

Natubhai V. Patel College of Pure & Applied Sciences  
B.Sc. Semester V  
Industrial chemistry  
US05CICH02: Unit process in organic manufacture  
UNIT – 2

**Syllabus**

**Sulfonation:** Introduction, sulfonating agents, chemical and physical factors in sulfonation, Kinetics and mechanism of sulfonation reaction. Commercial sulfonation of benzene (Barbet process) Batch v/s continuous sulfonation

**Oxidation:** Introduction, types of oxidation reaction, oxidizing reagents, kinetics and mechanism of oxidation of organic compounds, liquid phase oxidation, vapour phase oxidation. Commercial manufacturing of Benzoic acid, Phthalic anhydride and Acetic acid.

**SULFONATION AND SULFATION**

**2.0 INTRODUCTION**

**Sulfonation** may be defined as any chemical process by which the **sulfonic acid group (SO<sub>2</sub>OH)** or the corresponding salt or sulfonyl halide group (e.g. **-SO<sub>2</sub>Cl**) is **introduced** into an **organic compound**. These **groups** may be situated **on** either a **carbon or a nitrogen** atom. **Sulfonates** of the **second type** (e.g. RNHSO<sub>2</sub>ONa) are termed **N-sulfonates** or **sulfamates**.

Particular types of sulfonation include **sulfo-chlorination** (introduction of an -SO<sub>2</sub>Cl group into an alkane using sulfur dioxide and chlorine), **halo-sulfonation** (reaction of halosulfonic acid —ClSO<sub>3</sub>H or —FSO<sub>3</sub>H with an aromatic or heterocyclic compound to introduce an —SO<sub>2</sub>Cl or an —SO<sub>2</sub>F group), **sulfoxidation** (use of sulfur dioxide and oxygen to sulfonate an alkane), **sulfo-alkylation**, **sulfo-acylation** and **sulfo-arylation** (introduction of sulfalkyl, sulfoacyl or sulfoaryl groups).

**Sulfation** involves placement of **—OSO<sub>2</sub>OH** group on **carbon** yielding an acid sulfate (ROSO<sub>2</sub>OH) or of the **-SO<sub>4</sub>-** group **between two carbons**, forming the sulfate ROSO<sub>2</sub>OR

Sulfato-alkylation designate introduction of a sulfated alkyl group into an organic compound.

**2.1 CLASSIFICATION OF SULFONATES**

- Aliphatic and alicyclic
- Aromatic
- Heterocyclic and
- N-sulfonates or sulfamates.

The first three types have the - SO<sub>2</sub>OH group on carbon, the chemical nature of which determines the classification. Thus, C<sub>6</sub>H<sub>5</sub>OCH<sub>2</sub>SO<sub>2</sub>ONa (sodium-phenoxyethanesulfonate) would be considered an aliphatic sulfonate.

For **practical reasons**, it is also useful to refer to **three other types of sulfonates**, namely those **derived from petroleum fractions**, from **lignin**, and from **fatty oils**. These materials are mixtures of indeterminate or variable composition, probably comprising one or more of the main chemical types of sulfonates together with sulfates and other sulfur compounds, and are made largely by empirical procedures. All three types are commercially important.

**2.2 CLASSIFICATION OF SULFATES**

Sulfates may be classified as sulfated alkenes, alcohol sulfates, cyclic sulfates, sulfated carbohydrates and sulfated nitrogenous polysaccharides.

### 2.3 GENERAL PROCEDURES FOR PREPARING SULFONATES

- Treatment of an organic compound with SO<sub>3</sub> or a compound thereof
- Treatment with a compound of SO<sub>2</sub>
- Condensation and polymerization methods
- Oxidation of organic compound which already containing sulfur in a lower state of oxidation such as RSH.

Condensation procedures refer to the reaction of organic sulfonates building blocks (such as HOCH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na) with other organic compounds (such as long-chain acid chlorides) to form new sulfonates with altered properties; these methods include sulfoalkylation, sulfoacylation and sulfoarylation.

For the **preparation of sulfates**, the **first** and **third** (i.e. sulfatoalkylation) methods only are of interest.

