

CHAPTER 2

2) PROPERTIES AND USES:-

2.1) PHYSICAL AND CHEMICAL PROPERTIES :-

1.	Melting point	16.635 ± 0.002 °C
2.	Boiling point	117.87 °C
3.	Vapor pressure	$\log p = 7.55716 - 1642.54/(233.386+1)$
4.	Thermal conductivity	0.158 W/m °k at 20°C
5.	Heat of melting	207.1 J/g
6.	Heat of vaporization	394.5 J/g at boiling point
7.	Specific heat of vapor	5.029 J/g °k at 124°C
8.	Density, 20.0°C	1.04928 g/ml
9.	Refractive index, n_d	1.36965
10.	Specific heat of solid	0.837 J/g °k at 100°k 11.83 mPa.s or cp at 20°C 10.97 mPa.s or cp at 25°C
11.	Critical pressure	57.856 kPa (571.1 atm)
12.	Critical temperature	321.6°C
13.	Magnetic susceptibility	
	Solid	32.05 x 10 ⁻⁶ cm ³ /mol
	Liquid	31.80 x 10 ⁻⁶ cm ³ /mol
14.	Dielectric constant	
	Solid	2.665 at -10.0°C
	Liquid	6.710 at 20.0°C
15.	surface tension, mN/m or dyne/cm	27.57 at 20.1°C
16.	Flash point, open cup	57°C
17.	Autoignition point	465°C
18.	Lower limit of flammability	40°C
19.	Lower limit of flammability	5.4 vol % at 100°C

- Though the molecular weight of acetic acid is 60.05, its apparent molecular weight varies with both temperature and the other associating substances present.
- It is miscible in all proportions with water, ethanol and ether.
- It is an excellent solvent for organic compounds.
- A zero dipole moment for unsymmetrical acetic acid structure (is explained by the formation of symmetric dimers via hydrogen bonding in which the dipole moments cancel).
- No high dissociation ionic species in acetic acid solution.
- Possesses relatively low basicity or proton affinity.
- Has a very strong leveling effect on bases and solvolyzes all strong bases to acetate ion, CH_3COO^- .

2.2) APPLICATIONS AND USES :-

- Acetic acid has a broad spectrum of applications. They are as follows.
- Over 60% of acetic acid produced goes into polymers derived from either vinyl acetate (vinyl esters) or cellulose (cellulose esters).
- Most of poly (vinyl acetate) is used in paints and coatings or used for making poly (vinyl alcohol) and plastics.
- Also, cellulose acetate is used to produce acetate fibers
- Acetic acid and acetate esters are used extensively as solvents and in organic synthesis.
- In the production of white lead and chrome yellow pigments, it is used to make lead available in a soluble form for further reaction to give basic lead carbonate and lead chromate.
- Also used to provide the necessary acidity in the number of processes carried out in an aqueous media.
- Used in the mordanting process and in dyeing of wool in textile industry.

- Used as a coagulant for rubber latex in manufacture of elastic thread, as a component of photographic stopping and fixing baths and as a laundry sour.
- Also used in electroplating, engraving and in the processing of fish glue.
- Dilute acetic acid functions either or both as a preservative and flavoring agent in food stuffs such as pickled vegetables, condiments, jellies and confectionery.
- RDX - the high explosive cyclotrimethylenetrinitramine is furnished on nitration of hexamethylenetetramine with acetic acid.
- Also, lower alkyl esters such as methanol, ethanol, isopropanol and butanol are widely used as solvents for lacquers and adhesives.
- Other esters form basis for synthetic flavors for perfumes and bornyl acetate in the manufacture of synthetic camphor.

Acetic acid is mainly utilized in the manufacture of the following products:

1. Acetic Anhydride:

Acetic Anhydride is a very versatile product. It is a part of the manufacturing of Cellulose Acetate fiber, Plastics, Vinyl Acetate Monomer etc. The pharmaceutical industry uses Acetic Anhydride as a dehydration agent. The Dye industry also uses it for manufacturing Dyes and Dye intermediates. Ordnance factories use it in the manufacture of explosives. Perfumes are also made by the use of Acetic Anhydride. Aspirin, Paracetamol and other antibiotics are also made by using Acetic Anhydride.

2. Vinyl Acetate:

Vinyl Acetate is a basic raw material for Poly Vinyl Acetate and Poly Vinyl Alcohol. Vinyl Acetate Monomer is used in the manufacture of latex paint, paper coatings, Adhesives and textile finishing.

3. Cellulose Acetate:

Cellulose Acetate is an important constituent of thermoplastics and fibers. The textile industry uses cellulose acetate widely for the production of

cellulose acetate fiber. The other uses of Cellulose Acetate are the production of film, plastic sheets and the formulation of liquor.

