Chapter 3

MATERIAL BALANCES WITHOUT CHEMICAL REACTIONS

3.1 MATERIAL AND ENERGY BALANCES

- A material balance is simply an accounting for material.
- A chemical process plant is required to carry out the transformation of raw materials into desired products effectively and economically. In case of a process plant, we have to pay attention to the effective utilisation of materials and energy and to conserve the raw materials (to reduce costs and avoid wastage).
- For assessing the effectiveness of utilisation of raw materials and energy, we require some yardstick or minimum requirement that provides us the basis for judging the effectiveness (in performance) of the process units or the process plant as a whole.
- Material and energy balance calculations provide us the basis against which the actual performance of processing units can be assessed (provide the basis with which the actual performance of processing units is compared).
- Material and energy balance calculations help us (i) to evaluate the specific consumptions of materials and energy (e.g., benzene requirement per tonne of nitrobenzene production, steam consumption for concentrating a weak solution from 4% to 25% NaOH per tonne of the weak solution, kWh of electric energy consumption per tonne of caustic soda lye, etc.), (ii) to evaluate the losses of materials and energy and (iii) to find out the reasons for malfunctioning of processing units.
- Evaluation of the specific consumptions of materials and energy, in turn, help us to determine capacities of storage facilities, various utility generating units, etc. Finally, material and energy balance relationships are the starting points of all design calculations (starting points in the design of various process equipments).
- A material balance is an accounting of all the material that enters, leaves, accumulates, or is depleted in a process or in a process unit in a given time.

3.2.1 Law of Conservation of Mass

- All material balance calculations are based on the *law of conservation of mass, which states that matter can neither be created nor destroyed during a process (i.e., mass is conserved).* The law of conservation of mass can also be stated as :
  - (i) The total mass of all substances taking part in a process remains constant.
  - (ii) Within a given isolated system, the mass of the system remains constant, regardless of the changes taking place within the system.
  - (iii) The total mass of various components remains constant during an unit operation or a chemical reaction.
- The basis of the material balance of any process is the law of conservation of mass.
- We know that the chemical reactions involve conversion of one species to another, provided that we account for the masses of species disappearing and species appearing/generating the law of conservation of mass will hold.
- According to the law of conservation of mass, we have for any process

$$\text{Input} = \text{Output} + \text{Accumulation} \qquad \text{... (3.1)}$$

3.2.2 Steady-state and Unsteady-state Operations

- **Steady-state operations** are those in which there is no build-up of mass and energy within the system as well as there is no variation/change in operating conditions (temperature, flow rate, compositions, etc.) of the system with time.
- The steady state operation is that operation in which all the operating conditions remain constant with time and also the flow in and out of the system will not vary with time.
- As far as material balances are concerned for steady-state operations build-up (accumulation) within the system is constant or nil, i.e. it will not vary with time or it is zero within the system. So a material balance without chemical reaction for steady-state operations over a given system is

Input = Output

i.e. Input of materials = Output of materials

- **Unsteady-state operations** are those operations in which flow rates, build-up of material or energy and operating conditions within the system vary with time.
- The unsteady-state operation/process is that operation/process in which not all the operating conditions remain constant with time and/or the flow in and out of the system can vary with time and hence, the accumulation varies with time.
- An unsteady-state material balance without chemical reaction over a given system is

Input = Output + Accumulation

- For steady-state operations/processes wherein the accumulation of the material is constant or nil, equation (1) reduces to

Input of materials = Output of materials ... (3.2)

- [steady-state operations – operations that are carried out under steady-state conditions – in steady-state conditions, the input and output parameters (e.g., flow rate, composition) do not change with time (i.e., parameters are time invariant). An operation/a process is said to occur under steady state when the values of the variables (e.g., composition, flow rate) of the input and output streams of the operation/process do not change with respect to time (i.e., variables are time invariant).
- Accumulation refers to a change in mass or moles within the system with respect to time.

  Equation (3.2) written for total material ⇒ overall material balance.

  Equation (3.2) written for any component ⇒ component balance.
- When total mass/material balance is referred, Equation (3.2) is valid for systems involving no chemical reactions as well as those involving chemical reactions.
- When we make total material balance over the entire process we refer to it as overall material balance, for any one component it is referred as overall component balance.
- When the process involves a series of steps, total material balance across any one step is referred to as overall material balance across that step whereas for the component under consideration across any step it is called component balance.
- For processes with a chemical reaction under **steady-state** conditions (where the reactants are disappearing and the products are appearing/generating) :

Input = Output ... valid for total mass

- For any reacting component A across a chemical reactor :

A in input to the reactor = A in output from the reactor + A reacted by the reaction

... valid on mass or mole basis

As in case of chemical reactions, it is convenient to express the amounts on a mole (molar) basis, i.e. in *molar units, we have*

kmol A in input to the reactor = kmol A in output from the reactor + kmol A reacted

Note : A in output from the reactor = A remains unreacted

∴ A fed = A reacted + A unreacted

For any product R that is formed and for no R in the feed to a reactor,

R generated/formed = R in output from the reactor

[For systems with chemical reactions :

Input = Output + Consumption + Accumulation ... for any reactant A]

For steady-state operations :

Input = Output + Consumption]

For physical operations :

Input = Output + Accumulation

Input = Output ... under steady-state-conditions

3.3 CLASSIFICATION OF MATERIAL BALANCE PROBLEMS

The material balance problems are classified into two categories as follows :

(1) The material balance problems of processes involving no chemical reactions.

(2) The material balance problems of processes involving chemical reactions.

Further, each category is divided into :

(1) Steady-state operations, and (2) Unsteady-state operations.

MATERIAL BALANCES WITHOUT CHEMICAL REACTIONS

General methods for solving material balance problems of systems involving no chemical reactions are :

- Select a suitable basis of calculations. If the basis of calculations is specified in the statement of the problem, the same may be used or otherwise a convenient basis should be selected/assumed. The basis of calculations should be specified in weight units (as far as possible) ... kg, kg/h, etc.

(1) When the system involves a component material that appears in both the incoming and outgoing streams, whose quantity does not change during a given operation, then for the simplification of the problem, take a material balance of such a material (tie material). For example, in case of an evaporation operation, the quantity of the dissolved solids is the same in both thin (weak) and thick (concentrated) liquor. During this operation, the quantity of water (solvent) changes but the quantity of the dissolved solids remain unchanged, so the dissolved solids are treated as a tie material in the evaporation operation.

(2) Whenever we are dealing with the system involving an inert chemical species (which do not take part in the operation), the calculations may be simplified by making the material balance of the inert chemical species present. For example, in the combustion of coal, ash present in the coal does not take part in the combustion reaction, so the ash is an inert chemical species.

(3) Whenever the system involves two or more components and if all the components are undergoing change simultaneously during a particular operation (e.g., change in composition), then such material balance problems can be solved by generating and solving simultaneously the independent material balance equations. In such cases, the number of independent material balance equations should be equal to the number of unknown quantities to be computed.

For example, when a desired mixed acid is to be prepared from a given spent or waste acid by blending it with concentrated acids, all the acids get affected simultaneously. In case of distillation operation, the components present in a given system get affected simultaneously during the operation, so in such cases the material balance equations are generated and solved simultaneously.

General Procedure for Solving Material Balance Problems :

(1) Read and understand the problem statement. We have to read the problem given carefully to get an idea regarding what is given and what is to be accomplished.

(2) Assume a suitable basis of calculations such as quantity/amount or flow rate of the stream-entering or leaving the operation or process that is provided in the problem statement. If the basis is not specified in the statement of the problem, assume a new suitable/convenient basis (quantity or flow rate of a stream of known composition).

(3) Adopt weight units such as grams or kilograms in case of problems of operations/processes without chemical reactions (i.e., wherein no chemical reactions occur) and adopt/use molar units such as gram moles or kilogram moles in case of problems of processes with chemical reactions, i.e., processes involving chemical reactions as far as possible for the purpose of simplification.

(4) Draw a block diagram of the operation/process wherein the operation or each step is represented by a rectangular block. The input and output streams are represented by inflow and outflow arrows to or from the block.

(5) In the block diagram drawn, indicate the information provided related to the input and output streams given in the problem statement such as quantities, flow rates, stream compositions, materials, etc.

(6) Search out the unknown quantities : compositions, flow rates, etc.

(7) Search out the unknowns involved in the problem and ascertain them some x, y, z, etc. (depending upon the number of unknowns) and generate, with the help of the data given, the independent material balance equations in terms of x, y, z, etc. equal to the number of unknowns to be calculated. The material balance equations can be generated by making the overall material balance and individual material balances of components involved and solve them simultaneously.

(8) In case of problems involving a chemical reaction, write the balanced chemical equation, search out a limiting component and so on. Since the product produced during the reaction or the components reacted/consumed are to be calculated on the basis of the limiting reactant reacted and the chemical reaction under consideration.

(9) In the problems involving a chemical reaction, the quantity of the reacting component appearing in the product stream from a reactor is the quantity of that material remains unreacted (to be calculated by making its material balance : quantity of the reacting material charged minus the quantity of the reacting material reacted).