### 2.4 SULFONATING AND SULFATING AGENTS AND THEIR PRINCIPAL APPLICATION

Sulfonating and sulfating agents are of two types (1) inorganic and (2) organic. The latter type is employed in the condensation procedures.

#### 2.4.1 Principal sulfonating and sulfating agents

##### Sulfur trioxide and compounds thereof

- Sulfur trioxide, oleum, concentrated sulfuric acid (SO<sub>3</sub> plus water)
- Chlorosulfonic acid (SO<sub>3</sub> plus HCl)
- Sulfur trioxide adducts with organic compounds
- Sulfamic acid

##### The sulfur dioxide group

- Sulfurous acid, metallic sulfites
- Sulfur dioxides with chlorine
- Sulfur dioxide with oxygen

##### Sulfoalkylating agents

- Sulfo-methylating agents (hydroxy and aminomethanesulfonates)
- Sulfo-ethylating agents (hydroxy-chloro and methylaminoethanesulfonates, ethylenesulfonic acid)
- Miscellaneous sulfo-alkylating agents, sulfo-acylation, sulfo-arylation, sulfato-alkylation

#### 2.4.2 Uses and application of sulfonate and sulfates

Millions of tons of **sulfonates** are manufactured annually **lignin sulfonates** obtains as a **by-product** of **paper manufacture** constitutes the major single product. These compounds have achieved a wide variety of interesting and important uses. Most of them are employed as such in acid or salt form for application where the strongly polar hydrophilic -SO<sub>2</sub>OH group confers needed properties on a comparatively hydrophobic non-polar organic molecule. A **few sulfonates** are both marketed and used in acid form, including methane and toluenesulfonic acids as catalysts and phenolsulfonic acid as an **electroplating additive**. A considerably larger group is marketed in salt form and used in acid form; such compounds include **mothproofing agents**, and synthetic tanning agents. In these cases, the salts are applied in acid medium, thereby liberating the free -SO<sub>2</sub>OH group, which firmly attaches the organic molecule to the textile fiber or leather. The major quantity of **sulfonates and sulfates** is both marketed and used in **salt form**. This **category includes** detergents, emulsifying, deemulsifying, penetrating, wetting and solubilising agents, lubricant additives, and rust inhibitors. Polymeric sulfonates include dispersing agents, elastomers, water-soluble synthetic gums and thickening agents and ion exchange resins which function as strong acids with complete water insolubility and unusual combination of properties leading to many important applications.

**Aromatic sulfonyl chlorides** -RSO<sub>2</sub>Cl are useful for preparing sulfonamides (including sulfa drugs, dyes, tanning agents, plasticizers and the sweetening agents (saccharin) and sulfonate ester (insecticides).

**Sulfamates** include herbicide, sweetening agent and blood anticoagulant.

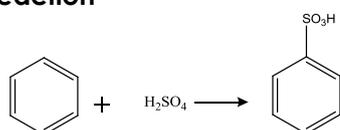
Sulfonates and sulfates find use **as intermediates** for preparing organic **compounds not containing sulfur**, notably phenols (prepared by caustic fusion of various sulfonates) and alcohols (made by hydrolysis of sulfated alkenes). Phenol, resorcinol, the naphthols, hydroxy-antraquinones and 8-hydroxyquinoline are phenols so produced while ethanol and isopropanol are examples of alcohols made from the sulfates.

## 2.5 BENZENE SULFONIC ACID OR MONOSULFONATION OF BENZENE

### 2.5.1 Raw materials

Under **optimum condition**, the **reaction time** for this process has been calculated at **1.5hr. at 180°C** using a seven-stage reactor, continuous process 10 moles of benzene per mole of sulfuric acid required. In contrast, the same process operated in batches at 160-180°C would require 14 hr. and 6-8 moles of benzene per mole sulfuric acid. Thus the continuous method increases by nearly ten times the capacity of the batch method. It is further estimated that the ratio of benzene used, to benzene reacted could be reduced as low as 3 :1 by doubling the time of reaction. The efficiency of the process can be further increased by using 10% oleum instead of sulfuric acid, thereby reducing the required water removal without substantially raising by product sulfone formation.

