

## **EXECUTIVE SUMMARY**

Acetic acid is one of the important carboxylic acids. It is a colourless corrosive liquid. Acetic acid and its derivatives are widely used in chemical, pharmaceutical, food processing and textile industry.

There are basically three specifications of acetic acid viz. Technical grade, Pure and Analytical reagent.

There are three main processes to manufacture acetic acid viz.

1. Oxidation of acetaldehyde
2. Direct oxidation on n-butane
3. Carbonylation of methanol

Acetic acid is mainly used in the manufacture of Purified Terephthalic Acid, Vinyl Acetate Monomer, Acetic Anhydride, Esters, Monochloroacetic acid, etc.

There are about 20 companies manufacturing acetic acid in India with a total installed capacity of approximately 150,000 TPA. The major concentration of units is in Western India followed by South and North India. In the Eastern region, there is only one plant with an installed capacity of 4,500 TPA.

The production was 95,600 MT in 1991-92 with a capacity utilization of 65% on the whole. The capacity utilisation is only indicative as there are certain units which have been utilising more than 90% of their capacity. During the decade of 1980-90, the average annual growth rate was 11%.

The sudden increase in production during the period 1986-90, is attributed to the increased demand of PTA and VAM in India, and to the increased and sustained availability of industrial alcohol.

The demand is expected to grow at an average rate of 13.6% annually during the period 1990-2000 AD. The demand is estimated at 1,69,108 TPA by 1995 and 2,92,147 TPA by the year 2000 AD. PTA, VAM and Acetic Anhydride would account for more than 70% of the total consumption of acetic acid.

There were large imports of acetic acid during the period 1985-87 when almost 3,500 MT of acetic acid was imported each year. In 1991-92, the import has reduced to 122 MT only. The exports during the last decade have been negligible, however, in the changing scenario there is good potential for export of acetic

acid. The major constraint in export of acetic acid pertains to its quality. India exported 637 MT during 1991-92.

The present manufacturing facilities are based on the process of acetaldehyde oxidation which in turn is manufactured from ethyl alcohol. The selectivity of conversion of acetaldehyde to acetic acid is in the region of 85-91%, while abroad, by the similar route, the selectivity is rather high, in the range of 94-97%. The power and steam required per tonne of acetic acid abroad, is low as compared to 400-600 KWH and 1.8-2.0 T in India.

The yield in acetic acid plants in India may be lower as compared to plants overseas as the plants are of small capacities and the dilute acid stream coming from the distillation column is rejected. If the plants are of larger capacities, the recovery of acetic acid from that stream would be economical and it will boost the yield factor of the plants. The manufacturers feel that the selectivity in the reactor in the Indian plants is equally good.

Quite a few Indian manufacturers produce acetic acid for captive consumption to produce further value added products. The technology to produce acetic acid using ethyl alcohol as the feedstock has been adapted successfully in India over a period of time.

The minimum economic capacity for an acetic acid unit based on ethyl alcohol route is 6,000 TPA. There is no methanol or hydrocarbon based manufacturing facility available in India though M/s. GNFC has entered into collaboration with BP Chemicals, UK to setup 50,000 TPA (100% EOU) methanol based acetic acid plant.

The present installed capacity in the world for acetic acid is estimated at over 5 million TPA. The major manufacturers worldwide include Hoechst, Walker Chemie, BASF, Huls in Germany; BP Chemicals in UK; Montedison in Italy; Daicel, Nippon Gosei Kagaku and Showa Acetyl Chemical in Japan; Celanese and Union Carbide Corp. in USA.

Only a few units use ethyl alcohol as feedstock and most of the large capacity plants are based on n-butane, naphtha or methanol as the feedstock.

Lenzing AG, the world's largest manufacturer of viscose fibre, produces acetic acid and furfural from exhaust vapour and condensates from evaporation of spent liquor from pulping process. This process achieves a purity level of 99.9% for acetic acid, with an extremely low content of formic acid and other impurities.

Lonza AG Ltd., Switzerland and Celanese, Mexico use acetaldehyde as the main raw material with a high selectivity of 94 and 97.7. The utilities consumption in the Lonza, AG plant is extremely low when compared with Indian Plants.