(10) The quantity of an excess reactant that is supplied is to be calculated from the theoretical requirement of that reactant based on the quantity of the limiting reactant fed/charged. One has to refer to the chemical reaction involved for the stoichiometric proportion between the excess and limiting components/reactants.

VARIOUS IMPORTANT OPERATIONS CARRIED OUT IN THE CHEMICAL INDUSTRY, THEIR SIGNIFICANCE AND BLOCK DIAGRAMS USEFUL FOR MAKING MATERIAL BALANCES OVER THEM :

(1) Distillation : This operation is used for the separation of the components of a liquid mixture by partial vaporization and condensation. Distillation with rectification or (fractional distillation) gives almost pure products. The product removed from the top is called the distillate or overhead product and that removed from the bottom is called the bottoms or bottom product.

The component material balance is generally based on the more volatile component.

The vapour phase is created by supplying thermal energy to the liquid to be distilled and this method of separation depends on the difference in vapour pressures of different components at a given temperature.

Block diagram of distillation operation for a binary system of (A + B) :

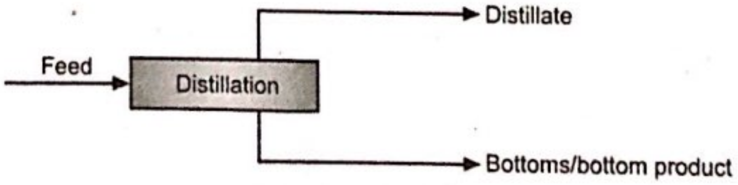

Fig. 3.1 : Distillation

Overall Material Balance :

$$\text{Feed} = \text{Distillate} + \text{Bottoms (on weight or mole basis)}$$

$$F = D + W$$

where F is the feed to a distillation column in kg or kg/h, D is the distillate in kg or kg/h and W is the bottom product in kg or kg/h.

Material Balance of Component A :

$$\text{A in feed} = \text{A in distillate} + \text{A in bottoms}$$

$$x_F \cdot F = x_D \cdot D + x_W \cdot W$$

where x_F, x_D and x_W are the weight fractions of A in the feed, distillate and bottoms respectively.

(2) **Evaporation :** This operation used in the chemical industry for the concentration of a weak liquor to produce a thick liquor by evaporating a portion of the solvent (generally water) by means of condensing steam (heating medium). It may be carried out in a single or a multiple effect evaporation system.

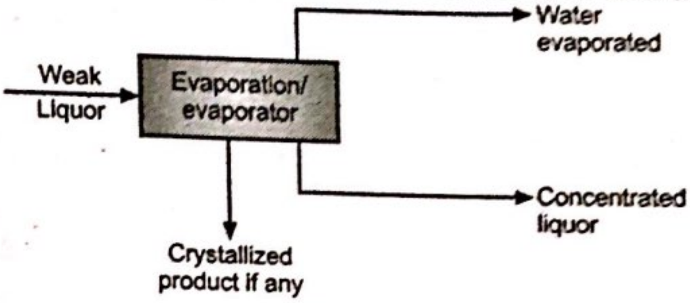

Fig. 3.2

Overall Material Balance :

$$\text{Weak liquor} = \text{Water evaporated} + \text{Crystallized product} + \text{Thick liquor}$$

If no product is crystallised, then the overall material becomes :

$$\text{Weak liquor} = \text{Water evaporated} + \text{Thick liquor}$$

Material balance of solids (solute) :

Solids (solute) in weak liquor = Solids (solute) in thick liquor

Material balance of water (solvent) :

Water in weak liquor = Water evaporated + Water in thick liquor

The above material balance equations may be written in terms of quantity in kg or flow rate in kg/h.

(3) **Absorption :** This operation is used in the chemical industry for the recovery/ removal of a solute gas component from its mixture with another component gases (called as inert gases with respect to absorption) with the help of a suitable liquid solvent in which the solute gas is absorbed.

Mechanically agitated vessels, packed columns, etc. are the equipments commonly used for absorption.

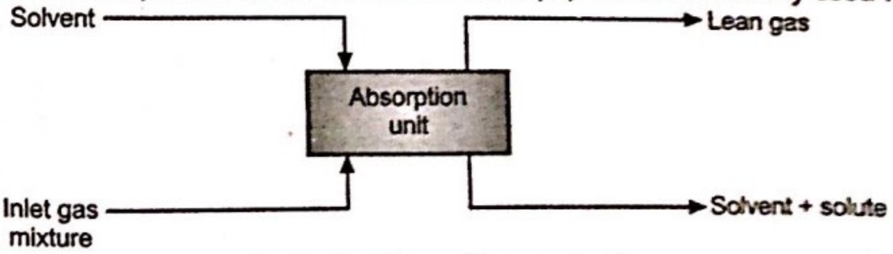

Fig. 3.3 : Absorption operation

Material balance of inert gas :

Inert gas in gas entering the tower = Inert gas leaving the tower (i.e., inert gas in the lean gas).

Material balance of solute gas (for no solute gas in the solvent used) :

Solute gas in inlet gas = Solute gas in lean gas (gas leaving the tower) + Solute gas in solvent leaving the tower

Solute gas removed by absorption = Solute in inlet gas – Solute in lean gas

(4) Extraction (liquid – liquid) : This operation is used in the chemical industry for the separation of th components of a liquid mixture with the help of a suitable liquid solvent wherein the solute from the feed solutio is transferred in the solvent yielding the raffinate phase (rich in the feed solvent) and extract phase (rich in th solvent used).

It does not give a pure product and needs further processing. Mixer settlers; packed columns etc. are used fo liquid – liquid extraction.

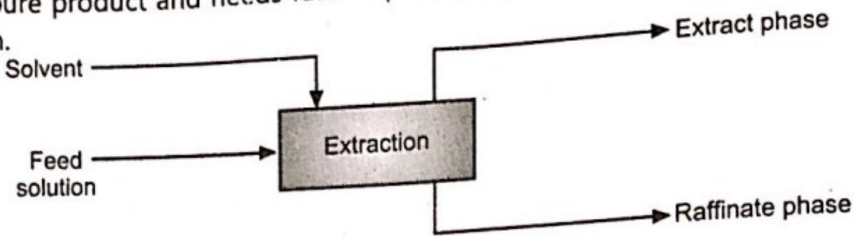

Fig. 3.4 : Extraction operation

Overall Material Balance :

Feed solution + Solvent = Extract phase + Raffinate phase

If A is the solute to be extracted, then the **material balance of A with a fresh solvent** is :

A in feed solution = A in extract phase + A in raffinate phase

Extraction operation is also carried out for the removal of a soluble constituent of solids with the help of suitable liquid solvent (it is called as solid extraction). For example, oil seed extraction or leaching of valuable meta from mineral ores.

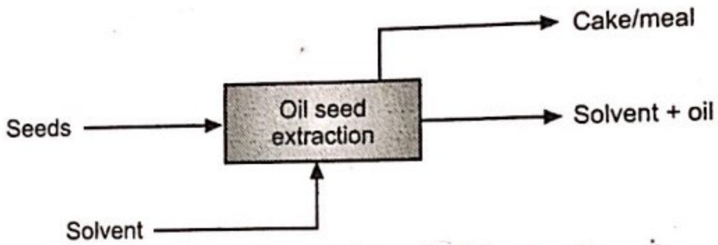

Fig. 3.5 : Solvent extraction of oil from oil seeds

Material Balance of Solids :

Solids in seeds = Solids in meal ... if no solids in solvent

Material Balance of Oil :

Oil in seeds = Oil in meal + Oil in solvent (extracted oil)

(5) Drying : This operation is carried out in the chemical industry for the removal of a residual moist (water) or volatile liquid associated with wet solids with the help of hot air, or inert gas (N_2) (drying medium). Wh the hot air is circulated over the wet solids, the moisture from the solids evaporates and gets added in the air. I generally the last operation carried out in the industry. Tray dryer, spray dryer, etc. are used industrially for dryin

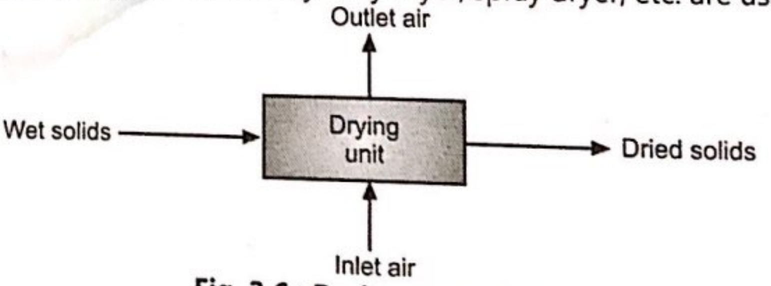

Fig. 3.6 : Drying operation

Dryer with Recycle of Air :

Material Balance of Moisture :

Moisture removed from solids = Moisture added in air

Initial moisture in wet solids – Moisture in dried solids

= Moisture in outlet air – Moisture in inlet air

The quantity of solids does not change during this operation.

Generally, hot air is used as a heating medium in drying operation.