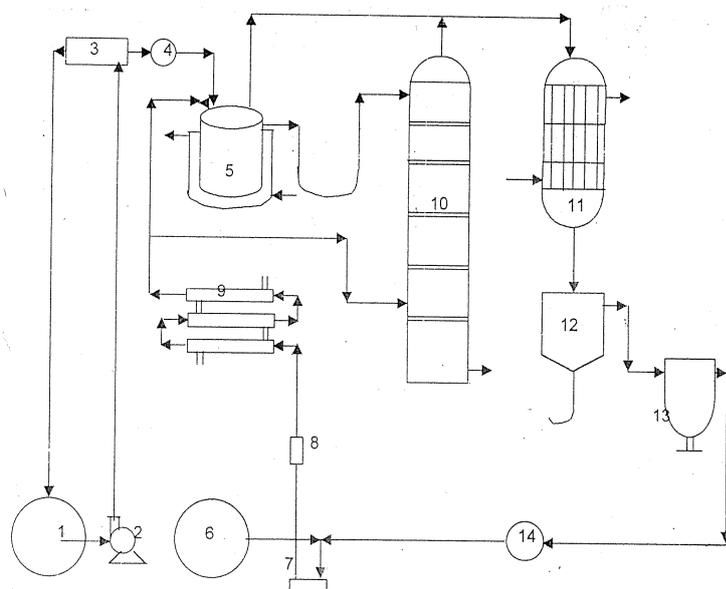
### 2.5.2 Reaction



### 2.5.3 Manufacture

Benzene can be monosulfonated efficiently and on a continuous basis by the partial pressure distillation method. A typical operating procedure based on the flow diagram shown in figure is as follow.

**Sulfuric acid** is continuously pumped from storage tank (1) by means of pump (2) through pressure regulator (3) and meter (4) to the sulfonator (5) **Liquid benzene** from storage tank (6 or 14) is continuously fed by pump (7) through meter (8) to the direct vaporizer super heater (9) and hence to the sulfonator (5) and the Sulfonation tower (10) In the Sulfonation,



1. H<sub>2</sub>SO<sub>4</sub> storage tank
2. Pump
3. Pressure regulator
4. Flow-meter
5. Sulfonator
6. Liquid benzene storage tank
7. Pump
8. Meter
9. Vaporizer
10. Sulfonation tower
11. Condensor
12. Separator
13. Neutralizing drier
14. Liquid benzene storage tank

**Sulfuric acid** reacts with **benzene**, and the **reaction mass** containing **30%** un-reacted sulfuric acid flows out continuously to the top of the Sulfonation tower (10) which is arranged like a plate column, the reaction mass flows downward through the tower while further reacting with a **countercurrent stream** of benzene vapour.

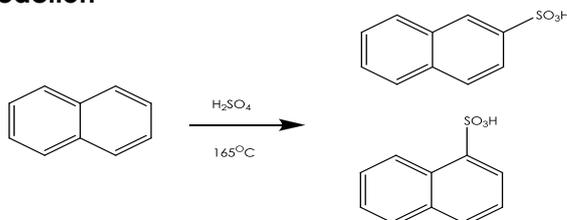
The exit benzene-water vapour are continuously discharged from top of tower (10) to condenser (11) and stratified in separator (12) and the benzene storage (14) while the benzenesulfonic acid, containing **2.5-3.5%** of sulfone and **3-4%** of sulfuric acid is continuously drawn off at the bottom of the tower.

## 2.6 NAPHTHALINE $\beta$ - SULFONIC ACID

### 2.6.1 Raw materials

Naphthalene, sulfuric acid, water, steam etc

### 2.6.2 Reaction



### 2.7.3 Manufacture

The hydrocarbon is reacted with sulfuric acid; in addition to the desired isomer, about 15% of the alpha isomer is also formed.

