

## PART I: Manufacture of Salicylic acid

### CHAPTER 1

#### Introduction

Salicylic Acid is a primary ingredient in many organic synthesis and pharmaceutical compounds. This thesis is a study on the industrial manufacturing process of Salicylic acid and design of an economic production plant with aid of material, energy and cost balance. In this chapter, general introduction to the chemical compound, its properties, occurrences, uses and synthetic manufacturing process are discussed.

#### 1.1. General Description of the compound:

Salicylic acid is a monohydroxybenzoic acid, a type of phenolic acid and a beta hydroxy acid. This colourless crystalline organic acid is widely used in organic synthesis and functions as a plant hormone. It is derived from the metabolism of Salicin. In addition to being an important active metabolite of aspirin, which acts in part as *prodrug* to Salicylic acid, it is probably best known for its use as a key ingredient in topical anti-acne products. The salts and esters of salicylic acid are known as Salicylates.

It has a formula of  $C_6H_4(OH)COOH$ , where the alcohol group ( -OH) is ortho to the carboxyl group. It is also known as 2-hydroxybenzoic acid. It is poorly soluble in water (2 g/L at 20°C). Aspirin is one of the many significant products with Salicylic acid as its precursor.

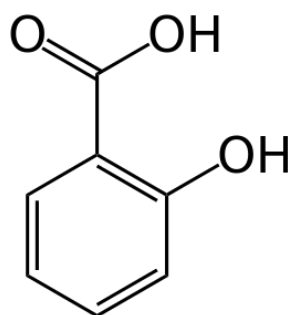


Fig 1.1: Chemical Structure of Salicylic acid

## **1.2. Occurrences**

Salicylic acid is a phenolic phytohormone and is found in plants with plant roles in growth and development, photosynthesis, transpiration, ion uptake and transport. Unripe fruits and vegetables are natural sources of Salicylic acid, particularly blueberries, blackberries, cantaloupes, dates, raisins, kiwi fruits, guavas, apricots, green pepper, olives, tomatoes, radish and chicory; also mushrooms. Some herbs and spices contain high amounts, while meat, poultry, fish, eggs and dairy products all have little to no Salicylates. Of the legumes, seeds, nuts and cereals, only almonds, water chestnuts and peanuts have significant amounts.

## **1.3. Physical Properties**

Chemical Formula	:	$C_7H_6O_3$
Molar Mass	:	138.12 g/mol
Density	:	1.443 g/cm <sup>3</sup>
Appearance	:	Colourless to white crystals
Odour	:	Odourless
Solubility in water	:	2g/L at 20°C
Solubility in other Chemicals	:	Ether, Benzene, Carbon tetrachloride, Ethanol, Toluene
Boiling Point	:	211°C
Flash Point	:	157°C
Sublimation Point	:	76°C
Heat of Sublimation	:	81.8 kJ/mol
Dissociation constants:		$K_1 = 1.05 \times 10^{-3}$ $K_2 = 4.0 \times 10^{-14}$ (19 °C)
Vapour pressure	:	1.66 mbar (110 °C) and 19.3 mbar (150 °C)

#### **1.4. Chemical Properties**

The difunctional Salicylic acid molecule combines the properties of phenols with those of aromatic carboxylic acids. It is esterified by alcohols in the presence of strong acids without significant etherification. Combined ether-ester can be prepared from dialkali salicylate in the presence of alkyl halide; these are converted by alkaline hydrolysis into the corresponding alkoxybenzoic acids. The phenolic OH group is etherified by an alkaline aqueous solution of dialkyl sulfate, and esterified by the action of acyl halides or acid anhydrides. Catalytic hydrogenation of salicylic acid esters over Raney nickel produces esters of *cis-trans*-2-hydroxycyclohexane carboxylic acid.

Since electrophilic reactants attack the less sterically hindered 5-position in preference to the 3-position, it is possible to obtain either 5-substituted or 3, 5-disubstituted derivatives directly. Derivatives substituted exclusively at the 3-position are obtained by indirect means, such as substitution of sulfosalicylic acid at the 5-position, followed by elimination of the sulfonic group. More severe conditions may lead to decarboxylation as well. Thus, 2,4,6-trinitrophenol (picric acid) is obtained upon treatment of salicylic acid with fuming Nitric acid and Tribromophenol results from treatment with bromine in the presence of water. When heated at or above its melting point Salicylic acid decomposes into phenol and carbon dioxide. Under a carbon dioxide atmosphere at 230 °C the main product is phenyl salicylate. At 250 °C, Xanthone is formed in parallel with phenol.

#### **1.5. Uses**

Salicylic acid is used in pharmaceutical and cosmetic applications, in many skin-care products both as a keratolytic and comedolytic agent. It is also used in chemical synthesis as a starting material for the synthesis of active pharmaceutical ingredients such as in Aspirin.

**Cosmetic Use:** Salicylic acid is used as preservative (up to 0.5 %) in cosmetic products. At a level up to 1 % in leave-on hair products and up to 2 % salicylic acid is used in leave-on cosmetics products (face and general creams) for its exfoliating and

cleansing properties and in rinse-off products (shower gels, shampoos, hair conditioners, make-up removers).

**Dermatological Uses:** Salicylic acid is widely used in the treatment of many common dermatological conditions because of its keratoplastic properties.

**Other Uses:** Salicylic acid is used: as a preservative in food, as a chemical raw material for the synthesis of dye and salicylates derivatives (aspirin), as an antiseptic and antifungal by topical application in veterinary medicine.

### 1.6. Industrial Synthesis of Salicylic acid

Sodium salicylate is commercially prepared by treating Sodium phenoxide with Carbon dioxide at high pressure (100 atm) and high temperature (390 K) using a method known as Kolbe-Schmitt reaction. The product is acidified using Sulphuric acid to produce Salicylic acid.

The main chemical reaction towards the production of Salicylic acid is shown below-

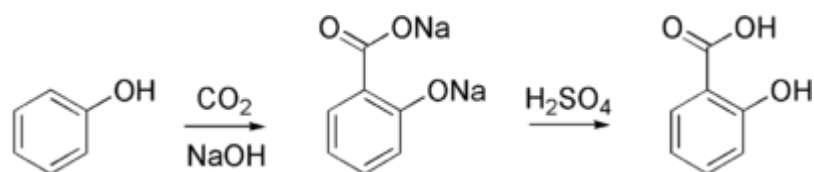


Fig. 1.2 Chemical Reaction in Salicylic acid Production

This reaction has a yield range of 40-59% in low pressures while on application of high pressure; the yield has been noted around 90%. It is usually conducted as a batch-wise operation in the industries.

## CHAPTER 2

### Literature Survey

#### 2.1. Methods of Production of Salicylic acid

Salicylic acid is found in various forms in nature but these cannot be efficiently harnessed. There are several methods by which it can be prepared synthetically to produce Salicylic acid of significant purity and yield. The following are a few methods-

- i. Oxidation of, or by fusion with Potassium hydroxide, or by electrolysis of one of the following substances- Salicin, Salicylaldehyde and Saligenin
- ii. Fusing Potassium hydroxide with one of the following substances- Benzoic acid, Coumarin, Indigo, Ortho-chloro-benzoic acid, ortho-cresol-sulphonic acid
- iii. Heating ortho-diazo-amidobenzoic acid with water
- iv. Dry distillation of Calcium salt of meta-oxybenzoic acid
- v. Reaction of Potassium permanganate on the potassium salt of ortho-cresosulphonic acid
- vi. Heating phenol with carbon tetrachloride and alcoholic potash
- vii. Distillation of Sodium phenyl-carbonate in a current of carbon dioxide with Sodium phenate
- viii. Action of nitrous acid on Anthranilic acid
- ix. Electrolysis of a solution of Benzoic acid in Acetic acid
- x. Photolytic exposure of a solution of Benzoic acid in the presence of ferric salt
- xi. Passage of dry carbon dioxide into a hot mixture of Phenol and Sodium hydroxide (Kolbe-Schmitt's reaction)

Kolbe-Schmitt's Process is used widely in industries for the large-scale production of Salicylic acid. This is essentially due to the relatively easier availability and safer handling of the reactants; Carbon dioxide and Phenol.

#### 2.2. Kolbe-Schmitt Process

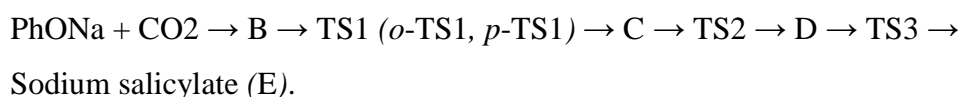
Kolbe-Schmitt reaction is the most convenient method of production of Salicylic acid. The conditions of the Kolbe-Schmitt reaction vary over a wide range, depending on the

starting alkali metal aryloxide, the procedure used for carrying out the reaction, the use of solvents or suspension media, the degree of dryness, and a few other factors. Kolbe first prepared salicylic acid by heating sodium phenoxide with carbon dioxide at atmospheric pressure, and acidifying the resulting sodium salicylate solution. Kolbe obtained yields below 50%. Schmitt later proposed a modification of the Kolbe reaction in which carbon dioxide introduced under pressure significantly improved the yield. A yield as high as 79% was reported when the operating conditions were maintained at 125 °C and Carbon dioxide pressure of 80-135 atm. This modification, known as the Kolbe–Schmitt reaction, remains the standard method for preparing a wide variety of hydroxy aromatic acids.

### **2.3. Proposed Mechanisms for Kolbe-Schmitt Reaction**

Several hypotheses have been proposed by various researchers over the years to elucidate the Kolbe-Schmitt Reaction. Following are a few proposed mechanisms-

- i. *Tijmstra* assumes a simple addition of carbon dioxide to sodium phenoxide, forming a 'phenyl sodium-σ-carbonic acid' (Ph(ONa) · COOH).
- ii. *Johnson* (1933) and *Luttringhaus* (1945) indicated that the initial chelate rearranges with the formation of a cyclic intermediate, followed by hydrogen atom migration in the synthesis of ortho substituted products.
- iii. *Kosugi* indicated that the reaction proceeded by direct carboxylation of the aromatic ring and that the PhONa.CO<sub>2</sub> complex was not an intermediate in this process. Thus, chelate formation constitutes a competing reaction with the formation of salicylic or *p*-hydroxybenzoic acid
- iv. *Markovic* employed Quantum mechanical calculations and proposed a complete mechanism with three intermediates and three transition states-



Markovic's study also provides a quantitative explanation for the low yield and equilibrium nature of Kolbe-Schmitt reaction.