Material Balance of Solids :

Solids in wet solids (feed) = Solids in dried product

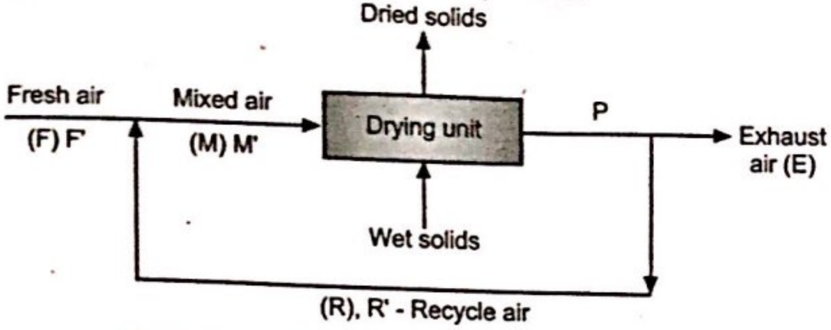

Fig. 3.7 : Drying operation with recycle of air

If F', R' and M' are the quantities of dry air in fresh air, recycle air and mixed air then,

$$F' + R' = M'$$

Moisture balance in F, R, and M :

Moisture in M = Moisture in F + Moisture in R

Moisture balance at the outlet of the dryer of Fig. 3.7 :

Moisture in P = Moisture in R + Moisture in E

Moisture content in P is the moisture content of the recycle stream of Fig. 3.7.

Moisture Balance over Dryer :

Moisture added in air = Moisture removed from solids

$$X_2M' - X_1M' = \text{Moisture removed from solids}$$

where X_2 and X_1 are kg moisture/water per kg dry air in the air leaving the dryer and the air entering the dryer respectively.

(6) **Filtration :** This operation is carried out in the industry for the separation of solids from a suspension in a liquid by using a porous medium that retains the solids and allows the liquid to pass through. Wet solids is the product of this operation. Various equipments used are : centrifuge machines, drum-fitter press, etc.

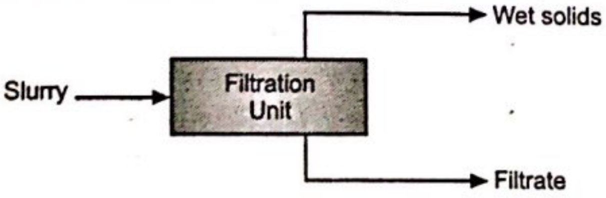

Fig. 3.8 : Filtration operation

Overall Material Balance :

Feed slurry = Wet solids + Filtrate

Material Balance of Solids :

Solids in slurry = Solids in wet solids product + Solids in filtrate (if any)

(7) **Mixing/Blending :** This operation is carried out in the chemical industry to obtain a product of the desired quality by mixing weak and concentrated streams. For example, preparation of a desired mixed acid, blending of solids from various batches to get solids of a specified quality, etc.

If a desired product stream is to be obtained by blending streams 1, 2 and 3, then

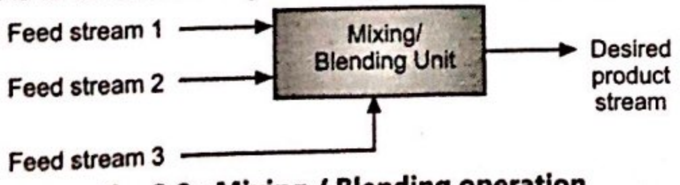

Fig. 3.9 : Mixing / Blending operation

Overall Material Balance :

Feed stream – 1 + Feed stream – 2 + Feed stream – 3 = Desired product stream

If the feed stream – 1 contains components A, B, and C, product stream contains A, B, and C, feed stream – contains A and C, and feed stream – 3 contains B and C, then

Material Balance of A :

A in feed stream – 1 + A in feed stream – 2 = A in desired product stream

Material Balance of B :

B in feed stream – 1 + B in feed stream – 3 = B in desired product stream

Mixing/blending of liquids may be carried out in a mechanically agitated vessel.

(8) Dissolution : It is an operation carried out for the preparation of solutions of a solute in a liquid solven e.g., KOH solution, NaOH solution, etc. **Dilution** is an operation carried out for dilution of a concentrated stream b the addition of a solvent, e.g., dilution of concentrated sulphuric acid, etc. Material balances of such process ar carried out in the same manner as done in the case of mixing. Dissolution and dilution operations are carried out i agitated vessels.

(9) Crystallization : It is the formation of solid particles within a homogeneous liquid phase. Crystallizatio gives almost pure product and crystallization from solution is very important industrially. Various equipments use for carrying out crystallization are stirred tanks, vacuum crystallizer, swenson-walker crystallizer, etc. Crystallizatio of the dissolved solids from a solution is based on the differences in solubilities at different temperatures. It usuall consists of concentrating a solution followed by cooling of the solution until it becomes supersaturated.

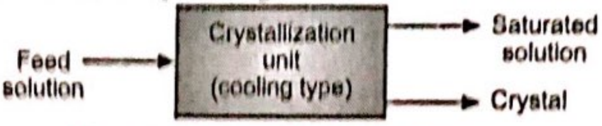

Fig. 3.10 : Crystallization operation

Overall Material Balance :

Feed solution = Saturated solution + Crystals obtained

Material balance of solute crystals :

Crystals in feed solution = Crystals obtained + Crystals in saturated solution

Example 3.1 : *A single effect evaporator is fed with 10000 kg/h of weak liquor containing 15% caustic by weigh and is concentrated to get thick liquor containing 40% by weight caustic (NaOH). Calculate : (a) kg/h of wate evaporated and (b) kg/h of thick liquor obtained.*

Hint : In this case, the weak liquor is an input stream to the evaporator, while the water evaporated and thick liquor are output stream from the evaporator. It is given in the problem statement that the evaporator is fed at the rate of 10,000 kg/h of weak liquor so tak 10,000 kg/h of weak liquor as a basis of calculations. As we have to calculate the water evaporated and thick liquor obtained, assume and y for these unknowns. Take an overall material balance and a material balance of NaOH to generate two material balance equation Solve these equations simultaneously to get x and y known.

Solution : Basis : 10,000 kg/h of weak liquor.

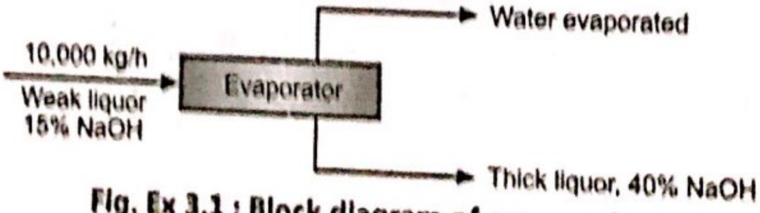

Fig. Ex 3.1 : Block diagram of evaporation

Let x be the kg/h thick liquor obtained and y be the kg/h water evaporated.

Overall Material Balance :

$$\Sigma \text{ kg/h input stream} = \Sigma \text{ kg/h output stream}$$

$$\text{kg/h weak liquor} = \text{kg/h thick liquor} + \text{kg/h water evaporated}$$

$$10000 = x + y$$

Material Balance of NaOH :

NaOH in input stream = NaOH in output stream

NaOH in weak liquor = NaOH in thick liquor

$0.15 \times 10000 = 0.40\,x$

∴ $x = 3750$ kg/h

We have, $x + y = 10000$

$3750 + y = 10000$

∴ $y = 6250$ kg/h

∴ Water evaporated = **6250 kg/h**

and Thick liquor obtained = **3750 kg/h** ... **Ans.**

Example 3.2 : *The ground nut seeds containing 45% oil and 45% solids are fed to expeller, the cake coming out of expeller is found to contain 80% solids and 5% oil. Find the percentage recovery of oil.*

Hint : Whenever the composition data of a particular stream is given, then in such cases it is more convenient to take a numerical value of 100 of that stream as a basis of calculations. For the basis of calculations, input stream should always be given preference. In this problem, we are supplied with composition in weight % of seeds so it is better to assume 100 kg of ground nut seeds as a basis of calculations. The quantity of the cake obtained is not known to us, so assume x for it. Take a material balance of solids over the expeller to get x known. Take a material balance of oil to know the oil recovered. Express the oil recovered as a percentage of oil in the seeds to get the % recovery of the oil.

Solution : Basis : 100 kg of ground nut seeds.

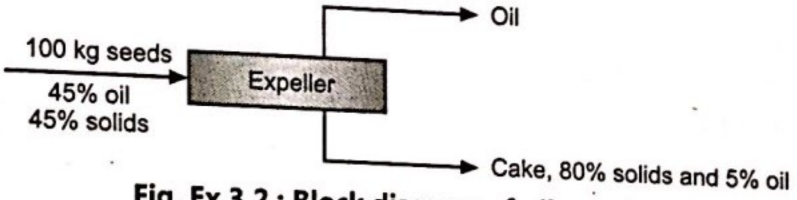

Fig. Ex 3.2 : Block diagram of oil expeller

Let x be the kg of cake obtained.

