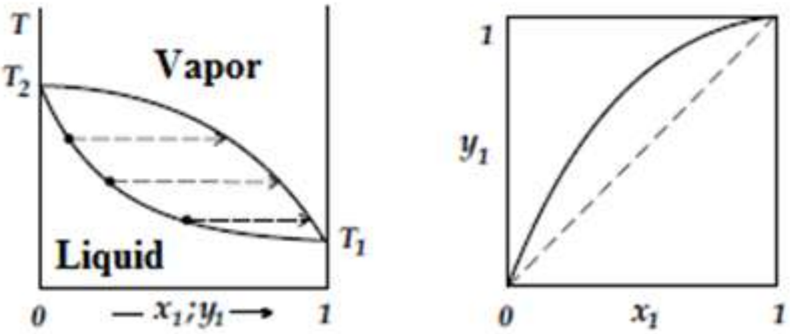
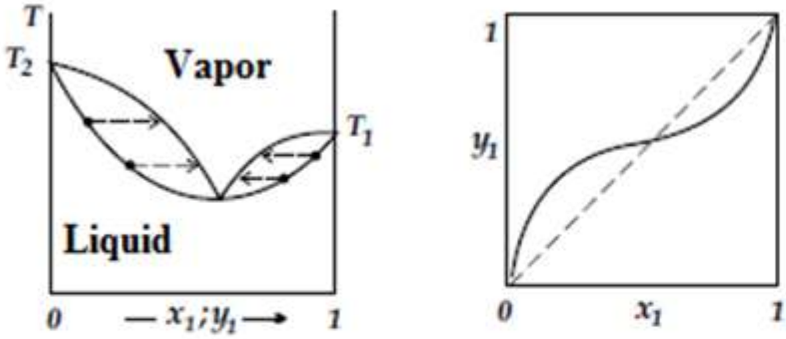


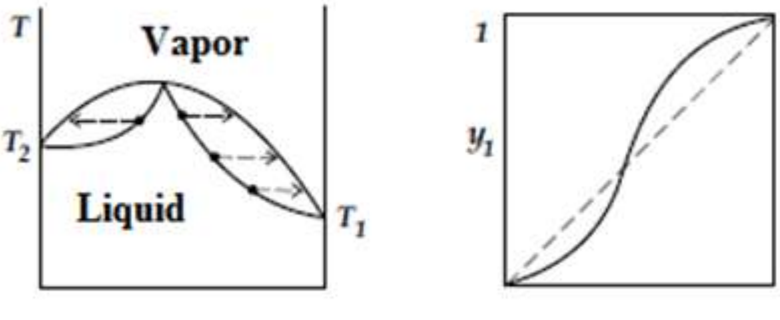
Figure 1.5 T- x-y and y=f(x) for zeotrope mixture.

1.3.2 Homogeneous azeotrope

Homogeneous azeotropic mixtures are systems that form an azeotrope in which the composition of the liquid phase is the same as that of the vapor phase, resulting in a fixed boiling point under a given pressure (as with a pure substance), which does not allow separation by ordinary distillation.



(a)



(b)

Figure 1.6 T- x-y and y=f(x) for azeotropes mixture with:
(a) minimum boiling point, **(b)** maximum boiling point.

1.3.3 Heterogeneous azeotrope

A heterogeneous azeotrope is an azeotropic mixture where the liquid phase is not uniform, meaning that it consists of two or more distinct liquid phases. These phases have different compositions, but when the mixture is vaporized, the vapor phase exhibits a constant composition.

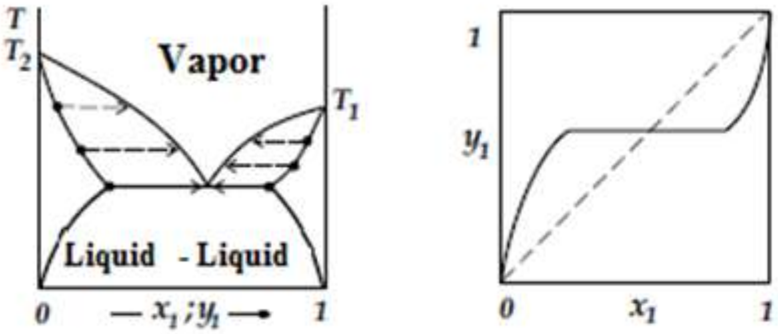


Figure 1.7 T- x-y and y=f(x) for heterogeneous azeotropic mixture.

1.4 Simple distillation

The aim of this process is to separate the most volatile compounds from a liquid mixture. A charge of the mixture to be treated is introduced into a boiler, where it boils under constant pressure. Steam escaping from the boiler is condensed, and the liquid is collected directly. The steam produced by the mixture is always richer in the most volatile constituent, so that the condensate titre is always higher than that of the initial mixture. Continued operation progressively depletes the boiler liquid of the most volatile constituents, resulting in a continuous decrease in condensate titre. The distillate can be collected in several fractions, each with a given average titre.

For an ideal mixture, where volatility is not constant, the quantity of condensate to be collected is obtained by establishing the material balance of the operation.

Consider **L** and **X_1** to be the quantity and respectively the titre of the initial charge in the boiler;

at time **t** of the flash distillation operation during the operation;

dL the quantity of liquid vaporized;

dX the titre of the liquid which has decreased during the distillation operation;

(L - dL) the quantity remaining in the boiler;

(X - dX) the molar titre of the liquid remaining in the boiler;

dV the vapor formed is equal to **dL,** and as it is in equilibrium with the liquid of titre **X** its titre is **Y***.

The material balance in terms of the most volatile component is :

$$X_1 L = (X_1 - dX_1)(L - dL) + Y^* dL \tag{1.27}$$

dX_1dL ⟶ **0** the result is:

$$\frac{dL}{L} = \frac{dX_1}{(Y^* - X_1)} \tag{1.28}$$

Integration of the equation above gives:

$$\int_{X_1}^{X_2} \frac{dL}{L} = Ln\left(\frac{L_1}{L_2}\right) = \int_{X_1}^{X_2} \frac{dX_1}{(Y^* - X_1)} \tag{1.29}$$

For ideal solutions, and when there is a linear relationship between Y^* and X in the range of strengths considered, we can determine the average strength X_{mD} of the distillate, by writing the material balance in terms of the most volatile component:

$$L_1 X_1 = L_2 X_2 + D X_{mD} \tag{1.30}$$

$$X_{mD} = \frac{L_1 X_1 - L_2 X_2}{L_1 - L_2} \tag{1.31}$$

1.4.1 Simple equilibrium distillation (flash)

In flash distillation, contact between vapour and liquid is prolonged for a sufficiently long time for equilibrium to be established between the two phases, liquid and vapour, which are collected separately. Figures 1.5 to 1.7 show the three operating modes of flash distillation: isothermal flash, adiabatic flash and partial condensation.

- **Isothermal flash:**

The liquid passes through a heat exchanger where partial vaporization occurs. The gas-liquid mixture at equilibrium is then separated in the flash drum. At the top of the drum is a device (demister) to retain any small drops of liquid that may be carried along with the steam. In the isothermal flash drum, the temperature is fixed.

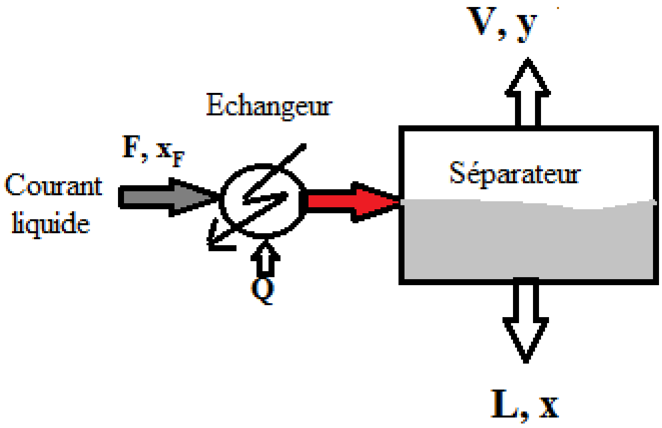


Figure 1.8 Isothermal flash process illustration

Adiabatic flash:

The pressurized liquid is heated in an exchanger and maintains its liquid state. Before entering the reservoir, the liquid passes through an expansion valve, and the resulting drop in pressure causes partial vaporization of the mixture. The energy required for vaporization is taken from the current, so the temperature of the current drops, and the liquid level in the boiler is maintained.

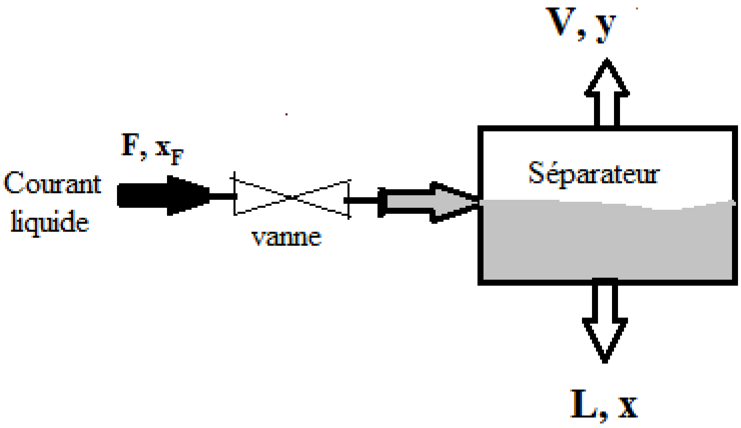


Figure 1.9 Adiabatique flash process illustration.

Partial condensation:

The vapor stream is introduced into a partial condenser and the liquid vapor mixture is then separated in the tank.

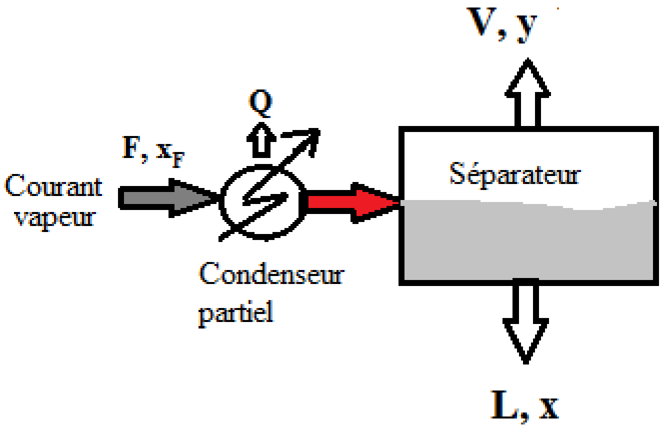


Figure 1.10 Partial condensation process illustration

The quantity of vaporized liquid is obtained from the total material balance:

$$\mathbf{F = V + L} \tag{1.32}$$

where **F** is the feed flow rate of titre $\mathbf{x_F}$, **V** the vapor flow rate formed of titre **y*** and **L** the remaining liquid flow rate of titre **x**.

These balances are written for one unit of time, the regime being assumed to be stationary. By explaining y, we deduce:

$$\mathbf{y = x_F + (L/V)\,(x_F - x)} \tag{1.33}$$

$$\mathbf{y = -(L/V)x + Z + (L/V)Z} \tag{1.34}$$

This equation is that of a straight line with inclination (- **L/V**) passing through the point with coordinates (x_F; x_F) (since $x_F = y_F$); the only unknowns in the equation are x and y. Another relationship required to solve the equation is the equilibrium curve. Their intersection gives the values of **x** and **y**, provided we know the equilibrium pressure **P** and the flow ratio **L/V**. The temperature corresponding to this equilibrium can be read from the temperature/molar fraction diagram.

The **L/V** ratio can vary between 0 and ∞.

- If **L/V** = 0, the entire feed mixture **F** will be in vapor form after distillation. This vapor will have mole fraction $\mathbf{x_F}$ and will be in equilibrium with an infinitely small quantity of liquid of mole fraction $\mathbf{x_{min}}$.

- If L/V is infinite, the entire mixture F is in liquid form after distillation.

Note: The equation for the feed line can be presented as a function of the vaporization rate **Ψ.**

$$\Psi = \frac{V}{F} \tag{1.35}$$

and can be written as follows:

$$\mathbf{y} = -\left(\frac{\mathbf{1-\Psi}}{\mathbf{\Psi}}\right)\mathbf{x} + \frac{\mathbf{z}}{\mathbf{\Psi}} \qquad \mathbf{(1.36)}$$

1.4.2 Flash equations for a multicomponent mixture

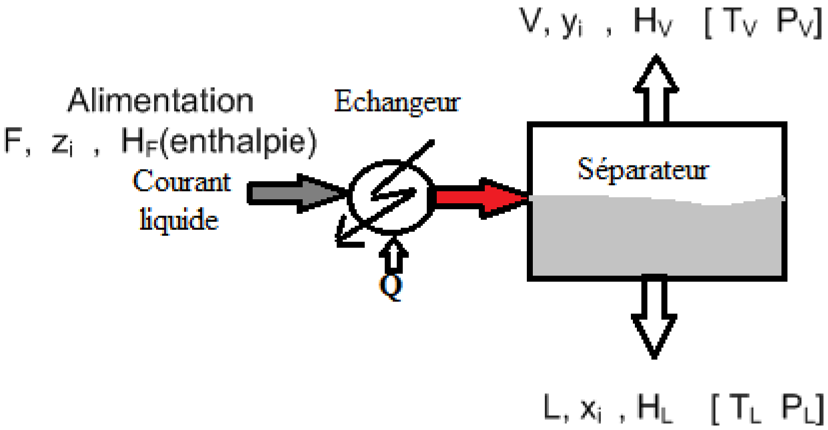


Figure 1.11 Illustration of the multi-component flash distillation

If C the number of components in the mixture, the variables are (3*C* +10) :

$\mathbf{F}$, $\mathbf{L}$, $\mathbf{V}$, $\mathbf{T_F}$, $\mathbf{T_L}$, $\mathbf{T_V}$, $\mathbf{P_{init}}$, $\mathbf{P_L}$, $\mathbf{P_V}$, $\mathbf{Q}$, $[\mathbf{z_i}, \mathbf{x_i}, \mathbf{y_i}]_{\text{i=1 à C}}$

The equations that can be written are as follows (2C + 6).

$$\mathbf{P_L= P_V}$$

$$\mathbf{T_L, T_V}$$

$$\mathbf{y_i=K\ x_i} \quad \text{with i=1 à C}$$

$$\mathbf{F\ z_i= L\ x_i+V\ y_i} \ \text{with i=1 à (C-1)}$$

$$\mathbf{F=L+V}$$

$$\mathbf{H_F\ F + Q=L\ H_L + VH_V} \qquad \mathbf{(1.37)}$$

$$\sum_1^C z_i = 1,\ \sum_1^C x_i = 1,\ \sum_1^C y_i = 1 \qquad \mathbf{(1.38)}$$

The number of variables subtracted from the number of equations gives us the number of degrees of freedom, giving us (C + 4).

But since (C + 2) supply variables are known *(**F**, $\mathbf{T_F}$, $\mathbf{P_F}$, $\mathbf{z_i}$ with i* =1 *to (C* −1) this leaves 2 degrees of freedom to choose from in order to solve the system of equations. The most frequent cases are as follows:

a) Fix $\mathbf{P_V}$ (ou $\mathbf{P_L}$) et $\mathbf{\Psi}$ and calculate $\mathbf{T_L}$, **Q** and $\mathbf{x_i}$, $\mathbf{y_i}$

b) Fix $\mathbf{P_V}$ (or $\mathbf{P_L}$) and T_L (flash isotherm) and calculate Ψ, Q et les x_i, y_i

c) Fix P_V (or P_L) and Q=0 (adiabatic flash) and calculate T_L, Ψ et les xi, yi

with:

$$\mathbf{Q=LH_L+VH_V-H_FF} \qquad \mathbf{(1.39)}$$

1.5 Bubble and dew points of multicomponent mixtures

In distillation, it's important to know the pressure and temperature conditions under which the liquid and vapor phases coexist.

1.5.1 Point de bulle

Consider a mixture containing C components of respective compositions zi. At the bubble point, the mixture containing C components is a saturated liquid in equilibrium with the first vapor bubbles. The composition of the liquid is that of the initial mixture. Using volatility and the property of mole fractions, we find the criterion characterizing conditions at the bubble point:

$$\boldsymbol{\sum_i^C y_i = 1 \;\; and \;\; x_i = z_i \;\leftrightarrow \sum_i^C z_i k_i = 1} \qquad \mathbf{(1.40)}$$

If the temperature is known, we determine the pressure at which the first steam bubbles will appear. If Dalton and Raoult's laws apply, the pressure at the bubble point is:

$$\boldsymbol{k_i = \frac{P_i^{\circ}}{P} \rightarrow \sum_i^C \frac{P_i^{\circ} z_i}{P} = 1 \rightarrow P_{bulle} = \sum_i^C P_i^{\circ} z_i} \qquad \mathbf{(1.41)}$$

1.5.2 Dew point

At the dew point, the mixture containing C components, of respective compositions zi, is a saturated vapor in equilibrium with the first drops of liquid. The composition of the vapor is that of the initial mixture. The criterion characterizing conditions at the dew point is:

$$\boldsymbol{\sum_i^C y_i = 1 \; et \; y_i = z_i \rightarrow \sum_i^C \frac{z_i}{k_i} = 1} \qquad \mathbf{(1.42)}$$

If the temperature is known, we determine the pressure at which the first drops of liquid will appear. If Dalton and Raoult's laws apply, the pressure at the dew point is:

$$\boldsymbol{k_i = \frac{P_i^{\circ}}{P} \rightarrow \sum_i^C \frac{z_i}{\frac{P_i^{\circ}}{P}} = 1 \rightarrow P_{bulle} = P_{ros\acute{e}e} = \frac{1}{\sum_i^C \left[\frac{z_i}{P_i^{\circ}}\right]}} \qquad \mathbf{(1.43)}$$

1.5.3 Determining the phases of a current

To determine the nature of the phases of a current, there is a set of criteria derived from the above equations for bubble and dew points. The different states of a current and the associated criteria are as follows:

Table 1.2 Nature of the phases of a current from the bubble point and dew point.

	$\sum_i^C z_i k_i$	$\sum_i^C \frac{z_i}{k_i}$
Sub cooled liquid	<1	>1
Saturated liquid	=1	>1
Liquid-steam mixture	>1	>1
Saturated steam	>1	=1
Superheated steam	>1	<1

- **Application 1.1**

  The following mixture is flash vaporised at 149°C under 19.06 atm**.**

Composés	**Flow (kmol/h)**	**Volatility K_i**
C_3	40	2.93
nC_4	35	1.55
nC_5	35	0.87
nC_6	35	0.49
nC_7	20	0.138
nC_8	10	0.11

1. Confirm that these operating conditions produce a liquid-vapour phase.

- **Solution:**

We calculate z_i, the bubble point and the dew point in the table below and use Table 1.2 to check that we have a liquid-vapour mixture.

Therefore we verify that $\sum K_i * z_i > 1$ and $\sum K_i / z_i > 1$

Compounds	**Flow (kmol/h)**	**Volatility K_i**	**z_i**	**K_i*z_i**	**K_i/z_i**
C_3	40	2.93	0.228	0.668	12.85
nC_4	35	1.55	0.200	0.310	7.75
nC_5	35	0.87	0.200	0.174	4.35
nC_6	35	0.49	0.200	0.098	2.45
nC_7	20	0.138	0.114	0.157	1.21
nC_8	10	0.11	0.057	0.006	1.93

$\sum K_i * z_i = 1.41$ $\sum K_i / z_i = 30.54$

So the condition of the mixture is liquid - vapour.

1.6 McCabe-Thiele method in continuous distillation of binary mixtures

The distillation column is a device for exchanging matter and heat between an ascending vapor phase and a descending liquid phase. It is a multi-stage gas-liquid contactor consisting of a set of trays, as illustrated below. The mixture to be distilled, called feed F (composition z_F), is introduced at a certain level of the column. To obtain the liquid gas counter flow, two pieces of equipment are very important

At the bottom of the column, there's a reboiler to vaporize the liquid, while at the top, there's a condenser to condense the outgoing V vapor stream. Part of the liquid recovered from the condenser is then returned to the column: this is the reflux, L. The other part is recovered and constitutes the distillate, D (composition x_D). At the bottom of the column, residue B (composition x_B) is recovered. The areas of the column respectively above and below the feed are called the rectification (or enrichment) and depletion (or depletion) zones.

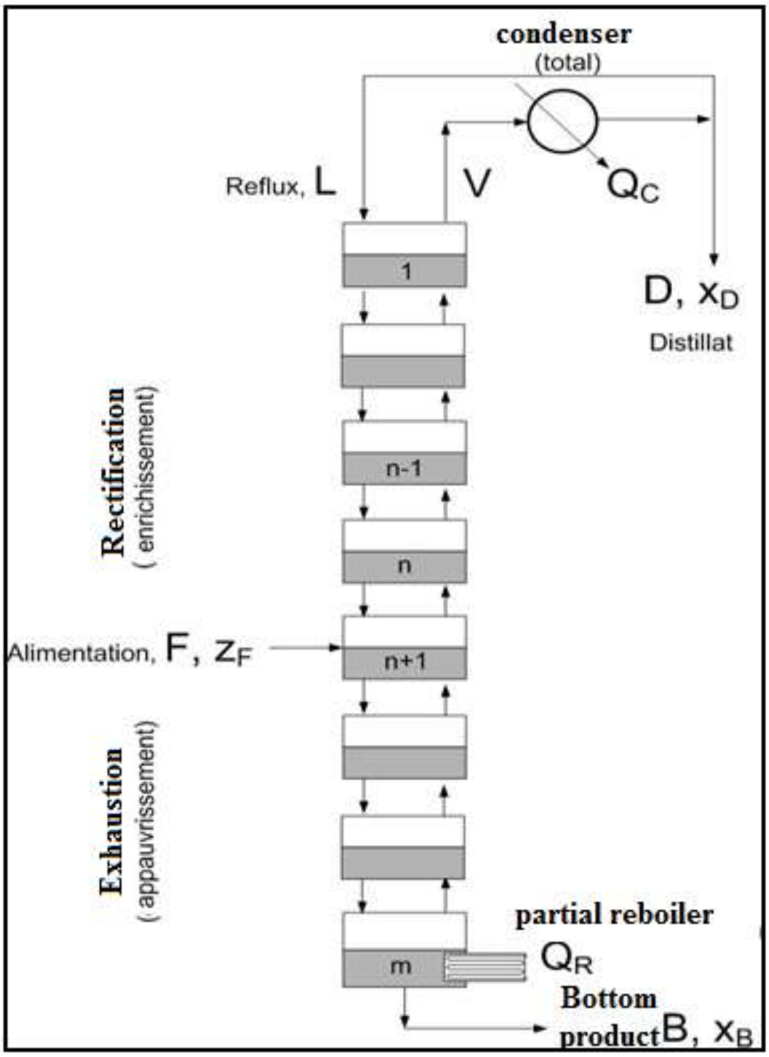


Figure 1.12 Stage distillation column configuration.

1.6.1 Reflux rate

Reflux, or liquid returning to the column, is characterized by the reflux rate. The internal reflux rate is the ratio of the liquid flow rate returned to the top, L, to the vapor flow rate leaving the column, V. The external reflux rate is the ratio of the liquid flow rate returned to the top, L, to the distillate flow rate, D.

internal reflux
$$R_{int} = \frac{L}{V} \tag{1.44}$$

external reflux
$$R_{ext} = \frac{L}{D} \tag{1.45}$$

The balance at the condenser is **V=L+D**, so we have:

$$\frac{L}{V} = \frac{L}{L+D} = (\frac{L+D}{L})^{-1} = (1 + \frac{D}{L})^{-1} \tag{1.46}$$

$$R_{int} = (1 + \frac{1}{R_{ext}})^{-1} \tag{1.47}$$

$$\frac{L}{D} = \frac{L}{V-L} = (\frac{V-L}{L})^{-1} = \left(\frac{V}{L} - 1\right)^{-1} \tag{1.48}$$

$$R_{ext} = (\frac{1}{R_{int}} - 1)^{-1} \tag{1.49}$$

1.6.2 Total Reflux

Total reflux is the condition when all the condensate is returned to the column as reflux: no product is taken off and there is no feed.