4. Monochloro Acetic acid:

- Monochloro Acetic acid [MCA] is used extensively in the manufacture of Herbicides, Preservatives, Bacteriostat and Glycine. Mainly it is used in the manufacture of Carboxy Methyl Cellulose which is a gummy and strong adhesive powder used in drilling for oil. MCA is also used for producing laboratory chemicals like EDTA and 2 4 D Thioglucolic acid.

2.3) OTHER ACETATES [ESTERS]:

- Acetic acid is used for the manufacture of organic and inorganic acetates like Methyl Acetate, Ethyl Acetate, Butyl Acetate etc.

2.4) PURIFIED TERPHTHALIC ACID [PTA]:

- Acetic acid finds use in the manufacture of PTA as a solvent. PTA is an alternative raw material for polyester fiber manufacture instead of Dimethyl Terephthalate [DMT].

2.5) FOOD ADDITIVES [VINEGAR]:

Acetic acid is widely used in the form of vinegar as a food additive. As vinegar it is used for the preservation of food and also to impart a sour taste to certain preparations.

2.6) NATURAL LATEX COAGULANT, OIL COAL ACIDIZER AND IN TEXTILE PRINTING:

Acetic acid is used in the textile industry for textile processing and printing. It is also used in the rubber industry as a natural latex coagulant.

Acetic acid is also used in the manufacture of plastics, pharmaceuticals, Dyestuff and Dye intermediates, insecticides and photographic chemicals.

CHAPTER 3

3.1) VARIOUS COMMERCIAL PROCESSES :

There are three main routes for the manufacture of Acetic acid. They are described below.

a) The direct oxidation of n-Butane (or to some extent LPG and light Naphtha).

This reaction can be carried out in three different ways as shown below:

- i. A vapor phase non-catalytic reaction at 350 to 400 deg. C. and 5-10 atm. pressure.
- ii. A liquid phase non-catalytic reaction at 160-180 deg. C. and 45-10 atm. pressure.
- iii. A liquid phase homogenous catalytic reaction at 160-180 deg. C. and 45-55 atm. pressure.



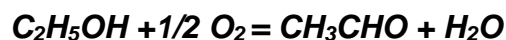
n-Butane Oxygen Acetic acid Water

b) ACETALDEHYDE OXIDATION

In India the majority of the Acetic acid plants follow this route. Alcohol is used to obtain Acetaldehyde (Alcohol is obtained by the fermentation and distillation of Molasses).

Acetic acid is produced by this route using a two step process.

- i. Oxidation of alcohol to Acetaldehyde:



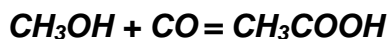
Ethyl alcohol Oxygen Acetaldehyde Water

- ii. Oxidation of Acetaldehyde to Acetic acid:



Acetaldehyde Oxygen Acetic acid

c) CARBONYLATION OF METHANOL: In 1995 the first Indian plant based on this process went online at G.N.F.C Bharuch.



Methanol Carbon Monoxide Acetic acid

3.2 (a) CHOICE OF PROCESS:

The production of acetic acid by acetaldehyde oxidation has an extensive patent literature. It has been in commercial operation since 1911 in Germany and 1920 in the US. Since the bulk of acetic acid in the world today is obtained from acetaldehyde, the acetaldehyde processes enjoy a leading position in any consideration of acetic acid manufacture.

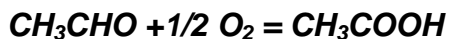
Even in many processes acetaldehyde is essentially an intermediate in the production of acetic acid and the four common main routes to acetaldehyde are:

- i) the vapor-phase dehydrogenation or partial oxidation of ethyl alcohol
- ii) the liquid-phase hydration of acetylene
- iii) the high-temperature oxidation of saturated hydrocarbons
- iv) the liquid-phase oxidation of ethylene.

Thus, the choice or selection of process leads to oxidation of acetaldehyde. Also, the overall yield is greater than 90% compared to other processes such as in oxidation of n-butane in liquid phase can exceed just about 60%.

3.2(b) PROCESS DESCRIPTION:

The continuous oxidation of acetaldehyde in the liquid phase is generally carried out by using air or oxygen in the presence of catalyst manganese acetate. The reaction mixture containing acetaldehyde diluted with crude acid and manganese acetate solution is circulated upward through the oxidation tower.



Reaction conditions when air is used are 55-65° C at 70-75 psi (about 5 atm); and when oxygen is used, 70-80°C at a pressure sufficient to keep the acetaldehyde liquid.

The reaction mixture is drawn off the top of the distillation tower and is diluted continuously in as many as 3 distillation columns. Now, crude acid is fed into the top of the distillation column and other volatile components are withdrawn overhead while a residue containing manganese acetate is removed at the bottom. A low boiling fore-run is taken off overhead in the second column and 99.6 - 99.8% pure acetic acid is taken off just above the reboiler.