Material Balance of Solids :

Solids in seeds = Solids in cake

∴ $0.45 \times 100 = 0.8\,x$

∴ $x = 56.25$ kg

Material Balance of Oil :

Oil in seeds = Oil in cake + Oil recovered

∴ $0.45 \times 100 = 0.05 \times 56.25$ + Oil recovered

∴ Oil recovered $= 45 - 2.81 = 42.19$ kg

$$\text{\% recovery of oil} = \frac{\text{kg oil recovered}}{\text{kg oil in seeds}} \times 100 = \frac{42.19}{45} \times 100 = \mathbf{93.75}$$ ... **Ans.**

Example 3.3 : *An evaporator is fed with 15000 kg/h of a solution containing 10% NaCl, 15% NaOH and rest water. In the operation, water is evaporated and NaCl is precipitated as crystals. The thick liquor leaving the evaporator contains 45% NaOH, 2% NaCl and rest water.*

Calculate : (a) kg/h water evaporated, (b) kg/h salt precipitated, (c) kg/h thick liquor.

Hint : Here the weak liquor is an input stream while the water evaporated, salts precipitated and thick liquor are output streams from the evaporator. The basis of calculations is specified in the problem statement which is 15000 kg/h of the weak solution. Since we have to calculate the unknowns such as water evaporated, salts precipitated and thick liquor leaving, assume x, y and z for them. Hence, we need three equations. Take an overall material balance and material balances of NaOH and NaCl to generate three material balance equations. Solve these equations simultaneously to get x, y and z known.

Solution : Basis : 15000 kg/h of weak solution fed to the evaporator.

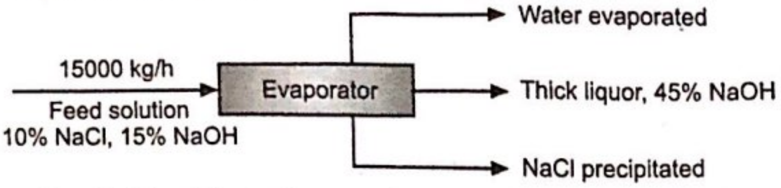

Fig. Ex 3.3 : Block diagram for crystallizing evaporator

Let x, y, and z be the kg/h of water evaporated, thick liquor and NaCl precipitated as crystals.

Overall Material Balance :

$$\Sigma \text{ Input stream} = \Sigma \text{ Output stream}$$

$$\therefore \quad 15000 = x + y + z$$

Material Balance of NaOH :

$$\text{NaOH in feed solution} = \text{NaOH in thick liquor}$$

$$0.15 \times 15000 = 0.45\, y$$

$$\therefore \quad y = 5000 \text{ kg/h}$$

Material Balance of NaCl :

$$\text{NaCl in feed solution} = \text{NaCl in thick liquor} + \text{NaCl precipitated as crystals}$$

$$0.10 \times 15000 = 0.02 \times 5000 + z$$

$$\therefore \quad z = 1400 \text{ kg/h}$$

We have, $x + y + z = 15000$

$$\therefore \quad x + 5000 + 1400 = 15000$$

$$\therefore \quad x = 8600 \text{ kg/h}$$

Check ⇒

Material Balance of Water :

$$\text{Water in feed solution} = \text{Water evaporated} + \text{Water in thick liquor}$$

$$0.75 \times 15000 = 8600 + 0.53 \times 5000$$

$$11250 = 8600 + 2650$$

$$11250 = 11250$$

As LHS = RHS, calculations done are correct.

$\therefore$ Water evaporated = **8600 kg/h**

Thick liquor obtained = **5000 kg/h**

NaCl precipitated as crystals = **1400 kg/h**

... An

Example 3.4 : *An evaporator system concentrating a weak liquor from 5% to 50% solids handles 100 kg of soli per hour. If the same system is to concentrate a weak liquor from 4% to 35%, find the capacity of the system in term of solids that can be handled per hour assuming water evaporation capacity to be same in both the cases.*

Hint : In this problem, for the case-I, i.e., for concentration of the liquor from 5% solids to 50% solids, the basis of calculations is defin which is 100 kg/h solid handling capacity of the evaporator system. For this capacity calculate the flow rates of the weak liquor enteri and thick liquor leaving. Take an overall material balance to get the water evaporated known.

For the case-II, i.e., for concentration of the liquor from 4% solids to 35% solids, the water evaporation is the same as that in t case-I, so take it as a basis of calculations. Assume x_1 and y_1 for the weak liquor and thick liquor flow rates. Take an overall mate balance and a material balance of solids to get two material balance equations, solve them to get x and y known. With the help of x_1 y_1, obtain the solid handling capacity in this case.

Chapter 4

MATERIAL BALANCES WITH CHEMICAL REACTIONS

The process of manufacture of a desired product from a given raw material(s) involves a series of steps wherein physical and chemical changes take place in the materials under consideration. The step wherein chemical change takes place, i.e., wherein raw materials undergo chemical reaction/reactions (with or without catalyst) to produce the desired product is the heart of the process as it decides the economics of the process as a whole.

Material balances of processes wherein a chemical reaction takes place are very important from the design point of view of chemical reactors. The occurrence of chemical reactions makes the material balance calculations complicated as in addition to the input and output terms (at steady-state), the formation or disappearance term is involved in the material balance equation.

The terminology and procedures used for solving the material balance problems of processes that involve chemical reactions are given in this chapter for getting clear idea of the subject matter.

In the processes involving chemical reactions, the total mass of various components entering a reactor is equal to the total mass of various components leaving the reactor but the sum of entering moles of components need not be equal to the sum of moles of components leaving. While doing the material balance calculations in such cases it is very convenient to use the basis of calculations in molar units. Generally, the calculations are based on a limiting reactant and the quantities of products formed are calculated by referring to the chemical reaction and the amount of the limiting reactant reacted.

4.1 TYPICAL PROBLEMS UNDERLYING THE SUBJECT INVOLVED

Providing the information of the composition and quantities of the stream(s) entering the reaction system and calculation of the composition and quantities of the stream(s) leaving the system for a specified degree of conversion or completion of the reaction or vice-versa.

4.2 DEFINITIONS OF THE TERMS INVOLVED

Stoichiometry : It is the theory of the proportions in which chemical species combine with one another.

Stoichiometry is defined as the quantitative relationships of reactants and products in a chemical reaction. It is based on the law of conservation of mass.

Stoichiometry is the calculations of the quantities of reactants and products in chemical reactions.

Stoichiometric Equation : The stoichiometric equation of a chemical reaction is the statement indicating relative moles of the reactants and products that take part in the reaction. For example, the stoichiometric equation

$$CO + 2\,H_2 \rightarrow CH_3OH$$

indicates that one molecule (mol or kmol) of CO reacts with two molecules (mol or kmol) of hydrogen to produce one molecule (mol or kmol) of methanol.

Stoichiometric Coefficient : It is the number that precede the formula of each component involved in a chemical reaction.

Thus, for example, in the above cited reaction, the stoichiometric coefficient of CO is one, the stoichiometric coefficient of H_2 is two and that of methanol is one. The stoichiometric requirements of components are given as :

$$\begin{aligned} 1\text{ kmol CO} &\equiv 1\text{ kmol } CH_3OH \\ &\equiv 2\text{ kmol } H_2 \end{aligned}$$

Stoichiometric Ratio : It is *the ratio of stoichiometric coefficients of two molecular species/components in the balanced reaction equation.*

e.g., stoichiometric ratio of H_2 to CO is 2/1 = 2.

Stoichiometric Proportion : Two reactants, A and B, are said to be present in the stoichiometric proportion if the ratio of moles of A present to the moles of B present is equal to the stoichiometric ratio obtained from the balanced reaction equation.

Consider the following chemical reaction : $CO + 2H_2 \longrightarrow CH_3OH$

For the reactants in the above reaction to be present in the stoichiometric proportion, there must be 2 moles of H_2 for every mole of CO (so that $n_{H_2}/n_{CO} = 2/1 = 2$) present in the feed to a reactor.

When the reactants are fed to a reactor in the stoichiometric proportion and the reaction goes to completion, all of the reactants are consumed. In case of the above cited reaction, for example, if 200 mol of H_2 and 100 mol of CO are initially present, the H_2 and CO would disappear at the same instant. It follows that if we start with 100 mol of CO and less than 200 mol of H_2 (i.e., if H_2 is present in less than its stoichiometric proportion) H_2 disappears before the CO_2, on the other hand, if there are more than 200 mol of H_2 initially present the CO disappears first.

Limiting Reactant / Component :

- *It is defined as the reactant that would disappear first if a reaction goes to completion.*
- It is the one which decides the extent to which a reaction can proceed. The limiting reactant is always present in less than its stoichiometric proportion relative to the other reacting components.
- It is the reactant which is present in the smallest stoichiometric amount, i.e., the reactant which is not present in excess of that required to combine with any of the other reactants.
- It is the reactant which is present in such proportions that its consumption/disappearance by the reaction will limit the extent to which the reaction can proceed (i.e., the extent of reaction).

Excess Reactant :

- It is defined as the reactant which is in excess of the theoretical or stoichiometric requirement as determined by the desired reaction. The excess component / reactant always found in the product stream though the reaction proceeds to completion.

For example, consider the following reaction : $C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O$

In industrial practice of producing ethylene oxide by oxidation of ethylene, oxygen/air fed to the reactor is always in excess of that theoretically required. Thus, ethylene is the limiting reactant and oxygen/air is the excess reactant.