## CHAPTER 3

### Industrial Process Description

#### 3.1 Unit Processes and Unit Operations

i. Mixing:

Mixing is a mechanical operation used to mix Phenol and Sodium hydroxide. Technical Phenol (39 °C) is mixed with a slight excess of Sodium hydroxide and is evaporated to dryness in equipment provided with a kneading or shearing type of agitation. After the transition from liquid to solid state occurs, the product is transferred to the autoclave for Carboxylation step and heated to 130 °C under vacuum to complete the dehydration.

ii. Autoclave Heating:

Carboxylation is carried out in the Autoclave. The dehydrated and finely divided Sodium phenate is cooled to 100 °C and treated with an excess of Carbon dioxide at about 6 atmospheric pressure. When the desired amount of Carbon dioxide has been absorbed, the autoclave is heated to 130 °C, and held at that temperature for several hours to complete the formation of Sodium salicylate. The autoclave is equipped with a plew-type agitator, and also with appropriate pressure-relieving devices to ensure safety of operation.

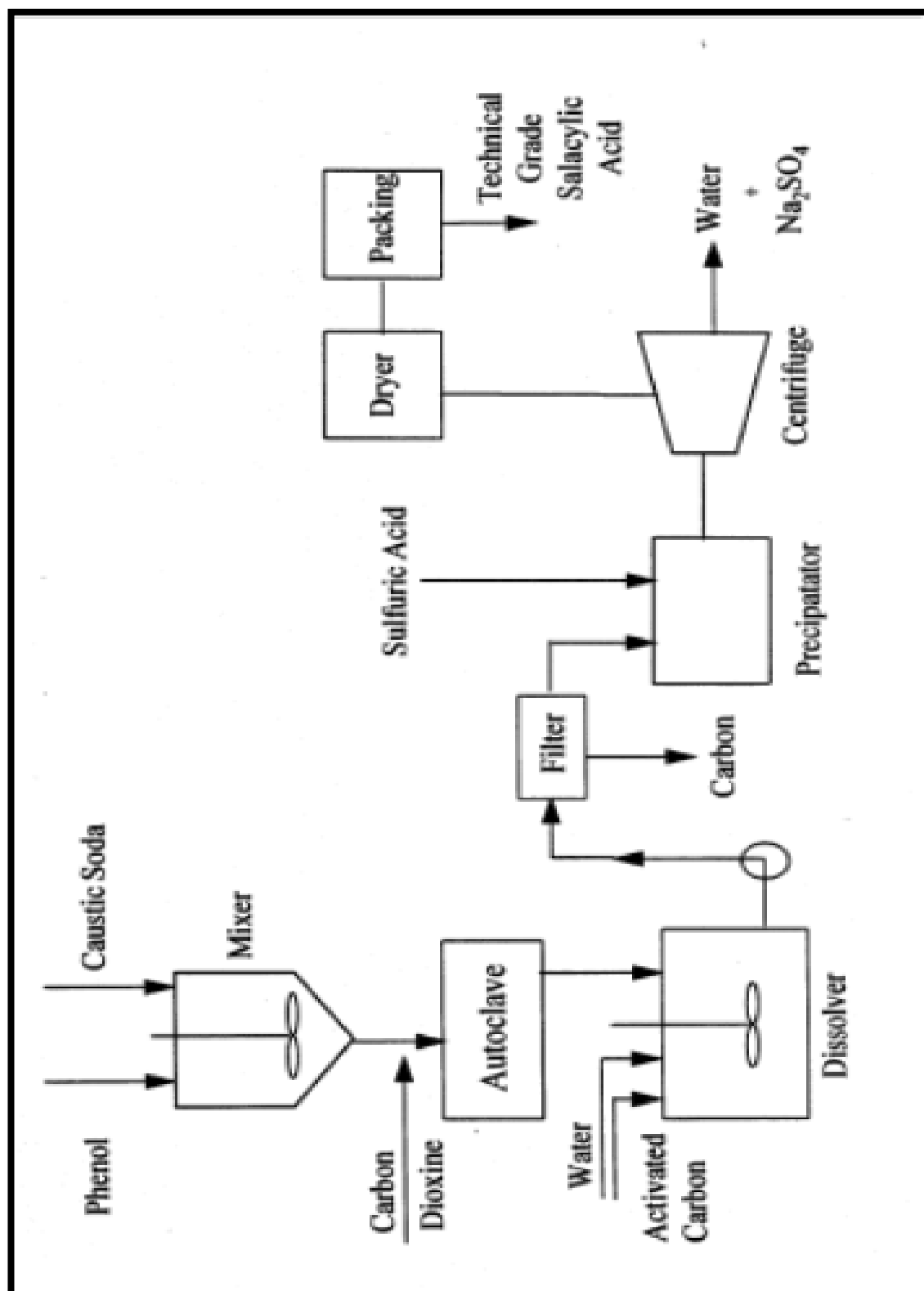
iii. Filtration and Dissolution:

Sodium salicylate is purified by dissolution followed by filtration. When carboxylation is judged to be complete, the autoclave is cooled to 100 °C and the contents are dissolved in water. The resulting solution is decolorized by filtration in the presence of a mixture of Zinc dust and Activated Carbon. It is then available for direct conversion into technical Salicylic acid. For higher purity levels of Salicylic acid, the solution can be cooled for crystallisation to be effected.

iv. Precipitation:

The clarified solution of Sodium salicylate is acidified with Sulphuric acid to precipitate Salicylic acid which is filtered on a centrifuge and dried in a rotary-

Fig. 3.1 Flowsheet for Industrial Manufacturing of Salicylic acid





dryer. It is essential to avoid contamination with Iron during these operations, and the equipment must be made of corrosion-resistant material.

v. Centrifugation:

In this stage, the salicylic acid crystals and the solution are separated with their densities as the separating factor.

vi. Drying:

The separated salicylic acid crystals are dried in a rotary-type drier in counter-current mode of operation through heat exchange with hot air. Moisture level from the crystals is decreased to dryness.

### **3.2. Selection of Equipments**

The type of reactants and products handled during the process and the operating conditions are important factors to be considered in order to select equipments. The following selections have been made for the unit operations involved in the manufacturing process-

i. Mixer: Static Mixer

Feed streams to the Mixer in the case of Salicylic acid manufacturing are liquids. Also, they are less viscous fluids. Thus, a static mixer is suitable for such operation.

Static mixer, also called motionless mixer, is in-line mixing device which consist of mixing elements inserted in a length of pipe. It consists of a stationary unit housed within a pipe. The material to be mixed is fed through the mixer via a pumping system. The material then undergoes a series of flow divisions and re-orientations as it travels down the pipe. The design of static mixers allows for continuous operation and a small working volume. Static mixer is typically used for short residence time applications. In laminar region, the mixing is independent of fluid flow rate and fluid properties. For liquid-liquid and gas –liquid dispersion mixing must occur in the turbulent region to generate sufficient mass transfer area.

ii. Filter: Cartridge Type

In filter, the Sodium phenolate solution is decolorized using activated Carbon. Cartridge filter can be used as it can house the decolorizing agent effectively.

Type of filter media : Cartridge filters

Filtration techniques : Depth bed filters

Filter cartridges consist of rolls of filter media wound so that several layers of filter media cover each other. These wound cartridges are usually contained in a housing which may hold more than one cartridge at a time. Cartridge filters may be used as surface filters or depth filters. When the cartridge is pleated, it functions as a surface filter, in which the filter media blocks the solid particles from flowing through. While when the cartridge consists of wound layers of filter media, it operates as a depth filter, in which the many layers collect the solid particles as the slurry flows through it.

iii. Centrifuge: Tubular bowl Centrifuge

Tubular bowl centrifuge can be used to separate both solid/liquid and liquid/liquid mixtures. In tubular-bowl centrifuges, feed enters from the bottom of the bowl. Since the streams to be separated are both in liquid phases, this centrifuge is appropriate for operation. Tubular-bowl centrifuges generally consist of a bowl, a motor, and a drive assembly. The bowl is suspended from an upper bearing and hangs freely. This allows the bowl to find its natural axis of rotation if it becomes unbalanced. The discharge ports at the top of the bowl are located at different radii and elevations depending on the properties of the components to be separated.

### **3.3. Quality Specifications, Storage and Environmental Protection**

**Quality Specifications:** Technical-grade salicylic acid obtained from the Kolbe – Schmitt process is extremely pure with salicylic acid content of 99.5 %; phenol, *p*-hydroxybenzoic acid, or 4-hydroxyisophthalic acid 0.05 – 0.1% (as impurity); ash <0.1 %; water 0.2 %.

**Storage and Handling:** Salicylic acid dust is combustible in air. The low combustion energy for the process indicates a high level of combustion sensitivity. Therefore,

appropriate measures are required to avoid sources of ignition and to protect against potentially severe explosive effects.

**Effect on Human Health:** The following are the Health effects of over exposure to Salicylic acid-

Eye: Causes severe eye irritation. It may result in corneal injury.

Skin: Contact with skin causes irritation and possible burns, especially if the skin is wet or moist. If absorbed, may cause symptoms similar to those for ingestion. It may cause skin rash and eruptions.

Ingestion: Causes gastrointestinal irritation with nausea, vomiting and diarrhoea. It may cause "salicylism"; characterized by headache, dizziness, ringing in the ears, hearing difficulty, visual disturbances, mental confusion, drowsiness, sweating thirst, hyperventilation, nausea, vomiting and diarrhoea. It may be harmful if swallowed. Severe salicylate intoxication may cause central nervous system disturbances such as convulsions and coma, skin eruptions, and alteration in the acid-base balance.

Inhalation: Causes irritation of the mucous membrane and upper respiratory tract.

Chronic: It may cause reproductive and foetal effects. Laboratory experiments have resulted in mutagenic effects. Also, it may cause salicylism with effects similar to those of skin absorption and damage to kidneys and pancreas.

**Environmental Effects:**

Salicylic acid is readily biodegradable and slightly bioaccumulable. It is readily soluble in water and hence has certain potential to add to the aquatic toxicity. However, there has been minimum toxicity reported to the aquatic organisms. Salicylic acid is susceptible to volatilization and thus requires careful disposal. Based on its impact on the environment, it is classified as harmless.