The processes used internationally to manufacture acetic acid are :

1. Oxidation of paraffin hydrocarbons
2. Carbonylation of methanol

The feedstocks used in the process using hydrocarbon include :

#### **FEEDSTOCK**

#### **ORGANISATIONS**

n Butane	Celanese, Union Carbide, USA; Huls, Germany
n Butane (2 Stage Oxidation)	Bayer, Germany
Light Gasoline	BP Chemicals, UK

Carbonylation of methanol was commercialised by BASF AG in 1960 based on a Cobalt/Iodine catalyst. Monsanto Co., USA patented the process which was later sold to BP Chemicals, UK, involving Rhodium/Iodine catalyst for production of acetic acid through carbonylation of methanol in 1970. Hestalloy and Stainless Steel are used for construction of the equipment as they are more suitable for use under the operating conditions. Production of acetic acid is highly capital intensive and the minimum economic capacity for using methanol as feedstock is 50,000 TPA.

A number of Indian manufacturers have well equipped laboratories with various sophisticated equipments such as Gas Liquid Chromatographs, Atomic Absorption UV Spectrophotometers, Polarograph, etc. These facilities are mainly used for end products and raw material testing and not for in-house R&D.

The R&D expenditure is quite low in the range of 0.2-0.8% of the total turnover as compared to 2-3% in the developed countries.

NCL, Pune have developed a low cost catalyst for carbonylation of methanol but it is not yet commercialised. It has also developed a One Step process to convert ethyl alcohol to acetic acid, using a metal oxide catalyst.

The BIS standards for acetic acid are IS 695 and IS 5208. There are various ISO standards pertaining to acetic acid. With the increased price benefit on account of its export potential, special emphasis is laid on the packaging, transportation and quality of acetic acid.

There are a number of technology suppliers for acetic acid units in India who have completely indigenised the design and the technology. India has a number of fabricators to supply equipments as per design requirements. The thrust areas for technology absorption include the development of a low energy consuming process by integrating the steps taken by various companies worldwide. At the same time, improving the selectivity of the conversion of acetaldehyde to acetic acid from the present level of 86-90 to 94 is required.

As per projections (Annexure 8) by 1995 5.54 million T of molasses would be produced and the total availability of ethyl alcohol would be in the range of 1073 million litres. Going by the growth trends of alcohol based chemicals, the requirement by that sector alone would be in the range of 800-900 million litres.

### **RECOMMENDATIONS**

1. The thrust, should be on the ethyl alcohol-based route for acetic acid. With the growth of the sugar industry, the disposal of molasses can pose problems. The available molasses can be effectively used.
2. However, the success of the alcohol based industries would mainly depend upon the location of the production units, besides other salient factors. In the earlier days of alcohol and alcohol based industries, the locational factor had been ignored in many cases, where the units were located far out from the point of availability of molasses and/or alcohol viz; ICI in collaboration with Union Carbide at Bombay, ACCI at Calcutta and another one at Sirsilk which are all located about 300 to 500 Kms away from the source of alcohol or molasses. As many alcohol-based plants are located in areas of alcohol scarcity, the capacity utilisation had been poor. This created problems for the allocation arranged supplies from other states, which had surplus. Besides, this amounted to heavy transport/handling cost of the raw material. In recent years, the trend is in favour of integrated complexes. Liberalised issue of licenses for production of alcohol by the sugar factory would help, is the opinion of some experts. The concept of integrated complexes with sugar as the core industry have also to be planned. In such complexes, the by-products like molasses and bagasse should be utilised in captive productions. Such a planning will lead to the advantages of using cogenerated power, common infrastructure, easy effluent and pollution control, better management leading to better profitability.
3. Development of various alcohol-based chemical and polymer industries should be encouraged, as also new derivatives and high value added products. At the same time, a rational product mix should be in the

planning depending upon the local demand projections and the export potential. Such a rational planning is very imperative so as to save glut of one product and shortage of the other. Expansion of the existing units should also be planned on this rational.

4. The manufacturers are strongly of the opinion that ethyl alcohol should be rationally priced to suit the alcohol-based industries. Taxes and levies should be kept at the minimum. They also feel that there should be a special price of alcohol for the alcohol-based industries which are export oriented as this will enable foreign exchange earning, and that there should be preferential allotment of alcohol to EOUs.
5. There are many alcohol-based units which are suffering for timely availability of the raw material. Hence, the manufacturers feel that in order to avoid the same, there should be free interstate movement of alcohol.
6. In addition, the manufacturers strongly opine that the molasses price, for delivery to the distilleries, should be adjusted so as to suit the alcohol industry's viability. This can be done through reduction of excise or taxes or a combination of both to ensure lower price of alcohol for chemical industries. With the decontrol of molasses, it is imperative that the demand of alcohol based industries should be met by maintaining 60% share of ethyl alcohol for alcochemical industries.
7. Selectivity of acetic acid in the Indian industry is in the range of 86% to 90%, while in almost similar conditions and plants, the selectivity is 94% to 97%. Secondly, the energy consumption, both power and steam, is comparatively higher in the Indian plants in terms of per tonne of acetic acid produced. Thirdly, there are problems of high cost which adversely effect competitiveness in the export market and profitability. Such problems would need in-house research by the industry, which is mostly applied research related to the specific problems faced by the units.