- **It is a reactant present in excess of the limiting reactant.**

When all reactants are present in the stoichiometric proportion, then none of the reactants involved is limiting.

For example, $N_2 + 3H_2 \rightarrow 2NH_3$

N_2 and H_2 are always fed to the reactor in their stoichiometric proportion i.e. 1 mole N_2 to 3 moles H_2. Therefore none of the reactants is limiting.

Percent Excess : The excess reactant involved in the reaction is generally specified in terms of percent excess. It is the amount in excess of the stoichiometric (theoretical) requirement expressed as a percentage of the stoichiometric/theoretical requirement.

Consider the reaction : $A + B \rightarrow C$

wherein B is the excess reactant. Then

$$\therefore \boxed{\begin{bmatrix}\text{Percent}\\ \text{excess of B}\end{bmatrix} = \left[\frac{\begin{array}{l}\text{moles of B}\\ \text{supplied}\\ \text{or fed}\end{array} - \begin{array}{l}\text{moles of B}\\ \text{theoretically}\\ \text{required}\end{array}}{\begin{array}{l}\text{moles of B}\\ \text{theoretically}\\ \text{required}\end{array}}\right] \times 100} \quad \dots (4.1)$$

Moles of B theoretically required are the moles of B that would correspond to stoichiometric proportion and are calculated based on limiting reactant charged.

Equation (4.1) is also valid on weight basis.

The above equation can be rearranged to calculate the quantity of the excess reactant actually supplied.

$$\boxed{\begin{bmatrix}\text{moles of B}\\ \text{actually fed}\\ \text{or supplied}\end{bmatrix} = \begin{bmatrix}\text{Stoichiometric}\\ \text{requirement or}\\ \text{theoretical}\\ \text{requirement of B}\end{bmatrix}\left(1 + \frac{\%\text{ excess B}}{100}\right)} \quad \text{... (4.2)}$$

The quantity of an excess reactant must be found based on the quantity of the limiting reactant fed to the reactor. Consider, for example, the reaction

$$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$$

and suppose that 100 mol SO_2/h and 75 mol O_2/h are fed to a reactor. SO_2 is clearly the limiting reactant, and to be in stoichiometric proportion, moles of O_2 would have to be 50 mol/h. Therefore, the percent excess of O_2 is

$$\%\text{ excess } O_2 = \left(\frac{75-50}{50}\right) \times 100 = 50$$

4.3 CONVERSION

The conversion is always based on the limiting reactant and it gives us an idea regarding the degree of completion of a reaction. The unreacted quantities of the raw materials are easily obtained knowing the charged quantities with the help of conversion. This, in turn, gives us an idea regarding whether recycling is to be done or not for the process to be economically feasible.

- **Conversion or fractional conversion of a reactant is the fraction of the reactant that has been converted into reaction products.** It ranges from 0 to 1.

  Consider the chemical reaction :

  $$A + B \rightarrow C$$

  where A is the limiting reactant and B is the excess reactant. Then,

- *The conversion or fractional conversion of A is the ratio of the amount of A reacted to the amount of A charged or fed to the reactor.*
- *The percentage conversion of A is the amount of A reacted expressed as a percentage of the amount of A charged or fed to the reactor. The percent conversion ranges from 0 to 100, whereas the fractional conversion ranges from 0 to 1.*

  The amount of A can be expressed on mole or weight basis. If amount of A is expressed in moles then

$$\boxed{\%\text{ conversion of A} = \frac{\text{moles (or mass) of A reacted}}{\text{moles (or mass) of A charged or fed}} \times 100}$$

In case of recycle operations, the term namely per pass conversion is commonly used. The per pass conversion is defined as the *quantity of the limiting reactant reacted/consumed expressed as percentage of the limiting reactant in the mixed feed.*

If 100 mol of reactant A are fed and 75 of them react, the fractional conversion is 0.75 (the percentage conversion is 75%) and the fraction unreacted is 0.25. If 50 mol of reactant A are fed and the percentage conversion is 80%, then (0.80) (50) = 40 mol of reactant A are reacted and (0.20) (50) = 10 mol of A remain unreacted.

The degree of completion of a reaction is expressed as a percentage of the limiting reactant converted into the product.

The conversion of a chemical reaction tells us how efficiently a process is conducted from the point of view of the utilisation of the starting materials, i.e., the reactants.

4.4 YIELD AND SELECTIVITY

In most of the chemical processes, though the objective is to produce a desired product, the raw materials ma also undergo a series or parallel reactions (side-reactions) resulting into the production of undesired materia which has an reverse effect on the economics of the process. In such cases (in industrial practice), the steps a taken to depress the side reactions by use of selective catalyst, addition of inhibitors in the feed, etc.

The terms yield and selectivity are used in case of multiple reactions to give the information regarding th degree to which the desired reaction predominates over the side reaction (or reactions) involved.

Consider the reactions :

$$A + B \rightarrow C$$

$$C + B \rightarrow D$$

i.e., $A \rightarrow C \rightarrow D$ ... (reactions in series)

or $A \rightarrow C$

$A \rightarrow D$ ... (parallel reactions)

where C is the desired product, D is the undesired product and A is the limiting reactant. Then, the yield of 'C' i given as :

$$\boxed{\text{Yield of C} = \frac{\text{moles of A reacted to produce C}}{\text{moles of A totally reacted}} \times 100}$$

The yield of a desired product is also defined as the ratio of the quantity of the desired product actuall produced to its maximally obtainable quantity.

The percent yield of a desired product is the quantity of the limiting reactant reacted to produce it expressed a a percentage of the quantity of the limiting reactant reacted totally (i.e., by all the reactions involved).

Selectivity is the ratio of the moles of the desired product produced to the moles of the undesired product (by-product) produced.

Consider the parallel reactions :

$A \rightarrow C$ and $A \rightarrow D$, where C is the desired product and D is the undesired product, in this case, selectivity i given as :

$$\boxed{\text{Selectivity of C relative to D} = \frac{\text{moles of C (desired product) formed}}{\text{moles of D (undesired product) formed}}}$$

Selectivity is also defined as the ratio of the amount of the limiting reactant reacted to the desired product to the amount of it reacted to produce the undesired product. If yield is 100%, then the selectivity is 1. The yield of a desired product tells us how efficient a given process is in terms of the reaction product.

It may be noted that the conversion may have low values but the yield should have higher values.

4.5 COMPOSITION OF PRODUCT AND REACTANT

- The composition of a product stream as well as of a reactant stream can be expressed in terms of weight % or mole % (or volume % if the stream is gaseous).
- A reactant stream is one that contains all reactants entering a reactor.
- A product stream/product mixture is one that leaves a reactor and contains the product formed, unreacted reactants and inerts.
- If we are supplied with the feed composition, % conversion and yield, we can calculate the composition of a product stream using chemical reaction(s) which gives us an idea regarding reactants and products and vice-versa.

SOLVED EXAMPLES

Example 4.1 : *The carbon monoxide is reacted with hydrogen to produce methanol. Calculate from the reaction : (a) The stoichiometric ratio of H_2 to CO. (b) kmol of CH_3OH produced per kmol CO reacted. (c) The weight ratio of CO to H_2 if both are fed to a reactor in stoichiometric proportion. (d) The quantity of CO required to produce 1000 kg of CH_3OH.*

Solution : Reaction : $CO + 2H_2 \rightarrow CH_3OH$

From the reaction, we have

Stoichiometric coefficient of CO = a = 1

Stoichiometric coefficient of H_2 = b = 2

$$\therefore \quad \text{Stoichiometric ratio of } H_2 \text{ to CO} = \frac{b}{a} = \frac{2}{1} = \mathbf{2}$$

... **Ans. (a)**

From the reaction, we have : 1 kmol CO ≡ 1 kmol CH_3OH

$$\therefore \quad CH_3OH \text{ produced from 1 kmol CO} = \frac{1}{1} \times 1 = \mathbf{1\ kmol}$$

... **Ans. (b)**

CO fed to the reactor = 1.0 kmol ... on molar basis

∴ CO fed to the reactor = 1 × 28 = 28 kg ... on weight basis

H_2 fed to the reactor in the stoichiometric proportion with CO = 2 kmol

∴ H_2 fed to the reactor = 2 × 2 = 4 kg

$$\therefore \quad \text{Weight ratio of CO to } H_2 \text{ fed} = \frac{\text{Amount of CO in kg}}{\text{Amount of } H_2 \text{ in kg}} = \frac{28}{4} = \mathbf{7}$$

... **Ans. (c)**

From the reaction, the stoichiometric relationship between CO and CH_3OH is

1 kmol CO ≡ 1 kmol CH_3OH ... on molar basis

28 kg CO ≡ 32 kg CH_3OH ... on weight basis

i.e., to produce 32 kg CH_3OH, 28 kg CO must react

$$\therefore \quad \text{Amount of CO required to produce 1000 kg } CH_3OH = \frac{28}{32} \times 1000 = \mathbf{875\ kg}$$

... **Ans. (d)**

Example 4.2 : *Ammonia is produced by the following reaction : $N_2 + 3 H_2 \rightarrow 2 NH_3$*

Calculate : (a) The molal flow rate of hydrogen corresponding to nitrogen feed rate of 25 kmol/h if they are fed in the stoichiometric proportion.