## CHAPTER 4

### Material and Energy Balance

#### 4.1 Material Balance

**Basis- 0.5 ton/day of Salicylic Acid**

Raw Materials Required-

Phenol - 800 kg

Caustic Soda - 350 kg

4.1.1. Material Balance across Mixer:

Reaction in Mixer-

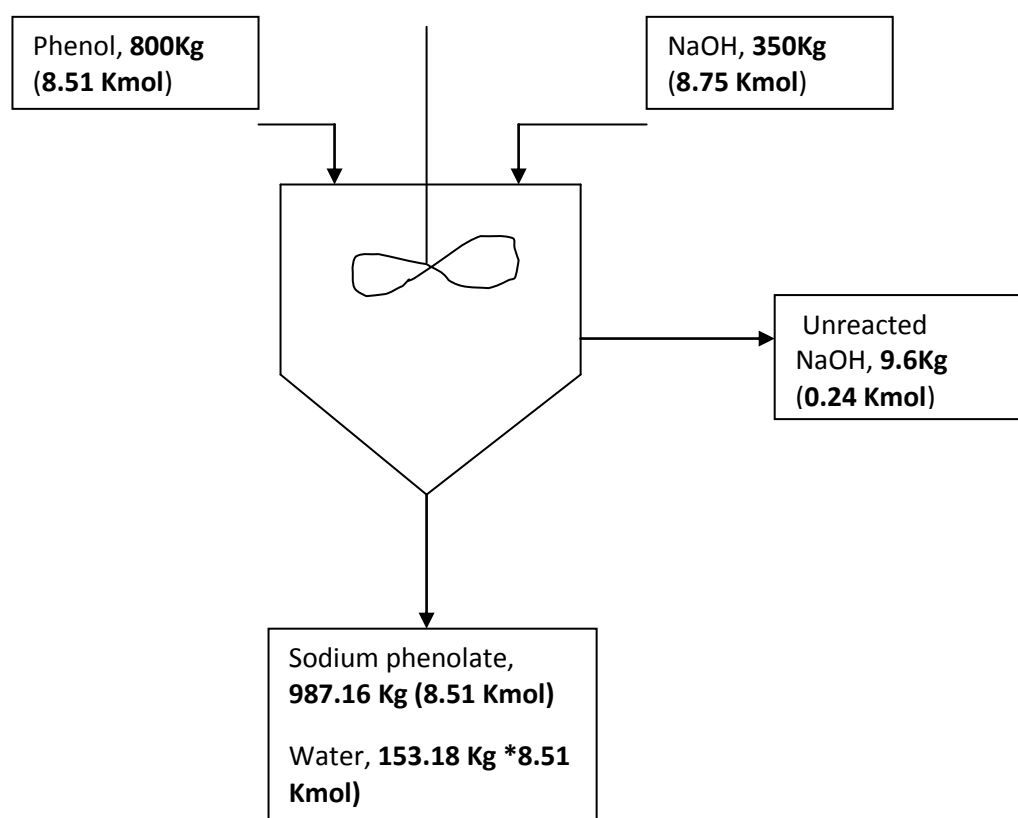
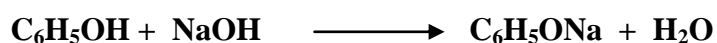


Fig. 4.1 Schematic Diagram of Material Balance across Mixer

1 mole of Phenol reacts with 1 mole of Caustic Soda to give 1 mole of Sodium phenolate

**Molecular Weight of Phenol = 94 kg/Kmol**

**Molecular Weight of Caustic soda = 40 Kg/Kmol**

⇒ No. of moles in 800 Kg of Phenol =  $800/94 = 8.51 \text{ Kmol}$

According to the Stoichiometry of the reaction, it is found that Phenol is the limiting reagent. Thus, 8.51 Kmol of Phenol will react with 8.51 Kmol of Caustic soda only, while leaving 0.24 Kmol of unreacted Caustic soda.

Amount of NaOH reacting =  $8.51 \text{ Kmol} * 40 = 340.4 \text{ Kg}$

Amount of unreacted NaOH =  $0.24 * 40 = 9.6 \text{ Kg}$

Chemical	Mass In (in Kg)	Mass Out (in Kg)
Phenol	800	-
Caustic Soda	350	9.6
Sodium phenolate	-	987.15
Water	-	153.18
<b>Total</b>	<b>1150</b>	<b>1149.94</b>

Table 4.1. Material Balance across Mixer

#### 4.1.2. Material balance in an autoclave

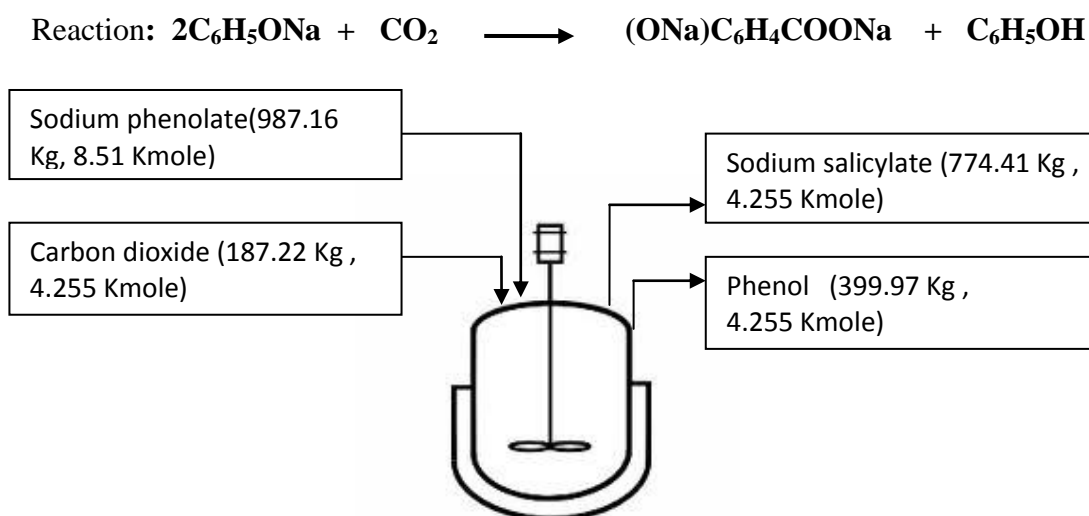


Fig 4.2. Schematic Diagram of Material Balance across Autoclave

The Sodium phenolate is dried in an autoclave to finely divided powder. The autoclave is a revolving, heated ball mill. It operates under vacuum and 130deg C. Carbon dioxide gas is introduced under pressure (700 kPa) and temperature (100 deg C). Sodium phenol carbonate is formed and this isomerizes to Sodium salicylate. Phenol is regenerated and recovered.

**Molecular weight of sodium phenolate is 116 Kg/ Kmole.**

**Molecular weight of sodium salicylate is 182 Kg/ Kmole.**

**Molecular weight of phenol is 94 Kg/ Kmole.**

According to the stiochiometric equation, 2 Kmole of sodium phenolate reacts with 1 Kmole of carbon dioxide to give 1 Kmole of sodium salicylate and 1 Kmole of phenol. therefore 8.51 Kmole of sodium phenolate reacts with (8.51/2) 4.255 Kmole of carbon dioxide to give 4.255 Kmole of sodium salicylate and 4.255 Kmole of phenol.

Chemicals	Mass in ( in kg)	Mass out ( in Kg)
sodium phenolate	987.16	-
carbon dioxide	187.22	-
sodium salicylate	-	774.41
Phenol	-	399.97
TOTAL	1174.38	1174.38

Table 4.2. Material Balance across Autoclave

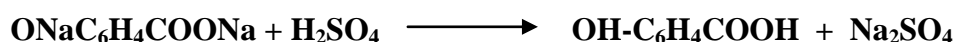
#### 4.1.3. Dissolver and Filter

Water dissolves the Sodium salicylate and activated carbon (~20 Kg) is added to remove any colour by adsorption. The solid activated carbon is removed in the filter.

**Amount of water used = 971.41 Kg**

#### 4.1.4. Material Balance across Precipitator

Reaction in Precipitator-



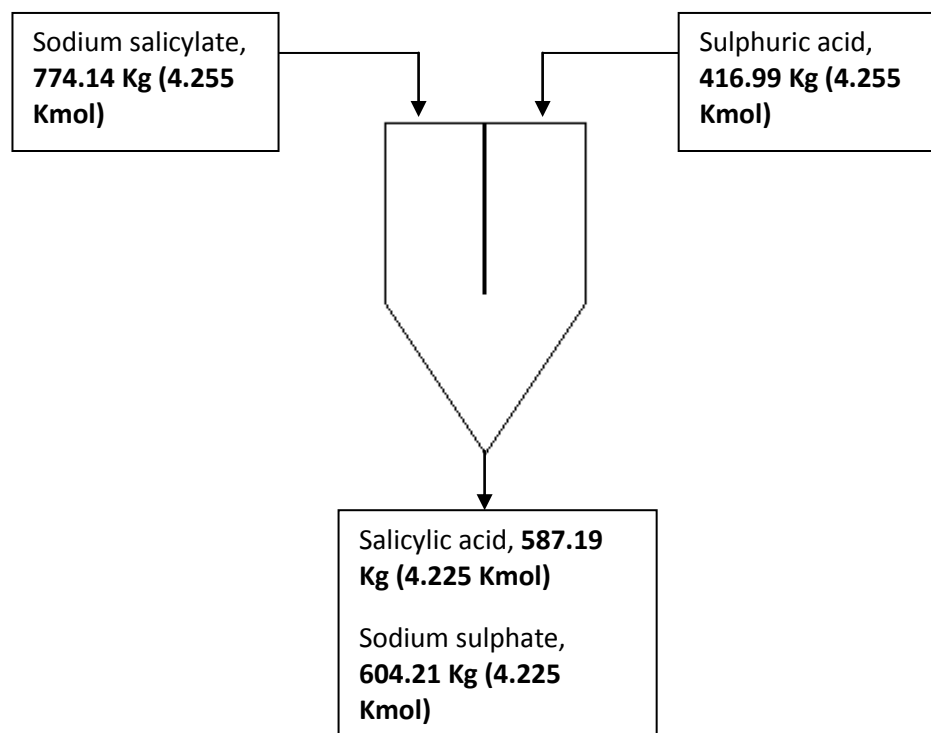


Fig. 4.3 Schematic Diagram of Material Balance across Precipitator

Sodium salicylate solution is mixed with Sulphuric acid which precipitates Salicylic acid along with the formation of Sodium sulphate.