At total reflux the number of stages required for a given separation is the minimum at which it is theoretically possible to achieve the separation. Though not a practical operating condition, it is a useful guide to the likely number of stages that will be needed.

Columns are often started up with no product takeoff and operated at total reflux until steady conditions are attained. The testing of columns is also conveniently carried out at total reflux.

1.6.3 Minimum Reflux

As the reflux ratio is reduced, a pinch point will occur at which the separation can be achieved only with an infinite number of stages. This sets the minimum possible reflux ratio for the specified separation.

1.6.4 Optimum Reflux Ratio

Practical reflux ratios will lie somewhere between the minimum for the specified separation and total reflux. The designer must select a value at which the specified separation is achieved at minimum cost. Increasing the reflux reduces the number of stages required, and hence the capital cost, but increases the service requirements (steam and water) and the operating costs. The optimum reflux ratio will be that which gives the lowest annual operating cost. No hard and fast rules can be given for the selection of the design reflux ratio, but for many systems the optimum will lie between 1.2 and 1.5 times the minimum reflux ratio.

1.6.5 Theoretical stage

Each tray is a gas-liquid contactor. The liquid and vapor streams entering the tray are not in equilibrium. The liquid and vapor streams leaving the tray are at thermodynamic equilibrium (in the ideal case where the tray is equivalent to a theoretical stage). The function of each tray is to bring the outgoing streams to equilibrium.

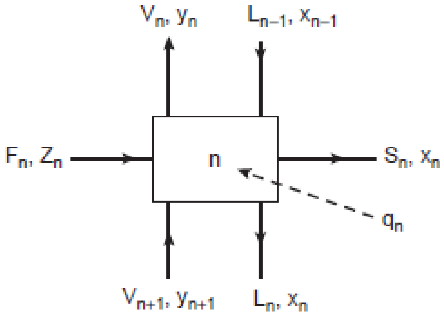


Figure 1.13 Stage flows.

1.6.6 Material balance

Material balance of the complete unit for a steady state

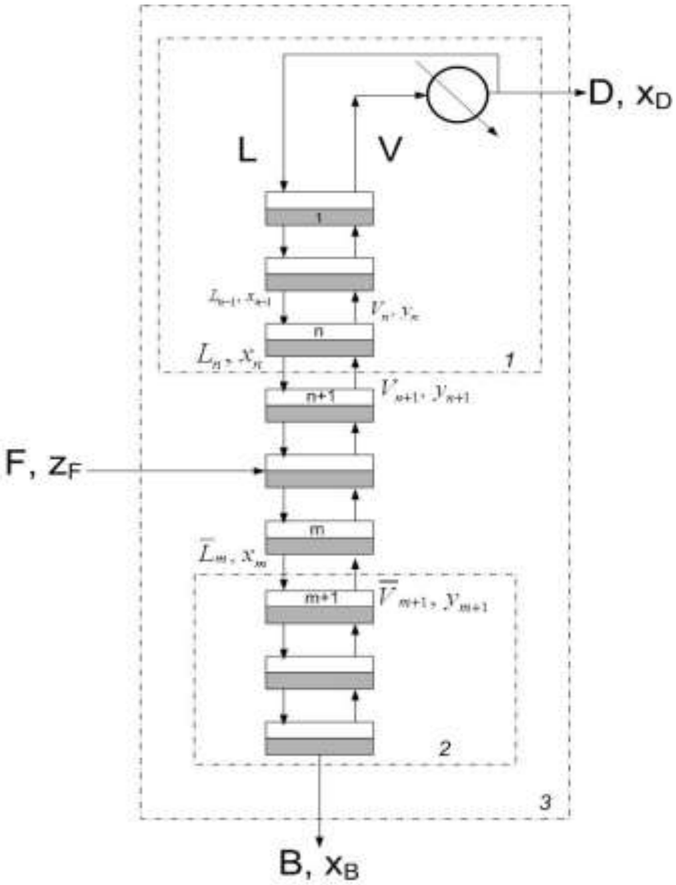


Figure 1.14 Presentation of the continuous distillation column with rectification and exhaustion zones.

$$\mathbf{F = D + B} \tag{1.50}$$

$$\mathbf{z_F\, F = x_D\, D + x_B\, B} \tag{1.51}$$

$$\mathbf{z_F\, F = x_D\, D + x_B\, (F - D)} \tag{1.47}$$

$$\mathbf{F(z_F - x_B) = D(x_D - x_B)} \tag{1.48}$$

$$\frac{D}{F} = \frac{z_F - x_B}{x_D - x_B} \tag{1.49}$$

$$\Longrightarrow \qquad D = F\,\frac{z_F - x_B}{x_D - x_B} \tag{1.50}$$

$$\frac{B}{F} = \frac{z_F - x_D}{x_B - x_D} \tag{1.51}$$

$$\Longrightarrow \qquad B = F\,\frac{z_F - x_D}{x_B - x_D} \tag{1.52}$$

Material balance in the rectification zone:

$$V_{n+1} = L_n + D \tag{1.53}$$

and

$$y_{n+1}V_{n+1} = L_n x_n + D x_D \tag{1.54}$$

$$y_{n+1} = x_n \frac{L_n}{V_{n+1}} + x_D \frac{D}{V_{n+1}} \tag{1.55}$$

Material balance in the exhaustion zone:

$$\bar{L}_m = \bar{V}_{m+1} + B \tag{1.56}$$

and

$$x_m \bar{L}_m = y_{m+1}\bar{V}_{m+1} + B x_B \tag{1.57}$$

$$y_{m+1} = x_m \frac{\bar{L}_m}{\bar{V}_{m+1}} + x_B \frac{B}{\bar{V}_{m+1}} \tag{1.58}$$

1.6.7 Lewis simplifying assumptions for the McCabe-Thiele method:

Lewis's simplifying assumptions simplify the expressions of the operating line equations. These assumptions are:

1. The distillation column is adiabatic;

2. The heats of mixing of the two binary compounds are negligible;

3. The heats of vaporization of the two compounds are equal;

These 3 assumptions imply that when part of the vapor condenses on a plate, the heat recovered is not dissipated to the outside, since the system is adiabatic, and is therefore available to vaporize part of the liquid. Since the heats of mixing are negligible and the heats of vaporization are equal, the condensation of one mole of steam leads to the vaporization of one mole of liquid.

$$\bar{V}_m = \bar{V}_{m+1} = \bar{V} = constant\ et\ \bar{L}_m = \bar{L}_{m+1} = \bar{L} = constant$$

$$V_n = V_{n+1} = V = constant\ \text{et}\ L_n = L_{n+1} = L = constant$$

In these conditions:

- Equation of the operating line in the concentration zone

$$y = \frac{L}{V}x + \frac{D}{V}x_D \tag{1.59}$$

- Equation of the operating line in the exhaustion zone

$$y = \frac{\bar{L}}{\bar{V}}x + \frac{B}{\bar{V}}x_B \tag{1.60}$$

1.6.8 Balance on the feed tray

The redistribution of the supply current on the feed tray depends on its thermodynamic conditions in relation to those on the tray.

If the feed is in the form of a saturated liquid, all the flow introduced will flow back down to the exhaustion zone. Similarly, in the case of saturated steam, it will rise in the rectification zone. In the case of a gas-liquid feed, the mixture will be distributed in each of the zones.

An undercooled liquid will not only drop into the depletion zone, but will also cause some of the steam on the plate to condense. Similarly, overheated steam will vaporize part of the liquid.

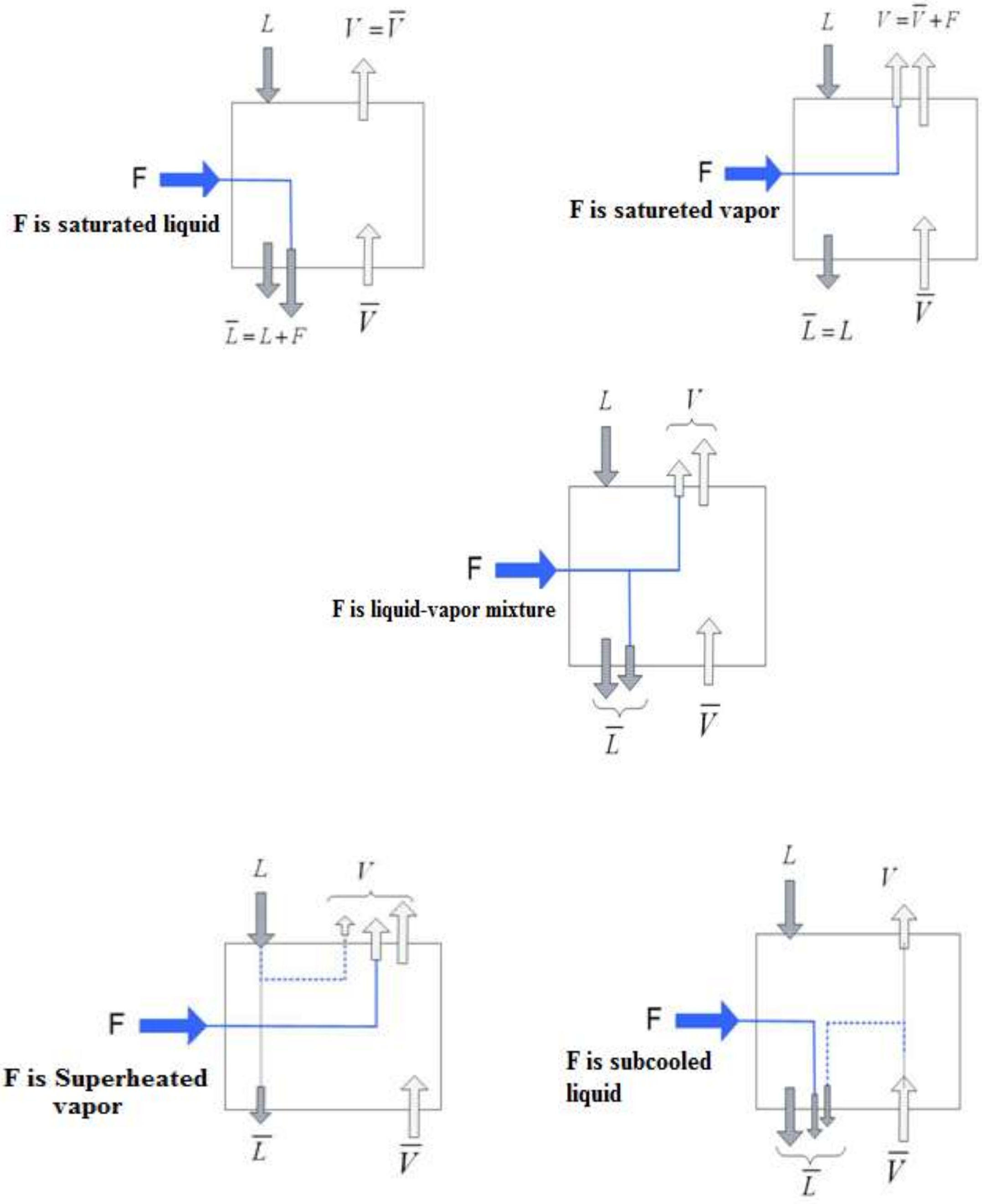


Figure 1.15 different states of feed in distillation.

The point of intersection of the two operating lines verifies the equation of the feed line mentioned below.

$$y = x\frac{(L-\bar{L})}{(V-\bar{V})} + z_F\frac{F}{(V-\bar{V})} \qquad (1.61)$$

$$\Longrightarrow \qquad y = \frac{(q)}{(q-1)}x + \frac{z_F}{(1-q)} \qquad (1.62)$$

$$\Leftrightarrow \qquad \text{With: } \bar{L} = L + qF \qquad q = \frac{\bar{L}-L}{F} \qquad (1.63)$$

$$\Leftrightarrow \qquad V = \bar{V} + (1-q)F \qquad (1-q) = \frac{V-\bar{V}}{F} \qquad (1.64)$$

q: Coefficient characterizing liquid flow variations between rectification and exhaustion zones; q represents the rate of liquefaction in feed **F**.

The q coefficient can also be related to the enthalpy balance on the feed stage (assumed to be adiabatic.

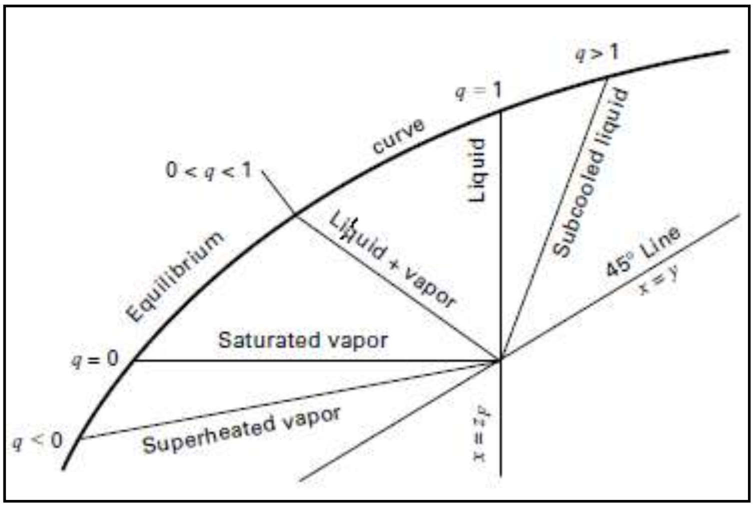
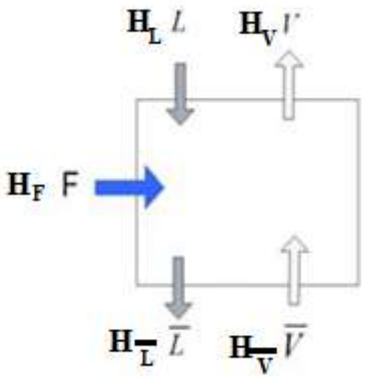


Figure 1.16 Effect of thermal condition of feed on slope of the q-line.

$$y = \frac{\Psi-1}{\Psi}x + \frac{z_F}{\Psi} \qquad (1.65)$$

$$\Longrightarrow \qquad \text{With: } V = \bar{V} + \Psi F \qquad \Psi = \frac{V-\bar{V}}{F} \qquad (1.66)$$

$$FH_F + LH_L + \bar{V}H_{\bar{V}} = \bar{L}H_{\bar{L}} + VH_V \qquad \textbf{(1.67)}$$



Lewis' hypotheses assume that:

$$H_L = H_{\bar{L}} \text{ and } H_{\bar{V}} = H_V$$

$$FH_F + LH_L + \bar{V}H_V = \bar{L}H_L + VH_V \qquad \textbf{(1.68)}$$

$$FH_F = H_L(\bar{L} - L) + H_V(V - \bar{V}) \qquad \textbf{(1.69)}$$

$$\mathbf{q} = \frac{(H_V - H_F)}{(H_V - H_L)} \qquad \textbf{(1.70)}$$

1.6.9 Subcooled liquid feed

For a feed that is a subcooled liquid, the term ($\mathbf{H_V}$ - $\mathbf{H_F}$) corresponds to the energy required to heat the liquid to its boiling temperature (bubble point, $\mathbf{T_b}$) and then to vaporize it $\mathbf{\Delta H_{Vap}}$ and ($\mathbf{H_V}$ - $\mathbf{H_L}$) corresponds to the latent heat of vaporization of the liquid:

$$\mathbf{q} = 1 + \frac{C_{PL}(T_b - T_F)}{\Delta H_{Vap}} \qquad \textbf{(1.71)}$$

1.6.10 Feed is superheated steam

For superheated steam, the term ($\mathbf{H_V}$ - $\mathbf{H_F}$) corresponds to the energy required to cool the steam to its condensation temperature (dew point, $\mathbf{T_r}$). We therefore have a for superheated steam:

$$\mathbf{q} = - \frac{C_{PL}(T_F - T_r)}{\Delta H_{Vap}} \qquad \textbf{(eq. 1.72)}$$

1.6.11 Principle of the McCabe-Thiele method

To solve a distillation problem, we need to satisfy equations for liquid-vapor equilibrium on each stage, and for material balance (total and partial) between stages.

On a y-x graph.

The principle behind Mc Cabe and Thiele's graphical method is as follows:

1) Currents leaving a stage are at equilibrium, and therefore correspond to a point on the equilibrium curve.

2) Currents crossing between stages correspond to points on the operating lines.

The construction consists of a staircase plot that passes successively from the operating line to the equilibrium curve.

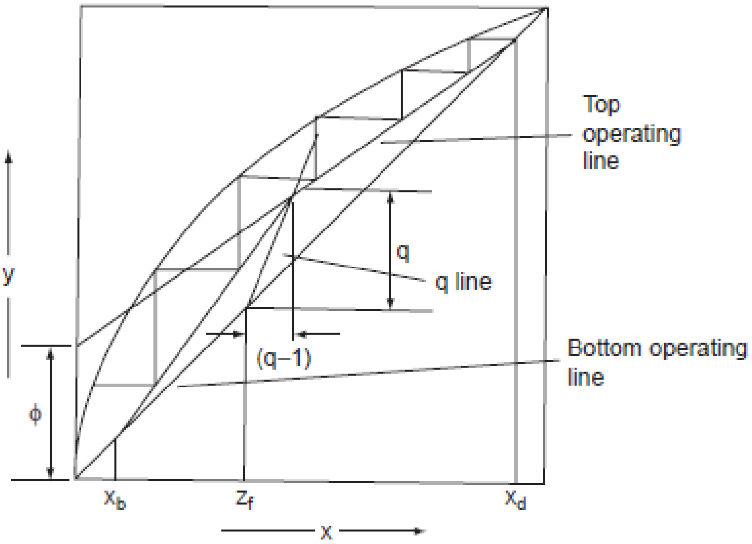
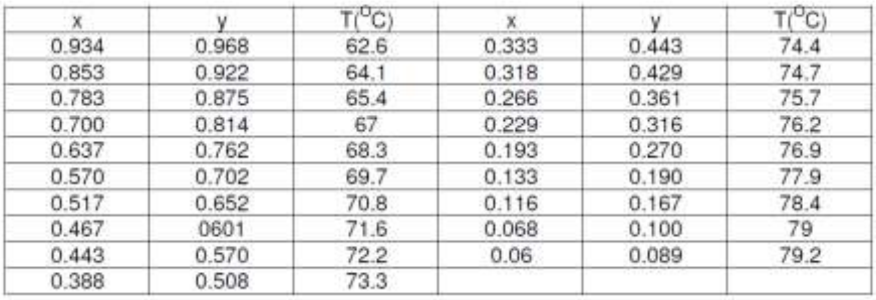


Figure 1.17 Determination of the number of stages using the McCabe-Thiele method.

- **Application 1.2**

Consider a mixture of chloroform and benzene with a molar composition of 65-35%. The equilibrium data is as follows:



x	y	T(^{o}C)	x	y	T(^{o}C)
0.934	0.968	62.6	0.333	0.443	74.4
0.853	0.922	64.1	0.318	0.429	74.7
0.783	0.875	65.4	0.266	0.361	75.7
0.700	0.814	67	0.229	0.316	76.2
0.637	0.762	68.3	0.193	0.270	76.9
0.570	0.702	69.7	0.133	0.190	77.9
0.517	0.652	70.8	0.116	0.167	78.4
0.467	0601	71.6	0.068	0.100	79
0.443	0.570	72.2	0.06	0.089	79.2
0.388	0.508	73.3			

We want to separate this mixture into a rich fraction containing 95% chloroform and a lean fraction containing 13%.

1. Draw the y vs x diagram.

2. What is the minimum number of trays required for this separation?

3. Given that the feed is a saturated liquid, what is the minimum reflux ratio (L/V)?

Fixing the reflux ratio at L/V=0.75,

4. What is the number of theoretical stages and the optimal feed tray position (taking tray 1 at the top of the column)?

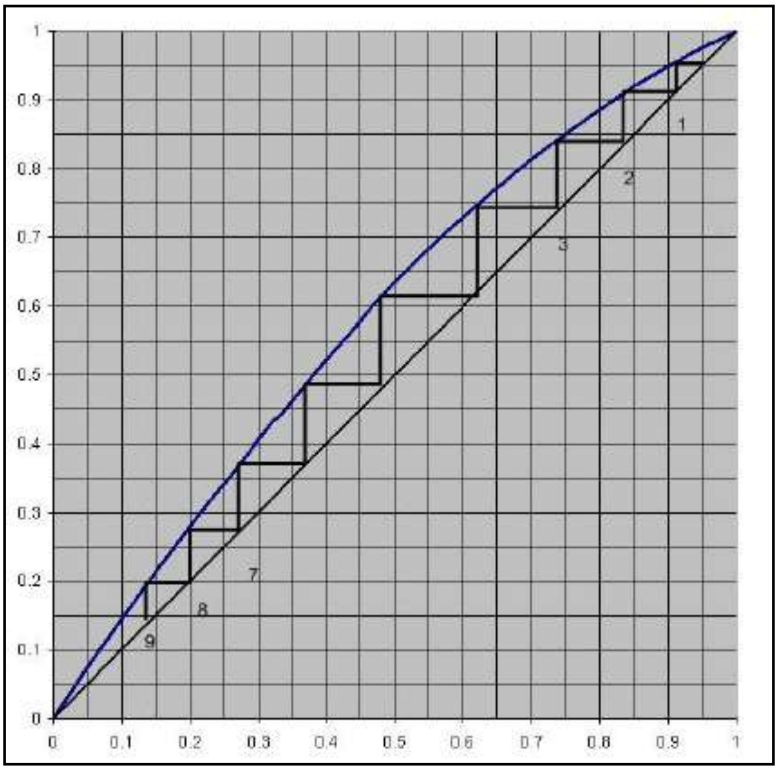
5. What are the flow rates of the streams recovered at the top and bottom of the column, considering the feed rate is 100 kmol/hour?

6. What are the flow rates of the liquid and vapor streams that intersect in the rectification and stripping sections?

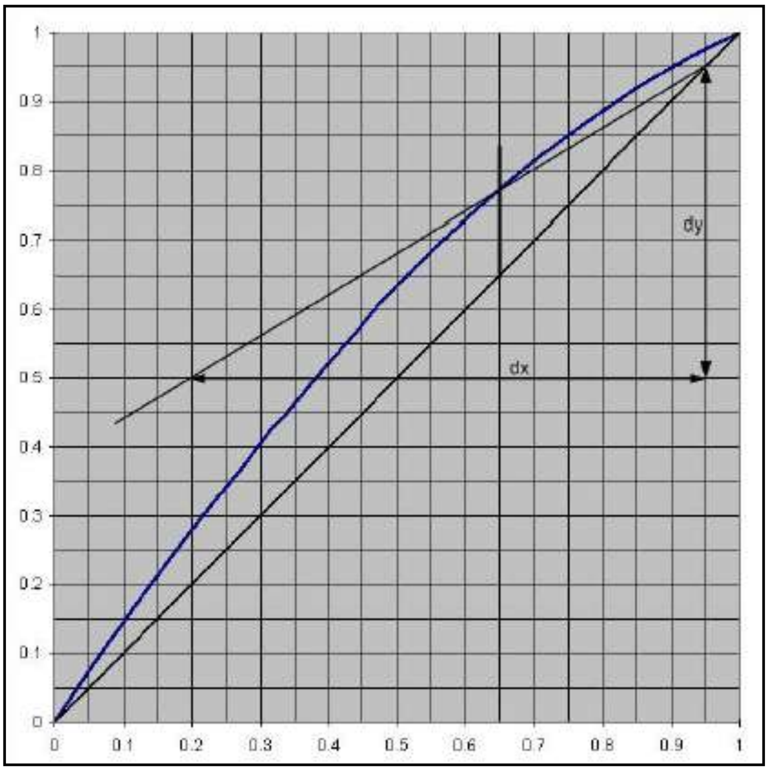
7. What are the temperatures at the top, bottom of the column, and at the feed?

