

EXECUTIVE SUMMARY

1. INTRODUCTION

Butanol is an aliphatic saturated C₄ alcohol. It is termed normal butyl alcohol, n-butyl alcohol, butyric alcohol, n-butanol or 1-butanol. The structure is represented by CH₃ CH₂ CH₂ CH₂ OH or C₄H₉OH. There are four structural isomers of this alcohol; two primary, one secondary and one tertiary. n-Butanol occurs in nature in compound form. It also occurs sometimes in high concentrations, in fusel oils obtained by fermentation.

It is a colourless liquid, having characteristic vinous odour. The vapour has an irritant effect on mucous membranes and narcotic effect in higher concentration. It is partly miscible with water. The autoignition temperature, freezing point and boiling point is 365°C (-) 89°C and 117°C respectively with flash point of 35°C. It is a major product since world war II and serves as a starting material for a wide range of substances.

Butyl alcohols can cause fat accumulations in the liver, heart and kidneys of experimental animals. The largest use for butanol and its derivations is in the coating industry for the formulation of nitrocellulose lacquers. An emerging market for butanol is latex in the form of butyl acrylate. The more important derivatives of butanol are butyl acetate, butyl glycol ether and plasticizers as an extraction solvent for oils, drugs and perfumes. It is an excellent diluent for brake fluid formulations and also used as an extractant in the manufacture of antibiotics, vitamins and hormones. Isobutanol can also be used in practically all of the applications that have been mentioned for butanol.

Butanol is moderately dangerous; toxic fumes are emitted when heated to decomposition. Excessive exposure can cause headache, dizziness, nausea etc. The liquid effluent is degradable and can be disposed after neutralisation with lime followed by biodegradation. Liquid and gaseous effluents can also be incinerated.

2. DEVELOPMENT OF TECHNOLOGY

Between 1852 and 1871 butyl alcohols were discovered and their structures established. In 1871 Lieben and Rossi prepared n-butyl alcohol by reducing n-butyraldehyde. The original observation of the butanol production by 'Clostridia' was made by pasteur and acetone fermentation by Schardinger. Interest in commercializing butanol-acetone fermentation occurred in 1909 primarily as a means of obtaining butadiene as a raw material for a synthetic rubber.

In 1914 Weizmann established a fermentation process in USA using 'Clostridium acetobutylicum' to ferment starchy material. With the outbreak of World War I demand for acetone increased and large scale fermentation operation were established in Canada, USA, India and elsewhere. After world war; DuPont developed fast-drying nitrocellulose lacquers for the automobile industry requiring butyl acetate as solvent. By 1930's synthetic production began and fermentation process using molasses instead of grain were developed. Fermentation industry thrived until the end of World War II. There were quite a few producers but currently only one plant in South Africa is reportedly working with fermentation process.

The most wide spread means of producing butanol today is the oxo process where propylene and syngas (CO and H₂) are reacted. The oxo or hydroformylation reaction was discovered by O. Roelen in 1938. The products were both aldehydes and ketones. Most of the aldehydes produced are either reduced to alcohol directly or subjected to aldol condensation prior to hydrogenation. High pressure cobalt catalysts oxo process was commercialised since 1950. Ruhrchemie (Germany) used this process for producing detergent range alcohols. Many variations of the above process have been developed and commercialised.

The next improvement came with the range of catalyst to phosphine-modified cobalt carbonyls with reduced operating pressure. Two step rhodium oxo hydrogenation process uses rhodium carbonyls as oxo catalyst with reactivities about 10² to 10³ times higher than cobalt carbonyls. The process also required less pressure. Rhodium based catalyst has been further modified in recent years.

The aldol process uses acetaldehyde as the precursor. Acetaldehyde is produced by direct ethylene oxidation or by dehydrogenation of ethanol.

3. PROCESS OF MANUFACTURE AND RAW MATERIALS

The processes of manufacture of butanol are propylene hydroformylation (oxo synthesis), crotonaldehyde hydrogenation starting with acetaldehyde or ethanol, Reppe synthesis and fermentation. The raw materials for oxo process are propylene and syngas. In Reppe process, the raw materials are propylene, carbon monoxide and water. For the production of acetaldehyde ethanol or ethylene can be used. Acetaldehyde is aldolized followed by hydrogenation. Fermentation process uses molasses or starch grains to produce simultaneously butanol, acetone, ethanol, carbon dioxide, livestock feed, hydrogen and riboflavin.