**Molecular weight of Sodium salicylate = 182 Kg/ Kmol**

**Molecular weight of Sulphuric acid = 98 Kg/ Kmol**

**Molecular weight of Salicylic acid = 138 Kg/ Kmol**

Chemical	Mass In (in Kg)	Mass Out (in Kg)
Sodium salicylate	774.14	-
Sulphuric acid	416.99	-
Sodium phenolate	-	587.19
Sodium sulphate	-	604.21
Water	971.41	971.41
<b>Total</b>	<b>2162.82</b>	<b>2162.55</b>

Table 4.3. Material Balance across Precipitator

#### 4.1.5. Material Balance across Centrifuge

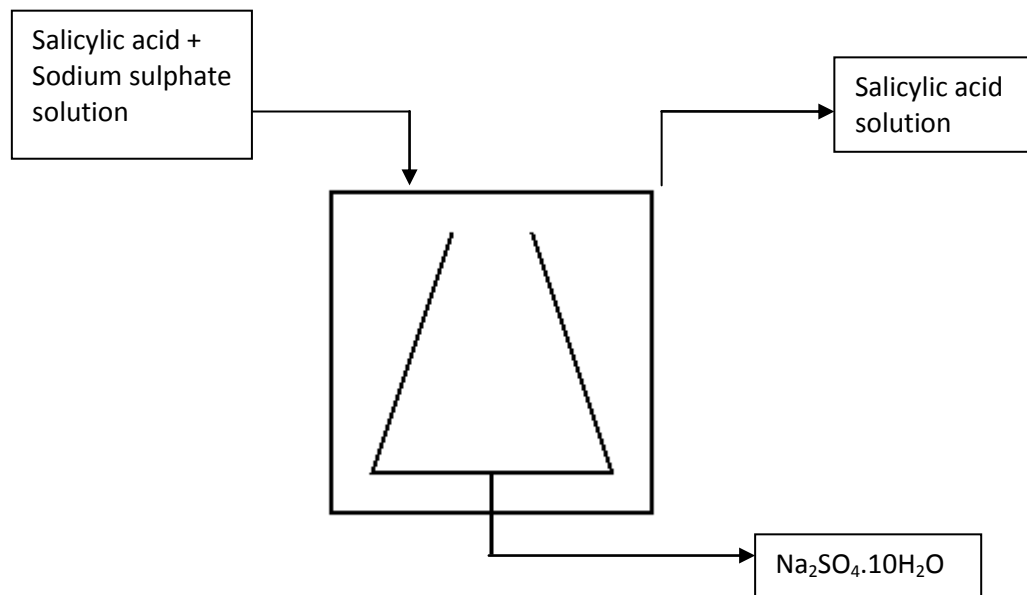


Fig. 4.4 Schematic Diagram of Material Balance across Centrifuge

Precipitated Salicylic acid is removed from the Sodium sulphate solution. Sodium sulphate is removed with water of crystallisation and Salicylic acid solution

Sodium sulphate is removed in the form of Glauber's salt.

4.225 Kmol of Sodium sulphate enters the centrifuge and must be separated from Salicylic acid solution in the centrifuge.

1 mole of Glauber's salt contains 1 mole of dehydrated Sodium sulphate with 10 molecules of water of crystallisation.

Hence, 4.225 Kmol of Sodium sulphate will be present with 42.25 Kmol of water of crystallisation.

Hence, mass of water separated with Glauber's salt =  $42.25 \text{ Kmol} \times 18 = \mathbf{765.9 \text{ Kg}}$

Assuming Salicylic acid enters dryer with a moisture content of 35%, the amount of water in Salicylic acid solution at the outlet of centrifuge is given by-

$$0.35 = (\text{moisture content})/(\text{dry bone weight of salicylic acid solution})$$



$$\Rightarrow 0.35 = \text{Moisture content}/587.19$$

$$\Rightarrow \text{Moisture content} = \mathbf{205.52 \text{ Kg}}$$

Chemical	Mass In (in Kg)	Mass Out (in Kg)
Salicylic acid (dry)	587.19	587.19
Water	971.41	205.516
Sodium sulphate	604.21	-
Sodium sulphate as Glauber's salt	-	1370.11
<b>Total</b>	<b>2162.81</b>	<b>2162.816</b>

Table 4.4. Material Balance across Centrifuge

#### 4.1.6. Material balance in a drier

35 % of moisture in the salicylic acid slurry is reduced to 10 % in the industrial drier.

Salicylic acid is purified by sublimation and then sent to packing.

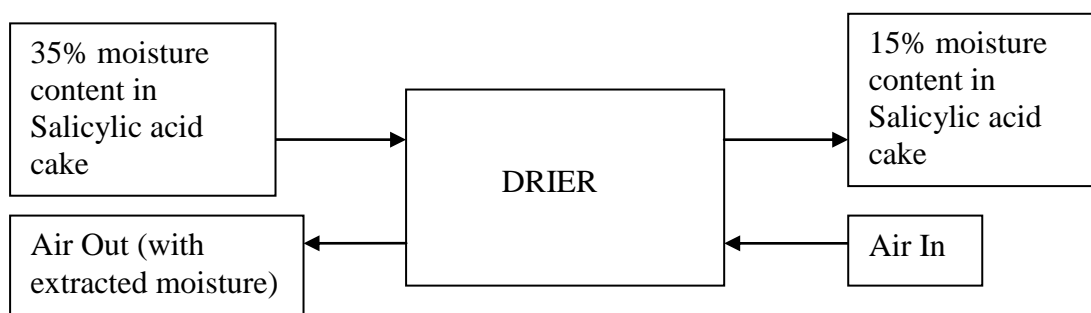


Fig. 4.5 Schematic Diagram of Flow of Materials across Drier

$$\text{Amount of moisture at entry} = 205.52 \text{ Kg}$$

$$\text{Amount of moisture at entry} = 0.1 \times 587.19 = 58.719 \text{ Kg}$$

$$\text{Amount of moisture removed} = 205.52 - 58.719 = 146.801 \text{ Kg}$$

## 4.2. Heat Balance:

### 4.2.1. Heat balance across Mixer:

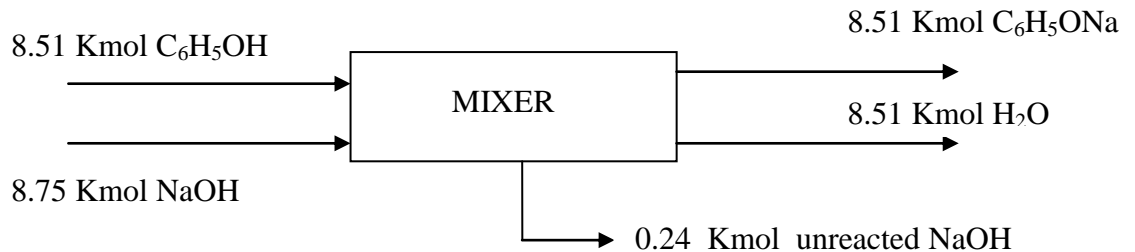
Conditions:

Inlet feed temperature = 39 °C ;                      Reaction temperature=39 °C

Outlet temperature=130 °C ;                      Reference Temperature = 25 °C

Equation for Heat conservation:

$$\text{Heat Input} + \text{Heat supplied} = \text{Heat Output}$$



Heat Input:

$$\Delta T = T_{\text{feed}} - T_{\text{ref}} = 39^{\circ}\text{C} - 25^{\circ}\text{C} = 14^{\circ}\text{C}$$

$$\begin{aligned} &= mC_p \Delta T_{(\text{C}_6\text{H}_5\text{OH})} + mC_p \Delta T_{(\text{NaOH})} \\ &= [(8.51 * 10^3 * 106.57 * 14) + (8.75 * 10^3 * 87.29 * 14)] \\ &= 2.3389 * 10^7 \text{ J/day} \end{aligned}$$

Heat Output:

$$\Delta T = T_{\text{outlet}} - T_{\text{ref}} = 130^{\circ}\text{C} - 25^{\circ}\text{C} = 105^{\circ}\text{C}$$

$$\begin{aligned} &= mC_p \Delta T_{(\text{C}_6\text{H}_5\text{ONa})} + mC_p \Delta T_{(\text{H}_2\text{O})} + mC_p \Delta T_{(\text{unreacted NaOH})} \\ &= [(8.51 * 10^3 * 126 * 105) + (8.51 * 10^3 * 36.35 * 105) + (0.24 * 10^3 * 86.9 * 105)] \\ &= 1.4725 * 10^8 \text{ J/day} \end{aligned}$$

Heat Supplied = Heat Output - Heat Input

$$= 1.4725 * 10^8 - 2.3389 * 10^7 = 1.2386 * 10^8 \text{ J/day}$$

To calculate the amount of steam required to supply the required heat,

$$\text{Heat Supplied} = 1.2386 * 10^8 = m * \lambda_{\text{steam}}$$

$$\lambda_{\text{steam at } 130^{\circ}\text{C}} = 2687 \text{ KJ/Kg}$$

$$m = 1.2386 * 10^8 / (2687 * 10^3) = 46.099 \text{ Kg}$$

**Quantity of Steam to be supplied= 46.1 Kg/day**

#### 4.2.2. Heat balance across Autoclave:



Conditions:

Inlet feed temperature = 130 °C

Reaction temperature=100 °C

Outlet temperature =100 °C

Reference Temperature = 25 °C

Equation for Energy conservation,

$$\text{Heat Input} = \text{Heat Output} + \text{Heat Removed}$$

Heat Input:

$$\Delta T = T_{\text{Outlet}} - T_{\text{ref}} = 130\text{ }^{\circ}\text{C} - 25\text{ }^{\circ}\text{C} = 105\text{ }^{\circ}\text{C}$$

$$\begin{aligned} &= mC_p \Delta T_{(\text{C}_6\text{H}_5\text{ONa})} + mC_p \Delta T_{(\text{CO}_2)} \\ &= [(8.51 \times 10^3 \times 126 \times 105) + (4.255 \times 10^3 \times 105 \times 42.28)] \\ &= 1.3147 \times 10^8 \text{ J/day} \end{aligned}$$

Heat Output:

$$\begin{aligned} &mC_p \Delta T_{(\text{C}_6\text{H}_4(\text{OH})\text{COONa})} + mC_p \Delta T_{(\text{C}_6\text{H}_5\text{OH})} \\ &= [(4.255 \times 10^3 \times 75 \times 243.64) + (4.255 \times 10^3 \times 75 \times 121.36)] \\ &= 1.1648 \times 10^8 \text{ J/day} \end{aligned}$$

Heat Removed = Heat Input – Heat Output

$$\begin{aligned} &= 1.3147 \times 10^8 - 1.1648 \times 10^8 \text{ J/day} \\ &= 1.4996 \times 10^7 \text{ J/day} \end{aligned}$$

To calculate the amount of water required to remove heat,

$$\begin{aligned} mC_p \Delta T_{\text{water}} &= 1.4996 \times 10^7 \\ m \times 4.18 \times (86 - 30) &= 1.4996 \times 10^7 \end{aligned}$$

**m=64,080 Kg/day of water is required for cooling**

#### 4.2.3. Heat Balance across Drier:

Inlet Temperature of Salicylic acid crystals = 30 °C

Outlet Temperature of Salicylic acid crystals = 110 °C

Inlet Temperature of Air = 135 °C

Outlet Temperature of Air = 60 °C

The quantity of heat  $Q$  to be transferred is calculated from the following three principal terms.