- **Solution:**

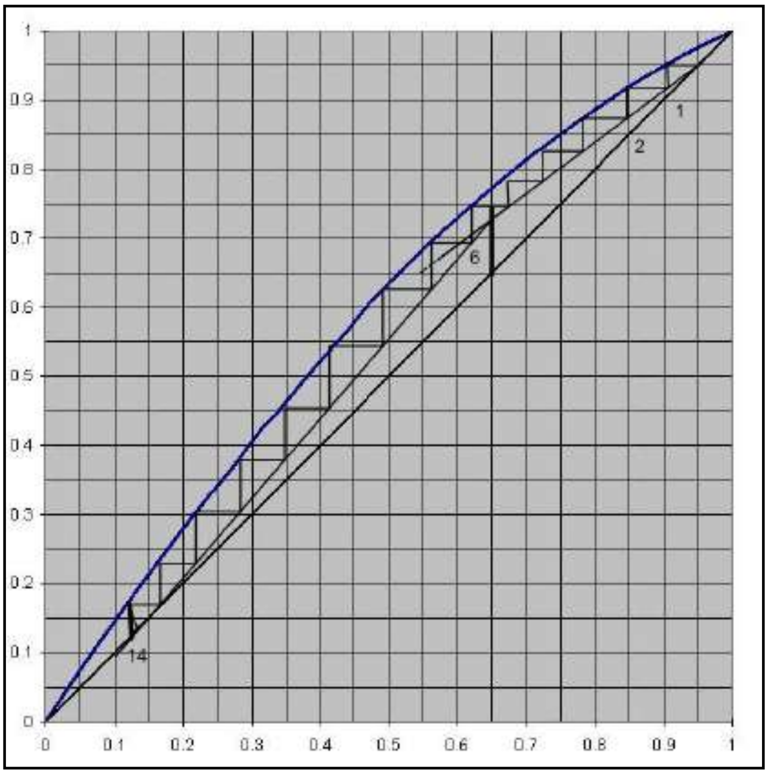
1. Plotting the equilibrium diagram y=f(x) and constructing it with the first bisector gives 9 stage.



3. The feed line for a saturated liquid (vertical) is drawn through $x=y=z_F$. We find the intersection of the operating line through $x=y=X_D$ with the equilibrium curve with the equilibrium curve and the feed line. The slope of this line is (dy/dx)=9/15=0.6



4. Draw the operating line for the enrichment zone L/V=0.75(=3/4=6/8), between 13 and 14 trays are required and the optimum tray for feeding is tray 6.



5. The flow rates of the currents recovered at the top and bottom of the column, given that the feed rate is 100 kmole/hour:

$\boldsymbol{F = D + B} \quad \boldsymbol{z_F F = x_D D + x_B B}$

$\boldsymbol{z_F F = x_D D + x_B (F\text{-}D) \Longrightarrow (z_F - x_B) F = (x_D - x_B) D}$

$\boldsymbol{D = \frac{(zF - xB)}{(xD - xB)} F} \Longrightarrow$ ***D= 63.41*** kmol/hour and ***B=36.59*** kmol/h

6. The flow rates of the liquid and vapour streams that cross in the rectification and exhaustion zones are:

In the rectification zone:

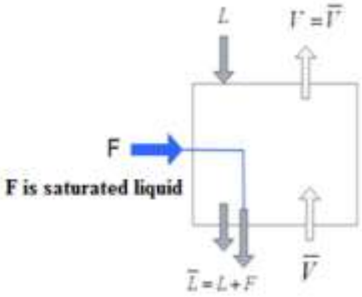
$$\boldsymbol{\frac{L}{V} = \frac{L}{V-L} = \left(\frac{V-L}{L}\right)^{-1} = \left(\frac{V}{L} - 1\right)^{-1} = \left(\frac{1}{0.75} - 1\right)^{-1} = 3} \Longrightarrow \boldsymbol{L} = 3(63.41) = \boldsymbol{190.23} \text{ kmol/h}$$

$$\boldsymbol{\frac{L}{V} = 0.75} \Longrightarrow \boldsymbol{V} = \frac{\boldsymbol{L}}{0.75} = \frac{190.23}{0.75} = \boldsymbol{253.64} \text{ kmol/h}$$

Feed is a saturated liquid:

$\bar{L} = L + F = 190.23 + 100 = 293.23$ kmol/h

$\bar{V} = V = 253.64$ kmol/h



1.7 Reboilers and condensers

1.7.1 Reboilers

A reboiler is said to be total if all the liquid feed to the reboiler is vaporized. Otherwise, the reboiler is said to be partial. A partial reboiler that leads to the formation of a liquid-vapor mixture in equilibrium is therefore equivalent to a theoretical stage.

In the figure below, only the thermo-siphon (b and c) is a total reboiler (one liquid inlet and one vapour outlet) and the reboiler shown in (a) is a partial reboiler (one liquid inlet and one liquid outlet and one vapour outlet).

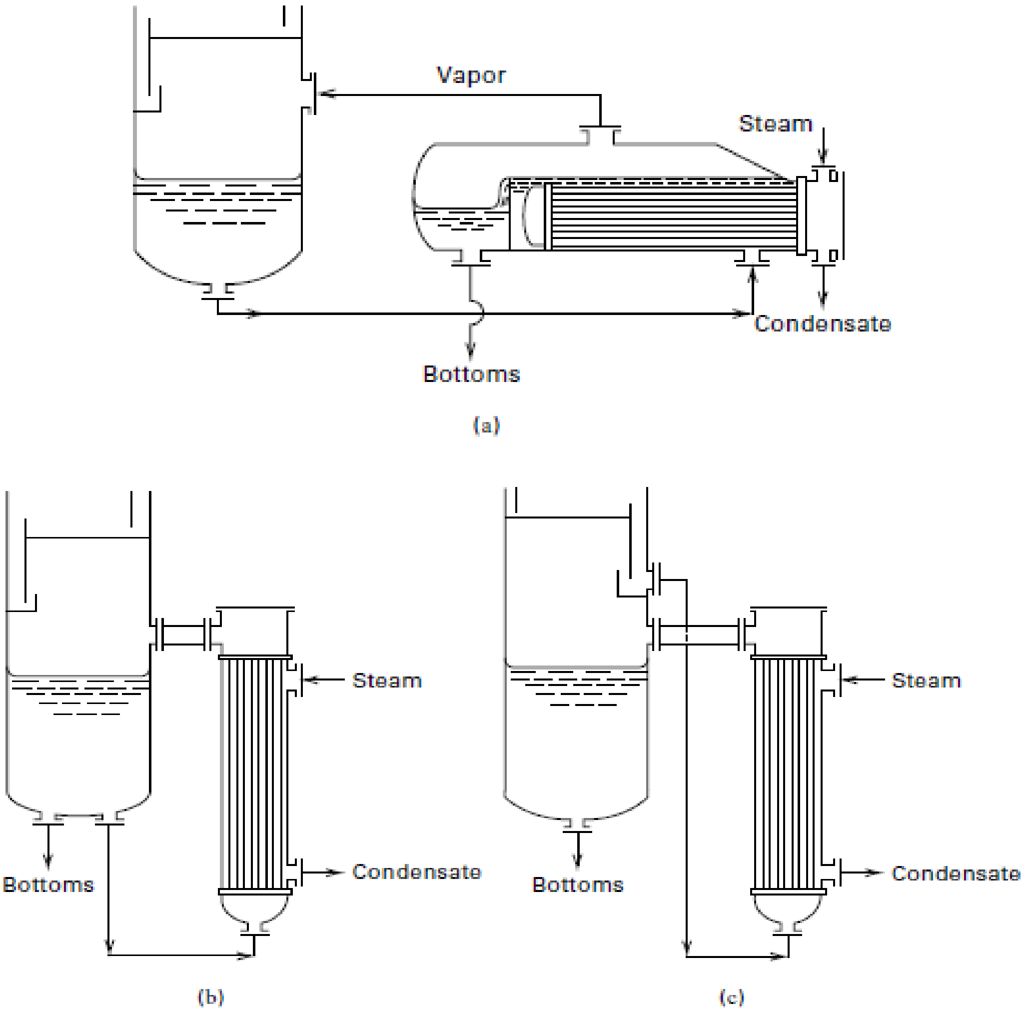


Figure 1.18 Reboilers for plant-size distillation columns: (a) kettle-type reboiler; (b) vertical thermosyphon-type reboiler, reboiler liquid withdrawn from bottom sump;(c) vertical thermosyphon-type reboiler, reboiler liquid withdrawn from bottom-tray downcomer.

1.7.2 Condensers

A parallel distinction is made for condensers:

- The total condenser, which condenses all the steam leaving the column.
- The partial condenser, which leads to the formation of a liquid-vapor mixture in equilibrium. The partial condenser is equivalent to a theoretical stage.

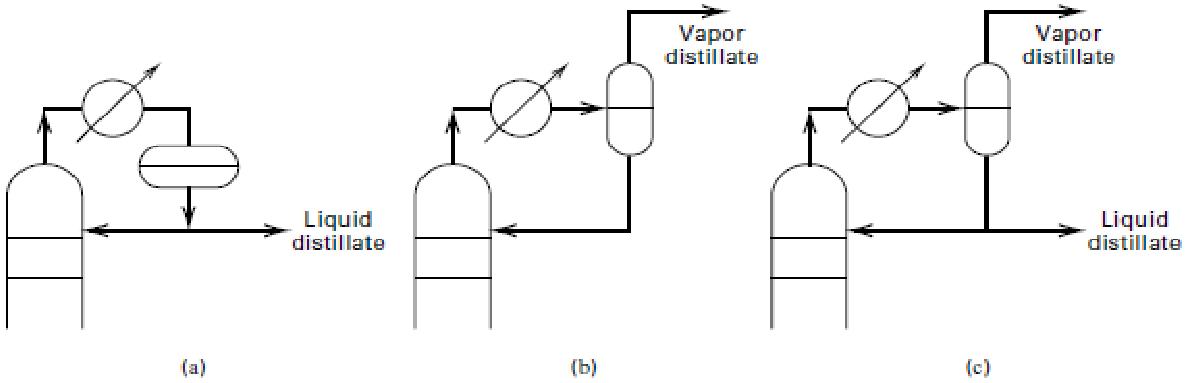


Figure 1.19 Condenser types: (a) total condenser; (b) partial condenser; (c) mixed condenser.

1.8 Stage efficiency

The theoretical plateau corresponds to the ideal case where the vapor $\mathbf{V_n}$ and liquid $\mathbf{L_n}$ currents flowing out of it are in thermodynamic equilibrium. In real conditions, the currents $\mathbf{V_n}$ and $\mathbf{L_n}$ do not always reach this equilibrium.

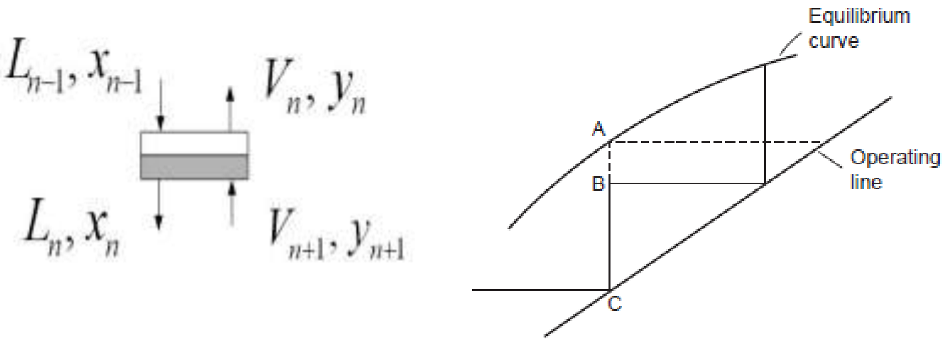


Figure 1.20 Stage efficiency.

1.8.1 The Murphree efficiency

We characterize this deviation from equilibrium by defining the Murphree efficiency in the vapor phase as:

$$E_{MV} = \frac{y_n - y_{n+1}}{y_n^* - y_{n+1}} = \frac{BC}{AC} \qquad \textbf{(1.73)}$$

where $\mathbf{y_n*}$ is the composition of a hypothetical steam in equilibrium with the liquid $\mathbf{L_n}$. Similarly, Murphree efficiency in the liquid phase is defined by:

$$E_{ML} = \frac{x_n - x_{n-1}}{x_n^* - x_{n-1}} \qquad \textbf{(1.74)}$$

où $\mathbf{x_n*}$ is the composition of a hypothetical steam in equilibrium with the vapor $\mathbf{V_n}$.

Murphree's efficiency can change from tray to tray. Murphree efficiency is a precise information, but difficult to calculate. We often use the concept of overall column efficiency, which is defined as the ratio of the number of theoretical trays needed to obtain a certain separation to the number of trays actually used.

$$\boldsymbol{E_{global}} = \frac{\textbf{number of theoretical stages}}{\textbf{Number of real stages}} \tag{1.75}$$

- **Application 1.3**

An old distillation column is found in a refinery and is identified as consisting of 5 trays. To determine the efficiency of this column, it is installed and fed with an isopropanol-ethybenzene mixture with the following equilibrium data isopropanol-ethybenzene mixture with the following equilibrium data**:**

x	5	10	20	30	40	50	60	70	80	90
y	30	48	67	78	84	88	91	93	94	97

Under conditions of total reflux, measurements of the concentrations of the phases on each plate are obtained the following results:

No du plateau	1 (tête)	2	3	4	5 (pied)
x(iso-prop)	0.8	0.5	0.4	0.15	0.05
Y(iso-prop)	0.9	0.8	0.5	0.4	0.15

1. Determine the vapour phase efficiencies of each tray and comment on them.

- **Solution:**

The points of the currents leaving each stage are placed (pseudo-equilibrium curve) and the construction allows the efficiencies of each stage to be calculated using relationship (1.73) For No. 3:

$$E_3 = \frac{(50-40)}{(84-40)} = \frac{10}{44} = 0.23$$

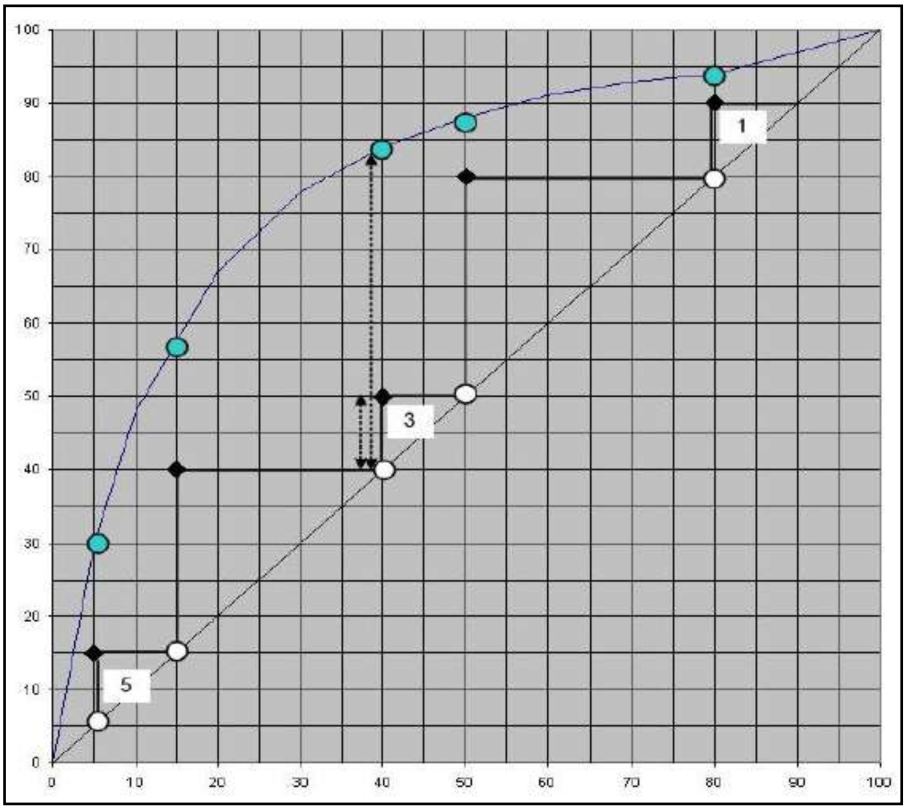
$$E_1 = 0.71$$

$$E_2 = 0.79$$

$$E_4 = 0.60$$

$$E_5 = 0.40$$

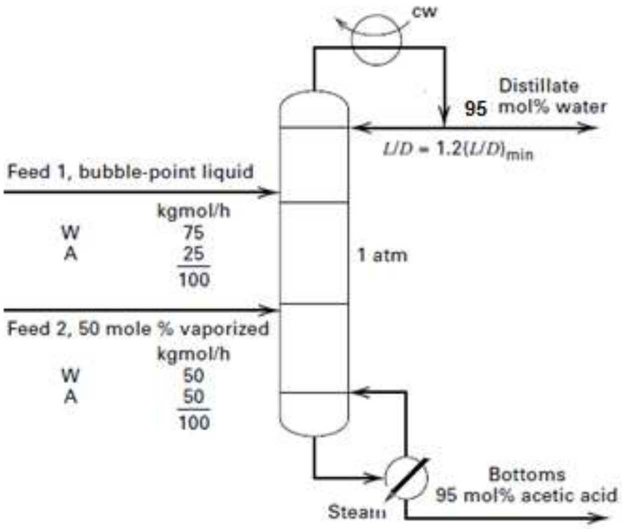
Tray 3 is defective.



- **Application 1.4** Optimum stages of feeder for two feeders

Using the liquid-vapour equilibrium data in mole fractions of water given in the table below;

- Determine the optimum stage location for each feed and the theoretical number of stages required for distillative separation of the water/acetic acid mixtures specified in the following figure.



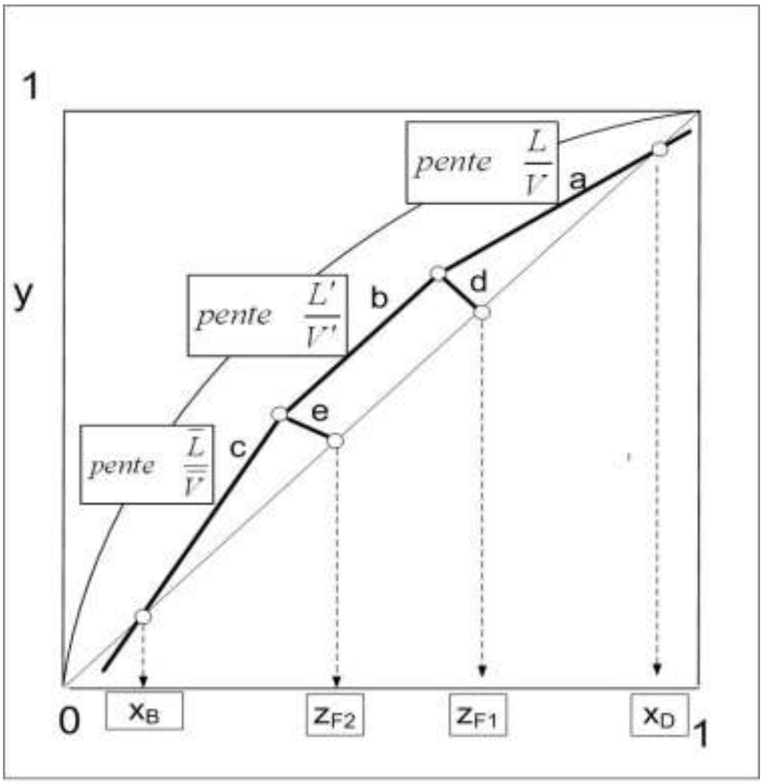
Data:

Table 1: Liquid-vapour equilibrium acetic acid/water (W) at 1 atm.

x_W	0.0055	0.053	0.125	0.206	0.297	0.510	0.649	0.803	0.9594
y_W	0.0112	0.133	0.240	0.338	0.437	0.630	0.751	0.866	0.9725

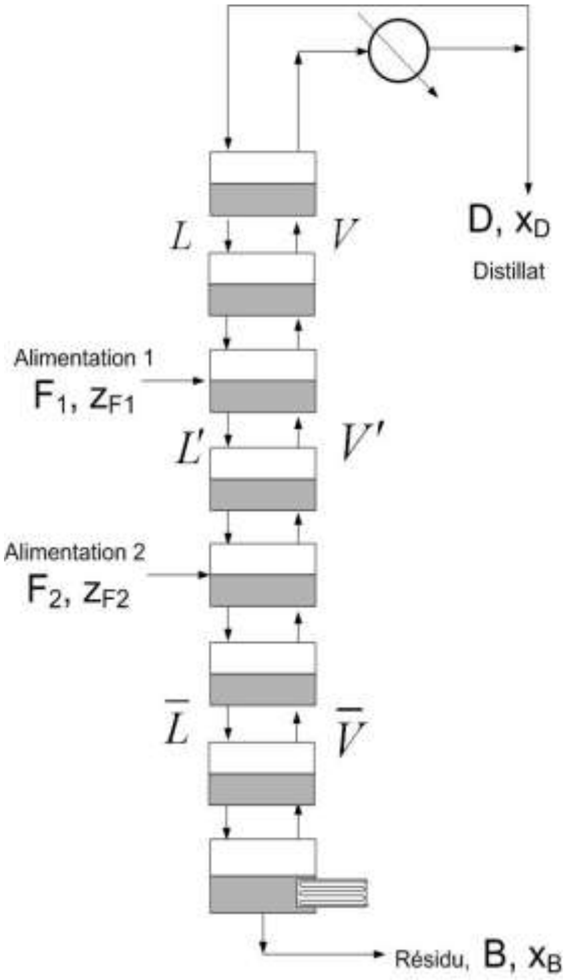
- Solution

The principle of the McCabe and Thiele method for two power supplies is identical to that for a single feed. For each feed, the corresponding feed line is defined. In addition, a new operating line is defined in the intermediate zone, with a slope of (L'/V').



Each feed line is cocurrent with the operating lines of the zones adjacent to it.

By application we have:



$(x_D/R+1)_{min}=0.34$

$R_{min}=1.79$

$R_{min}=(L/D)_{min}$

L/D=1.79x1.2=2.148

F1+F2=D+B=100+100=200 kmole/h

x_w F1+ x_w F2=x_wD+x_wB

0.75(100)+0.5(100)=0.95D+0.05B

D=127.77 kmole/h

B=72.22 kmole/l

V=L+D et L=2.148(D)=274.45 kmole/h

V=402.22 kmole/h

V=V'=402.22 kmole/h

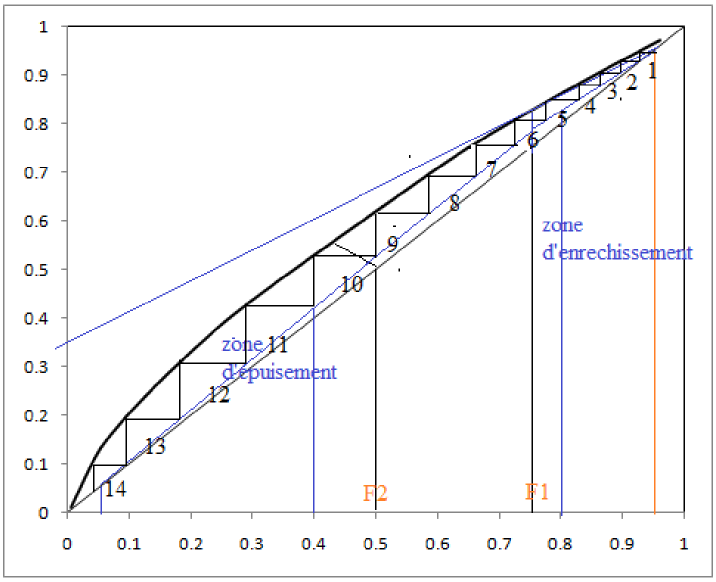
et L'=L+F1=274.45+100=374.45 kmole/h

$\bar{L} = L' + qF2 = 374.45 + 0.5(100) =$ 425.45 kmole/h

$\bar{V}$=V'+(1-q)F2=402.22+50=452.22 kmole/h

The operating line for the enrichment zone has slope L/V and passes through (x_D,x_D). Its equation is therefore y=0.68x+0.3.