**Naphthalene** (3,350 lb - 26.2 lb moles) is charged to a **cast iron sulfonation kettle**, 500 gal capacity, equipped with propeller or anchor agitator and heated either directly with generator gas or by **high-pressure** (100 lb) jacket steam. It is melted by heating to **90-110 °C**. **Sulfuric acid** (3,350 lb of 96% strength - 32.8 lb moles) is then added with agitation, the temperature being allowed to rise to about **160 °C**. The batch is held at **160 -165°C** for about **2hrs** to complete reaction, during which time **water** (approx. 400 lb-22.2 lb moles) and **naphthalene** (approx. 350 lb -2.7 lb moles) distill off and are collected by condensation. The reaction **products contains** mainly monosulfonic acids (85 % beta and 15% alphas) plus some **sulfone**, free sulfuric acid, disulfonic acids and tar. The **undesired  $\alpha$ - sulfonate** is now removed by blowing **dry steam** into the charge to effect **hydrolytic desulfonation**, the liberated naphthalene being distilled and recovered. It is essential to employ dry steam to avoid foaming and to maintain a temperature in the range **160-165°C** to ensure rapid reaction. About **16% or 540 lb** of the original naphthalene employed is recovered, leaving the  **$\beta$ -sulfonate** contaminated with only about 0.1% alpha isomer.

The **hydrolyzed** sulfonation mixture is discharged into the water with good agitation and the resulting solution is run into the brine to form the sodium sulfonate salt. The **slurry** so obtained is **agitated** for **10 hr** as it **cooled to 30 °C** this yields an easily **filterable precipitate**. The filtration is accomplished by pumping or blowing the sodium sulfonate suspension into a pressure filter containing wooden plate filters and rubber-coated frames. The shell of the filter is coated with tar to minimize corrosion. The filtrate is permit to stand and more salt added if necessary and then it is refiltered to collect any additional sulfonate that has crystallized out.

The **second crop** of sodium sulfonate is not as pure as the first. The filter cakes are washed with a minimum of water and these washings are employed to advantage as part of the liquor in the sulfonation dilution tank. The filter cake of sodium sulfonate containing about 70 % water is pressed hydraulically to a water content of about 30%. The press cakes are dried to moisture content of about 5%, disintegrated and delivered to the **caustic fusion kettles** for conversion to  **$\beta$  -naphthol**. The **yield** is about **90%** of theory on the basis of naphthalene consumed.

#### Factors ensure rapid and complete sulfonation

- use of about **25% excess acid**, corresponding to about 40% excess over that actually converted to sulfonate
- Distillation of a **quantity of water** (22.2 moles) only **slightly less** than the amount of naphthalene (23.5 moles) sulfonated
- Use of an **elevated reaction temperature**. At this temperature, water will distill from dilute acid until it has increased to 68% in concentration, which is above the concentration (64%) required to sulfonate naphthalene at this temperature.

- As in every important sulfonation, **several modified procedures** have been suggested to reduce the acid factor more closely to theoretical, including the use of excess naphthalene or operation under vacuum. Continuous operation has also been studied. None of these expedients has been adopted commercially. Variations in the working up procedure have however sometimes proved advantageous.

## OXIDATION

### 2.8 TYPES OF OXIDATIVE REACTIONS

In the organic chemical industry, oxidation constitutes one of the most powerful tools used in the synthesis of chemical compounds. The oxidation processes are many and varied and are manifested in a variety of net effects. The principal types of oxidative reactions may be set forth as follows:

- Dehydrogenation** is illustrated in the transformation of a primary alcohol to an aldehyde:  

$$\text{C}_2\text{H}_5\text{OH} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$$
 Or a secondary alcohol to a ketone:  

$$\text{CH}_3\text{CHOH}\cdot\text{CH}_3 + \frac{1}{2} \text{O}_2 \longrightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2\text{O}$$
- An atom of oxygen may be introduced** into a molecule, as is illustrated by the oxidation of an aldehyde to an acid:  

$$\text{CH}_3\text{CHO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CH}_3\text{COOH}$$
 Or of a hydrocarbon to an alcohol:  

$$(\text{C}_6\text{H}_5)_3\text{CH} + \frac{1}{2} \text{O}_2 \longrightarrow (\text{C}_6\text{H}_5)_3\text{COH}$$
- A combination of dehydrogenation and introduction of oxygen** may occur, as in the preparation of aldehyde from hydrocarbons:  

$$\text{CH}_4 + \text{O}_2 \longrightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$$
 Or the preparation of benzoic acid from benzyl alcohol  

$$\text{C}_6\text{H}_5\text{CH}_2\text{CH}\cdot\text{OH} + \text{O}_2 \longrightarrow \text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O}$$
- Dehydrogenation may also be accompanied by molecular condensation**, as is the case when two molecules of benzene form diphenyl or two molecules of toluene form stilbene or when methyl, anthraquinone is converted to anthracene yellow C.  