Besides, there appears to be a scope for improving the designs of some of the critical equipments viz. reactors. This calls for organising a Design Development & Improvement Cell at the manufacturers' workshops.

There is need for research on development of catalysts, leading to higher selectivity and cost saving. Conservation and saving of energy & process improvements etc. will also come within this ambit. The national institutes like National Chemical Laboratories Pune, Indian Institute of Chemical Technology, Hyderabad and other Government research organisations etc. could undertake such fundamental research.

There should be a proper interaction between the research organisations, industry and the plant manufacturers on the problems and the results of R&D efforts.

8. The areas of research are identified as under :

- i) To effect improvement in selectivity of acetic acid.
- ii) Studies on catalysts, on their substitution where possible in the interest of cost reduction and efficiency.
- iii) Energy conservation and process improvement.
- iv) Design development & improvement of the critical equipment.
- v) To improve the quality of the product to meet the rising standards in India and the stringent quality standards prevalent abroad.
- vi) To improve plant and equipment designs for process convenience/better performance and higher product recovery and overall plant efficiency.
- vii) To modify the process techniques and renovate the material flow so as to reduce the quantity/cost of consumables, power and energy and thus reduce the cost of production to ensure better market competitiveness.
- viii) To innovate and renovate the process with a view to search for intermediates, co-products and by-products from the main stream.
- ix) To incorporate modern developments in the process control and instrumentation by using microprocessor based electronic instruments.
- x) To effect improvement in acetaldehyde recovery system.
- xi) To develop an efficient system to remove the light products i.e. formic acid and waste water so as to improve the product quality.
- xii) Development of better material of construction in collaboration with Bhaba Atomic Research Centre and Defence Metallurgical Research Laboratory.

9. Acetic acid being an input for many valuable and sophisticated endproducts, in process quality control is very important and so is the testing. This aspect is more important in the case of export oriented products. Central Regional Testing Centers should extend testing facilities. The production units should also have proper Quality Control, Research & Testing Laboratories.
10. Research should be carried out for development of higher capacity acetaldehyde/reactors by designing tubular reactors with metal oxide catalyst pellets and adequate cooling facilities.

The present acetaldehyde coolers are limited to the capacity of 20-22 TPD using the silver netting system. Designs of efficient and higher capacity coolers have to be developed.

11. There is need to develop a direct link between the ethanol distillation system and the acetaldehyde reactor. The system could have a feed of 80 to 95% ethanol vapour with balance water direct into the acetaldehyde reactor (with air) with energy savings on both sides.
12. Oxidation of acetaldehyde to a mixture of acetic acid and acetic anhydride under special conditions. There is a need to develop effective azeotrope forming compound to remove the water as it is formed, so that the anhydride/acid ratio is good.
13. Process development for ketene-based products other than acetic anhydride. The process for manufacturing acrylate esters from ketene and formaldehyde reaction has not yet been commercialised. Steps should be taken to commercialise the same.
14. Development of process to oxidise ethylene to the glycol diacetate and make MEG and acetic acid as coproducts. This needs detailed study followed by research.
15. Use of catalyst in acetic acid, as in any other industry, is very vital from all aspects viz. quality, recovery efficiency and cost. Types and quality of catalysts have been standardised, but research has got to be continued in this regard for possible substitution for better results and savings in costs. The substitute catalyst for carbonylation of methanol developed indigenously by NCL, Pune should be commercially exploited for future indigenous production and possible exports. NCL, in collaboration with the user industry is trying to develop the new formula of the catalyst by using Iron Molybdate as a catalyst which may give 100% conversion of

ethyl alcohol to acetaldehyde as against 50% per pass, converting over silver catalyst. In case this research is successful, it would be extremely beneficial to the industry.

16. Emphasis should be given to improve the conversion and efficiency of the Acetic Acid/Anhydride reaction system. The Andhra Sugars have done in-house research on this and have improved the ratio of acetic anhydride and acetic acid from 40:60 to 60:40.
17. Maintenance of gas compressors is difficult and they also consume a lot of energy. If replaced by blower systems, energy consumption and plant down time, are both reduced. The blower system is also easier to operate. More research should be carried out in the field of improving efficiency by using blower systems. This changeover would help in upgradation of the existing technology.
18. As the scale of operations in India is small when compared with international standards, the technology suppliers should aim to export the technology to developing/under developed countries where agro based ethyl alcohol is available. This can yield results as most of the international technological developments relate to petro based raw materials only.