The operating line for the exhaustion zone has a slope of $\bar{L}/\bar{V}$ and passes through (x_B,x_B). Its equation is therefore y=0.94x+0.003



The theoretical number of stages is 14;

the F1 feed stage is 6;

F1 feed stage is 10.

1.9 Ponchon-Savarit method in continuous distillation of binary mixtures

The McCabe–Thiele method assumes that molar vapor and liquid flow rates are constant. This, plus the assumption of no heat losses, eliminates the need for stage energy balances.

When component latent heats are unequal and solutions nonideal, the McCabe–Thiele method is not accurate, but the Ponchon–Savarit graphical method, which includes energy balances and utilizes an enthalpy-concentration diagram of the type shown in Figure 1.19, is applicable. This diagram includes curves for enthalpies of saturated-vapor $\mathbf{H_V}$ and liquid mixtures, where the terminal points of tie lines connecting these two curves represent equilibrium vapor and liquid compositions, together with vapor and liquid enthalpies, at a given temperature. Isotherms above the saturated-vapor curve represent enthalpies of superheated vapor, while isotherms below the saturated-liquid curve represent subcooled liquid. In Figure 1.17, a mixture at 100°F (Point A) is a subcooled liquid. By heating it to Point B at 204°F, it becomes a liquid at its bubble point. When a mixture at 100°F (Point G) is heated to 243°F (Point E), at equilibrium it splits into a vapor phase at Point F and a liquid phase at Point D.

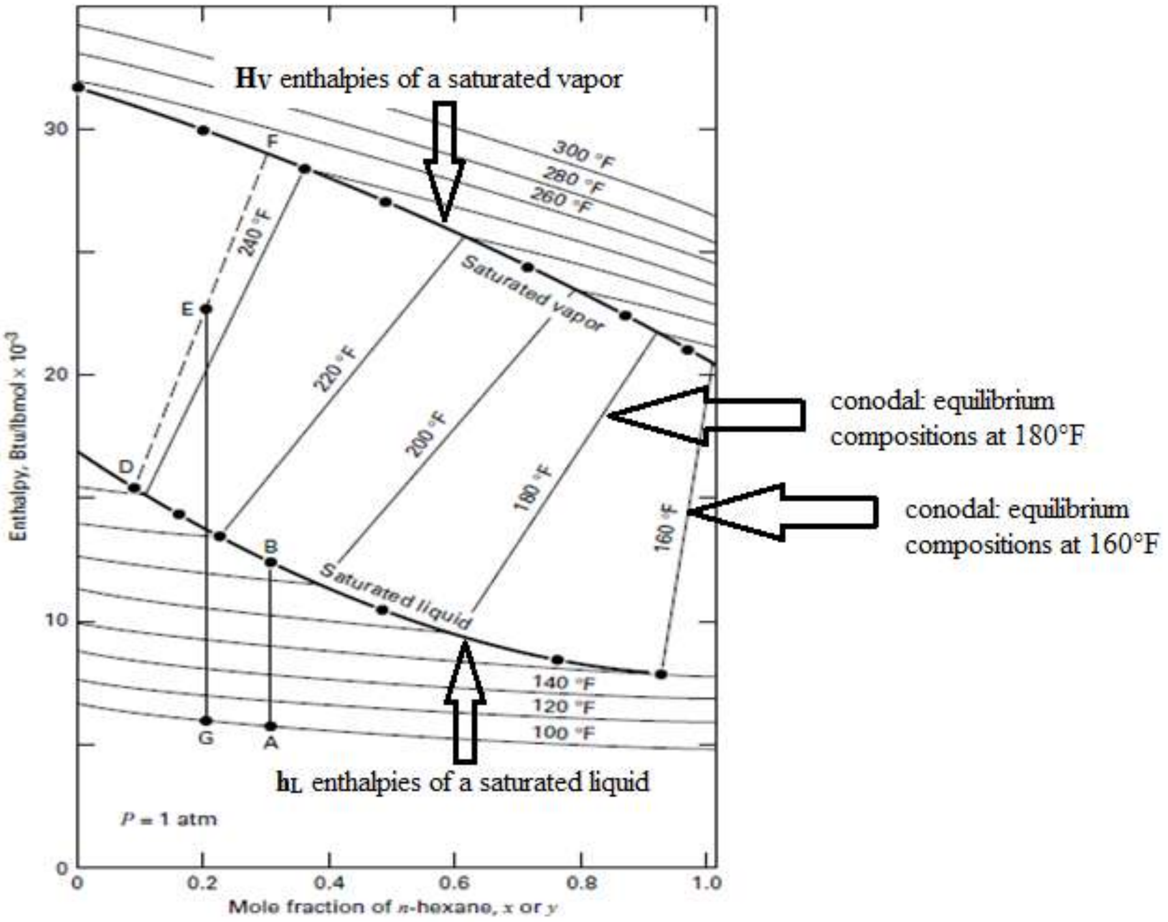


Figure 1.21 Enthalpy-concentration diagram.

1.9.1 Enthalpy-concentration diagram (pressure fixed)

The abscissa represents the mole fraction x (liquid) or y (vapor) and the ordinate represents the enthalpy.

The curves $\mathbf{h_L}$ and $\mathbf{H_V}$ represent the enthalpies of a saturated liquid and a saturated vapor. The lower and upper parts of the graph correspond to the domains of the liquid and vapor phases. Between the two curves, there is the domain of existence of the two phases liquid and vapor whose equilibrium compositions at a certain temperature are at the extremities of a conodal.

1.9.2 Material and enthalpy balances on a distillation column (see figure 1.11)

- **Material and enthalpy balances in the concentration zone**
  - **Total and partial material balance**

$$V_{n+1} = L_n + D \tag{1.76}$$

$$y_{n+1}V_{n+1} = x_nL_n + x_nD \tag{1.77}$$

  - **Enthalpy balance:**

Let D and B be the molar flow rates of distillate and $\mathbf{Q_D}$ and $\mathbf{Q_B}$ the heats exchanged at the condenser and boiler and of residue, we define $\mathbf{q_D}$ and $\mathbf{q_B}$ by:

$$q_D = \frac{Q_D}{D} \tag{1.78}$$

$$q_B = \frac{Q_B}{B} \tag{1.80}$$

$$H_{n+1}V_{n+1} + q_D D = h_n L_n + h_D D \tag{1.81}$$

$$y_{n+1}(L_n + D) = x_n L_n + x_n D \tag{1.82}$$

$$\frac{L_n}{D} = \frac{x_D - y_{n+1}}{y_{n+1} - x_n} \tag{1.83}$$

$$\frac{H_{n+1} - h_n}{y_{n+1} - x_n} = \frac{h_D - q_D - H_{n+1}}{x_D - y_{n+1}} \tag{1.84}$$

$$\frac{L_n}{D} = \frac{(h_D - q_D) - H_{n+1}}{H_{n+1} - h_n} \tag{1.85}$$

The internal reflux rate L/V at any level of the column is given by:

$$\Longrightarrow \qquad D = V_{n+1} - L_n \qquad y_{n+1}V_{n+1} = x_n L_n + x_D(V_{n+1} - L_n) \tag{1.86}$$

$$\frac{L_n}{V_{n+1}} = \frac{y_{n+1} - x_D}{x_n - x_D} \tag{1.87}$$

$$\frac{L_n}{V_{n+1}} = \frac{H_{n+1} - (h_D - q_D)}{h_n - (h_D - q_D)} \tag{1.88}$$

$$\frac{L_n}{V_{n+1}} = \frac{V_{n+1}P'}{L_n P'} \tag{1.89}$$

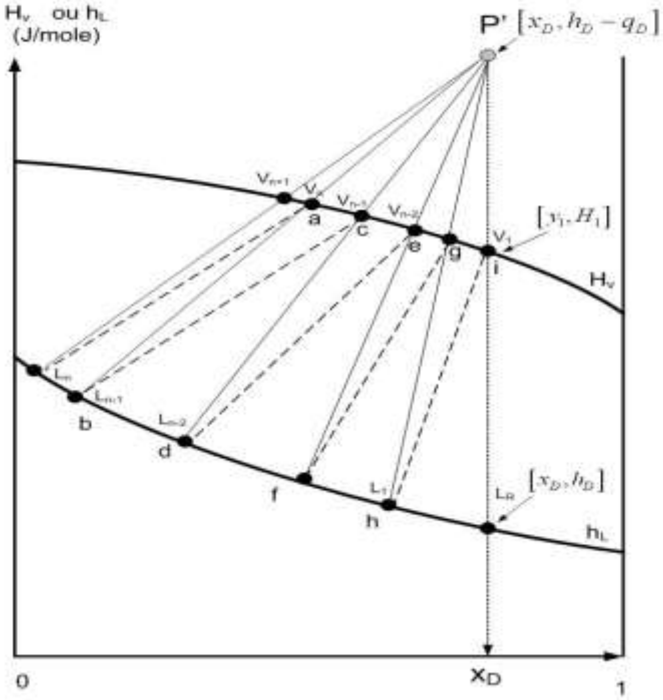


Figure 1.22 Representation of the P' pole in the enthalpy-concentration diagram.

- **Material and enthalpy balances on the exhaustion zone:**

$$\bar{L}_m = \bar{V}_{m+1} + \mathrm{B} \tag{1.90}$$

$$x_m \bar{L}_m = y_{m+1}\bar{V}_{m+1} + x_B \mathrm{B} \tag{1.91}$$

$$x_m \bar{L}_m + q_B B = H_{m+1}\bar{V}_{m+1} + h_B \mathrm{B} \tag{1.92}$$

$$\frac{(h_B - q_B) - H_{m+1}}{x_B - y_{m+1}} = \frac{H_{m+1} - h_m}{y_{m+1} - x_m} \tag{1.93}$$

Equation 1.62, on the enthalpy diagram (h-H) vs (x,y) operating line passing through the three points with coordinates [y_{m+1},H_{m+1}], [x_m,h_m] and [x_B,h_B-q_B]; the latter being the pole, P'', of the exhaustion zone.

In the exhaustion zone, all the operating straights that characterize the intersection of between two plates pass through the P'' pole.

Summary of the Ponchon-Savarit method:

1) The P' pole has the coordinate (x_D,h_D-q_D);

2) The P'' pole has the coordinate (x_B, h_B-q_B);

3) The three points (x_D,h_D-q_D), (z_F,h_F) and (x_B, h_B-q_B) are aligned;

4) Power supply F is placed at (x_D,h_D-q_D).

5) The intersecting currents in the enrichment zone belong to an operating straight line passing through the P' pole (compliance with partial, total and enthalpy balance equations);

6) Passing point zF, intersecting currents in the depletion zone belong to a straight line passing through pole P'' (compliance with partial, total and enthalpy balance equations).

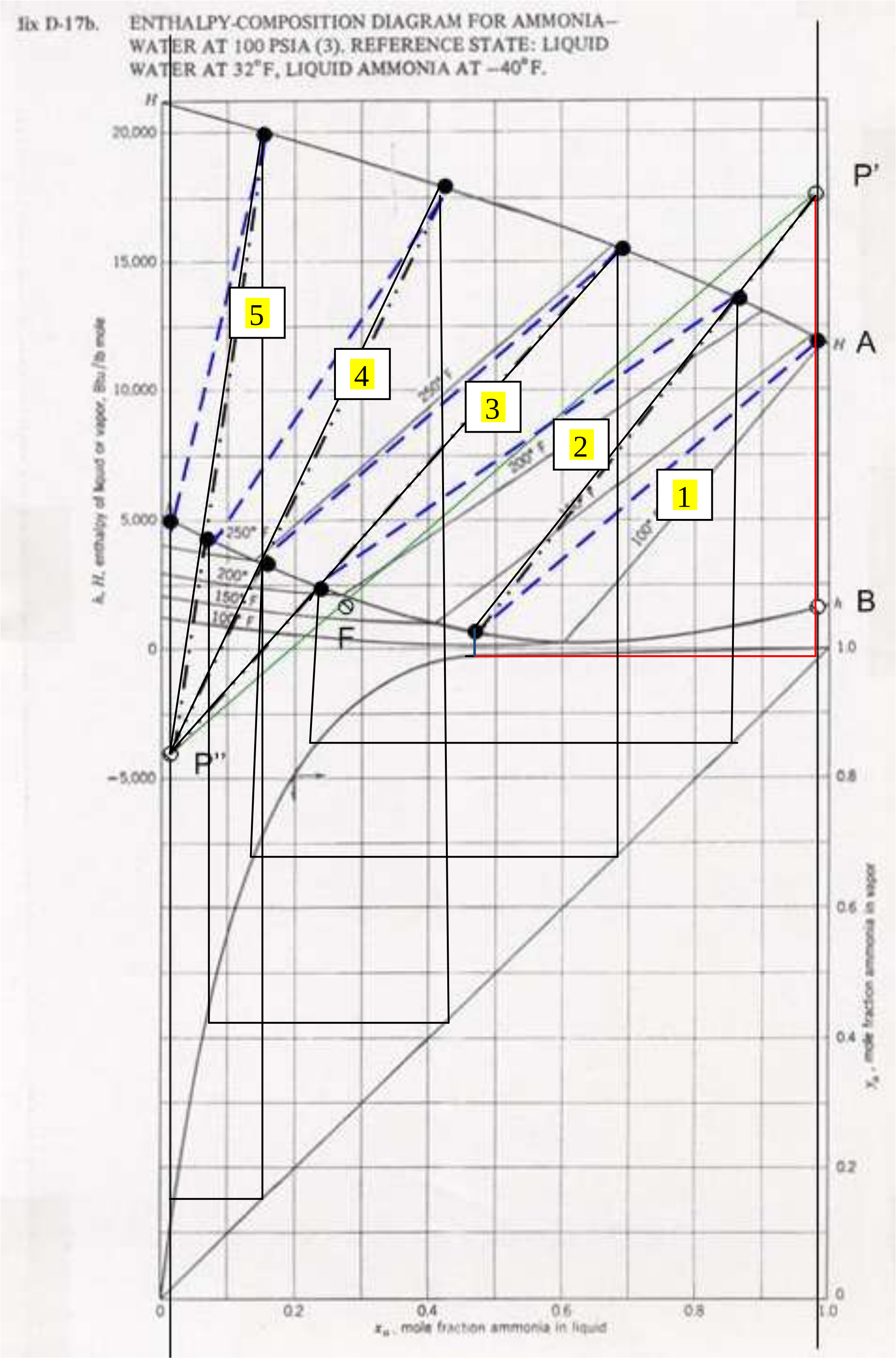


Figure 1.23 Determining the number of stages by the Ponchon Savarit method graphically.

1.9.3 Optimum position of the feed stage

The optimum position of the feed stage where the conodal line crosses the line connecting the poles P'P''. In the figure above, the feed stage is stage No. 2.

1.9.4 Minimum reflux with Ponchon Savarit Method

Minimum reflux corresponds to operation with an infinite number of stages. Graphically, an infinite number of stages is obtained as soon as an operating line can be superimposed on a conodal line. In general, and for simplicity's sake, we take as the minimum reflux value the value corresponding to the superposition of an operating line with the conodal passing through feeder F.

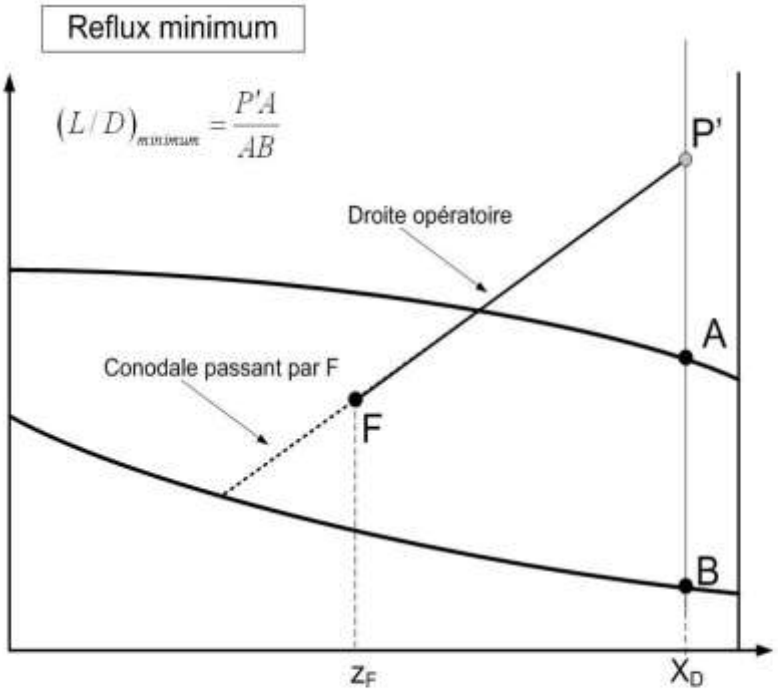


Figure 1.24 Determining the minimum reflux with Ponchon Savarit Method graphically.

- **Application 1.5**

An aqueous solution containing 30% ammonia is available, with a flow rate of 45 Kmole/hr. By distillation at 20 atm we want to recover 90% of the ammonia from the feed with a distillate containing 98% NH_3. There is a total condenser at the top of the column. There is no reboiler at the bottom but 27 Kmole/hr of saturated steam is injected directly. The feed is introduced in the form of a saturated liquid.

1. Determine the distillate and residue flow rates and the residue concentration.

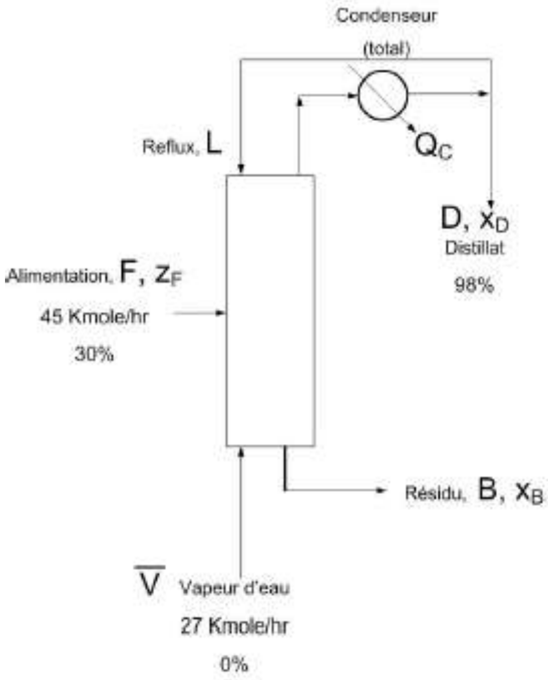
2. Determine the internal reflux rate L/V to be set at the top and the heat to be exchanged at the condenser.

3. What is the minimum reflux rate (determined from the feed composition)? Compare this with the operating reflux

4. How many trays are needed?

5. What is the optimum position of the feed?

6. What are the compositions of the liquid and vapour streams that cross between the 2nd and 3rd trays (f:rom the top of the column)?



- Solution:

1. The concentrations and flow rates of the distillate and residue streams are determined.

$$F + \bar{V} = D + B$$

0.90(0.30x45)=0.98xD

$\boldsymbol{D} = \frac{0.90 \text{ x } 0.30 \text{ x } 45}{0.98} = 12.4$

$\boldsymbol{B} = \boldsymbol{F} + \bar{\boldsymbol{V}} - \boldsymbol{D}$ = 45+27-12.4=59.6 Kmole/h

$\boldsymbol{z_F F + 0\text{x}\bar{V} = x_D D + x_B B}$

$\boldsymbol{x_B = \frac{z_F F - x_D D}{B} = \frac{0.3 \text{ x } 45 - 0.98 \text{ x } 12.4}{59.6} = 0.0226}$

At the bottom of the column, the intersecting vapour and liquid currents are $\bar{\boldsymbol{V}}$and ***B.***

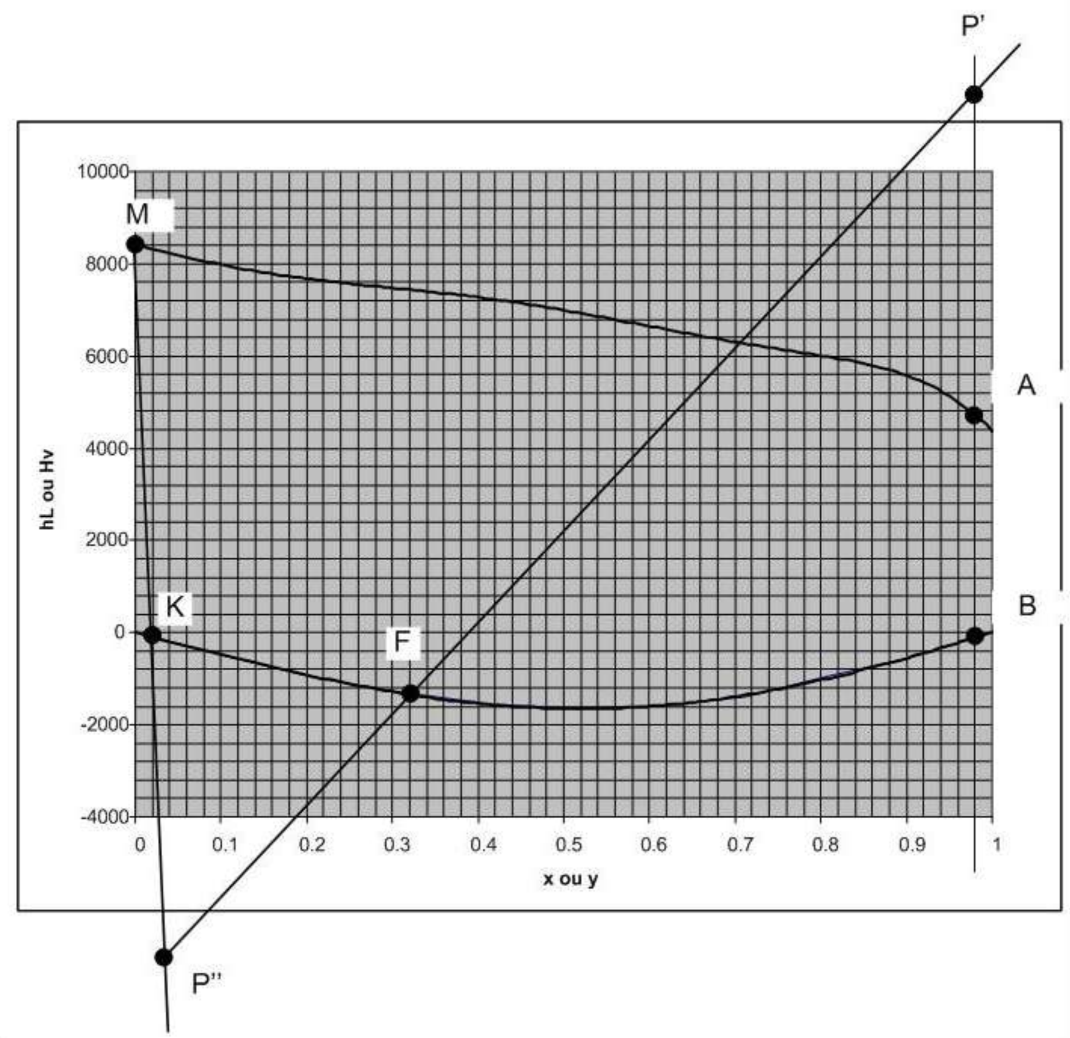
We therefore have :

$\boldsymbol{\frac{\bar{L}}{\bar{V}} = \frac{B}{\bar{V}} = \frac{59.6}{27} = 2.21}$

We can therefore place the P" pole using the following equation:

$\boldsymbol{\frac{\bar{L}}{\bar{V}} = \frac{MP''}{KP''} = \frac{MK + KP''}{KP''} = \frac{MK}{KP''} + 1 = 2.21 ===> \frac{MK}{KP''} = 1.21 ===>} KP'' = \boldsymbol{\frac{MK}{1.21}}$

Points ***M*** and ***K*** correspond to the vapour and liquid currents at the bottom of the column, and the distance measure the distance ***MK.*** The current F, trace P"F and find the point P'.