$$2\text{C}_6\text{H}_5 + \frac{1}{2} \text{O}_2 \longrightarrow \text{C}_6\text{H}_5 - \text{C}_6\text{H}_5 + \text{H}_2\text{O}$$

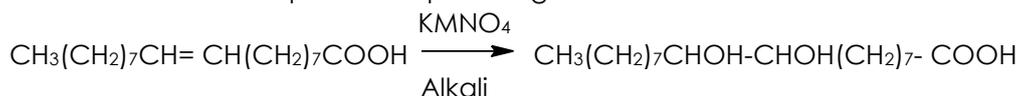
$$2\text{C}_6\text{H}_5\cdot\text{CH}_3 + \text{O}_2 \longrightarrow \text{C}_6\text{H}_5\cdot\text{CH} = \text{CH}\cdot\text{C}_6\text{H}_5 + 2\text{H}_2\text{O}$$
- Dehydrogenation, oxygen introduction and destruction of carbon linkages** may all occur in the same process of oxidation, e.g. in the oxidation of naphthalene to phthalic anhydride:  

$$\text{C}_{10}\text{H}_8 + 4.5\text{O}_2 \longrightarrow \text{C}_8\text{H}_4\text{O}_3 + 2\text{H}_2\text{O} + 2\text{CO}_2$$
- Oxidation may be accomplished indirectly** through the **use of intermediate** reaction.  

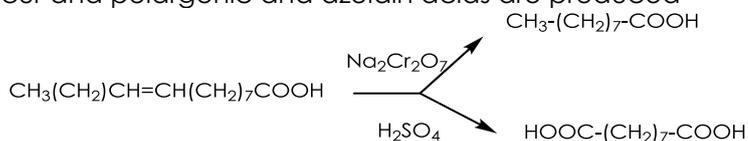
$$\text{C}_6\text{H}_5\cdot\text{CH}_3 \longrightarrow \text{C}_6\text{H}_5\text{CCl}_3 \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_5\text{COOH}$$

$$\text{C}_6\text{H}_6 \xrightarrow{\text{NaOH}} \text{C}_6\text{H}_5\text{SO}_3\text{H} \longrightarrow \text{C}_6\text{H}_5\text{OH}$$

$$\text{CH}_3\text{OH} + \text{CO} \longrightarrow \text{CH}_3\text{COOH}$$
- Olefin may be oxidized** under mild conditions to hydroxyl derivatives and may be converted to aldehydes and carboxylic acids of lower molecular weight when stronger oxidizers are employed. Thus, oleic acid can be converted to dihydroxystearic acid with alkaline potassium permanganate.



When sodium dichromate in acid solution is employed, fission as well as oxidation occur and pelargonic and azelain acids are produced





### 5. Sodium Chlorite and Chlorine Dioxide

Sodium chlorite,  $\text{NaClO}_2$  is marketed as **80% dry powder** for use in bleaching. When reacted with chlorine, sodium chlorite releases chlorine dioxide,  $\text{ClO}_2$ , a gas at normal temperatures and soluble in water. **Chlorine dioxide** is a powerful oxidizing and bleaching agent; but because of its instability, it cannot be produced and stored. The aqueous solution is decomposed by light to perchloric acid and chloric acid, oxygen and water.

### 6. Chlorates

**Chloric acid**,  $\text{HClO}_3$  is a powerful oxidizing agent. It may be obtained in aqueous solutions at concentrations up to about 40% and is **stable** at temperature **up to 40°C**.

**Potassium chlorate** is a powerful oxidizing agent. However its **solubility in water** is limited, being only **3.3gm/100gm** of water at **0°C** and **56.5 gm/100gm** of water at **100°C**. It has been widely used in the dry, finely divided state as an oxidizing agent and in the laboratory as a source of pure oxygen.

### 7. Peroxides

The principal peroxides used as oxidizing agents are those of lead, manganese and hydrogen.