1. The energy necessary to heat the given weight of air is given by:

$$Q_1 = M \times C \times (t_1 - t_0)$$

$M$  = amount of air entering = 221.5 kg/hr

$C$  = specific heat of air = 1.013 kJ/kg-K

Therefore  $Q_1 = 221.5 \times 1.013 \times (135 - 60) = 16828.4625$  KJ/hr

2. The heat necessary to evaporate the water contained in Salicylic acid is given by:

$$Q_2 = m \times [\lambda + C_p \times (t_1 - t_0)]$$

$m$  = amount of water evaporated = 5.73 kg/hr

Thus  $Q_2 = 5.73 \times [2257 + 4.219 \times 75]$

$$= 14745.72 \text{ kJ/hr}$$

3. The heat necessary to heat the vapour contained in the weight  $M$  of air, assumed

saturated is given by

$$Q_3 = M \times H_0 \times C \times (t_1 - t_0)$$

$C$  = specific heat of vapour = 1.16 kJ/kg°K

$H_0$  = it is expressed as kg of water per kg of air = 0.015

Therefore  $Q_3 = 221.5 \times 0.015 \times 1.16 \times 75 = 289.0575$  kJ/hr

The heat lost to ambient air is taken into account by writing the expression for  $Q$  as follows (Adding 25% for possible heat losses) :

$$Q = 1.25 \times (Q_1 + Q_2 + Q_3)$$

$$= 1.25 \times (16828.4625 + 14745.72 + 289.0575)$$

$$= 39829.05 \text{ kJ/hr}$$

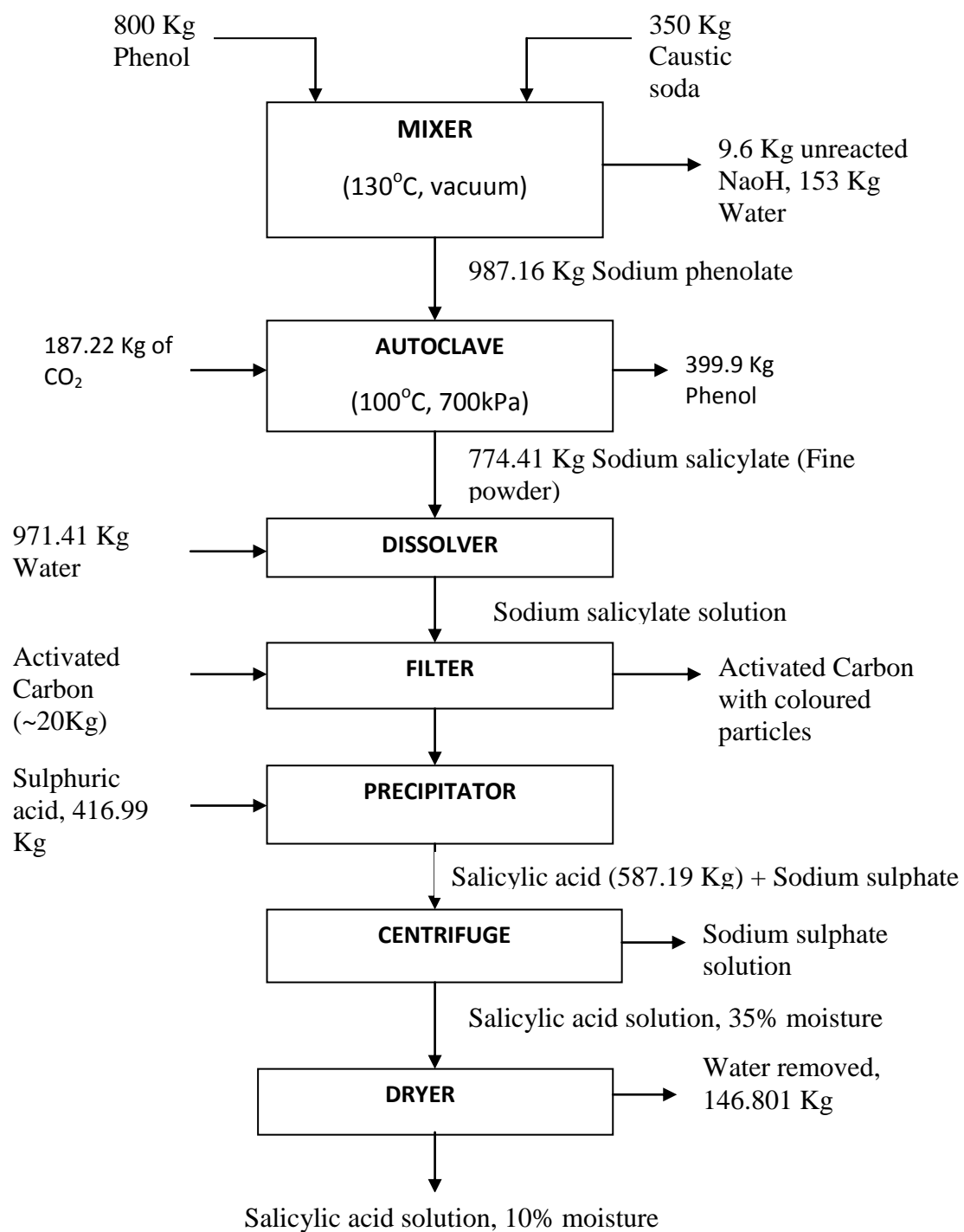


Fig.4.6 Flow of materials through various stages in manufacturing of Salicylic acid

## CHAPTER 5

### DESIGN OF EQUIPMENT

#### 5.1 Drier

Basis of calculation is 1 hr operation

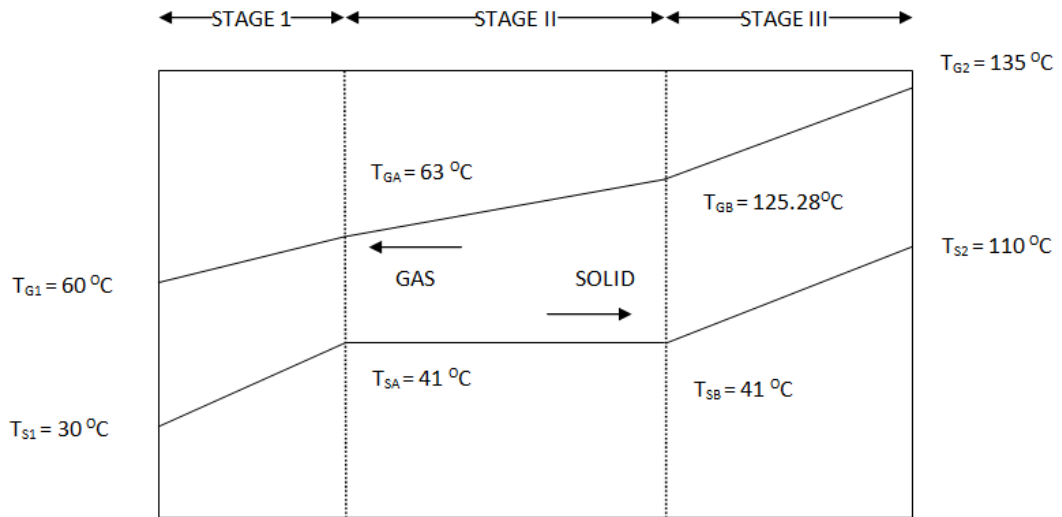


Fig. 5.1 Stages of Drying and Corresponding Temperatures

Production Rate = 587.19 kg/ day of Salicylic acid  
 =24.46 kg/hr

Solid contains 35% initial moisture

Mass of dry solid =  $M_S = 24.47 (1-0.35) = 15.91$  kg/hr

Moisture in the wet solid =  $X_1 = 35/65 = 0.54$

Moisture in the dry solid =  $X_2 = 0.15/0.85 = 0.018$

Water evaporated, mS, evaporated =  $M_S (X_1 - X_2)$   
 =  $15.91 (0.54 - 0.18) = 5.73$  Kg

Given data:

$T_{S1} = 30$  °C

$T_{G2} = 135$  °C

$Y_2 = 0.015$  kg/kg

$C_{PS} = 1.16$  KJ/kg-K

Let us assume that the exit temperature of the gas is  $T_{G1} = 60^\circ\text{C}$  and for solid  $T_{S2} = 110^\circ\text{C}$

Now enthalpy of different streams (Assuming Reference Temperature =  $0^\circ\text{C}$ )

$$\begin{aligned} H_{S1} &= [C_{PS} + (4.187) * X_1] [T_{S1} - 0] \\ &= [1.16 + (4.187) * 0.54] [30 - 0] = 102.62 \text{ KJ/kg dry air} \end{aligned}$$

$$\begin{aligned} H_{S2} &= [C_{PS} + (4.187) * X_2] [T_{S2} - 0] \\ &= [1.16 + (4.187) * 0.18] [110 - 0] = 210.503 \text{ KJ/kg dry solid} \end{aligned}$$

$$H_{g2} = [1.005 + (1.88) 0.015] [135 - 0] + (0.015) (2500) = 177 \text{ KJ/kg}$$

$$H_{g1} = [1.005 + (1.88) Y_1] [60 - 0] + Y_1 (2500) = \mathbf{60.3 + 2613 Y_1}$$

Overall mass balance

$$G_S (Y_1 - Y_2) = M_S (X_1 - X_2) = G_S (Y_1 - 0.015) = 5.73 \text{ Kg}$$

$$\Rightarrow G_S = \mathbf{5.73 / (Y_1 - 0.015)}$$

$$\begin{aligned} M_S [H_{S2} - H_{S1}] &= G_S [H_{g2} - H_{g1}] \\ \Rightarrow 15.91 [210.5 - 102.6] &= \{ 5.73 / (Y_1 - 0.015) \} \times (177 - 60.3 - 2613 Y_1) \end{aligned}$$

Thus,  $Y_1 = \mathbf{0.0416}$  and

$$G_S = 5.73 / (Y_1 - 0.015) = \mathbf{215.4 \text{ Kg/h}}$$

### Calculation of Shell Diameter

Volume of humid inlet gas ( $135^\circ\text{C}$  and  $Y_2 = 0.015$ )

$$V_{H2} = 8315 (1/M_B + Y_2/M_A) * (T_g + 273) / 101325)$$

$$\text{Thus, } V_{H2} = \mathbf{1.183 \text{ m}^3/\text{Kg dry air}}$$

Volume of humid exit gas ( $60^\circ\text{C}$  and  $Y_1 = 0.0416$ )

$$V_{H1} = \mathbf{1.0107 \text{ m}^3/\text{Kg dry air}}$$

$$\text{Maximum volumetric gas flow rate} = G_s \cdot V_{H_2} = 215.4 \times 1.183 = 254.83 \text{ m}^3/\text{h}$$

$$\begin{aligned} \text{The working velocity i.e. superficial velocity} &= 1.5 - (0.35 \times 1.5) \\ &= 0.975 \text{ m/s} \end{aligned}$$

(Air velocity must not exceed 1.5 m/s, hence working velocity = (1 - Y<sub>1</sub>)\*Max. Permissible Velocity )

$$\text{Gas Flow rate} = 3.14/4 \times d^2 \times (0.975)$$

$$\Rightarrow \text{Diameter, } \underline{\underline{d = 0.304 \text{ m}}}$$

### Heat Transfer Unit

Dryer is divided into three zones and therefore, the stage wise calculation of temperature and humidity of the stream can be obtained by material and energy balance.