At the top, we have $\frac{L}{V} = \frac{AP'}{BP'} \approx \mathbf{0.57}$

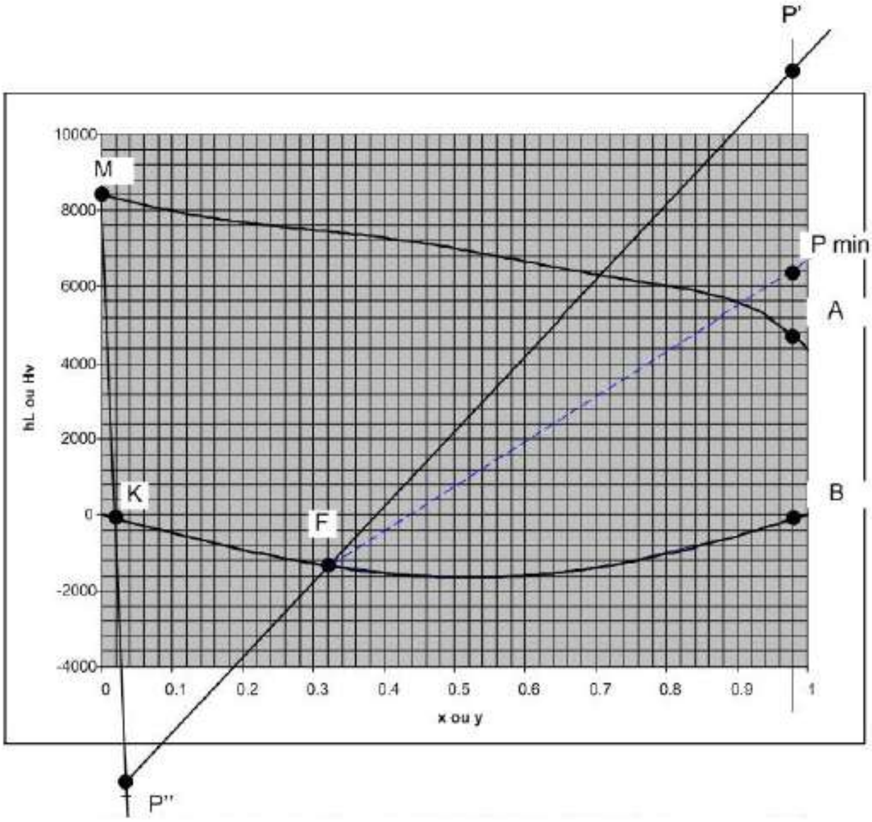
The heat to be exchanged at the condenser is given by the distance **P'B** :

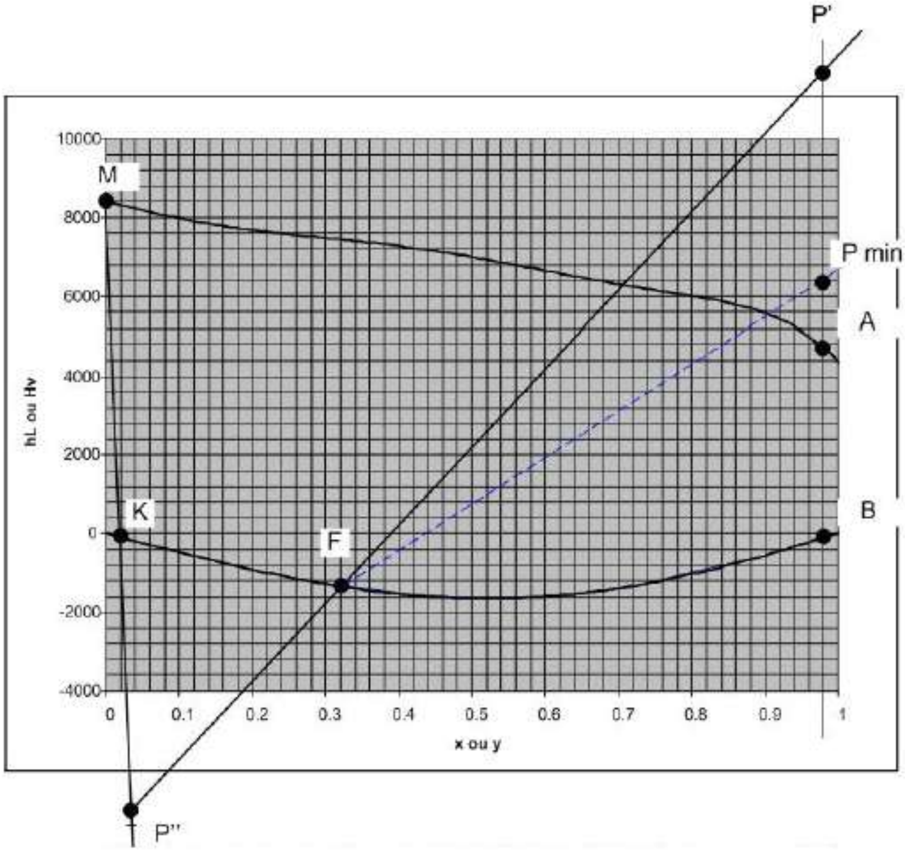
$\mathbf{q_D}$ ≈16,000 Kcal/Kmole of B

3. We plot the conodal line passing through F and its intersection with the vertical gives P_{min}

The minimum reflux:

$$\left(\frac{L}{V}\right)_{minimum} = \frac{AP_{min}}{BP_{min}} \approx \mathbf{0.27}$$





4. The construction gives 4 trays.

5. The optimum feed is from tray 2.

6. For the liquid leaving tray 2 x=0.25. For steam leaving tray 3 y=0.53

1.9.5 Case with two feed-in streams

Knowing the feed-in streams, F1 and F2, we can define the mixing point F, which is aligned with poles P' and P''. The P' pole is used above the F1 feed-in stream, the P'' pole below F2, and a new pole, P''', is used between the two feed-in streams, at the intersection of the straight lines P'F1 and P''F2.

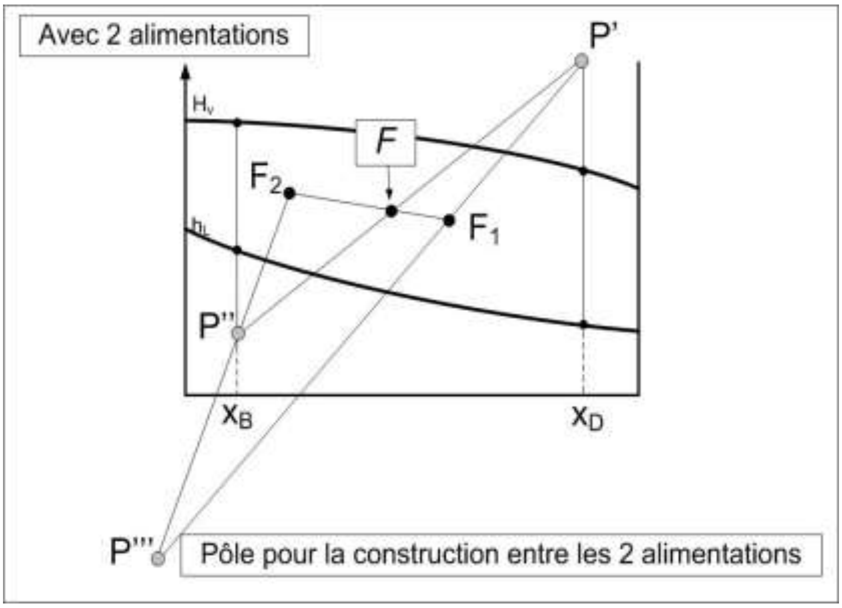


Figure 1.25 Determining of number stage in the case with two feed-in streams by Ponchon Savarit method.

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2.1 Introduction

Leaching, also known as solid-liquid (or liquid-solid) extraction, is a process that entails extracting a soluble portion (referred to as the solute or leachant) from a solid substance using a liquid solvent. The solute migrates from within the solid material into the surrounding solvent. The extracted solid fraction, the insoluble solids, or both, may constitute valuable products. This method finds extensive application in the metallurgical, natural product, and food industries.

The method of contacting solids with solvent is either by percolation of solvent through a bed of solids (or) by immersion of the solid in the solvent followed by agitation of the mixture. When percolation is used, either a stage wise or a differential contacting device is appropriate. When immersion is used, countercurrent multistage operation is commonly followed. Thus, the equipments used to conduct leaching can be under batch, semi-continuous or continuous operating conditions.

In Figure 2.1, the input solid material contains particles with components **A** and **B**. Solvent **C** selectively dissolves **B**. The stage's overflow is composed of a solvent **C** without solids and dissolved B. The underflow forms a slurry containing liquid and solid **A**. In an ideal leaching stage, the solvent completely dissolves all solutes, leaving **A** undissolved. Moreover, the composition of the retained liquid phase in the underflow slurry matches that of the liquid overflow, which is devoid of solids.

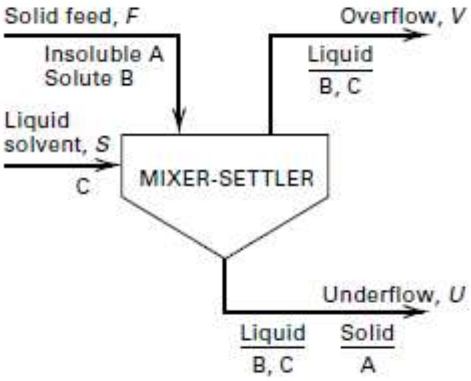


Figure 2.1 Components of solid-liquid extraction in a batch reactor.

The ratio of solid to liquid mass in the underflow is influenced by the characteristics of the phases and the equipment type, and is most accurately determined through practical experience or testing with prototype equipment. Typically, when the viscosity of liquid phases rises with an increase in solute concentration, the underflow's solid-to-liquid mass ratio decreases due to greater liquid retention by the solid.

2.2 Steps involved in Leaching

Leaching is the removal of a soluble fraction of a solid material by a liquid solvent. The solute diffuses from inside the solid into the surrounding solvent. Leaching is also termed solid-liquid extraction. Either the extracted solute or the insoluble solid portion may be the valuable product[81, 82].

The general steps involved in any solid-liquid extraction are:

1. Solvent is transferred from bulk solution to the surface of the solid.

2. Solvent penetrates into the solid.

3. Solute dissolves from the solid into the solvent.

4. Solute diffuses to surface of the solid.

5. Solute is transferred to bulk solution.

These steps are represented as a diagram in the following figure 2.2:

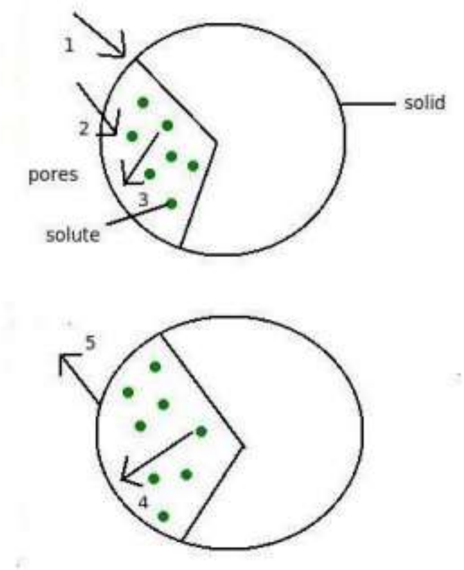


Figure 2.2 steps in leaching [1].

2.3 Industrial Example

- Extraction of vegetable oil from soybeans with a commercial hexane solvent in a pilot-plant-size, countercurrent-flow.

Leaching is more desirable than expression because a higher yield of oil is achieved using the former.

- Extraction of sugar from sugar beets using hot water.
- Removal of copper from ore using sulfuric acid.
- Recovery of gold from ore using sodium-cyanide solution
- Extraction of tannin from tree bark using water.

- Removal of caffeine from green coffee beans using supercritical CO_2.
- Recovery of proteins and other natural products from bacterial cells.

2.4 The solid-liquid equilibrium

2.4.1 Ternary solid–liquid systems

Ternary mixtures that undergo phase splitting to form two separate phases differ as to the extent of solubility of the three components in the two solid-liquid phases. The simplest case is in Figure 2.1, where only the solute, component **B**, has any appreciable solubility in either the carrier, **A**, or the solvent, C, both of which have negligible. solubility in each other. Here, equations can be derived for a single equilibrium stage, using the variables **F**, **S**, **V**, and **U** to refer, respectively, to the flow rates (or amounts) of the feed, solvent, exiting overflow **V** (**C**-rich), and exiting underflow **U** (**A**-rich). By definition, the overflow is the exiting liquid phase that contains the extracted solute; the underflow is the exiting solid phase that contains the portion of the solute, **B**, that is not extracted. If the entering solvent contains no **B**, it is convenient to write material-balance and phase-equilibrium equations for the solute, **B**, in terms of molar or mass flow rates. Often, it is preferable to express compositions as mass or mole ratios instead of fractions, as follows:

Let :

$\mathbf{F_A}$ = feed rate of carrier **A**;

S = flow rate of solvent **C**;

$\mathbf{X_B}$ = ratio of mass (or moles) of solute **B**; to mass (or moles) of the other component in the feed (**F**); underflow (**U**); or overflow (**V**).

Then, the solute material balance is:

$$X_B^F F_A = X_B^V S + X_B^U F_A \tag{2.1}$$

and the distribution of solute at equilibrium is given by:

$$X_B^V = K'_{D_B} X_B^U \tag{2.2}$$

where K'_{D_B} is the distribution or partition coefficient in terms of mass or mole ratios (instead of mass or mole fractions). By rearranging, this gives:

$$X_B^U = \frac{X_B^F F_A}{F_A + K'_{D_B} S} \tag{2.3}$$

A useful parameter is the extraction factor, $\mathbf{V_B}$, for the solute **B**:

$$V_B = K'_{D_B} S / F_A \tag{2.4}$$

Large extraction factors result from large distribution coefficients or large ratios of solvent to carrier. By rearranging, this gives:

$$\boldsymbol{X_B^U/X_B^F = \frac{1}{1+V_B}} \tag{2.5}$$

Thus, the larger the extraction factor, the smaller the fraction of **B** not extracted or the larger the fraction of **B** extracted.

Mass (mole) ratios, **X**, are related to mass (mole) fractions, **x**, by:

$$\boldsymbol{X_i = \frac{x_i}{1-x_i}} \tag{2.6}$$

Values of the distribution coefficient, $\boldsymbol{K'_{D_B}}$, in terms of ratios, are related to $\boldsymbol{K_D}$ in terms of fractions as given by the fraction of **B** not extracted as:

$$\boldsymbol{K'_{D_i} = \frac{x_i^1/(1-x_i^1)}{x_i^2/(1-x_i^2)} = K_{D_i}\left(\frac{1-x_i^2}{1-x_i^1}\right)} \tag{2.7}$$

- **Application 2.1**

Single-Stage Extraction of copper (**B**) from ore (**A**) using sulfuric acid as a solvent. Sulfuric acid is used as a solvent to remove copper (**B**) from a 13500 kg/h feed of 8 wt% copper in ore (**A**), If the underflow is to contain 1 w_t% copper, estimate the kg/h of solvent for a single equilibrium stage.

Data:

The ore and sulfuric acid are immiscible;

K_D=0.657 in mass-fraction units;

For the low concentrations of copper, assume $\boldsymbol{K'_D = K_D}$.

Solution

F_A=(0.92)(13500)=12420 kg/h

$$X_B^U = 0.01/(1-0.01) = 0.0101$$

$$V_B = \frac{X_B^F}{X_B^U} - 1 = \left(\frac{0.087}{0.0101}\right) - 1 = 7.617$$

The definition of extraction factor,

$$\boldsymbol{S} = \frac{V_B F_A}{K'_D} = 7.61(12420/0.657) = \mathbf{144000\ kg/h}$$

2.4.2 Solid-liquid system

Ideal leaching calculations can be done algebraically or with diagrams like Figure 2.3 Let:

F : total mass flow rate of feed to be leached;

S : total mass flow rate of entering solvent;

U : Total mass flow rate of the underflow, including solids;

V : Total mass flow rate of the overflow;

X_A : Mass ratio of insoluble solid **A** to (solute **B** + solvent **C**) in the feed flow, **F**, or underflow, **U**;

Y_A = Mass ratio of insoluble solid **A** to (solute **B** + solvent **C**) in the entering solvent flow, **S**, or overflow, **V**;

X_B : Mass ratio of solute **B** to (solute **B** + solvent **C**) in the feed flow, **F**, or underflow, **U**;

Y_B : Mass ratio of solute **B** to (solute **B** + solvent **C**) in the solvent flow, **S**, or overflow, **V**.

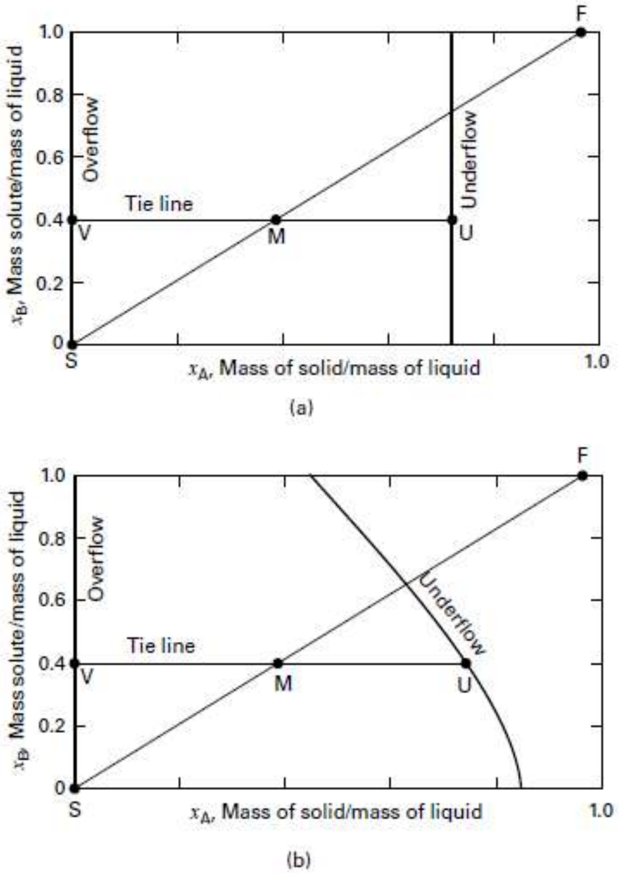


Figure 2.3 Underflow–overflow conditions for ideal leaching:
(a) constant-solution underflow; (b) variable-solution underflow.

Figure 2.3(a) illustrates ideal leaching conditions characterized by constant-solution underflow, where the mass ratio of insoluble solid to liquid (**X_A**) remains constant, regardless of the solute concentration (**X_B**) in the solids-free liquid. The resulting tie line is vertical in Conversely, Figure 2.3(b) represents ideal leaching conditions with variable-solution underflow, where **X_A** varies with **X_B**. In both cases, certain assumptions are made:

1. The entering feed, **F**, is devoid of solvent (X_B=1);

2. The solvent, **S**, is free of solids and solutes (Y_A=0, Y_B=0);

3. Equilibrium exists between the exiting liquid solutions in underflow (U) and overflow (V), ensuring X_B=Y_B;

4. The overflow, **V**, is free of solids (Y_A = 0).

A mixing point, M, is defined for (**F + S**), equal to the sum of the products of the leaching stage (**U + V**). Typical mixing points, as well as inlet and outlet compositions, are depicted in Figures 2.3(a) and (b). In both cases, the inverse-lever-arm rule can be applied to line **UMV** to determine the flow rates of **U** and **V**, as demonstrated in the subsequent example.

- **Application 2.2 Leaching of Soybeans to Recover Oil.**

Soybeans are a predominant oilseed crop, followed by cottonseed, peanuts, and sunflower seed. While soybeans are not consumed directly by humans, they can be processed to produce valuable products. Production of soybeans in the United States began after World War II, increasing in recent years to more than 140 billion lb/yr. Most soybeans are converted to soy oil and vitamins like niacin and lecithin for humans, and defatted meal for livestock. Compared to other vegetable oils, soy oil is more economical and healthier. Typically, 100 pounds of soybeans yields 18 lb of soy oil and 79 lb of defatted meal. To recover their oil, soybeans are first cleaned, cracked to loosen the seeds from the hulls, dehulled, and dried to 10–11% moisture. Before leaching, the soybeans are flaked to increase the mass-transfer rate of the oil out of the bean. They are leached with hexane to recover the oil. Following leaching, the hexane overflow is separated from the soy oil and recovered for recycle by evaporation, while the underflow is treated to remove residual hexane, and toasted with hot air to produce defatted meal. Modern soybean extraction plants crush up to 3000 tons of soybeans per day. Oil is to be leached from 100000 kg/h of soybean flakes, containing 19 wt% oil, in a single equilibrium stage by 100000 kg/h of a hexane solvent. Experimental data indicate that the oil content of the flakes will be reduced to 0.5 w_t%. For the type of equipment to be used, the expected contents of the underflows is as follows:

ß, Mass fraction of solids in underflow	0.68	0.67	0.65	0.62	0.58	0.53
Mass ratio of solute in underflow liquid, X_B	0.0	0.2	0.4	0.6	0.8	1.0

Calculate, both graphically and analytically, compositions and flow rates of the underflow and overflow, assuming an ideal leaching stage. What % of oil in the feed is recovered?

Data:

1 tons=1000 kg ; 1 lb=0.454 kg ; 1 billion=10^3 million ; yr: year.

Solution:

The flakes contain (0.19)(100000) = 19000 kg/h of oil and (100000 - 19000) = 81000 kg/h of insolubles. However, all of the oil is not leached. For convenience in the calculations, lump the unleached oil with the insolubles to give an effective A.

The flow rate of unleached oil = (81000)(0.5/99.5) = 407 kg/h.

Therefore, the flow rate of A is taken as (81000 + 407) = 81407 kg/h and the oil in the feed is just the amount leached, or (19000 - 407) = 18593 kg/h of B.

Therefore, in the feed, F, Y_A = (81407/18593) = 4.38, and X_B = 1.0.

The sum of the liquid solutions in the underflow and overflow includes 100000 kg/h of hexane and 18593 kg/h of leached oil.

Therefore, for the underflow and overflow, $X_B = Y_B$ = [18593/(100000+ 18593)] = 0.157

This is a case of variable-solution underflow. Using data in the above table, convert values of ß to values of X_A,

$$\boldsymbol{X_A = \frac{kg/hA}{kg/h(B+C)} = \frac{ßU}{(1-ß)U} = \frac{ß}{(1-ß)}}$$

Using (1), the following values of X_A are computed from the previous table.

X_A	2.13	2.03	1.86	1.63	1.38	1.13
X_B	0.0	0.2	0.4	0.6	0.6	1.0

Graphical Method

Figure 2.4 is a plot of X_A as a function of X_B. Because no solids leave in the overflow, that line is horizontal at X_A = 0. Plotted are the feeds, F, and hexane, S, with a straight line between them. A point for the overflow, V, is plotted at X_A = 0 and, from above, X_B = 0.157. Since $Y_B = X_B$ = 0.157, the value of X_A in the underflow is at the intersection of a vertical line from overflow, V, to the underflow line. This value is X_A = 2.05. Lines $\overline{FS}$ and $\overline{UV}$ intersect at point M. In the overflow, from X_B = 0.157, mass fractions of solute B and solvent C are, respectively, 0.157 and (1 - 0.157) = 0.843. In the underflow, using X_A = 2.05 and X_B = 0.157, mass fractions of solids B and C are [2.05/(1 + 2.05)] = 0.672, 0.157(1 - 0.672) = 0.0515, and (1 - 0.672 - 0.0515) = 0.2765, respectively.