(b) The kg of ammonia produced per hour if percent conversion is 25 and nitrogen feed rate is 25 kmol/h.

Hint : Here the basis of calculations is defined which is 25 kmol/h of N_2 fed. Write the chemical reaction ($N_2 + 3 H_2 \rightleftharpoons 2 NH_3$). Refer to the reaction. From the reaction, it is clear that the stoichiometric requirement of H_2 for 1 kmol N_2 is 3 kmol. So calculate the stoichiometric requirement of H_2 for 25 kmol/h of N_2 fed to get the answer (a).

With the help of % conversion and N_2 fed, calculate N_2 reacted. Refer to the chemical reaction. From the reaction, it is clear that 2 kmol of NH_3 will be produced from one kmol of N_2 reacted. So get the kmol NH_3 produced per hour for kmol/h N_2 reacted and convert kmol/h NH_3 to kg/h NH_3 using the molecular weight of NH_3 to get the answer (b).

Solution : Basis : 25 kmol/h of N_2 fed to the reactor.

Reaction : $N_2 + 3 H_2 \longrightarrow 2 NH_3$

Calculate the molar flow rate of H_2.

It is clear from the reaction that the stoichiometric proportion of N_2 to H_2 from the reaction is 1 : 3.

i.e., 1 kmol N_2 ≡ 3 kmol H_2

∴ The molal flow rate of hydrogen in stoichiometric proportion to the nitrogen flow rate is

... **Ans. (a)**

$$= \frac{3}{1} \times 25 = \mathbf{75\ kmol/h}$$

$$\text{Moles } N_2 \text{ reacted} = (\text{kmol } N_2 \text{ fed per hour}) \times \left(\frac{\%\text{ conversion}}{100}\right) = 25 \times \left(\frac{25}{100}\right) = 6.25 \text{ kmol/h}$$

Calculate NH_3 produced :

From the reaction, we have :

$$1 \text{ kmol } N_2 \equiv 2 \text{ kmol } NH_3 \text{ ... on molar basis}$$

i.e., 2 kmol of NH_3 will be produced when 1 kmol N_2 is reacted with 3 kmol hydrogen.

$$\therefore \quad NH_3 \text{ produced from } 6.25 \text{ kmol/h } N_2 = \frac{2}{1} \times 6.25 = 12.50 \text{ kmol/h}$$

Convert the amount of NH_3 produced from kmol to kg :

Amount of NH_3 produced = 12.50 × Molecular weight of NH_3 = 12.50 × 17 = **212.5 kg/h** ... **Ans. (b)**

Example 4.3 : *In the production of sulphur trioxide, 100 kmol of SO_2 and 200 kmol of O_2 are fed to a reactor. The product stream is found to contain 80 kmol SO_3. Find the percent conversion of SO_2.*

Hint : The basis of calculations is 100 kmol of SO_2 gas (it is defined in the statement of the problem). Write the chemical reaction involved $\left(SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3\right)$. From the reaction, it is clear that for 1 kmol SO_3 production, the stoichiometric requirement of SO_2, i.e., SO_2 required to be reacted is 1 kmol, so calculate SO_2 reacted for 80 kmol SO_3 production. Use the formula of calculating the percent conversion to get the answer.

Solution : Basis : 100 kmol of SO_2 entering the reactor.

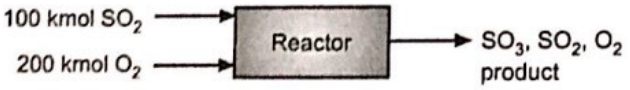

Fig. Ex 4.3 : Production of sulphur trioxide

Reaction : $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

Calculate SO_3 reacted :

From the reaction, the stoichiometric relationship between SO_2 and SO_3 is

$$\therefore \quad 1 \text{ kmol } SO_2 \equiv 1 \text{ kmol } SO_3$$

i.e., for prducing 1 kmol SO_3,1 kmol SO_2 must react by the reaction.

Amount of SO_3 in the product stream is 80 kmol.

$$\therefore \quad SO_2 \text{ reacted to produce } 80 \text{ kmol } SO_3 = 80 \times \frac{1}{1} = 80 \text{ kmol}$$

$$\%\text{ conversion of } SO_2 = \frac{\text{kmol } SO_2 \text{ reacted}}{\text{kmol } SO_2 \text{ charged}} \times 100 = \frac{80}{100} \times 100 = \mathbf{80}$$ ... **Ans.**

Example 4.4 : *In the manufacture of acetic acid by oxidation of acetaldehyde, 100 kmol of acetaldehyde is fed to a reactor per hour. The product leaving the reactor contains 14.81% acetaldehyde, 59.26% acetic acid, and the rest oxygen (on mole basis). Find the percentage conversion of acetaldehyde.*

Hint : Here the basis of calculations is defined which is 100 kmol/h of CH_3CHO fed to the reactor. Write the chemical reaction involved. We are supplied with the composition of the product stream but its amount is not known, so assume x kmol/h of the product stream. On the basis of the composition data, obtain kmol/h CH_3CHO and CH_3COOH in the product stream in the terms of x. Refer to the chemical reaction. From the reaction it is clear that for 1 kmol of CH_3COOH production, 1 kmol CH_3CHO is required to be reacted by the reaction, so calculate CH_3CHO reacted corresponding to CH_3COOH in the product stream. Take a material balance of CH_3CHO over the reactor to get x known. Then obtain kmol/h CH_3CHO reacted and use the formula of calculating the percent conversion to get the answer.

Solution : Basis : 100 kmol/h acetaldehyde charged to the reactor.

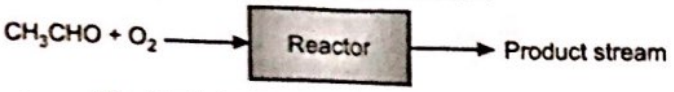

Fig. Ex 4.4 : Production of acetic acid

Reaction : $CH_3CHO + \frac{1}{2}O_2 \rightarrow CH_3COOH$

Let x be the kmol of product stream obtained per hour.

The product contains 14.81% acetaldehyde and 59.26% acetic acid by mole.

$\therefore$ Acetic acid formed = 0.5926 x kmol/h

Acetaldehyde unreacted (appearing in the product stream) = 0.1481 x kmol/h

Let us calculate acetaldehyde reacted.

From the reaction, we have

$$1 \text{ kmol } CH_3CHO \equiv 1 \text{ kmol } CH_3COOH$$

i.e., to produce 1 kmol CH_3COOH, 1 kmol CH_3CHO must react

$\therefore$ Acetaldehyde reacted to produce 0.5926 x kmol/h acetic acid $= \frac{1}{1} \times 0.5926\,x = 0.5926\,x$ kmol/h

Material Balance of CH_3CHO :

CH_3CHO fed to reactor = CH_3CHO reacted + CH_3CHO unreacted

$$100 = 0.5926\,x + 0.1481\,x$$

$$\therefore \quad x = 135 \text{ kmol/h}$$

$\therefore$ Acetaldehyde reacted = 0.5926 (135) = 80 kmol/h

$$\% \text{ conversion of acetaldehyde} = \frac{\text{acetaldehyde reacted}}{\text{acetaldehyde charged}} \times 100 = \frac{80}{100} \times 100 = \mathbf{80}$$ ... **Ans.**

Example 4.5 : *In the production of sulphur trioxide, 100 kmol of SO_2 and 100 kmol of O_2 are fed to a reactor. If the percent conversion of SO_2 is 80, calculate the composition of the product stream on mole basis.*

Hint : The basis of calculations is 100 kmol of SO_2 and 100 kmol of O_2. Write down the chemical reaction involved. With the help of % conversion, calculate kmol of SO_2 reacted. Refer to the chemical reaction for the stoichiometric proportions between SO_2 and O_2; and SO_2 and SO_3 and then calculate the kmol of O_2 reacted and SO_3 produced for kmol of SO_2 reacted. Take a material balance of SO_2 and O_2 to get kmol of SO_2 and O_2 unreacted which will appear in the product stream. Use the formula of calculating the mole % to get the answer.

Solution : Basis : 100 kmol of SO_2 and 100 kmol of O_2 charged to reactor.