(a)  $\text{PbO}_2$  (b)  $\text{MnO}_2$  (c)  $\text{H}_2\text{O}_2$  (d)  $\text{Na}_2\text{O}_2$  (e) Silver Oxides

### 8. Nitric acid and nitrogen tetroxide

The principle **disadvantages** of nitric acid as a partial oxidizing agent arises from the tendency to **act as a nitrating agent**. Even then dilute solutions are used; the products of oxidation may contain nitro derivatives.

### 9. Copper Salts

Copper is capable of existing in two states of oxidation and of passing readily from one to the other of these states by oxidation or reduction. In its **higher state of oxidation**, it is capable of **acting** as an **oxidizing agent** and in its **lower state**, as **reducing agent**. This property makes the metal a useful material as an oxygen carrier or oxidation catalyst.

### 10. Alkali Fusion

Fusion with alkali in the presence of air (oxygen) often accomplishes oxidation impossible to obtain otherwise.

### 11. Fuming Sulfuric Acid (Oleum)

Fuming sulfuric acid,  $\text{H}_2\text{SO}_4 + \text{SO}_3$ , in the presence of mercury salts is a powerful oxidizing agent.

### 12. Ozone

The powerful oxidizing potential of **ozone** has been made **use** of in textile bleaching, paper bleaching, for destruction of phenolic bodies in coke-oven waste liquors, and in limited ways for water purification.

Ozone in oxygen mixtures reacts slowly with lower-molecular weight paraffinic hydrocarbons at room temperatures. At temperature above 260°C the ozone reaction merges with normal slow combustion.

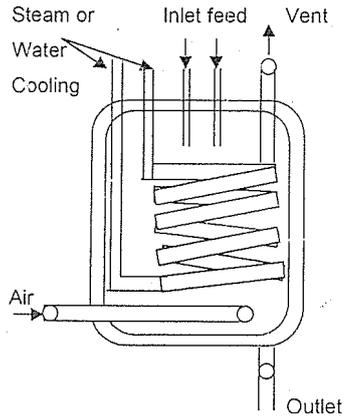
## 2.10 ACETIC ACID

The formation of acetic acid furnishes an excellent example of liquid-phase oxidation with molecular oxygen. Acetic acid may be obtained by the direct oxidation of ethanol, but the concentrated acid is generally obtained by oxidation methods from acetaldehyde that may have been formed by the hydration of acetylene or the oxidation of ethanol. The oxidation usually occurs in acetic acid solution in the presence of a catalyst and at atmospheric or elevated pressures.

Temperatures may range, up to 100°C, depending upon conditions, but are usually lower.

### 2.10.1 Acetic acid from acetaldehyde

Figure shows the general type of apparatus used and flow diagram of the manufacturing process. The reaction vessel consists principally of aluminum-lined steel vessel fitted with air distributor. Aluminum coils for heating and cooling, inlet and outlet opening and an air distributor. **In operation**, 4,500kg (10,000lb) of 99.00-99.8% **acetaldehyde** previously cooled to 0-5°C is introduced, and then 18-22kg (39.6-48.4lb) of **manganese acetate** is



added either in the form of **saturated acetic acid solution** or as a **powder** ground to pass a 200 mesh sieve. **Air** is introduced through the distributor head and at same time, **steam** is passed through the aluminum coils to raise the temperature gradually to the operating point. When the reaction starts oxygen absorption from the incoming air is almost complete and the heat of reaction must be removed by cooling water, which is substituted for the initial steam. The temperature is so controlled that after **1 hr** it approximates **27°C**, after **2 hr. 28-30°C** and after **4 hr. 60°C**.

The **most satisfactory** operating temperature is about **60°C**. The reaction is complete in about **12-14 hr**. The pressure is not allowed to exceed **5 kg/cm<sup>2</sup> (65.3 psi)**. The **nitrogen** being vented through a series of condensers attached to the dome. Condensed aldehyde is returned to the kettle. Before being released, the nitrogen is passed through **water scrubbers** to remove the last of the aldehyde, which is later recovered.