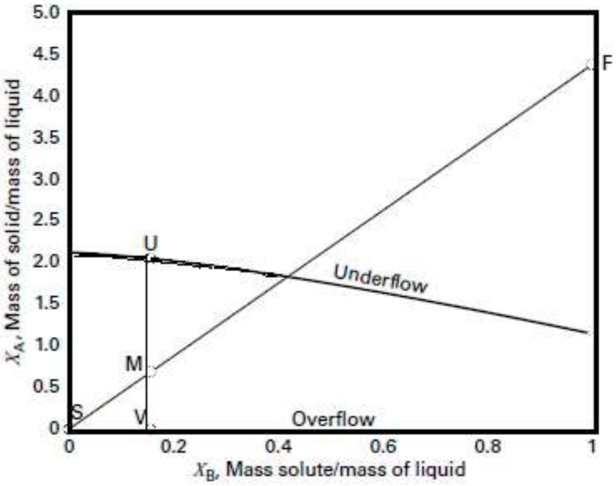


Figure 2.4 Constructions for Example 2.2

The inverse-lever-arm rule is used to compute the underflow and overflow. The rule applies only to the liquid phases in the two exiting streams because Figure 2.4 is on a solids-free basis. The mass ratio of liquid flow rate in the underflow to liquid flow rate in the overflow is the ratio of line $\overline{MV}$ to line $\overline{MU}$.

With M located at X_A = 0.69, this ratio = (0.69 - 0.0)/(2.05 - 0.69) = 0.51. Thus, the liquid flow rate in the underflow = (100000 + 18593)(0.51)/(1 + 0.51) = 40,054 kg/h. Adding the flow rates of carrier and unextracted oil gives U = 40054 + 81407 = 121461 kg/h or, say, 121000 kg/h. The overflow rate = V = 200000 - 121000 = 79000 kg/h.

Oil flow rate in the feed is 19000 kg/h. The oil flow rate in the overflow = Y_BV =0.157(79000) = 12400 kg/h. Thus, the oil in the feed that is recovered in the overflow = 12400/19000 = 0.653 or 65.3%.

Algebraic Method

As with the graphical method, X_B = 0.157, giving a value from the previous table of X_A = 2.05. Then, since the flow rate of solids in the underflow = 81407 kg/h, the flow rate of liquid in the underflow = 81407/2.05 = 39711 kg/h.

The total flow rate of underflow is U = 81407 + 39711 = 121118 kg/h.

By mass balance, the flow rate of overflow = 200000 - 121118 = 78882 kg/h.

These values are close to those obtained graphically. The percentage recovery of oil, and the underflow and overflow, are computed as before.

2.4.3 Solid–liquid cascades

The N-stage, countercurrent leaching–washing process in Figure 2.5 is an extension of the single-stage systems The solid feed entering stage 1 is comprised of two components, **A** and **B**, with mass flow rates $\mathbf{F_A}$ and $\mathbf{F_B}$, respectively.

The solvent, **C**, enters stage **N** at a flow rate **S** and selectively dissolves solute **B**, leaving insoluble carrier **A** unaffected. The concentrations of **B** are represented in terms of mass ratios of solute-to-solvent, denoted as **Y**. Consequently, the liquid overflow from each stage, j, contains $\mathbf{Y_j}$ mass of soluble material per mass of solute-free solvent. The underflow consists of a mass flow $\mathbf{F_A}$ of insoluble solids, a constant ratio of mass of solvent-to-mass of insoluble solids (**R**), and $\mathbf{X_j}$ mass of soluble material to mass of solute free solvent.

For a given feed, a relationship between the exiting underflow concentration of the soluble component ($\mathbf{X_N}$), the solvent feed rate (**S**), and the number of stages (**N**) is derived. In this process, all soluble material **B** in the feed is initially leached in stage 1. Subsequent stages (2 to N) serve as washing stages, aiming to reduce the amount of soluble material lost in the underflow leaving the last stage (N) and, consequently, increasing the amount of soluble material in the overflow from stage 1. Utilizing solvent material balances and assuming a constant R, the flow rate of solvent leaving in the reformulation can be determined.

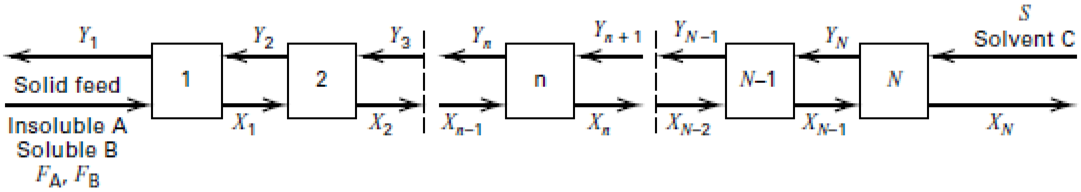


Figure 2.5 Countercurrent leaching or washing system.

The overflow from stages 2 to N carries a constant flow rate of solvent, denoted as **S**. Simultaneously, the solvent leaving in the underflow from stages 1 to N is characterized by the flow rate $\mathbf{RF_A}$. Consequently, the flow rate of solvent leaving in the overflow specifically from stage 1 can be expressed as the difference between the constant overflow rate (**S**) and the underflow rate ($\mathbf{RF_A}$). Therefore, the reformulated expression is:

Flow rate of solvent leaving in the overflow from stage 1 = $\mathbf{S - RF_A}$.

This equation signifies the amount of solvent leaving in the overflow from stage 1, considering the leaching of soluble material **B** in stage 1 and the subsequent washing stages.

A material balance for soluble material **B** around any interior stage n from n = 2 to N - 1 is

$$Y_{n+1}\,S + X_{n-1}\,RF_A = Y_n\,S + X_n\,RF_A \qquad \textbf{(2.8)}$$

For terminal stages 1 and N, the material balances on the soluble material are, respectively,

$$Y_2\,S + X_F\,F_B = Y_1\,(S - RF_A) + X_1\,RF_A \qquad \textbf{(2.9)}$$

$$X_{N-1}\,RF_A = Y_N\,S + X_N\,RF_A \qquad \textbf{(2.10)}$$

Assuming equilibrium, the concentration of solute **B** in each overflow is equal to the concentration of **B** in the liquid part of the underflow from the same stage. Therefore, at equilibrium, there is a balance in the concentrations of solute **B** between the liquid overflow and the liquid component of the underflow within each stage.

$$X_n = Y_n \tag{2.11}$$

In addition, it is convenient to define a washing factor, **W**, as

$$W = \frac{S}{RF_A} \tag{2.12}$$

If (2.8) to (2.10) are each combined with (2.11) to eliminate Y, and the resulting equations are rearranged to allow substitution of (2.12), then,

$$X_1 - X_2 = \left(\frac{F_B}{S}\right) \tag{2.13}$$

$$\left(\frac{1}{W}\right)X_{n-1} - \left(\frac{1+W}{W}\right)X_n + X_{n+1} = 0 \tag{2.14}$$

n = 2 to N-1

$$\left(\frac{1}{W}\right)X_{n-1} - \left(\frac{1+W}{W}\right)X_n = 0 \tag{2.15}$$

The description indicates that equations (2.13) to (2.15) constitute a set of N linear equations in N unknowns, denoted as X_n (where n takes values from 1 to N). Additionally, it is mentioned that these equations form a tridiagonal sparse matrix.

A tridiagonal matrix is a special kind of sparse matrix where all the elements are zero except for those on the main diagonal and the two diagonals adjacent to it (upper and lower diagonals). The main diagonal contains the coefficients corresponding to the variable X_n, and the adjacent diagonals contain other coefficients.

Equations of this form are solved by Gaussian elimination by removing the unknowns X_1, X_2, etc., to produce:

$$X_N = \left(\frac{F_B}{S}\right)\left(\frac{1}{W^{N-1}}\right) \tag{2.16}$$

By back-substitution, interstage values of **X** are given by:

$$X_n = \left(\frac{F_B}{S}\right)\left(\frac{\sum_{k=0}^{N-n} W^k}{W^{N-1}}\right) \tag{2.17}$$

For example, with N = 4

$$X_1 = Y_1 = \left(\frac{F_B}{S}\right)\left(\frac{1+W+W^2+W^3}{W^3}\right) \tag{2.18}$$

The cascade, given a certain solvent flow rate (**S**), aims to maximize $\mathbf{Y_1}$, the quantity of **B** dissolved in the solvent leaving stage 1, while simultaneously minimizing $\mathbf{X_N}$, the amount of **B** dissolved in the solvent leaving with **A** from stage N. Equation (2.18) suggests that achieving this objective for the feed rate $\mathbf{F_B}$ involves specifying a large solvent feed (**S**), increasing the number of stages (N), and/or employing a large washing factor (**W**). The washing factor can be enhanced by minimizing the liquid underflow compared to the overflow. It's important to note that the minimum amount of solvent required corresponds to zero overflow from stage 1. If there is no overflow from stage 1, it implies that all the soluble material **B** has been dissolved in the solvent, maximizing $\mathbf{Y_1}$. This condition aligns with the goal of the cascade to extract as much solute **B** as possible in the early stages while minimizing its presence in the solvent leaving with **A** from the last stage ($\mathbf{X_N}$).

$$S_{min} = RF_A \qquad \textbf{(2.19)}$$

2.5 Single-section, extraction cascades

Two-stage cocurrent, crosscurrent, and countercurrent, single section, solid–liquid extraction cascades are shown in Figure 2.6. The countercurrent arrangement is generally preferred because, as will be shown, this arrangement results in a higher degree of extraction for a given amount of solvent and number of equilibrium stages.

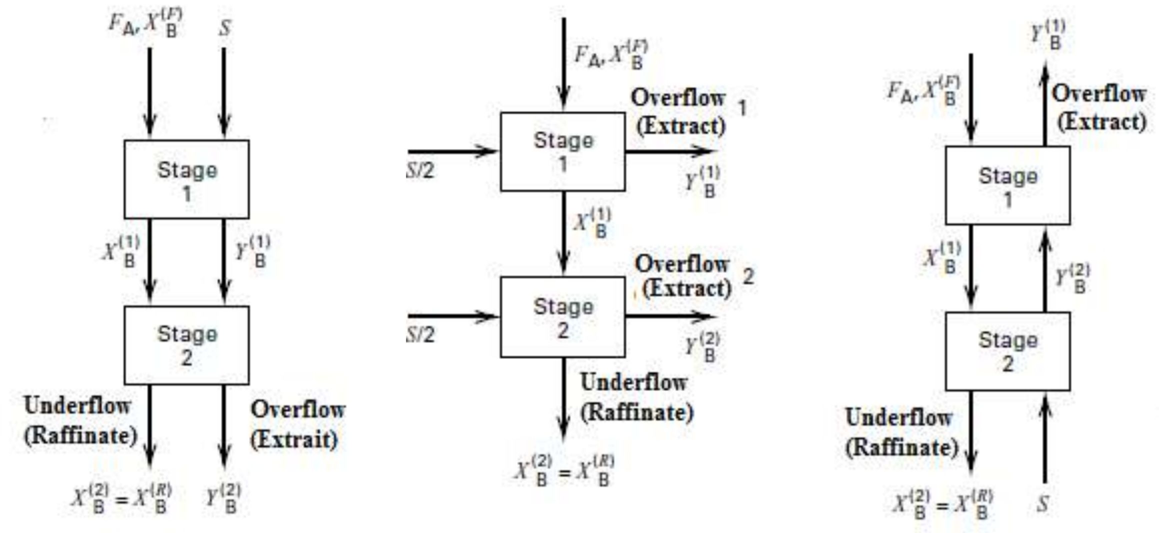
Equation (2.4), which pertains to the fraction of solute **B** that remains unextracted, was developed for a singular solid-liquid equilibrium extraction stage. This derivation is based on the assumption of employing a pure solvent and a consistent value for the distribution coefficient of **B**, which is dissolved in components **A** and **C**, both of which are mutually insoluble. This equation is formulated in relation to $\mathbf{X_B}$, representing the ratio of the mass of solute **B** to the mass of **A**, the other component present in the feed. Additionally, the expression incorporates the extraction factor.

$$V = K'_{D_B} S/F_A \qquad \textbf{(2.20)}$$

where:

$$K'_{D_B} = Y_B/X_B \qquad \textbf{(2.21)}$$

and $\mathbf{Y_B}$ is the ratio of mass of solute **B** to the mass of solvent **C** in the solvent-rich phase.



(a) **(b)** **(c)**

Figure 2.6 Two-stage arrangements:

(a) cocurrent cascade; (b) crosscurrent cascade; (c) countercurrent cascade.

2.5.1 Cocurrent Cascade

In Figure 2.6 (a), the fraction of B not extracted in stage 1 is Since $\boldsymbol{Y_B^{(1)}}$ is in equilibrium with $\boldsymbol{X_B^{(1)}}$ by:

$$\boldsymbol{Y_B^{(1)}/Y_B^{(F)} = K'_{D_B}/(1+V)} \qquad \textbf{(2.22)}$$

For the second stage, a material balance for B gives:

$$\boldsymbol{X_B^{(1)}F_A + Y_B^{(1)}S = X_B^{(2)}F_A + Y_B^{(2)}S} \qquad \textbf{(2.23)}$$

With: $$\boldsymbol{K'_{D_B} = Y_B^{(2)}/Y_B^{(2)}} \qquad \textbf{(2.24)}$$

However, no further extraction occurs after the initial stage because the two streams leaving are already at equilibrium when they are recontacted in subsequent stages. Therefore, a cocurrent cascade does not offer any advantages unless the required residence times are sufficiently long to prevent the achievement of equilibrium in a single stage, necessitating additional capacity. Regardless of the number of cocurrent equilibrium stages, denoted as N,

$$\boldsymbol{\frac{X_B^{(N)}}{X_B^{(F)}} = \frac{1}{1+V}} \qquad \textbf{(2.25)}$$

2.5.2 Crosscurrent Cascade

For the crosscurrent cascade in Figure 2.6 (b), the feed progresses through each stage, starting with stage 1.

The solvent flow rate, S, is divided into portions that are sent to each stage. The overall mass balance on stage 1 refers to the equation expressing the total conservation of mass during a unit operation, such as a liquid-liquid extraction process. This equation takes into account the incoming and outgoing flows on this specific stage.

The overall mass balance on stage 1 can be expressed as follows (assuming a solid-liquid extraction operation:

$$F_B + S_B = x_B U_1 + y_B V_1 \qquad \textbf{(2.26)}$$

Le bilan sur le soluté de l'étage 1:

$$x_F^B F + y_{S_1}^B S_1 = x_{U_1}^B U_1 + y_{V_1}^B V_1 \qquad \textbf{(2.27)}$$

Where:

F_B is the inflow of the solute **B** in feed **F** to stage 1.

S_B is the inflow of the solute **B** in solvent **S** to stage 1.

x_B is the mass or mole fraction of the solute **B** in the underflow to stage 1.

U_1 is the underflow rate from stage 1.

y_B is the mass or mole fraction of the solute **B** in the overflow to stage 1.

V_1 is the overflow rate from stage 1.

The solvent and the solute being immiscible, all the diluent entering **F** will be recovered in U_1 and all the solvent in V_1.

U_1' Quantity or flow rate of pure diluent.

$$U' = F(1 - x_F^B) \rightarrow F = \frac{U'}{(1 - x_F^B)} \qquad \textbf{(2.28)}$$

$$U' = R_1\left(1 - x_{U_1}^B\right) \rightarrow \quad U_1 = \frac{U'}{\left(1 - x_{U_1}^B\right)} \qquad \textbf{(2.29)}$$

S' : Quantity or flow rate of pure solvent.

$$S' = S_1(1 - y_{S1}^B) \rightarrow S_1 = \frac{S'}{(1 - y_{S1}^B)} \qquad \textbf{(2.30)}$$

$$.S' = V_1(1 - y_{V1}^B) \rightarrow V_1 = \frac{S'}{(1 - y_{E1}^B)} \qquad \textbf{(2.31)}$$

By replacing equations (2.28), (2.29), (2.30), (2.31) in equation (2.27), the equation becomes:

$$x_F^B \frac{U'}{(1 - x_F^B)} + y_{S_1}^B \frac{S'}{(1 - y_{S1}^B)} = x_{U_1}^B \frac{U'}{\left(1 - x_{U_1}^B\right)} + y_{V_1}^B \frac{S'}{(1 - y_{V1}^B)} \qquad \textbf{(2.32)}$$

$$U'(X_F^B - X_{U_1}^B) = S'\left(Y_{V1}^B - Y_{S1}^B\right) \qquad \textbf{(2.33)}$$

$$-\frac{U'}{S'} = \frac{(Y_{S1}^B - Y_{V1}^B)}{(X_F^B - X_{U_1}^B)} \qquad \textbf{(2.34)}$$

With:

$$\boldsymbol{X_F^B = \frac{x_F^B}{(1-x_F^B)}}\ , \qquad \boldsymbol{X_{U_1}^B = \frac{x_{U_1}^B}{\left(1-x_{U_1}^B\right)}}\ , \boldsymbol{Y_{S1}^B = \frac{y_{S1}^B}{(1-y_{S1}^B)}}\ , \ \boldsymbol{Y_{V1}^B = \frac{y_{V1}^B}{(1-y_{V1}^B)}}$$

The operating line equation for a crosscurrent extraction process, where the solvent and diluent are immiscible, for stage 1 is as follows:

$$\boldsymbol{-\frac{U'}{S'} = \frac{(Y_{S1}^B - Y_{V1}^B)}{(X_F^B - X_{U_1}^B)}} \tag{2.35}$$

The operating line equation for a crosscurrent extraction process, where the solvent and diluent are immiscible, for stage 2 is as follows:

$$\boldsymbol{-\frac{U'}{S'} = \frac{(Y_{S2}^B - Y_{V2}^B)}{(X_F^B - X_{U_2}^B)}} \tag{2.36}$$

If the equilibrium and operating curves are linear, the graphical representation of material transfer in a Y=f(X) crosscurrent cascade extraction is as follows:

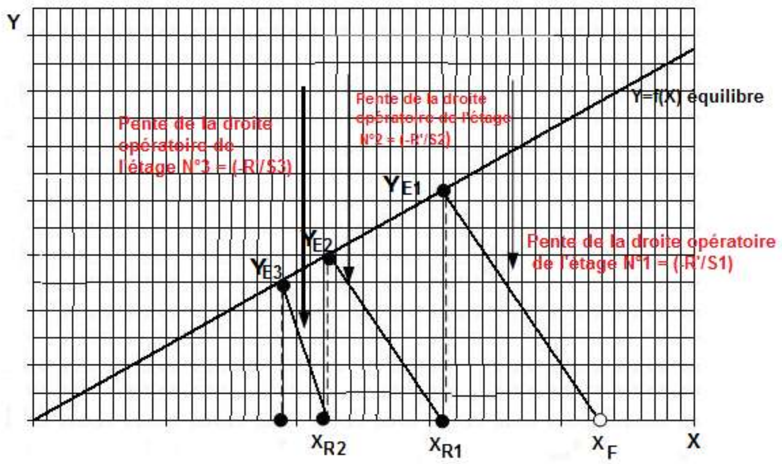


Figure 2.7 Graphical representation of the X and Y ratios obtained through crosscurrent solid-liquid extraction processes, assuming immiscibility between the solvent and diluent.

If the solvent flow rate is evenly distributed in each stage, for a total of N stages, the solvent flow rate at each stage is **S/N** and the equilibrium equation becomes:

$$\boldsymbol{\frac{X_B^{(1)}}{X_B^{(F)}} = 1/(1+V/N)} \tag{2.37}$$

$$\boldsymbol{\frac{X_B^{(2)}}{X_B^{(1)}} = 1/(1+V/N)} \tag{2.38}$$

$$\boldsymbol{\frac{X_B^{(N)}}{X_B^{(N-1)}} = 1/(1+V/N)} \tag{2.39}$$

By combining the equations (2.37), (2.38), (2.39) together, it gives:

$$\boldsymbol{X_B^{(N)}/X_B^{(F)} = X_B^{(U)}/X_B^{(F)} = \frac{1}{(1+V/N)^N}} \tag{2.40}$$

2.5.3 Countercurrent Cascade

A countercurrent cascade (Figure 2.6 (c)) refers to a process or system in which the flows of two substances, move in opposite directions. In a countercurrent cascade, the solid being processed and solvent move in opposite directions through a series of stages or components. the material-balance and equilibrium equations for solute **B** for each stage are:

Stage 1:

$$\boldsymbol{X_B^{(F)}\,F_A + Y_B^{(2)}\,S = X_B^{(1)}\,F_A + Y_B^{(1)}\,S} \tag{2.41}$$

$$\boldsymbol{X_B^{(2)}/X_B^{(F)} = X_B^{(U)}/X_B^{(F)} = \frac{1}{1+V+V^2}} \tag{2.42}$$

Extending (2-43) to N countercurrent stages gives:

$$\boldsymbol{X_B^{(U)}/X_B^{(F)} = 1/\sum_{n=0}^{N} V^n} \tag{2.43}$$

2.6 Janecke diagrams

In 1906, Janecke [10] proposed a data representation depicted in Figure 2.8. In this representation, the mass of solvent per unit mass of solvent-free liquid, solvent/(solute **A** + solute **B**), is graphed on the ordinate against the mass ratio, on a solvent-free basis, of solute **B**/(solute **A** + solute **B**) on the abscissa. Both phases share the same ordinate and abscissa. Equilibrium conditions are connected by tie lines. Mole ratios can also be employed to create Janecke diagrams.

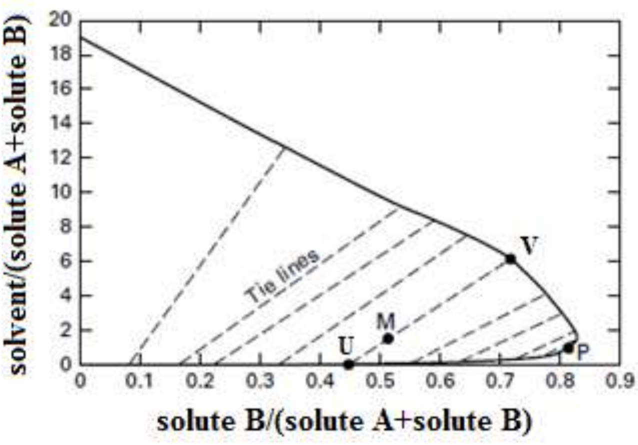


Figure 2.8 Janecke diagram.

M is a point representing the composition of the initial mixture **F** (containing solute **A** and solute **B**) and the solvent **S**. At equilibrium, **M** is fractionated into two phases, **V** (overflow) and **U** (underflow), along the equilibrium coexistence Tie lines.

2.7 Equilibrium-stage model for leaching and washing

The simplest model for a continuous, countercurrent leaching and washing system, as shown in Figure 2.9. It assumes that the solid feed consists of a solute that is completely soluble in the solvent and an inert substance or carrier that is not soluble. Leaching is assumed to be rapid such that it is completed in a single leaching stage, which is followed by a series of one or more washing stages to reduce concentration of solute in the liquid adhering to the solids in the underflow. All overflow streams are assumed to be free of solids. In Figure 2.9:

S : Mass flow rate of inert solids, which is constant from stage to stage;

V : Mass flow rate of entering solvent or overflow liquid (solvent plus solute), which varies from stage to stage;

L : Mass flow rate of underflow liquid (solvent plus solute), which varies from stage to stage;

y : Mass fraction of solute in the overflow liquid;

x : Mass fraction of solute in the underflow liquid.

Alternatively, **V** and **L** can refer to mass flow rates of solvent on a solute-free basis and the symbols **Y** and **X** can be used to refer to mass ratios of solute to solvent in the overflow liquid and underflow liquid, respectively. Mole or volume flow rates can also be used.