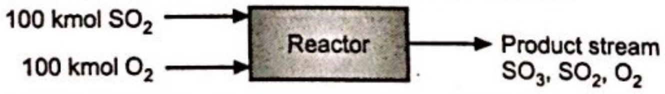

Fig. Ex 4.5 : Production of SO_3 by oxidation of SO_2

Reaction : $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

Percent conversion = 80

$$\% \text{ conversion of } SO_2 = \frac{\text{Moles of } SO_2 \text{ reacted}}{\text{Moles of } SO_2 \text{ charged}} \times 100$$

$$\therefore \quad \text{Moles of } SO_2 \text{ reacted} = \frac{\% \text{ conversion}}{100} \times \text{Moles of } SO_2 \text{ charged} = \frac{80}{100} \times 100 = 80 \text{ kmol}$$

Material Balance of SO_2 :

SO_2 charged = SO_2 reacted + SO_2 unreacted

$\therefore$ SO_2 unreacted = 100 – 80 = 20 kmol

Calculate SO_3 produced :

From the reaction, 1 kmol $SO_2 \equiv 1$ kmol SO_3

$$\therefore \quad SO_3 \text{ produced from 80 kmol } SO_2 = \frac{1}{1} \times 80 = 80 \text{ kmol}$$

Calculate O_2 reacted :

From the reaction, 1 kmol $SO_2 \equiv 0.5$ kmol O_2

$$\therefore \quad O_2 \text{ reacted with 80 kmol } SO_2 = \frac{0.5}{1} \times 80 = 40 \text{ kmol}$$

Material Balance of O_2 :

$$O_2 \text{ charged} = O_2 \text{ reacted} + O_2 \text{ unreacted}$$

$$\therefore \quad O_2 \text{ unreacted} = 100 - 40 = 60 \text{ kmol}$$

Composition of Product Stream :

Component	Quantity, kmol	Mole %
SO_2	20	12.5
SO_3	80	50.0
O_2	60	37.5
Total	160	100

RECYCLE OPERATIONS

5.1 RECYCLING AND RECYCLE OPERATIONS

Recycling is returning back a portion of the stream leaving a process unit to the entrance of the process unit for further processing (along with the fresh stream entering the process unit).

Recycling operations, commonly encountered in unit operations and unit processes (chemical reactions), are performed for :

(i) Maximum utilisation of the valuable reactants (so that the loss of reactants is minimised).
(ii) Improvement of the performance of the equipment/operation.
(iii) Utilisation of the heat being lost in the exit stream (conservation of heat).
(iv) Better operating conditions of the system, such as temperature, concentration, etc.
(v) Improvement of the selectivity of a product.
(vi) Maintaining process rate at a high value.
(vii) Enrichment of a product.

- In distillation operations, a part of the distillate is fed back/returned back (as reflux) to the column to enrich the product, so that almost pure product can be obtained.
- In drying operations, a major portion of the hot air leaving the dryer is recirculated to conserve heat - to utilise the heat being lost in the exit air.
- In the manufacture of methanol, the gas mixture leaving the reactor after separating it from the product stream is recycled to the reactor for their maximum utilisation.
- In absorption towers, better wetting of tower packings is done by recycling a part of the exit solvent stream.
- In chemical reactions, exit catalyst or spent catalyst is returned to the reactor for reuse after being regenerated.
- Recycling is extensively used in processes, such as the manufacture of methanol, ammonia, ethanol, etc. for achieving complete conversion, keeping the yield of byproduct to minimum and effecting reactions at a high rate.

A recycle stream is a process stream that returns material leaving a process unit back to the entrance of the ame unit (or to a process unit which is at the upstream of the process unit).

Recycle operations are carried out under steady-state conditions. That is, in these operations there is no build- p or depletion of material takes place inside the process or in the recycle stream.

A schematic diagram of the recycle operation is shown in Fig. 5.1.

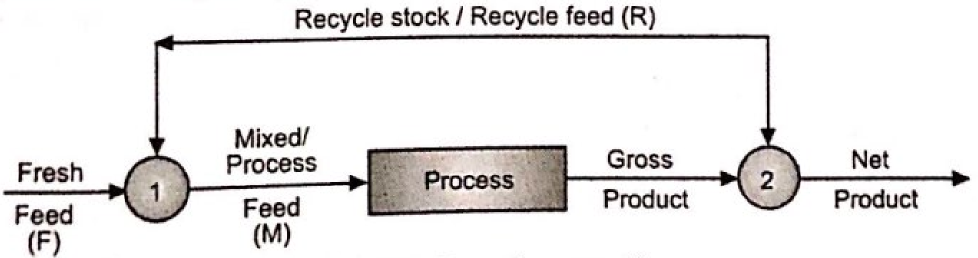

Fig. 5.1 : Recycle operation

Material balances for the recycling operation can be written :

(i) about the entire process including the recycle stream - wherein the fresh feed is equated with the net product.

(ii) about the junction point (1) at which the fresh feed combines with the recycle stream.

(iii) about the junction point (2) at which the gross product is divided into recycle and net product.

(iv) about the process itself (involving only process feed and gross product streams).

While solving the problems involving recycle, these balances can be written in terms of any one component present in the streams under consideration or in terms of streams as a whole.

Let F, R and M be the kg/h fresh feed, recycle feed and mixed feed respectively. Let A be the component present in these streams and x_F, x_R and x_M are the weight fractions of A in the respective streams. Then,

Overall material balance at the junction (1) :

$$F + R = M$$

Material balance of the component at/across/over the junction (1) :

$$x_F \cdot F + x_R \cdot R = x_M \cdot M$$

Recycle operations with chemical reactions :

In recycling operations/processes with a chemical reaction, there are two bases for the conversion, namely overall conversion and single-pass (per pass) or once-through conversion. In these operations, a process stream is recycled in order to increase the conversion of the reactant.

If A is the limiting reactant, then

$$\text{Overall fractional conversion of A} = \frac{\text{A in fresh feed} - \text{A in output of the overall process}}{\text{A in fresh feed}}$$

$$\text{\% overall conversion of A} = \text{Overall fractional conversion of A} \times 100$$

$$\text{Per pass fractional conversion of A} = \frac{\text{A in feed to the reactor} - \text{A in exit stream from the reactor}}{\text{A in feed to the reactor}}$$

$$\text{\% per pass conversion} = \text{per pass fractional conversion} \times 100$$

Per pass conversion is also termed as single-pass conversion.

$$\text{Single-pass conversion} = \frac{\text{reactant input to the reactor} - \text{reactant output from the reactor}}{\text{reactant input to the reactor}}$$

$$\text{Overall conversion} = \frac{\text{reactant input to the process} - \text{reactant output from the process}}{\text{reactant input to the process}}$$

Note that : reactant input to the reactor = reactant in the mixed feed

reactant input to the process = reactant in the fresh feed

reactant output from the process = reactant in the product stream leaving the overall process.

reactant output from the reactant = reactant in the stream leaving the reactor.

Single-pass conversion gives the fraction of the reactant converted on a single pass through the reactor whereas the overall conversion gives the fraction of the reactant converted by the process as a whole.

Note that the feed to the reactor is the mixed feed. The above equations are valid on a weight basis as well as on a mole basis.

For the amounts of reactant A as given below the per pass and the overall conversions of A are :

A in the fresh feed = 40 mol, A in the mixed feed = 160 mol,

A in the exit stream from the reactor = 125 mol,

A in the output of the overall process/in the net product = 5 mol.

The overall conversion of A is : $\left(\frac{40-5}{40}\right) \times 100 = 87.5\%$.

The per pass conversion of A is : $\left(\frac{160-125}{160}\right) \times 100 = 21.87\%$.

5.2 PURGING OPERATION

In this operation, a fraction (or portion) of the recycle stream is continuously bled-off in order to limit the concentration of inerts to a desired/tolerable level in the mixed stream.

Whenever some inerts are present in the fresh feed, recycling of fluid streams gradually accumulates inerts in the recycle stream (hence in the recycle loop) and if the concentration of inerts exceeds beyond a tolerable limit/level, then they (inerts) adversely affect the conversion in the reactor (e.g., argon in the synthesis of ammonia). Consequently, the concentration of inerts in the reactor has to be controlled within specified limits. A practical approach is to purge or bleed a small fraction of the recycle stream to ensure the removal of the required quantities of inerts from the recycle loop.

For steady-state operation : inerts in purge = inerts in fresh feed ... otherwise inerts will accumulate in the recycle loop.

Purge : It is a part of recycle stream which is continuously purged (removed) to the atmosphere in order to maintain the concentration of an undesired component in the recycle loop within a tolerable limit.

Purge stream is the fraction of the recycle stream which is continuously bled-off in order to avoid an accumulation of inerts in the recycle loop.

In the synthesis of ammonia, some of the gas stream must be purged to prevent build up of Ar and CH_4.

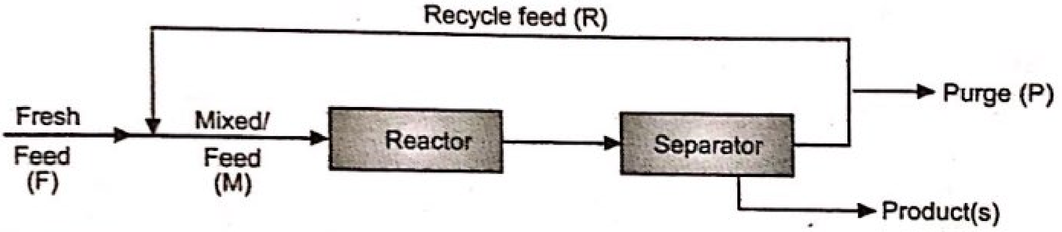

Fig. 5.2 : Recycle operation with purge stream (Process with chemical reaction)

The recycling of air/recirculation of air in the drying of solids is shown diagrammatically in Fig. 5.3.