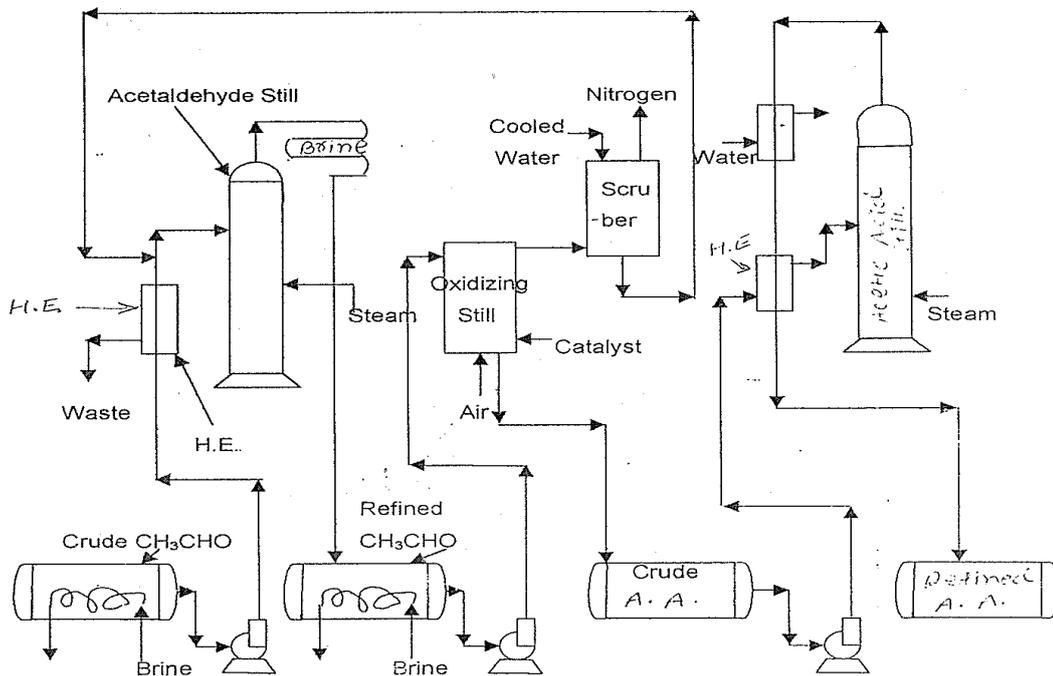


Figure. Flow sheet for oxidation of acetaldehyde to acetic acid.

A concentrated **acetic acid, exceeding 96%** in strength, results Distillation is used for final concentration and purification of acid. The **yield** varied from **88-95%** of the theoretical. A retort of this size will produce about 60 tones of 99% acid per month when operated normally or about 80-100 tones per month when forced.

Through **study of the mechanism** by which the catalyzed **liquid phase oxidation** of acetaldehyde to acetic acid proceeds, it has been found that at temperatures **below 15°C**

and in **suitable solvents** the **acetaldehyde** forms an **unstable compound**, acetaldehyde monoperacetate. At controlled low temperatures this compound can be made to yield peracetic acid and acetaldehyde, salts of the metal cobalt, copper and iron catalyze the first-stage reaction in a manner used in acetic acid manufacture.

This process is significant in that it is now in pilot-plant operation and commercial production of peracetic acid is being planned. Previously, *in situ* use of this peracetic acid oxidation of unsaturated natural fatty acid to epoxy derivatives. Commercial availability of low cost peracetic acid will open new areas of epoxidation reaction since almost any olefinic double bond is capable of epoxidation by peracetic acid. Because of the resulting co-production acetic acid, it is possible that custom epoxidation by use of acetic acid might be a logical result or that an added incentive will be given for product diversification by acetic acid user.

Oxidations of fatty oils by peracetic acid results in products, which are epoxidized, hydroxylated and acetylated and have properties of value for use in vinyl plasticizers and greases.