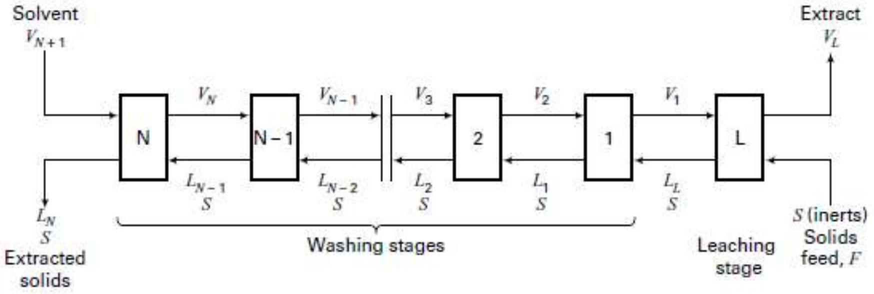


Figure 2.9 Continuous, countercurrent, ideal-stage leaching and washing system.

An ideal leaching or washing stage is defined by Baker [8] as one where:

1. Any entering solid solute is completely dissolved into the liquid in the stage (assuming the liquid contains sufficient solvent).

2. The composition of liquid in the stage is uniform throughout, including any liquid within pores of the inert solid.

3. Solute is not adsorbed on the surfaces of the inert solid.

4. Inert solids leaving in the underflow from each stage are wet with liquid, such that mass ratio of solvent in that liquid (or the total liquid) to inert solids is constant from stage to stage.
5. Because of item 2, concentration of solute in the overflow is equal to that in the liquid portion of the underflow. This is equivalent to an equilibrium assumption.
6. Overflows contain no solids.
7. Solvent is not vaporized, adsorbed, or crystallized.

For the continuous, countercurrent system of ideal leaching stages in figure 2.9, solute and total-liquid material balances can be used to solve problems, including:
1. determination of ideal stages required to achieve a specified degree of washing; and
2. determination of the effect of washing for a specified degree of washing with a certain number of ideal stages. Depending on the problem, either an algebraic or a graphical method may be preferred.

2.7.1 McCabe–Smith Algebraic Method

When the ideal-stage model applies, a more accurate algebraic method, developed by McCabe and Smith [9] from the Kremser can be used. The method is developed here using solute concentrations in mass fractions, but the final equations can also be derived with mass ratios.

$$\boldsymbol{y_{N+1} = y_1\left(\frac{1-A^{N+1}}{1-A}\right) - y_0^{*}A\left(\frac{1-A^{N}}{1-A}\right)} \qquad \textbf{(2.44)}$$

where N = number of ideal washing stages and

$$\boldsymbol{y_0^{*} = Kx_0 = Kx_L = y_L} \qquad \textbf{(2.45)}$$

For washing, ***K=y/x = 1*** **(2.45)**

and , therefore, ***A=L/KV = L/V*** **(2.46)**

Equation (2.45) can be written as follows by collecting terms in A^{N+1} and A:

$$\boldsymbol{A^{N+1}(y_1 - y_L) = A(y_{N+1} - y_L) + (y_1 - y_{N+1})} \qquad \textbf{(2.47)}$$

and simplified by writing an overall solute balance around all washing stages

$$\boldsymbol{y_{N+1}V_{N+1} + x_L L_L = y_1 V_1 + x_N L_N} \qquad \textbf{(2.48)}$$

But for ideal washing stages, since:

$$\boldsymbol{V_{N+1}=V_1} \qquad \textbf{(2.49)}$$

$$\boldsymbol{L_L=L_N} \qquad \textbf{(2.50)}$$

Equation **(2.48)** simplifies to:

$$y_{N+1} = y_1 + Ax_N - Ax_L \qquad \textbf{(2.51)}$$

But $y_L = x_L$, therefore, **(2.51)** becomes

$$(y_1 - y_{N+1}) = A(y_L - x_N) \qquad \textbf{(2.52)}$$

Combining **(2.47)** and **(2.52)** and rearranging gives:

$$A^N = \left(\frac{y_{N+1} - y_N}{y_1 - y_L}\right) \qquad \textbf{(2.53)}$$

for **N** with **A = L/V** gives:

$$N = \frac{\log\left(\frac{x_N - y_{N+1}}{y_L - y_1}\right)}{\log(L/V)} \qquad \textbf{(2.54)}$$

The argument of the log term of the denominator can be written in terms of end points to give:

$$\frac{L}{V} = \left(\frac{y_1 - y_{N+1}}{y_L - x_N}\right) = \left(\frac{y_1 - y_{N+1}}{y_L - x_N}\right) \qquad \textbf{(2.55)}$$

Combining **(2.54)** and **(2.55)**

$$N = \frac{\log\left(\frac{x_N - y_{N+1}}{y_L - y_1}\right)}{\log\left(\frac{y_1 - y_{N+1}}{y_L - x_N}\right)} \qquad \textbf{(2.56)}$$

2.8 Equipment for leaching

Leachable solids generally undergo pretreatment before being fed to leaching equipment so that reasonable leaching times are obtained. Industrial equipment for solid–liquid extraction is designed for batchwise or continuous processing. The method of contacting solids with solvent is either by percolation of solvent through a bed of solids or by immersion of the solid in the solvent followed by agitation of the mixture.

When immersion is used, countercurrent, multistage operation is common. With percolation, either a stagewise or a differential contacting device is appropriate. An extractor must be efficient to minimize the need for solvent because of the high cost of solvent recovery.

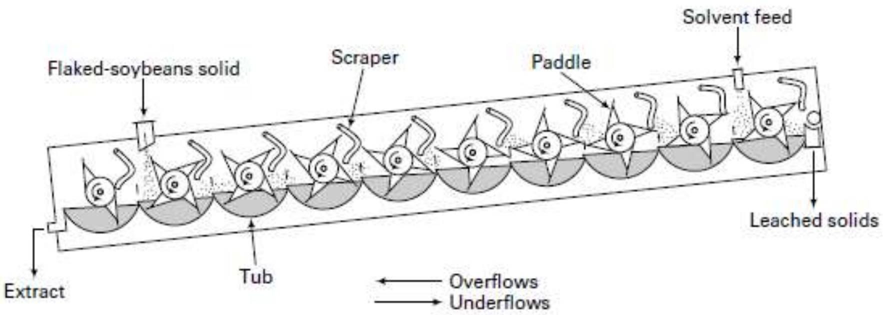


Figure 2.10 Kennedy extractor for leaching of oil from soybeans.

2.8.1 Batch Extractors

When the solids to be leached are in the form of fine particles, perhaps smaller than 0.1 mm in diameter, batch leaching is conveniently conducted in an agitated vessel. A simple configuration is the Pachuca tank [2] depicted in Figure 2.11 and used extensively in the metallurgical industry. The tank is a tall, cylindrical vessel and the solvent and solids are placed in the tank and agitation is achieved by an air lift, whereby air bubbles entering at the bottom of a circular tube, concentric with the tank, cause upward flow and subsequent circulation of the solid–liquid suspension. During agitation, air continuously enters and leaves the vessel. When the desired degree of leaching is accomplished, agitation stops and solids are allowed to settle into a sludge at the bottom, where it is removed with the assistance of air. The supernatant extract is removed by siphoning from the top of the tank. Agitation can also be achieved by a paddle stirrer or by the use of a propeller mounted in a draft tube to provide upward flow and circulation of the solid–liquid suspension, much like that in the Pachuca tank.

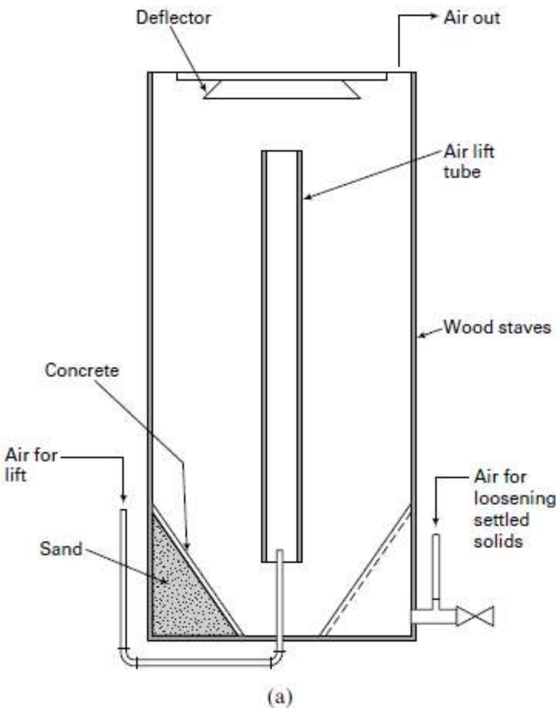


Figure 2.11 Pachuca tank for batch leaching of small particles.

When the solids are too coarse to be easily suspended by immersion in a stirred solvent, percolation techniques can be used. Solids to be leached are dumped into the cylindrical vessel, followed by percolation of solvent down through the bed of solids, much like in fixed-bed adsorption. To achieve a high concentration of solute in the solvent, a series of vessels is arranged in a multibatch, countercurrent-leaching technique developed in 1841 by James Shanks and called a Shanks extraction battery [3]. Where Vessel 1 is off-line for emptying and refilling of solids. Solvent enters and percolates down through the solids in Vessel 2, and then percolates through Vessels 3 and 4, leaving as final extract from Vessel 4. The extraction of solids in Vessel 2 is completed first. When that occurs, Vessel 2 is taken off-line for emptying and refilling of solids and Vessel 1 is placed on-line. Fresh solvent first enters Vessel 3, followed by Vessels 4 and 1. In this manner, fresh solvent always contacts solids that have been leached for the longest time, thus realizing the benefits of countercurrent contacting.

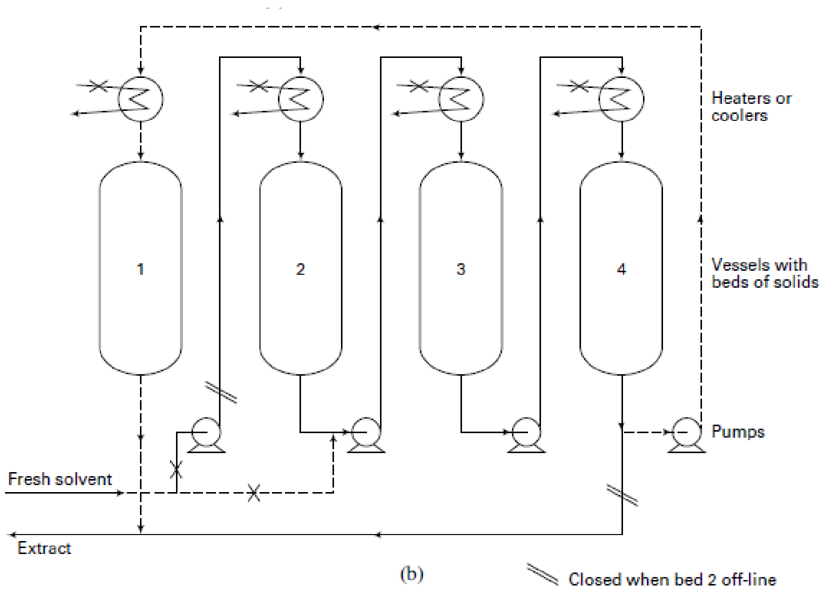


Figure 2.12 Shanks countercurrent, multibatch battery system for leaching of large particles by percolation [3].

2.8.2 Continuous Extractors [2,4,5]

When leaching is carried out on a large scale, it is preferable to use an extraction device that operates with continuous flow of both solids and liquid. Many such patented devices are available, especially for the food industry. These differ mainly with respect to the manner in which solids are transported and the degree to which agitation of solid–liquid mixtures is provided. The Kennedy extractor in Figure 2.10 for oil extraction from soybeans may have a low efficiency in some applications, but it is still used and still available. The Bollman vertical, moving-basket, conveyor extractor in Figure 2.13 is used to extract oil from flaked seeds and beans. Baskets with perforated bottoms are moved around a vertical loop by a motor-driven chain drive. Solvent percolates down, from basket to basket, through the solids. When a basket reaches the top of the extractor, it is inverted to dump extracted solids and then filled with fresh solids. Flow of liquid is countercurrent to solids in ascending baskets and cocurrent in descending baskets. Fresh solvent enters near the top of the ascending leg and collects as ‘‘half miscella’’ in the left-hand part of the bottom sump. From there, half miscella is pumped to the top of the descending leg, from which it flows down to the right-hand part of the sump and is withdrawn as final extract, ‘‘full miscella.’’ A typical Bollman extractor is 14 m high, with each basket filled with solids to a depth of about 0.5 m.

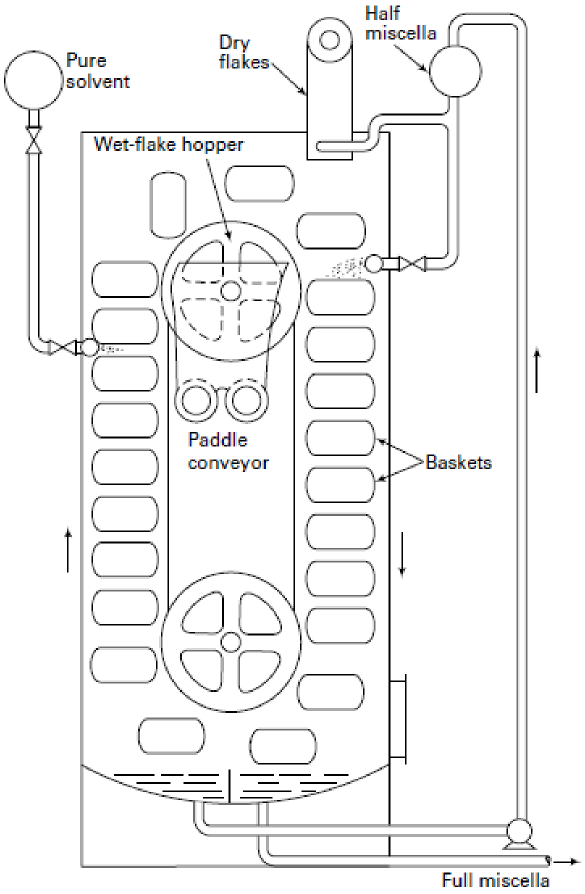


Figure 2.13 Bollman vertical, moving-basket, conveyor extractor.

Another widely used continuous extractor for flaked seeds and beans is the Rotocel extractor in figure 2.13. In this device, which resembles a carousel and simulates a Shanks system, walled, annular sectors, called cells, on a horizontal plane, are slowly rotated by a motor. The cells, which hold solids and are perforated for solvent drainage, successively pass a solids-feed area, a series of solvent sprays, a final spray and drainage area, and a solids-discharge area. Fresh solvent is supplied to the cell located just below the final spray and drainage area, from where drained liquid is collected and pumped to the preceding cell location. The drainage from that cell is collected and pumped to the cell preceding that cell and so on. In this manner, a countercurrent flow of solids and liquid is achieved. Rotocel extractors are typically 3.4–11.3 m in diameter, 6.4–7.3 m in height, and with bed depths of 1.8–3.0 m. They process up to 3 million kg/day of flaked soybeans.

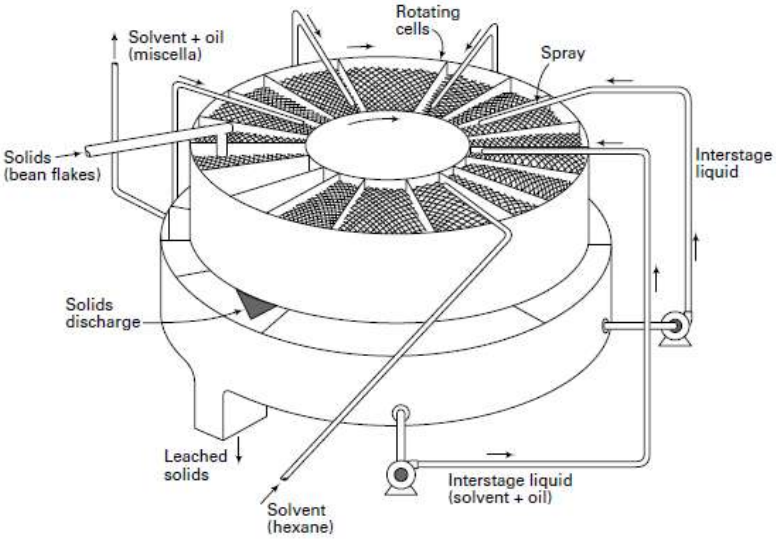


Figure 2.14 Rotocel extractor.

Continuous, perforated-belt extractors, as shown in figure 2.14, are used to process sugar cane, sugar beets, oil seeds, and apples (for apple juice). The feed solids are fed from a hopper to a slow-moving, continuous, and nonpartitioned perforated belt driven by motorized sprockets at either end. The height of solids on the belt can be controlled by a damper at the feed hopper outlet. Belt speed is automatically adjusted to maintain the desired depth of solids. Extracted solids are discharged into an outlet hopper at the end of the belt by a scraper, and side walls prevent solids from falling off the sides of the belt. Below the belt are compartments for collecting solvent. Bed depths range from 0.8 to 2.6 m and units from 7 to 37 m long with belts from 0.5 to 9.5 m wide have processed as much as 7,000,000 kg/day of sugar cane or sugar beets.

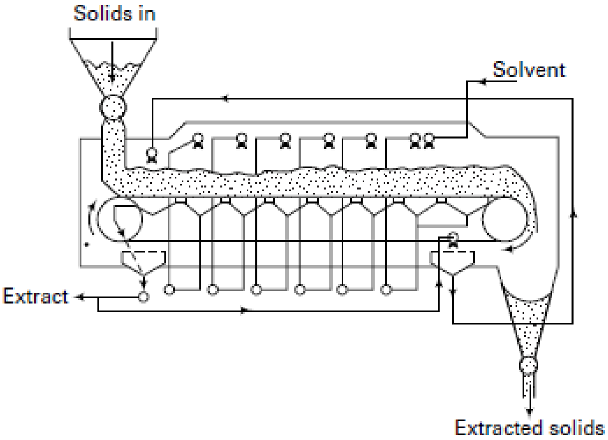


Figure 2.15 Continuous, perforated-belt extractor.

2.8.3 Continuous, Countercurrent Washing [2]

When leaching is very rapid, as with small particles containing very soluble solutes or when leaching has already been completed or when solids are formed by chemical reactions in a solution, it is common to countercurrently wash the solids to reduce the solute concentration in the liquid adhering to the solids. This can be accomplished in a series of gravity thickeners or centrifugal thickeners, called hydroclones, arranged for countercurrent flow of the underflows and overflows as shown in figure 2.16, and sometimes called a continuous, countercurrent decantation system.

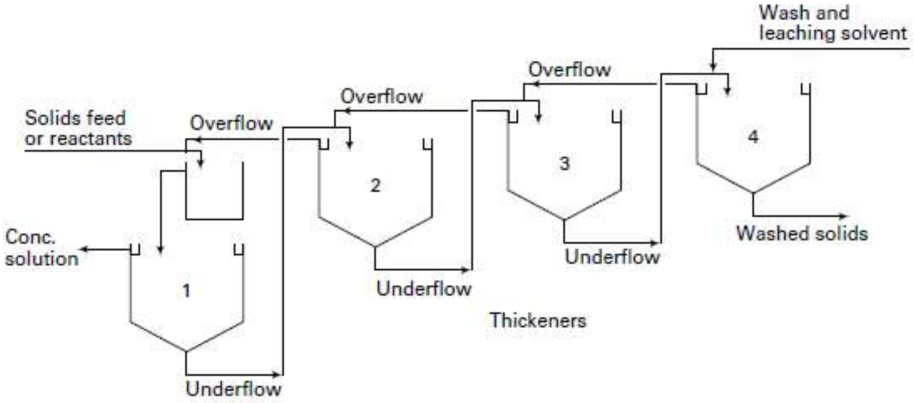


Figure 2.16 Continuous, countercurrent washing system using thickeners.

Residence times of solids and liquids in a gravity thickener are often large (minutes or hours) and, as such, are sufficient to provide adequate residence time for mass transfer and mixing when small particles are involved. When long residence times are not needed and the overflow need not be perfectly clear of solids, the hydroclone, shown in Figure 2.17, may be appropriate. Here, pressurized feed slurry enters tangentially to create, by centrifugal force, a downward-spiraling motion. Higher-density, suspended solids are, by preference, driven to the wall, which becomes conical as it extends downward, and discharged as a thickened slurry at the hydroclone bottom. The liquid, which is forced to move inward and upward as a spiraling vortex, exits from a vortex-finder pipe extending downward from the closed hydroclone top to a location just below feed entry.

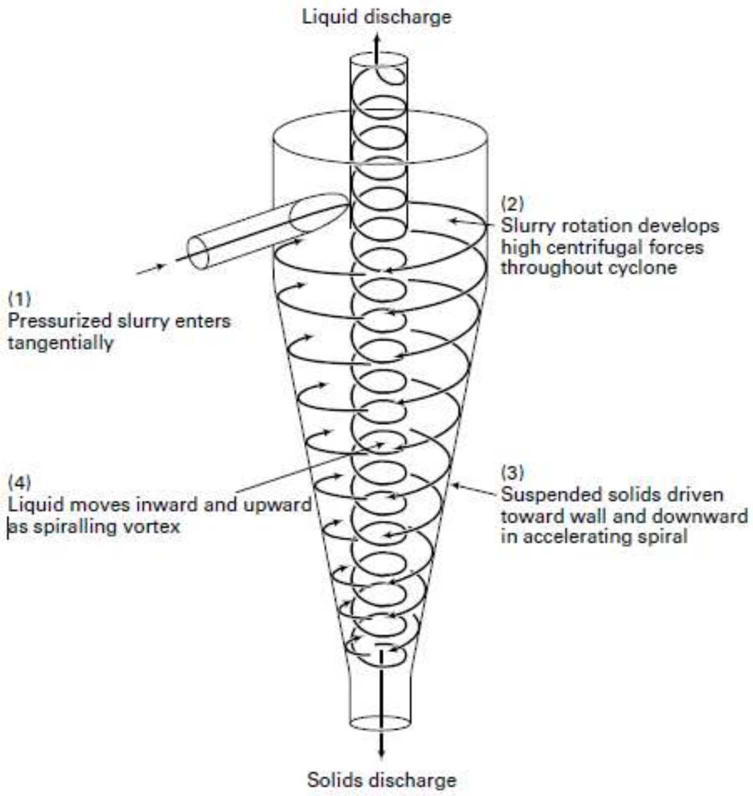


Figure 2.17 Hydroclone, centrifugal thickener.

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3.1 Introduction

En industrial practice, the term "mélange" defines the operation of dispersing, through mechanical means (forced movement), one material into another material, typically regardless of the nature or physical state of the constituents subjected to mixing. Terms such as "agitation" are also used for operations occurring in a tank or reactor stirred by a movable rigid element, usually related to the mixing of low-viscosity liquids or liquids with solids. " kneading " is employed for mixing highly viscous media. A frequent operation in the chemical industry, mixing occurs when it is necessary to achieve intimate contact between multiple phases, either to induce a reaction or to facilitate mass or heat transfer among them.

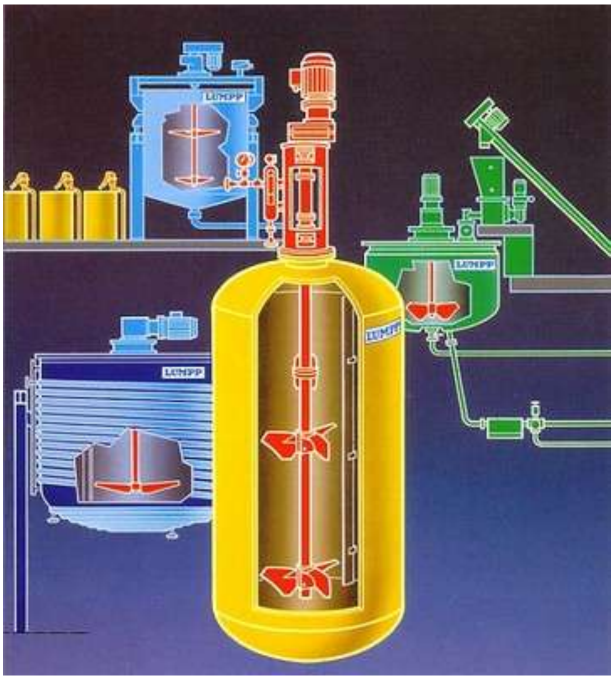

Figure 3.1 Schematic representation of different tanks.

