

Natubhai V. Patel College of Pure & Applied Sciences

T. Y. B.Sc. (Industrial chemistry)

IC – 302: Unit Process, Synthetic dyes and Pharmaceuticals

UNIT – 2B

Syllabus

Oxidation: Introduction, types of oxidation reaction, oxidizing reagents and commercial manufacturing of Benzoic acid, Phthalic anhydride and Acetic acid.

OXIDATION2.8 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:

$$\text{CH}_3\text{CHOH}.\text{CH}_3 + \frac{1}{2} \text{O}_2 \longrightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2\text{O}$$
- 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

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

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

$$2\text{C}_6\text{H}_5.\text{CH}_3 + \text{O}_2 \longrightarrow \text{C}_6\text{H}_5.\text{CH} = \text{CH}.\text{C}_6\text{H}_5 + 2\text{H}_2\text{O}$$
- 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.

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

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

$$\text{CH}_3\text{OH} + \text{CO} \longrightarrow \text{CH}_3\text{COOH}$$
- 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.

$$\text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_7\text{COOH} \xrightarrow[\text{Alkali}]{\text{KMNO}_4} \text{CH}_3(\text{CH}_2)_7\text{CHOH} - \text{CHOH}(\text{CH}_2)_7 - \text{COOH}$$

3. Chromic Acid Solution

Chromic anhydride, CrO_3 , dissolves in glacial acetic acid is sometimes used as an oxidizing agent.

4. Hypochlorous Acid and Salts

The **lithium, sodium and calcium salts** of **hypochlorous acid** are known in the solid state. Although they decompose easily when wet, they are stable if thoroughly dry.

5. Sodium Chlorite and Chlorine Dioxide

Sodium chlorite, NaClO_2 is marketed as **80% dry powder** for use in bleaching. When reacted with chlorine, sodium chlorite releases chlorine dioxide, 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, 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) PbO_2 (b) MnO_2 (c) H_2O_2 (d) Na_2O_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.

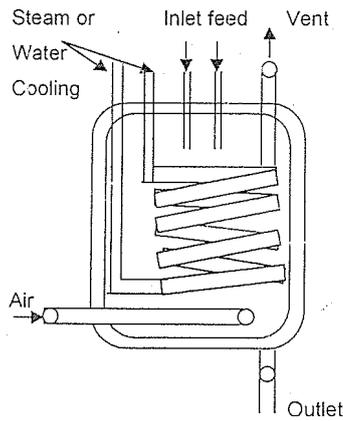
Temperatures may range, up to 100°C, depending upon conditions, but are usually lower.

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/cm² (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.

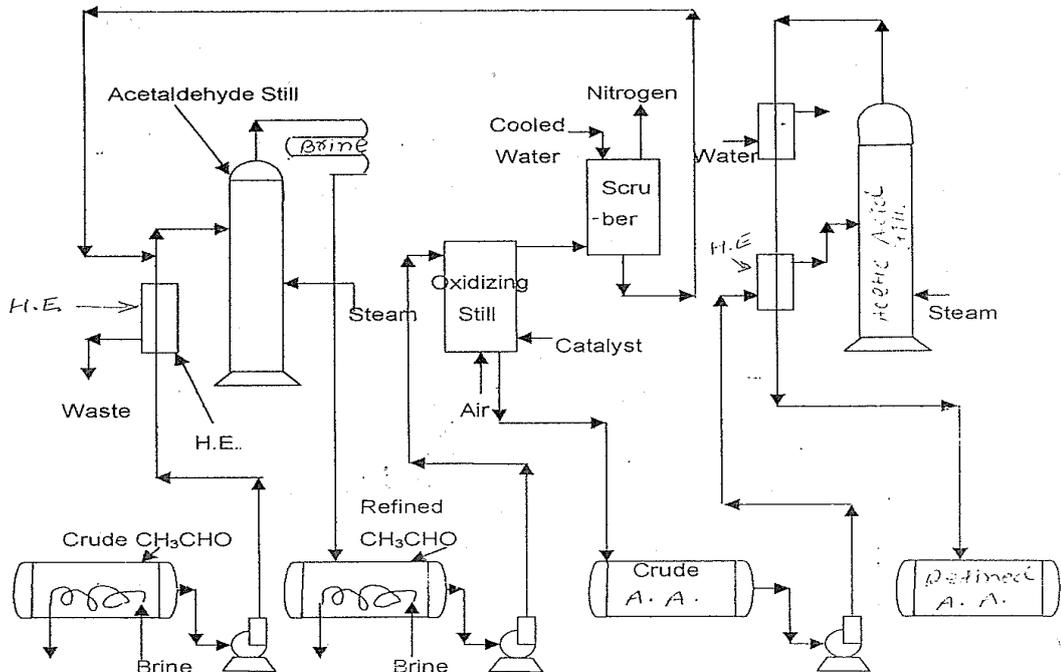


Figure. Flow sheet for oxidation of acetaldehyde to acetic acid.

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 tons 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 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 user 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.

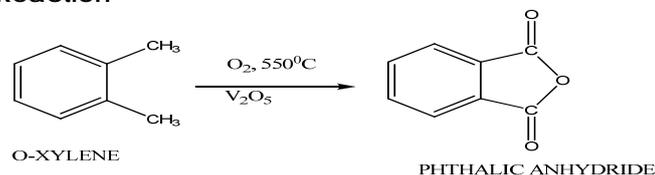
In the presence of catalysts, such as the acetates of the eighth group of metals, particularly cobalt, oxidation of acetaldehyde by air to acetic anhydride is claimed to occur directly at temperatures of 30-35 °C and to result in 85-95 percent conversion per pass

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.