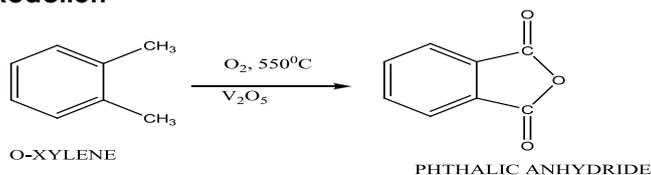
In the presence of catalysts, such as the acetates of the eighth group of metals, particularly cobalt, oxidation of acetaldehyde by air to acetic anhydride is claimed to occur directly at temperatures of 30-35 °C and to result in 85-95 percent conversion per pass

## 2.11 PHTHALIC ANHYDRIDE

### 2.11.1 Raw materials

O-xylene, Air, Vanadium pentoxide as catalyst

### 2.11.2 Reaction



### 2.11.3 Manufacture

**O-xylene** oxidation in presence of a **catalyst** like **vanadium pentoxide** at **550°C** yields phthalic anhydride.

As shown in figure preheated **o-xylene** is sent into a **hot stream of air** which is kept at **140–150°C** and under a pressure of **2 bars**. Air is enriched with vapours of o-xylene and care should be taken that the mixture is outside to combustion, where the catalyst packed in tubes.

Exothermic heat is absorbed by circulating molten salt in the space between tubes and shell. The hot vapours are allowed to exchange heat to waste heat boiler. By cooling

further phthalic anhydride is sub lined and is a deposit on the surface of switch condenser. The deposited film of phthalic anhydride is melted by means of circulation of steam.

The molten anhydride is again distilled under vacuum for purification. Along with phthalic anhydride a small amount of benzoic acid and maleic anhydride are also there. Phthalic anhydride is converted into phthalic acid through potassium phthalates. By hydrolyzing potassium terephthalic acid can be obtained.

## 2.12 BENZOIC ACID

The use of **manganese dioxide** for the **oxidation of toluene** to benzaldehyde and benzoic acid was formerly extensive. With manganese dioxide the principle product is benzaldehyde, for high yield to benzoic acid, a stronger oxidizing agent such as chromic acid is required.

**Considerable** benzoic acid is **manufactured by decarboxylation of phthalic** acid, a process that yields a chlorine free product. The development of this process has served to restrict the investigation of air oxidation method.

The **products of toluene oxidation**, chiefly benzaldehyde, benzoic acid, maleic acid and anthraquinone are obtain in proportions that **depend upon** catalyst, temperature, oxygen ratio and time of contact. **High oxygen ratios** and **long time of contact** are in general conducive to **Benzoic acid formation**. At temperature of **280 – 300°C**, reaction begins in presence of **vanadium oxide** catalyst, but reaction slow, long time of contact are required and benzoic acid tend to be the major product.

Oxidation of **toluene** with large excess of **air** over an **alumina- supported vanadium oxide catalyst** has been claimed to be an effective method for benzoic acid production. Thus the use of air: toluene weight ratios of **39 – 49: 1**, temperature on the order of **410–430°C** and contact time of **0.25 – 0.75 sec.** are claimed to result in **yields of benzoic acid** of about **34%** with corresponding maleic acid yields of 7–11% based on toluene consumed in the process.

## 2.13 EXERCISE

Sr. No.	Question	Marks	Exam/year
1.	Explain sulfonation and sulfation. State the principle sulfonating and sulphating agents	03	SPU 2005
2.	Give an account of different type of oxidising agents and oxidative reaction	08	SPU 2005
3.	With the help of flow diagram describe the manufacture of vinyl acetate	05	SPU 2006
4.	Write manufacture of acetic acid from acetaldehyde	05	SPU 2006, 2007
5.	Explain the term sulphonation and sulfation giving suitable examples	03	SPU 2006
6.	Write note on various oxidative reactions	06	SPU 2006
7.	Write manufacture of benzoic acid	04	SPU 2006
8.	Write note on different hydrolysing agents used for hydrolysis	03	SPU 2006
9.	With the help of flow diagram describe the continuous partial sulfonation of benzene	05	SPU 2007
10.	Describe manufacture of benzoic acid from toluene	04	SPU 2007
11.	Define the term hydrolysis. Write note on alkali hydrolysis	04	SPU 2007
12.	Using neat flow diagram describe the manufacture of ethyl acetate	05	SPU 2007
13.	Define term sulfonation and sulfation giving suitable examples. Also write various sulfonating and sulphating agents used for sulfonation and sulfation	04	SPU 2007

## 2.26 FURTHER READING

- Unit Processes in Organic Synthesis by P. H. Grogins.