The objectives of the operation include:

- Homogenization of a system with multiple components in terms of concentration and temperature by increasing the interfacial surface and/or creating favorable hydrodynamic conditions.
- Enhancement of thermal exchange between the liquid and the container surface.
- Formation of a suspension (also possible dilution and dissolution) of a solid in the liquid.
- Dispersion (potentially emulsion) of two immiscible liquids.
- The dispersion of a gas in the liquid (gas/liquid contact);
- The mixing of two or more solid products, such as powders, pastes, or granules.

3.2 Mixing and dispersion applications in separation processes

The operations of mixing and dispersion are often used in conjunction with separation processes to improve their efficiency. Here are some specific applications in separation processes:

3.2.1 Liquid-Liquid Extraction:

- Liquid Mixing: Before extraction, the liquid phases containing the components to be separated are often mixed to promote contact between solutes and the extracting solvent.
- Dispersion: Dispersion can be used to increase the contact surface between liquid phases, thereby improving the efficiency of extraction.

3.2.2 Distillation:

- Liquid Mixing: The liquids to be distilled are typically mixed before entering the distillation column to ensure a uniform composition.
- Dispersion: Vapor dispersion in the distillation column can enhance the separation of components.

3.2.3 Adsorption:

- Mixing: During the preparation of the adsorbent phase, mixing steps may be necessary to ensure a homogeneous distribution of adsorbents.
- Dispersion: Gas or liquid dispersion in the adsorbent bed can improve the efficiency of adsorption.

3.2.4 Chromatography:

- Mixing: Samples to be analyzed are often mixed with stationary phases to enhance interaction with the mobile phase.
- Dispersion: Homogeneous dispersion of mobile and stationary phases is crucial for obtaining accurate results in chromatography.

3.2.5 Membrane Separation:

- Mixing: Solutions to be treated can be mixed to ensure a uniform composition before coming into contact with the membrane.
- Dispersion: Dispersion of particles or solutes can influence the performance of separation membranes.

By skill fully integrating mixing and dispersion into separation processes, one can optimize separation conditions and improve the quality of the obtained products.

3.3 Different types of agitators in separation processes

In separation processes, agitators are devices used to effectively mix phases, disperse components, promote chemical reactions, or maintain homogeneous conditions. Here are some types of agitators commonly used in separation processes:

3.3.1 Paddle Agitators:

It is one of the most basic types of agitator. It contains blades which are paddle shaped; the blades stretch throughout the vessel and reach the walls of the vessel. They are primarily used in applications where a uniform laminar flow of the liquids and little shearing is desired. This type of agitator is especially used for viscous materials. These are mostly used in food, chemicals, pharmaceuticals, sorbitol etc industries.

Figure 3.2 Paddle agitators.

3.3.2 Turbine agitators:

These agitators have an axial input and the output is radial. Turbine agitators are very versatile; they are able to handle a wide variety of mixing operations because these agitators can create turbulent movement of the fluid due to the combination of rotational as well as centrifugal motion. They are popularly used in metal extraction industries and also for chemical reactions and have a very high blending efficiency. These are mostly used in chemical, pharmaceuticals, grease, cosmetics industries.

Figure 3.3 Turbine agitators

3.3.3 Propeller agitator:

These have impellers that similar to marine type propellers. They have blades which taper towards the shaft to minimize centrifugal force and to promote axial flow. It means when this agitator operates the motion of fluid is such that the inlet flow is parallel to the shaft and the outlet flow is also parallel to the shaft, the ideal flow is axial in nature. They are primarily used in applications to stir low viscosity liquids. They are used in pharmaceuticals industries and also other industries which use suspensions as the agitators don’t let the solid particles settle.

Figure 3.4 Propeller Agitators.

3.3.4 Anchor Agitators:

As the name indicates the shape of the impeller resembles that of the anchor. These agitators also extend and spread throughout the vessel such that there is very less clearance between the blades and the walls of the vessel. These agitators are also used when laminar flow conditions are desirable. These impellers sweep the whole batch because the blades are almost in physical contact with the walls of the vessels. These agitators are used in ink, paint and adhesive industries.

Figure 3.5 Anchor Agitators

3.3.5 Helical Agitators:

The blades of the helical agitators are arranged in a structure of helix. The appearance is similar to how a threaded screw looks. The motion of the liquids in this type of agitator is also axial in nature due to the way the blades or the ribbons move while helical agitator is in operation. There is a vigorous motion of the fluids within the vessel when the agitator is in operation. It is used in polymer industries and other industries which require the use of quite viscous materials.

Figure 3.6 Helical Agitators.

3.3.6 Air agitator:

Air agitators use compressed air to create bubbles in the liquid, promoting mixing and dispersion. The choice of the agitator depends on the properties of the liquid, viscosity, tank volume, and specific goals of the separation process.

3.4 Inline Mixing

Static devices that promote turbulent mixing in pipelines provide an inexpensive way of continuously mixing fluids. Some typical designs are shown in Figures 3.1 to 3.6. A simple mixing tee, as shown in Figure 3.7 a, followed by a length of pipe equal to 10 to 20 pipe diameters, is suitable for mixing low-viscosity fluids (≤ 50 mN s/m^2), providing the flow is turbulent and the densities and flow rates of the fluids are similar. With injection mixers (see Figures 3.7 b, c), in which the one fluid is introduced into the flowing stream of the other through a concentric pipe or an annular array of jets, mixing will take place by entrainment and turbulent diffusion. Such devices

should be used where one flow is much lower than the other and will give a satisfactory blend in about 80 pipe diameters. The inclusion of baffles or other flow restrictions will reduce the mixing length required.

The static inline mixer shown in Figure 3.8 is effective in both laminar and turbulent flow, and can be used to mix viscous mixtures.

The division and rotation of the fluid at each element cause rapid radical mixing [1-3].

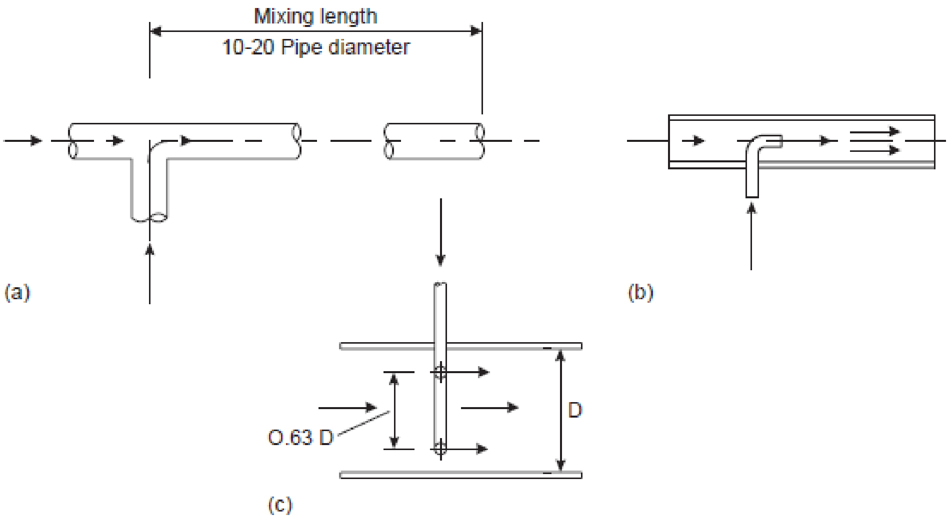

Figure 3.7 Inline mixers. (a) Tee. (b) Injection. (c) Annular.

Figure 3.8 Static mixer (Kenics Corporation).

3.5 Stirred Tanks [4-7]

Mixing vessels fitted with some form of agitator are the most commonly used type of equipment for blending liquids and preparing solutions.

A typical arrangement of the agitator and baffles in a stirred tank and the flow pattern generated are shown in Figure 3.9. Mixing occurs through the bulk flow of the liquid and, on a microscopic scale, by the motion of the turbulent eddies created by the agitator. Bulk flow is the predominant mixing mechanism required for the blending of miscible liquids and for solids suspension. Turbulent mixing is important in operations involving mass and heat transfer, which can be considered as shear controlled processes.

The most suitable agitator for a particular application will depend on the type of mixing required, the capacity of the vessel, and the fluid properties, mainly the viscosity.

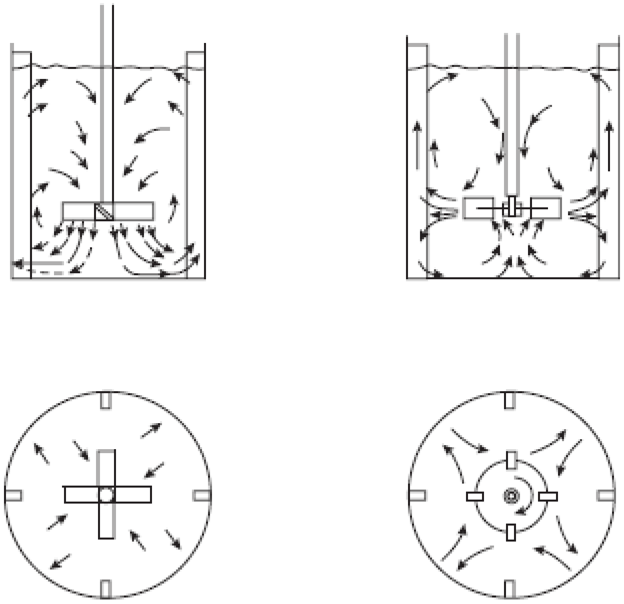

Figure 3.9 Agitator arrangements and flow patterns.

3.6 Agitator Power Consumption

The shaft power required to drive an agitator can be estimated using the following generalized dimensionless equation:

$$N_p = KRe^b Fr^c \tag{3.1}$$

Where:

$$N_p = power\ number = \frac{P}{D^5N^3\rho} \tag{3.2}$$

$$R_e = Reynolds\ number = \frac{D^2N\rho}{\mu} \tag{3.3}$$

$$N_p = power\ number = \frac{P}{D^5N^3\rho} \tag{3.4}$$

$$F_r = Froude\ number = \frac{DN^2}{g} \tag{3.5}$$

P = shaft power, W;

K= a constant, dependent on the agitator type, size, and the agitator-tank geometry**;**

ρ = fluid density, kg/m^3 ;

μ = fluid viscosity, Ns/m^2 ;

N = agitator speed, s^{-1} (revolutions per second) (rps) ;

D = agitator (impeller) diameter, m ;

g = gravitational acceleration, 9.81 m/s^2.

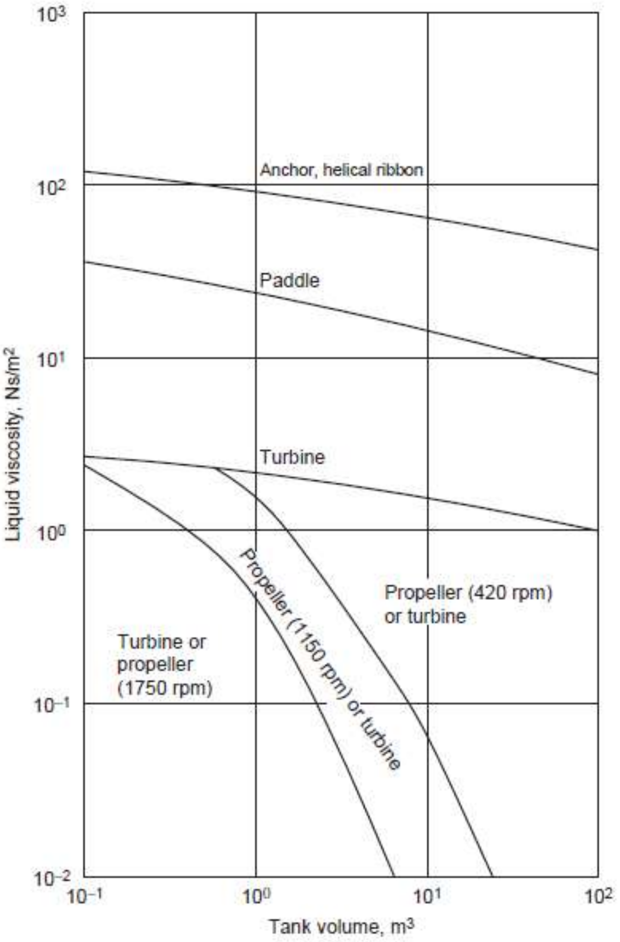

Figure 3.7 Agitator selection guide.

Values for the constant **K** and the indices **b** and **c** for various types of agitator, tank-agitator geometries, and dimensions can be found in the literature [8]. A useful review of the published correlations for agitator power consumption and heat transfer in agitated vessels is given by Wilkinson and Edwards [9]; they include correlations for non-Newtonian fluids. Typical power curves for propeller and turbine agitators are given in Figures 3. 8 and 3. 9. In the laminar flow region, the index ‘‘b’’=1; and at high Reynolds number, the power number is independent of the Froude number; index ‘‘c’’ = 0.

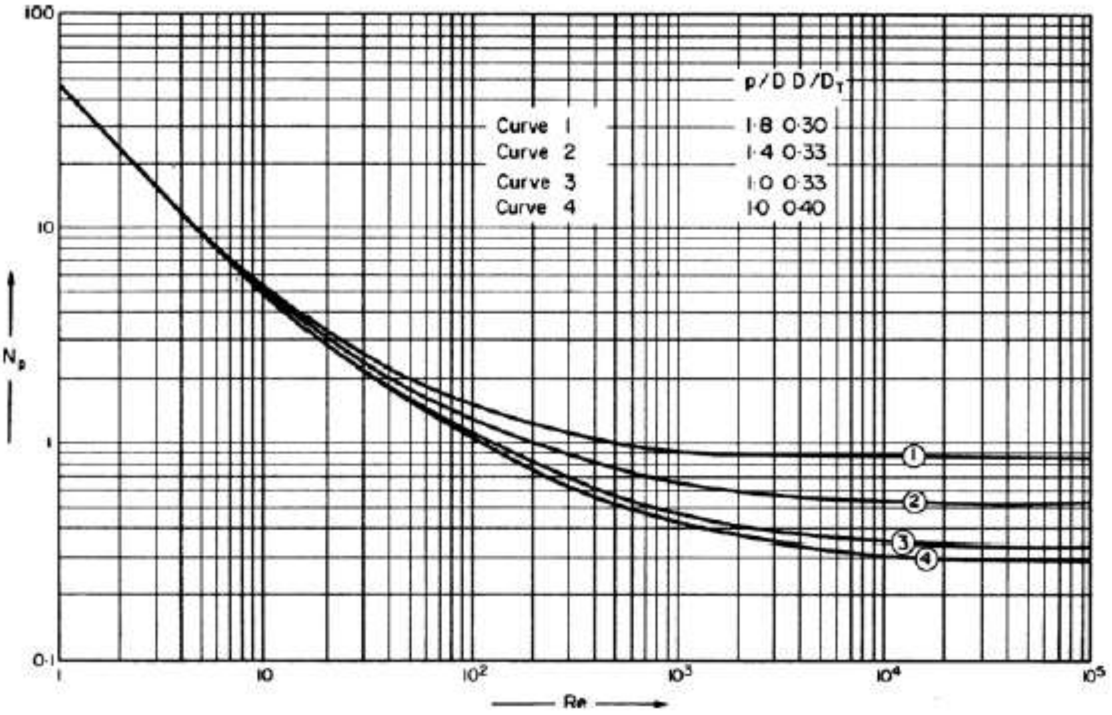

Figure 3.8 Power correlation for single three-bladed propellers baffled [4].

p = D blade pitch, D = impeller diameter, D_T = tank diameter.

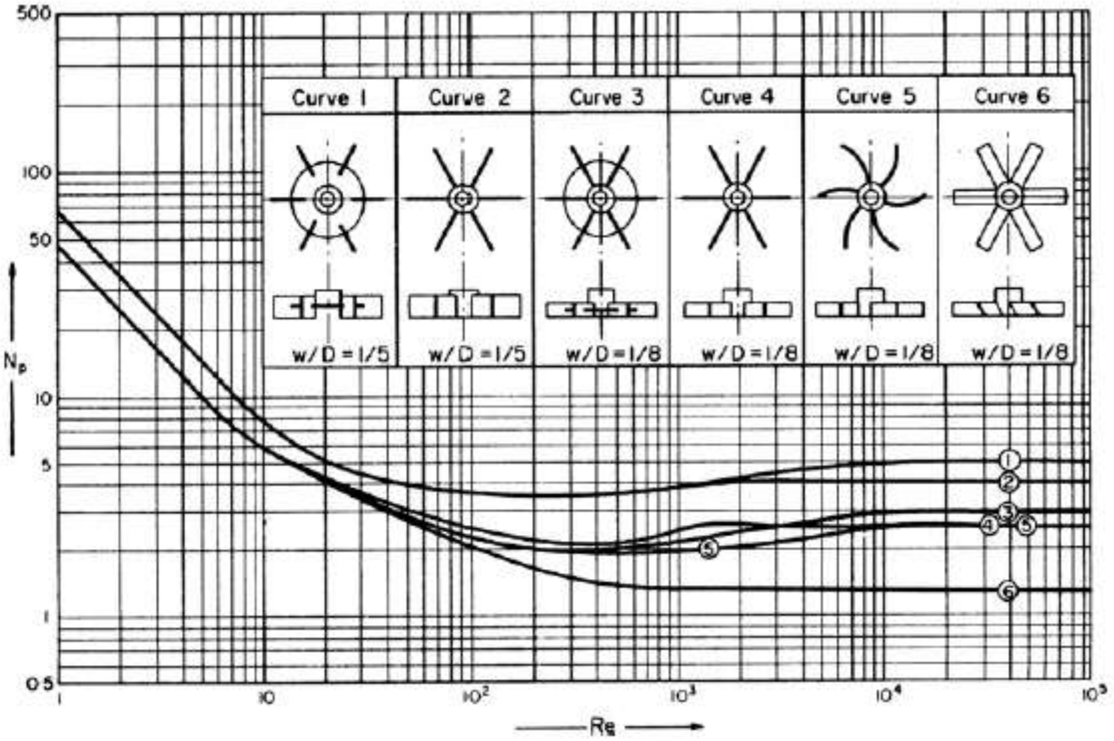

Figure 3.9 Power correlations for baffled turbine impellers, for tank with 4 baffles [4].

w = impeller width, D = impeller diameter

An estimate of the power requirements for various applications can be obtained from Table 3.1

Table 3.1 Power Requirements-Baffled Agitated Tanks

Agitation	Applications Power	kW/m^3
Mild	Blending mixing	0.04–0.10
	Homogeneous reactions	0.01–0.03
Medium	Liquid-liquid mixing	0.03–1.0
	Heat transfer	1.0–1.5
Severe	Slurry suspension	1.5–2.0
	Gas absorption	1.5–2.0
	Emulsions	1.5–2.0
Violent	Fine slurry suspension	> 2.0

3.7 Agitation system sizing

Sizing of the agitation system refers to the process of determining the appropriate specifications and characteristics for an agitation system in a particular environment. This involves evaluating the diameter of the agitator, the number of baffles, the power, and the positioning of the agitator. The sizing of the agitation system aims to ensure effective agitation, homogeneous material distribution, and optimal performance within a given operation.

3.7.1 Diameter of the agitator

The equation for calculating the diameter of an agitator depends on various factors, including the specific application, the type of agitator, and the characteristics of the fluid being agitated. However, a common empirical equation used in the industry is the Rushton Turbine Equation, which provides an estimation for the agitator diameter (D_a) based on the impeller diameter (D) and the tank diameter (D_T):

$$D_a = 0.3 \times D_T + 0.1 \times D \qquad (3.6)$$

This equation is a general guideline and may be modified based on the specific requirements and characteristics of the agitation system. It's essential to consider factors such as the fluid properties, desired mixing intensity, and the purpose of the agitation when determining the agitator diameter.

3.7.2 The number of baffles

Baffles are typically used in various engineering applications to control the flow of fluids, improve heat transfer, or enhance mixing in a vessel. In the context of a shell-and-tube heat exchanger or a vessel, baffles are flat plates or obstacles placed perpendicular to the flow of a fluid. These baffles disrupt the flow pattern, creating turbulence and promoting better heat transfer. The number of baffles in a vessel is an important design parameter, and it depends on factors such as the size of the vessel, the desired level of mixing or heat transfer, and the specific application.

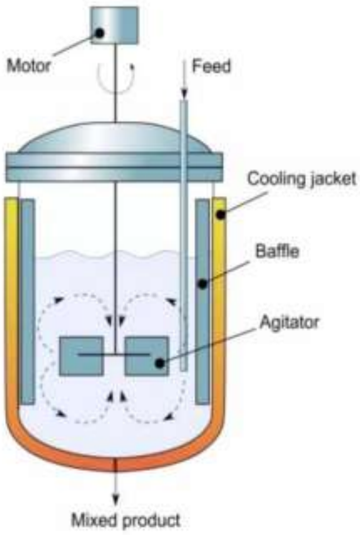

Figure 3.10 Tank baffle design.

The equation for determining the number of baffles may vary based on the design standards or empirical correlations used. One common empirical correlation for determining the number of baffles in a shell-and-tube heat exchanger is the Kern's method, which provides a guideline for the baffle spacing. The number of baffles (N) can be estimated using the following equation:

$$N = L/(B + D) \tag{3.7}$$

where:

- N is the number of baffles,
- L is the shell length,
- B is the baffle spacing, and
- D is the shell diameter.

This equation is just one example, and depending on the specific application or design standards, other correlations or methods may be used.

3.7.3 Positioning of the agitator

The positioning of an agitator in a vessel is an important aspect of mixing system design and impacts the efficiency of the mixing process. The goal is to place the agitator in a way that ensures effective mixing throughout the entire volume of the vessel. The positioning is influenced by factors such as the type of agitator, vessel geometry, fluid properties, and the specific mixing requirements of the process.

There is no single universal equation for determining the optimal positioning of an agitator because it depends on the specific characteristics of the mixing application. However, some general guidelines and considerations are commonly followed:

- **Off-Center Positioning:**
  - Placing the agitator off-center can create a swirling or circulating motion, promoting better mixing.
  - The off-center positioning is often determined based on the vessel diameter, fluid properties, and the desired flow pattern.
- **Clearance from Vessel Wall:**
  - Maintaining a proper clearance between the agitator blades and the vessel wall is essential to prevent dead zones and ensure effective mixing.
  - The clearance is typically determined based on the agitator diameter, blade design, and the vessel dimensions.
- **Clearance from Vessel Bottom:**
  - Avoiding the agitator from being too close to the vessel bottom prevents sedimentation and ensures proper mixing in the lower regions.
  - The clearance from the vessel bottom is influenced by factors such as the agitator design, vessel shape, and the characteristics of the fluid.
- **Impeller Submersion:**
  - The impeller (the rotating part of the agitator) should be properly submerged in the liquid to prevent aeration and ensure efficient mixing.
  - The impeller submersion is determined based on factors such as the impeller design, vessel geometry, and the desired mixing intensity.

While there is no specific equation for determining the positioning of an agitator, computational fluid dynamics (CFD) simulations and empirical correlations may be used to optimize the agitator placement for specific applications. These approaches involve considering factors such as flow patterns, velocity profiles, and mixing efficiency.

In practice, the optimal agitator positioning is often determined through experience, experimentation, and by referring to guidelines provided by equipment manufacturers, industry standards, or relevant literature on mixing technology.

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