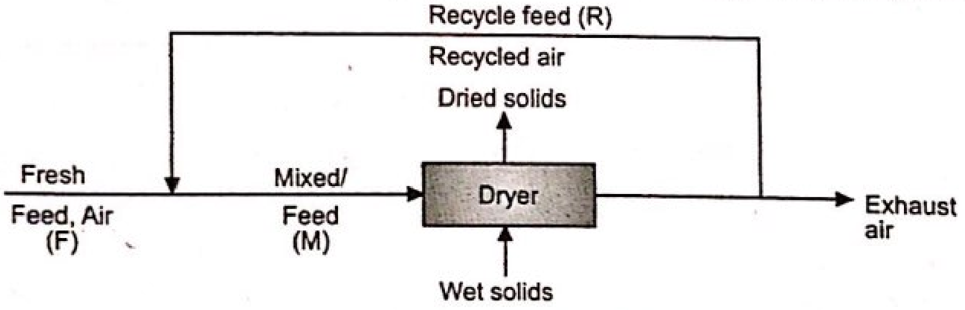

Fig. 5.3 : Drying of solids

In a recycling operation :

$$\text{Combined feed} = \text{Fresh feed} + \text{Recycle feed}$$

$$M = R + F$$

The combined feed is a mixture of the fresh feed (also called net feed) and the recycle feed/recycle stock.

$$\text{Gross product} = \text{Recycle feed} + \text{Net product}$$

The gross product is a mixture of the net product and the recycle feed.

Recycle ratio : It is the ratio of the quantity of recycle feed to the quantity of fresh feed.

$$\text{Recycle ratio} = \frac{R}{F} \quad \text{... (5.1)}$$

$$\left[\begin{array}{l}\text{Recycle ratio based} \\ \text{on any component 'A'}\end{array}\right] = \frac{\text{'A' in recycle feed}}{\text{'A' in fresh feed}} \quad \text{... (5.2)}$$

Combined feed ratio : It is the ratio of the quantity of mixed feed to the quantity of fresh feed.

$$\text{Combined feed ratio} = \frac{M}{F} \quad \text{... (5.}$$

$$\begin{bmatrix}\text{Combined feed ratio} \\ \text{based on any component 'A'}\end{bmatrix} = \frac{\text{'A' in mixed feed}}{\text{'A' in fresh feed}} \quad \text{... (5.}$$

The recycling in case of any reactor is shown in Fig. 5.4.

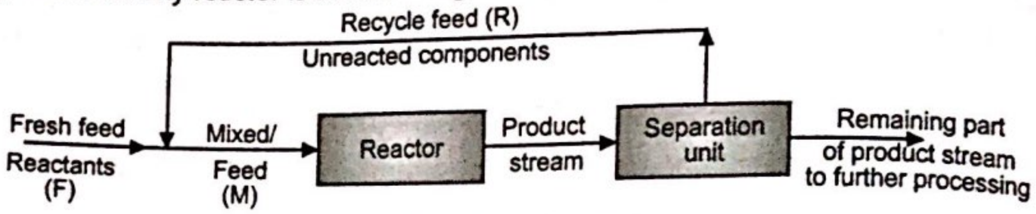

Fig. 5.4 : Recycle reactor

Purge Ratio : It is the ratio of the *quantity of purge stream to the quantity of recycle feed. It can also be expresse on the basis of a particular component present in the purge stream and recycle feed.*

$$\therefore \qquad \text{Purge ratio} = \frac{P}{R} \quad \text{... (5.5}$$

$$\begin{bmatrix}\text{Purge ratio based on} \\ \text{any component 'A'}\end{bmatrix} = \frac{\text{'A' in purge}}{\text{'A' in recycle feed}} \quad \text{... (5.6}$$

Purging can be shown diagrammatically as follows :

In the manufacture of ammonia, built up of CH_4 in the recycle loop beyond a certain tolerance limit is avoide by purging.

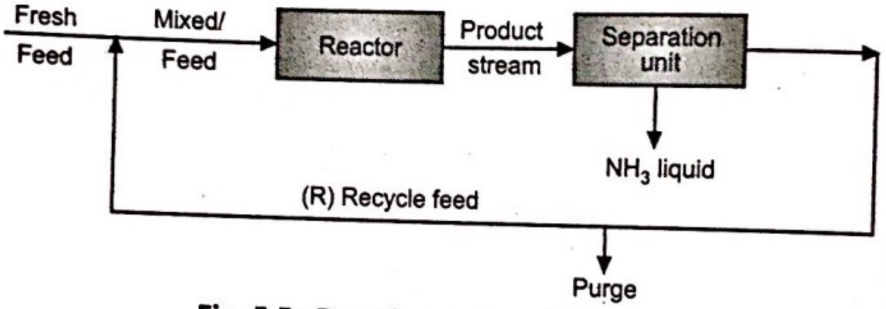

Fig. 5.5 : Recycle reactor with purge

SOLVED EXAMPLES

Example 5.1 : *A dryer is used to dry 100 kg/h wet solids from 20% to 1% moisture (by weight) by hot air. The fresh air containing 0.02 kg water vapour per kg dry air is available at 303 K (30°C) and 101.325 kPa. Air leaving the dryer is found to contain 0.1 kg water vapour per kg dry air. If the recycle ratio is maintained at 3 kg dry air in the recycle ai per kg dry air in the fresh air, calculate the volumetric flow rate of fresh air assuming the molecular weight of fresh ai to be 28.8.*

Solution : Basis : 100 kg/h wet solids.

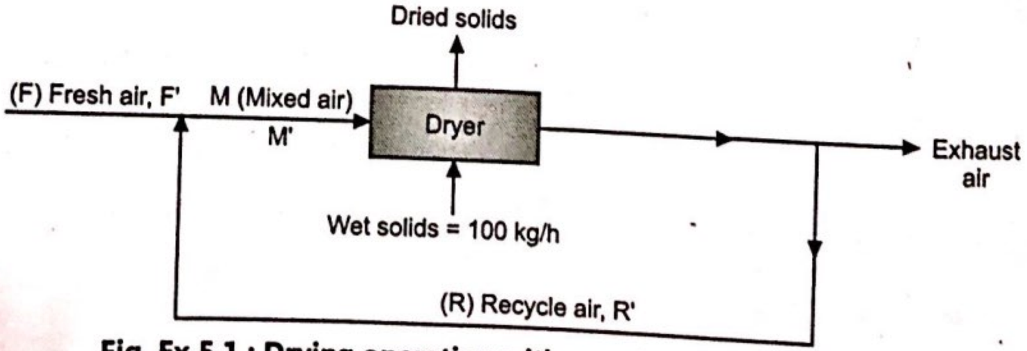

Fig. Ex 5.1 : Drying operation with recycle of drying medium

Let F', M' and R' be the kg of dry air per hour in the fresh air, mixed air and recycle air.

Material Balance of Dry Air :

$$F' + R' = M'$$

$$\text{Recycle ratio} = \frac{R'}{F'} = 3$$

$$R' = 3F'$$

$$\therefore \quad M' = 4F'$$

and

Initial moisture (water) in the wet solids = 0.2 (100) = 20 kg

Solids (bone-dry) in the wet solids = 100 − 20 = 80 kg

Let the final moisture in the product solids be y kg.

Solids (dried) contain 1% moisture.

$$\therefore \quad \left(\frac{y}{80 + y}\right) \times 100 = 1.0$$

$$\therefore \quad y = 0.81 \text{ kg}$$

Moisture removed from the solids = 20 − 0.81 = 19.19 kg/h

Let the moisture in the mixed air be $x \dfrac{\text{kg water}}{\text{kg dry air}}$

Moisture / Water Balance at inlet to the Dryer :

Moisture in mixed air = Moisture in fresh air + Moisture in recycle air

$$x \cdot M' = 0.02\,F' + 0.1\,R'$$

$$= 0.02\,F' + 0.1 \times 3F' \text{ ...... (as } R' = 3\,F')$$

$$\therefore \quad x \cdot M' = 0.32\,F'$$

We have, $M' = 4F'$

$$\therefore \quad x\,(4F') = 0.32\,F'$$

$$\therefore \quad x = 0.08$$

Material Balance of Moisture over Dryer :

Moisture gained by air = Moisture removed from solids

$$0.1\,M' - 0.08\,M' = 19.19$$

$$\therefore \quad M' = 959.5 \text{ kg/h}$$

We have, $M' = 4F'$

$$\therefore \quad F' = 959.5/4 = 239.8 \text{ kg/h}$$

Water associated with dry air in the fresh air $= \dfrac{0.02}{1} \times 239.8 = 4.8$ kg/h

∴ Fresh air fed to the dryer = 239.8 + 4.8 = 244.6 kg/h

Moles/h fresh air entering the dryer = n'

$$\therefore \quad n' = \frac{244.6}{28.8} = 8.5 \text{ kmol/h}$$

If V' is the volumetric flow rate of the fresh air, then

$$V' = \frac{n'RT}{P}$$

where, n' = 8.5 kmol/h, P = 101.325 kPa, R = 8.31451 $m^3 \cdot kPa/(kmol \cdot K)$, T = 303 K

∴ Volumetric flow rate of the fresh air $= \dfrac{8.5 \times 8.31451 \times 303}{101.325}$ = **211.34 m³/h** ... **Ans.**