#### Stage III

Very less water left for vaporization in stage III. Consider solid is at T<sub>SB</sub>, the wet bulb temperature of the air at location between III & II.

$$\text{Assume } T_{SB} = T_{SA} = 41 \text{ }^\circ\text{C}$$

Enthalpy of solid at the inlet to stage III

$$\begin{aligned} H_{SB} &= [0.85 + (0.18) (4.187)] (41-0) \\ &= 78.46 \text{ KJ/kg dry solid} \end{aligned}$$

Humid heat of gas entering stage III

$$\begin{aligned} C_{HB} &= [1.005 + (1.88) (0.015)] \\ &= 1.003 \text{ KJ/kg-K} \end{aligned}$$

Heat balance over stage III

$$\begin{aligned} M_s [H_{S2} - H_{SB}] &= G_s (C_{HB})_{III} (135 - T_{GB}) \\ \Rightarrow 15.91(210.5 - 78.46) &= 215.4 \times (1.003) \times (135 - T_{GB}) \\ \Rightarrow T_{GB} &= 125.276 \text{ }^\circ\text{C} \end{aligned}$$

Adiabatic saturation temperature of air entering stage II (125.276 °C & humidity of 0.015) is 41 °C.



At the boundary B,  $\Delta T_B = 125.276 - 41 = 84.276 \text{ }^\circ\text{C}$

At end 2,  $\Delta T_2 = 135 - 110 = 25 \text{ }^\circ\text{C}$

$$\text{LMTD}_{\text{III}} = (\Delta T)_m = (84.276 - 25) / \ln(84.276/25) = 48.78 \text{ }^\circ\text{C}$$

$$(N_{tG})_{\text{III}} = T_2 - T_{GB} / (\Delta T)_m = (135 - 125.276) / 48.78 = 0.1993$$

## Stage II

Using heat balance equation over stage I, the value of  $T_{GA}$  is calculated. The calculated  $T_{GA}$  value can be used to estimate the number of transfer units.

Since  $Y_B = 0.015$

$$H_{GB} = [1.005 + 1.88 Y_B] (125.276 - 0) + 2500 (Y_B) = 166.935 \text{ KJ/Kg}$$

$$H_{AS} = [1.16 + 4.187 X_1] (T_{SA} - 0) = [1.16 + (4.187) (0.54)] (41)$$

$$\text{Thus, } H_{AS} = 140.26 \text{ KJ/(Kg dry solid)}$$

Enthalpy balance:

$$M_S (H_{SB} - H_{SA}) = G_S (H_{GB} - H_{GA})$$

$$\Rightarrow 15.91 (78.46 - 140.26) = 215.4 (140.26 - H_{GA})$$

$$\Rightarrow H_{GA} = 144.824 \text{ KJ/Kg}$$

Once  $H_{GA}$  value is known then  $T_{GA}$  can be calculated using the following equation

$$H_{GA} = 144.824 = [1.005 + 0.0416 (1.88)] [T_{GA} - 0] + 0.0416 (2500)$$

$$\Rightarrow T_{GA} = 63 \text{ }^\circ\text{C}$$

At section A temp diff.  $\Delta T_A = 63 - 41 = 22 \text{ }^\circ\text{C}$  and  $\Delta T_B = 84.276 \text{ }^\circ\text{C}$

$$(\Delta T)_M = (84.276 - 22) / \ln(84.276/22) = 46.37 \text{ }^\circ\text{C}$$

$$\begin{aligned} \text{Number of transfer unit} &= (N_{tG})_{\text{II}} = (T_{GB} - T_{GA}) / (\Delta T)_M \\ &= (125.276 - 63) / 46.37 = 1.343 \end{aligned}$$

Stage I:

$$(\Delta T_1) = (60 - 30) = 30 \text{ }^\circ\text{C}$$

$$(\Delta T_A) = 22 \text{ }^\circ\text{C}$$

$$(\Delta T_M) = (30-22)/\ln(30/22) = 25.79 \text{ }^\circ\text{C}$$

$$\text{Hence, } (N_{tG})_I = (T_{GA} - T_{GI})/(\Delta T_M) = (63-60)/25.79 = 0.1163$$

$$\text{Total } (N_{tG}) = (N_{tG})_I + (N_{tG})_{II} + (N_{tG})_{III} = 0.1163 + 1.343 + 0.1993 = 1.658$$

**Length of Transfer Unit:**

$$\text{Average mass flow rate} = [215.4 (1.015) + 215.4(1.04306)]/2 = 221.5 \text{ Kg/h}$$

$$\text{The gas mass flow rate, } G'' = (221.5/3600)/(\pi/4 \times (0.304)^2) = 0.84768 \text{ Kg/m}^2.\text{S}$$

$$\text{Volumetric heat transfer coefficient} = U = (237 (G'')^{0.67})/d$$

$$U = (237 \times (0.848)^{0.67})/0.304 = 698.07 \text{ W/m}^3.\text{K}$$

Humid heat at the ends

$$C_{H2} = 1.005 + 1.88 (0.015) = 1.033$$

$$C_{H1} = 1.005 + 1.88 (0.04306) = 1.083$$

Average humid heat,

$$C_H = (1.033 + 1.083)/2 = 1.058 \text{ KJ/Kg. K}$$

$$\text{Length of transfer unit, } L_T = G'' C_H / U = (0.848 \times 1058)/698.07 = 1.285 \text{ m}$$

$$\text{Length of dryer, } L = N_{tG} \cdot L_T$$

$$= 1.658 \times 1.285 = 2.13 \text{ m}$$

Thus, **d = 0.304 m** and **L = 2.13 m**

A Rotary-type Drier of diameter 0.304 m and length of 2.13m must be used to hold the given rate of inlet and outlets.

## **5.2. Centrifuge**

### **High Speed Tubular centrifuge**

In case of high speed tubular centrifuge the velocity of the particle for size upto 10 micron does not perceptibly exceed 1 m/sec. The Reynolds number can be considered between  $10^{-4}$  to 10 and this is the region where Stoke's law is applicable.

$$u = [D_p^2 (\rho_p - \rho_r) \omega^2 r] / 18 \mu$$

Standard dimensions:

Particle diameter,  $D_p = 22$  mesh size = 0.71 mm

Centrifuge diameter,  $d = 1.75$  in = 4.445 cm

Density of crystals,  $\rho_r = 1444$  Kg/m<sup>3</sup>

Density of solution,  $\rho_p = 2660$  Kg/m<sup>3</sup>

Number of revolutions per minute = 1400

Angular velocity centrifuge,  $\omega = 2\pi \times 1400 / 60 = 146.6$  sec<sup>-1</sup>

Viscosity of solution,  $\mu = 0.008$  Ns/m<sup>2</sup>

$$u = [ (0.71 \times 10^{-3})^2 \times 2660 \times (146.6)^2 \times 0.04445 ] / (18 \times 0.008 \times 2) = 0.5856 \text{ m/s}$$

For gravity separation:

$$U = [D_p^2 (\rho_p - \rho_r) g] / 18 \mu$$

$$u = [(0.71 \times 10^{-3})^2 \times 2660 \times 9.81] / 18 \times 0.008$$

$$u = 0.04176 \text{ m/sec}$$

For centrifugal separation:

$$U = [D_p^2 (\rho_p - \rho_r) r \omega^2] / 18 \mu = 0.5856 \text{ m/s}$$

Ratio of sedimentation rate in centrifugal to gravity separator =  $0.5856 / 0.04176 = 14.02$ .

This ratio is an indication of extent of separation by Centrifugal means and Gravity. Hence, it shows that Centrifugal separation is more than Gravity separation. It is also indicative of the D/L ration of the centrifuge.

Thus, the Centrifuge must be designed with the specification of  $D/L \geq 14.02$

## **CHAPTER 6**

### **COST ESTIMATION**

Cost Estimation is done to check the profitability of the proposed tonnage of the manufacturing plant.

#### **6.1 Calculation of Fixed Cost Investment:**

Cost of Salicylic acid plant of 182.5 TPY capacity in 1953 = Rs. 11,16,000

Chemical Engineering Plant Cost Index in 1953 = 84.5

Chemical Engineering Plant Cost Index in 2014 = 600

Fixed Cost Investment includes investment in physical assets such as machinery, land, buildings, installations, vehicles and technology.

Present Fixed Cost Investment = (Present Cost Index/ Cost Index in reference year) \*

Fixed Cost Investment in reference yr

$$= (600/84.5) * 1116000 = \text{Rs. 79, 24, 260.355}$$

#### **6.2 Estimation of Total Investment Cost:**

##### **6.2.1 Direct Cost**

Direct costs include prices that can be completely attributed to the production of specific goods and services. In construction, the costs of materials, labour, equipment and all directly involved efforts or expenses for the cost object are direct costs. The following are the constituents of Direct cost and their contributing factors-

- |   |   |                                 |
|---|---|---------------------------------|
| a. Purchased Equipment Cost                 | : | 15-40 % of FCI (0.4)            |
| b. Installation Cost                        | : | 35-50% of Purchased Cost (0.45) |
| c. Instrumentation and Control Installation | : | 30% of Purchased Cost           |
| d. Piping Installation Cost                 | : | 10-80% of Purchased Cost (0.75) |
| e. Electricity Installation Cost            | : | 10-40% of Purchased Cost (0.35) |
| f. Building and Process Auxiliary           | : | 10-70% of Purchased Cost (0.65) |
| g. Service Facility                         | : | 30-80% of Purchased Cost (0.75) |
| h. Yard Improvement                         | : | 10-15% of Purchased Cost (0.12) |
| i. Land                                     | : | 4-8% of Purchased Cost (0.6)    |

<b>Investment</b>	<b>Cost (in Rupees)</b>
Purchased Equipment Cost	31, 69, 704
Installation Cost	14, 26, 266
Instrumentation and Control Installation	9, 50, 911
Piping Installation Cost	23, 77, 278
Electricity Installation Cost	11, 09, 396
Building and Process Auxiliary	20, 60, 307
Service Facility	23, 77, 278
Yard Improvement	3, 80, 364
Land	1, 90, 182
<b>Total Direct Cost</b>	<b>1, 40, 41, 686</b>

Table 6.1.Direct Cost Components

### 6.2.2 Indirect Cost

**Indirect costs** are costs that are not directly accountable to a cost object (such as a particular project, facility, function or product). Indirect costs may be either fixed or variable. Indirect costs include administration, personnel and security costs. These are those costs which are not directly related to production. Some indirect costs may be overhead. But some overhead costs can be directly attributed to a project and are direct costs.