In the oxo reaction, carbon monoxide and hydrogen are added to carbon-carbon double bond of propylene, in the liquid phase in the presence of catalyst, (cobalt hydrocarbonyls) producing 1-butanol and some amount of isobutanol. Though there

are several variations of this process, the differences being in the reaction conditions (pressure, temperature). In the high pressure process, operation pressure is 200-300 kg/cm² and temperature 100-180° C. The catalyst is Co and the product is 75% or more of butanol and the rest isobutanol. The new process using Rh catalyst operates at much lower pressure (7-20 kg/cm²). The isomeric ratios achieved are about 92:8 or 95:1-butanol to isobutanol. Catalytic hydrogenation of the aldehydes lead to the formation of the corresponding alcohols. As only primary alcohols can be obtained via the oxo synthesis it is not possible to produce secondary and tertiary butyl alcohol by this process.

In Reppe process developed in 1942, propylene, carbon monoxide and water are made to react under pressure in the presence of a catalyst (tertiary ammonium salt of polynuclear iron carbonyl hydrides). The difference between this process and classic Co catalyst hydroformylation is that at low temperature (100° C) and pressure alcohol is formed directly. This process has not been commercially successful in spite of certain advantages it offered compared to conventional oxo process. This is attributed to more expensive process technology.

Until the mid 1950s the manufacture of n-butanol based on acetaldehyde was the preferred process. With the development of the oxo synthesis, this process has lost its importance in developed countries. Acetaldehyde is produced either from ethanol or ethylene and is aldolized to acetaldol at normal temperature and pressure in the presence of alkaline catalyst. With conversion of about 60% the acetaldol yield is about 95%. Unreacted acetaldehyde can be distilled off and recycled.

Various gas and liquid phase processes have proved their value for the hydrogenation of crotonaldehyde to butanol. Copper catalyst are particularly useful. For tropical countries with large supplies of cheap biomass as well as for the more developed countries of the third world who do not have their own oil resources this process is alternative to oxo process. The plants producing butanol from alcohol have been generally located near alcohol distilleries. Propylene-syngas based plant is located as down stream of naphtha cracker or very close to that naphtha cracking unit which is normally a part of a petrochemical complex.

4. CAPITAL EQUIPMENT

Propylene is a co-product of ethylene from a naphtha cracking unit or alternatively from natural gas cracking unit. Syngas is produced by reforming naphtha or natural gas. Naphtha/natural gas cracking unit and reformer are two main capital equipment of a petrochemical complex. The capital cost for these units is substantial.

The other capital equipment required for oxo process are syngas compressors, alcohol reactors, blowers, waste heat boilers besides various safety and control equipment. NOCIL imported most of the capital equipment for their butanol plant except waste boilers. For the alcohol route some of the plant and equipment were imported by Somaiya and Oswal units, but today they are all available indigenously.

In the late 1960s, Indian capability in terms of capital equipment fabrication was restricted compared to what is today. Nevertheless there are certain proprietary or patented design equipment like reformer furnace, syngas compressors, reactor and blowers are supplied by technology supplier. Fabrication facility for reformer furnace is available in India.

5. STRUCTURE AND STATUS OF INDIAN INDUSTRY

AT present, five units, all in private sector, are engaged in the manufacture of butanol. The present installed capacity is about 25,700 TPA against licensed capacity of 33,200 TPA. Only one unit has been issued with licence for expansion. There are three units in Maharashtra, and one each in U.P. and A.P. Only two units are using petrochemical feed stock. There are large number of organisations in the organised sector who have been issued with letters of intent or industrial licenses for the manufacture of butanol and the approved capacity is close to 92,000 TPA. Out of these, only Andhra Petro and Reliance Industries plant will be based on petrochemical feed stock. Butanol production in 1982 was 10,740 MT and in 1992 about 20,000 MT.