- a. Engineering and Supervision Costs : 5-30% of Direct Cost (0.25)
- b. Construction Expenses : 10% of Direct Cost (0.07)

- c. Contractors' Fees : 2-7% of Direct Cost (0.05)
- d. Contingency : 8-20% of Direct Cost (0.15)

<b>Investment</b>	<b>Cost ( in Rupees)</b>
Engineering and Supervision Costs	35, 10, 421
Construction Expenses	9, 82, 918
Contractors' Fees	7, 02, 084
Contingency	21, 06, 252
<b>Total Indirect Cost</b>	<b>73, 01, 675</b>

Table 6.2 Indirect Cost Constituents

#### 6.2.3. Fixed Capital Investment:

Fixed Capital Investment (FCI) = (Direct + Indirect) Costs = **Rs. 2, 13, 43, 361**

#### 6.2.4. Working Capital Investment:

Working Capital Investment = 10-20% FCI

Assuming 15%, we get, Working Capital Investment = **Rs. 32, 01, 504**

#### 6.2.5. Total Capital Investment:

Total Capital Investment = (Fixed + Working) Capital Investment

**= Rs. 2, 45, 44, 865**

### **6.3. Estimation of Total Production Cost:**

#### 6.3.1. Fixed Charges:

1. Depreciation : 10% of Fixed Cost Investment = Rs. 21, 34, 383
2. Local Taxes : 3% of Fixed Cost Investment = Rs. 6, 40, 314
3. Insurances : 1% of Fixed Cost Investment = Rs. 2, 13, 438
4. Rent : 9% of Fixed Cost Investment = Rs. 19, 20, 944

Total Fixed Charges = **Rs. 49, 09, 079**

Generally, Fixed Costs = 10-20% of Total Product Cost (Assuming 10%, here)

Therefore, **Total Product Cost** = 49, 08, 973/0.1 = **Rs. 4, 90, 90, 790**

#### 6.3.2. Direct production:

- a. Raw material : 10-50% of Total Production Cost (0.25)
- b. Operating Labour (OL) : 10-20% of Total Production Cost (0.15)
- c. Direct supervisory and electric labour: 10-25% of Operating Labour (0.15)
- d. Utilities : 10-20% of Total Production Cost (0.15)
- e. Maintenance : 2-10% of Fixed Cost Investment (0.05)
- f. Operating supplies (OS) : 10-20% of Maintenance Cost (0.15)
- g. Laboratory charges : 10-20% of Operating Labour (0.15)
- h. Patent and royalties : 2-6% of Total Production Cost (0.04)

<b>Investment</b>	<b>Cost (in Rupees)</b>
Raw material	1, 22, 72, 697
Operating Labour (OL)	73, 63, 618
Direct supervisory and electric labour	11, 04, 542
Utilities	73, 63, 618
Maintenance	10, 67, 168
Operating supplies (OS)	1, 60, 075
Laboratory charges	11, 04, 542
Patent and royalties	1, 96, 391
<b>Total Direct Production</b>	<b>3, 06, 32, 651</b>

Table 6.3 Costs of Direct Production

### 6.3.3. Plant overhead cost:

Generally, it is 50-70% of (Operating Labour + Operating Supplies + Maintenance)

Assuming 60%, **Plant Overhead Cost** =  $0.6 \times 85,90,861 = \text{Rs. } 51,54,516$

### 6.3.4. General expenses:

- a. Administration cost : 40-60% of Operating Labour (0.55)
- b. Distribution and selling price : 2-30% of Total Production Cost (0.20)
- c. Research and development cost : 3% of Total Production Cost

Investment	Cost (in Rupees)
Administration cost	40,49,989
Distribution and selling price	98,18,158
Research and development cost	14,72,723
<b>Total General Expenses (GE)</b>	<b>1,53,40,870</b>

Table 6.4 General Expenses Constituents

Therefore, **Manufacturing Cost (MC)** = Product cost + Fixed Charges + Plant overhead expenses = **Rs. 5,91,54,385**

Thus, **Total Production Cost** = MC + GE = **Rs. 7,44,95,255**

## 6.4. Gross earnings and rate of return:

The plant is working for say 300 days a year

Selling price =Rs. 900/kg ; Tax =50%

Total income =  $500 \times 300 \times 900 = \text{Rs. } 13,50,00,000 = \text{Rs } 2,91,00,00,000$

**Gross income** = Total Income – Total Production Cost =  $13,50,00,000 - 7,44,95,255 = \text{Rs. } 6,05,04,745$

Thus, the proposed capacity of Salicylic acid plant is estimated to earn a **Net profit** = **Rs 3,02,52,372.5**



## PART II: Steady State Analysis of Sieve Tray Gas Absorption Column using MATLAB

### CHAPTER 7

#### Introduction

##### 7.1. Objective:

The objective of this analysis is to develop a steady state model for the coupled hydrodynamics and mass transfer of a sieve tray gas absorption column. It is an attempt at showing the dependence of gas phase composition profiles on the tray number using Murphree tray efficiency as a parameter to account for the failure to achieve equilibrium. MATLAB is used for effective computation.

##### 7.2. Sieve Tray Gas Absorption Column:

Absorption is a gas-liquid mass transfer operation in which a gas mixture is contacted with a liquid for the purposes of preferentially dissolving one or more components of the gas and to provide a solution of these in the liquid. Generally, these operations are used for purification of gas streams by selective solute distribution between the two participating phases. Sieve Tray Gas Absorption Column is a type of Absorption column with Sieve Trays as the contacting medium between the two phases. For the thesis study, a real industrial bioethanol gas absorption process is chosen. In this the two contacting phases are the gas mixture of Carbon dioxide and Ethanol and water as the absorbent. The motive of the control is to keep the ethanol concentration low in the gas effluent stream.

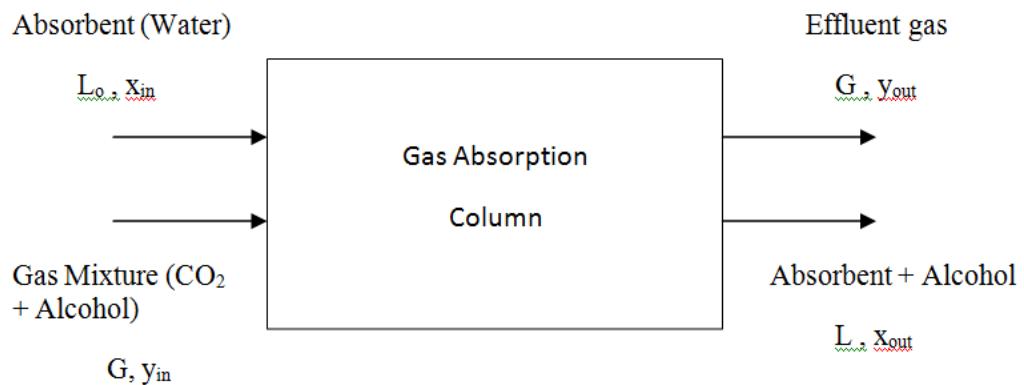


Fig.7.1.The input-output block diagram for the Absorption Column

## CHAPTER 8

### Steady State Analysis

#### 8.1. Working Assumptions

The operation of Absorption column involves a lot of parameters such as the Gas and Absorbent flow rate, the number of stages in the column, the tray efficiency and the operating conditions inside the column, at each tray. It is difficult to conduct a study with so many degrees of freedom in a system. Hence, certain assumptions are made to accommodate fewer changing attributes and easier study of the general performance behaviour of the model.

The following are the assumptions made for the Steady State Model-

- Liquid on the tray is perfectly mixed and incompressible
- Vapour holdup of the tray is negligible
- Vapour and liquid streams are in thermal equilibrium, but not in phase equilibrium
- Total Gas flow rate (G) is kept constant throughout
- The equilibrium relationship is linear
- Murphree Tray Efficiency is same for all the trays inside the column

#### 8.2. Derivation of Equations of study from Mass and Component Balance

To obtain the steady state model of the tray gas absorption column, the steady state condition is applied to the governing equations. The governing equations in the study are the Mass balance and Component (solute) balance across a tray.

For a generalised equation, the balance is carried out across  $j^{\text{th}}$  tray. In the  $j^{\text{th}}$  tray, the unsteady state material balance is given by-

$$(dM_j / dt) = L_{j-1} + G - L_j - G \quad \text{----- (1)}$$

where,  $M_j$  is the total liquid holdup (kmol) on the  $j^{\text{th}}$  tray, while  $L_{j-1}$ ,  $L_j$  (mol/s) are the inlet and outlet liquid flow rates respectively, while the total gas flow rate is  $G$  (mol/s)

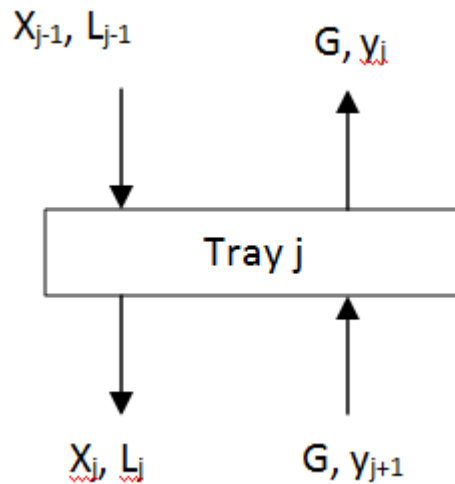


Fig.8.1.Schematic Tray Diagram

Solute Balance on the  $j^{\text{th}}$  tray-

$$\frac{d(M_j x_j)}{dt} = x_{j-1} L_{j-1} - x_j L_j + G(y_{j+1} - y_j) \quad \text{-----(2)}$$

At steady state, both equations 1 and 2 will become 0

$$L_{j-1} + G - L_j - G = 0$$

$$\Rightarrow L_{j-1} = L_j = L_0 \text{ (say)} \quad \text{----- (3)}$$

Also,

$$x_{j-1} L_{j-1} - x_j L_j + G(y_{j+1} - y_j) = 0 \quad \text{----- (4)}$$

From (3) and (4), we get

$$(L_0/G) (x_{j-1} - x_j) = y_j - y_{j+1} \quad \text{----- (5)}$$

For  $j=1$ ,

$$(L_0/G) (x_0 - x_1) = y_1 - y_2 = -\Delta y_1$$

For  $j=2$ ,

$$(L_1/G) (x_1 - x_2) = y_2 - y_3 = -\Delta y_2$$

So on, and

For  $j=n$ ,

$$(\mathbf{L}_n/\mathbf{G}) (\mathbf{x}_{n-1} - \mathbf{x}_n) = \mathbf{y}_n - \mathbf{y}_{n+1}$$

Transforming the above set of equations to matrix form for easier computation in MATLAB, we get

$$\mathbf{A}_x \mathbf{x} = -\Delta \mathbf{y} + \mathbf{B} \mathbf{u} \quad \text{----- (6)}$$

Where

$$(\mathbf{a}_x)_{i,j} = \begin{pmatrix} -\left(\frac{L_o}{G}\right) \text{ if } i = j \\ \left(\frac{L_o}{G}\right) \text{ if } j = i + 1 \end{pmatrix} ; \mathbf{u} = \begin{pmatrix} \left(\frac{L_o}{G}\right) x_{in} \\ y_{in} \end{pmatrix} \quad \text{For all } i, j = 1, 2, 3 \dots N$$

$$\mathbf{B} = \begin{pmatrix} -1 & 0 \\ 0 & 0 \\ \dots & \dots \\ \dots & \dots \\ 0 & -1 \end{pmatrix} ; \Delta \mathbf{y} = \begin{pmatrix} \Delta y_1 \\ \Delta y_2 \\ \Delta y_3 \\ \dots \\ \dots \\ \Delta y_n \end{pmatrix} ; \mathbf{y} = \begin{pmatrix} y_1 \\ y_2 \\ y_3 \\ \dots \\ \dots \\ y_n \end{pmatrix} ; \mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ \dots \\ \dots \\ x_n \end{pmatrix}$$

Murphree Tray Efficiency-

$$\eta = (\mathbf{y}_j - \mathbf{y}_{j+1}) / (\mathbf{y}_j^* - \mathbf{y}_{j+1}) \quad \text{----- (7)}$$

From equilibrium data,

$$\mathbf{y}^* = \mathbf{k} \mathbf{x}_j \quad \text{----- (8)}$$

From (7) and (8)

$$\eta = (\mathbf{y}_j - \mathbf{y}_{j+1}) / (\mathbf{k} \mathbf{x}_j - \mathbf{y}_{j+1}) \quad \text{----- (9)}$$

Rewriting Equation (9),

$$\Rightarrow \mathbf{k} \mathbf{x}_j \eta = \mathbf{y}_j - \mathbf{y}_{j+1} (1 - \eta) \quad \text{----- (10)}$$

For the above equation, for j=1,

$$\mathbf{k} \mathbf{x}_1 \eta = \mathbf{y}_1 - \mathbf{y}_2 (1 - \eta)$$

For j=2,

$$k x_2 \eta = y_2 - y_3 (1 - \eta)$$

•  
•  
•

For  $j=n$ ,

$$k x_n \eta = y_n - y_{n+1} (1 - \eta) \text{ where } y_{n+1} = y_{in}$$

Transforming the above set of equations to matrix form, we get

$$A_y y = -k \eta x - (1 - \eta) y_{in} v \quad \text{----- (11)}$$

Where

$$(a_y)_{i,j} = \begin{pmatrix} -1 & \text{if } i = j \\ (1 - \eta) & \text{if } j = i + 1 \end{pmatrix} \quad \text{For all } i, j = 1, 2, 3 \dots N$$

$$v = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{pmatrix}$$

Thus, the governing equations of the absorption column have been established in the form of Matrices.

### **8.3 Implementation of Steady State Model Algorithm**

The steady state system of equations given by (6) and (11) is coupled through the Murphree tray efficiency. An initial estimate value for the distribution of liquid phase compositions ( $x$ ) throughout the trays in the column is found using these steady state equations. Equation (6) reduces to  $Ax_o = Bu$  as  $\Delta y \rightarrow 0$  for steady state condition. Also,  $(1-\eta)$  can be neglected from Equation (11) for high tray efficiency.

## 8.4 Graphical Result

### Program Inputs:

The iteration for initial guess is run using the following input constants-

Inlet Absorbent flow rate,  $L_o = 2.25$  mol/s

Inlet Gas flow rate,  $G = 1.2$  mol/s

Inlet solute concentration in the absorbent,  $x_{in} = 0$

Inlet solute concentration in the feed (mole/mole),  $y_{in} = 0.02$

Slope of the Equilibrium curve,  $k = 1.0682$

Murphree Tray Efficiency,  $\eta = 0.6$

Tolerance value = 0.001

### Program Output:

The following plot was obtained between the solute concentration in gas and liquid phases ( $y, x$ ) and the tray number. Both the measured variables follow non-linear trend which is attributed to the Murphree Tray Efficiency.

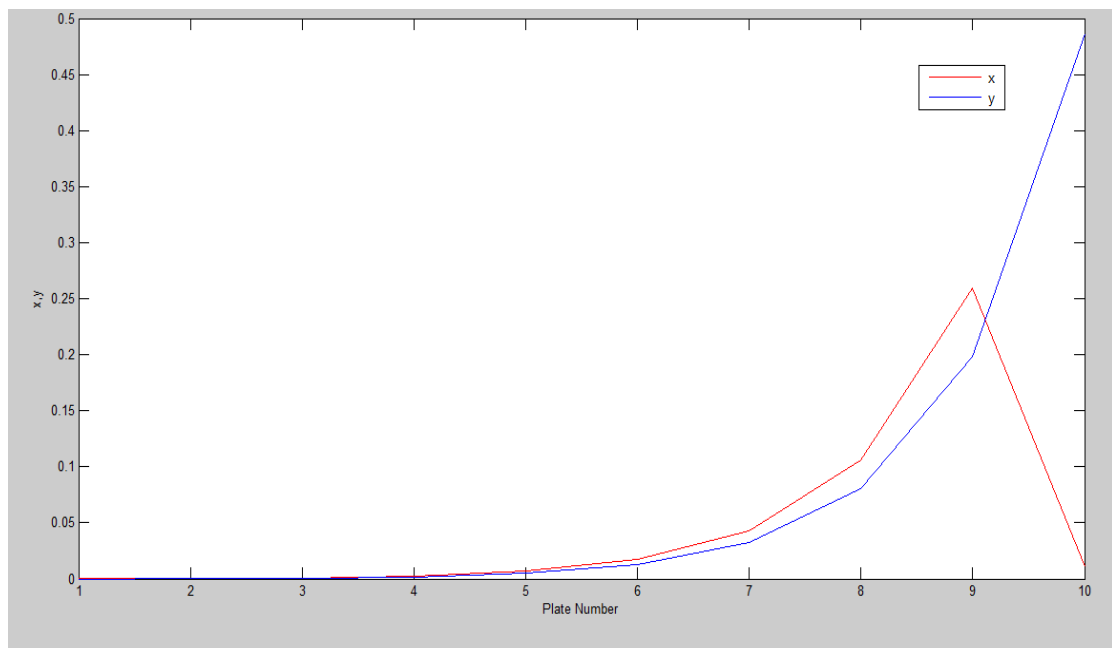


Fig. 8.2 Result Plot between  $x, y$  and Tray Number ( $N$ )

## **CHAPTER 9**

### **Summary**

#### **9.1 Contribution of the Project**

The work on designing the entire Plant operation involved in manufacturing Salicylic acid has given an estimate of the materials required, energy and utility consumption and the costs involved in setting up a Salicylic acid plant of 0.5 tonnes per day capacity. With the study carried out on the properties of Salicylic acid and its behaviour under various operating conditions in the Kolbe-Schmitt Process, the equipment selections have been made which can be implemented by any large scale industry for efficient handling of materials and energy conservation.

The steady state analysis of the sieve tray absorption column has allowed us to obtain the variations in gas and liquid phase compositions in the column across different trays. The MATLAB code used to obtain the Steady state solution can be implemented for different values of Murphree Tray Efficiency to analyse the performance and extent of absorption with respect to the efficiency. It can be incorporated in industries which have processes involving Absorption columns to simulate performance based on efficiency and number of trays.

#### **9.2 Future Scope of the Project**

The present work on Salicylic acid manufacturing is based on ideal conditions such as complete reaction conversion, no recycle and negligence of equipment heat loss. This work can thus be furthered towards more reliable results by introducing variance in losses and other operating parameters. Higher temperatures and pressure conditions can be implemented with appropriate means in the process to obtain higher yields. Crystallisation unit can be added to improve the purity level of Salicylic acid crystals. It can also lead to the formation of needle-like crystals which improve flowability, which in turn allow production of Salicylic acid in tablet form rather than powder.

The Steady state behaviour obtained can be extended to simulate the performance of Absorption column in dynamic operation. Since most of the industrial operations exhibit dynamic conditions, it is essential to establish control systems that monitor dynamic behaviour of the process too. Steady state analysis is a precursor in achieving command over dynamic control systems.

## APPENDIX I: MATLAB .m file for computing the initial guess of $x_0$

```
Lo=2.25; %Initial absorbent flow rate
G=1.2;   %Inlet gas flow rate
xin=0;   %Inlet solute concentration in absorbent
yin=0.02;%Inlet solute concentration in feed
N=10;    %Number of stages
eta=0.6; %Murphee's stage efficiency
k=1.0682;%Slope of equilibrium curve
xo=[0;0;0;0;0;0;0;0;0;0;0];
B=[-1,0;0,0;0,0;0,0;0,0;0,0;0,0;0,0;0,0;0,-1];
u=[(Lo/G)*xin;yin];
v=[0;0;0;0;0;0;0;0;0;0;1];
tol=0.001;
error=1;
A=zeros(10);
for n=1:1:10
    for m=1:1:10
        if n==m
            A(n,m)=-1*((eta*k)+(Lo/G));
            Ay(n,m)=-1;
            Ax(n,m)=-1*(Lo/G);
        else if n==(m+1)
            A(n,m)=Lo/G;
            Ay(n,m)=1-eta;
            Ax(n,m)=Lo/G;
        else
            A(n,m)=0;
            Ay(n,m)=0;
            Ax(n,m)=0;
        end
    end
end
xo=inv(A)*(B*u);
display('Tolerance=0.01');
display('Displaying xo initialised to x');
x=xo
while error>tol
    display('-----');
    display('Iteration');
    y=inv(Ay)*((-eta*k*x)-(1-eta)*v)

    for i=1:1:9
        dely(i,1)=y(i+1,1)-y(i,1);
    end
    dely(10,1)= -1*y(10,1);
    x=inv(Ax)*((B*u)-dely)
    plot(x,'r');
    hold
    plot(y);
    hold
```



```
xlabel('Plate Number');  
ylabel('x,y');  
e=(x-xo).^2;  
sum=0;  
for j=1:1:10  
    sum=sum+e(j,1);  
end  
xo=x;  
error=sqrt(sum)  
end
```

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