The main producing units are Oswal Petro Chemicals, National Organic Chemical Industries Limited, Somaiya Organic (I) Limited, Kolhapur Sugar Mills Limited and recently commissioned Andhra Petro having installed capacities of 4,200, 6,000, 7,500, 3,000 and 5,000 TPA respectively. The product quality of NOCIL, Oswal and Somaiya is satisfactory and very close to international specifications. NOCIL, one of the oldest petrochemical complex in India commissioned their butanol plant in 1969 with capital investment of Rs. 452 lakhs, the present replacement value of which is Rs. 5,437 lakhs. For Somaiya's plant original project cost was Rs. 411 lakhs and the present cost of expansion is Rs. 194 lakhs. The performance of these units, over the years was satisfactory. None of the units are exclusively making butanol but manufacturing other chemicals also. The ex works price of butanol of NOCIL is Rs 30,000 per MT while that of Oswal and Somaiya it is Rs 38,000 and Rs. 30,500 respectively.

The major problem with the industry is feed stock, besides other constraints like power, infrastructure etc. Both naphtha and alcohol are allocated feed stock. While

one is controlled by Central Government the other is controlled by States. Industrial alcohol prices are altered and allocations changed by the States at times causing problem for industry. This requires a uniform policy on alcohol by the States.

6. DEMAND / EXPORT / IMPORT

The demand of normal butanol by the end users was more than what industry could produce. This necessitated import. The major sectors of consumption are paints and resins, pharmaceuticals, esters, plasticizers and others. The demand in 1984-85 was 13,465 MT while the production was 11,965 MT and import was 1500 MT. The corresponding figures for the year 1991-92 are 22,000, 20,000 and 5,000 MT respectively, Estimated demand for the year 1999-2000 AD is 46,700 MT. Unless the price is internationally competitive, export possibility is remote.

7. TECHNOLOGY

The technologies for butanol manufacture are the followings

- Oxo-synthesis, propylene hydroformylation
- Crotonaldehyde hydrogenation starting from acetaldehyde or ethanol.
- Fermentation.
- Reppe synthesis,

The most important and widely commercialised technology is the oxo-synthesis. It is in use in the developed countries having substantial petrochemical feed stock. The oxo-synthesis technology in use in NOCIL plant is from Shell, Netherlands for the alcohol section and Holdor - Topsoe for reformer section. Davy McKee, U.K. is the technology supplier for Andhra Petro's oxo alcohol plant.

The technologies for Somaiya Organics plant is from Melle-Beznos, France. Oswal plant technology is from UCC, USA. Somaiya, Oswal and Kohlapur Sugar plants are alcohol based. The plants of NOCIL, Somaiya and Oswal are in operation for a considerable period of time and technologies are fully absorbed. The state of the art technology is based on rhodium catalyst. None of the oxo-synthesis technologies are available indigenously. Catalysts are very critical for the technologies referred above. Both indigenous and imported catalysts are in use by the units.

8. TECHNOLOGY SUPPLIERS AND ENGINEERING CONSULTANTS

Internationally there are several technology suppliers. Some of the technology suppliers are Shell, Netherlands, Union Carbide, Celanese Chemical, Dow Chemical all from USA, BASF, Huls, Hoechst, Germany and Koeichemical, Tokuyama

Petrochemical and few others from Japan. The other technology suppliers are Davy Mckee, U.K. & Barsou & Consultors Associados, Brazil. The engineering consultants are Shell/Haldor-Topsoe, Davy Mckee and few others. Davy Powergas (India), Lurgi India Company Pvt. Ltd. and NOCIL Technical Service are the Engineering consultants. Molasses to ethanol technology is available indigenously as was seen in the case of EO/EG manufacture. None of the national laboratories is in a position to provide the technology for butanol be it oxo process or ethanol based route.

9. INTERNATIONAL SCENARIO

USA is the largest producer of butanol as well as isobutanol followed by Germany and Japan and other Countries in Europe. Most of the butanol manufacturers do not exclusively manufacture butanol but other chemicals as well. Oxo process is the predominant process in operation all over the world. Countries having biomass and ethanol are following the ethanol route and a limited few are following the fermentation process. These countries are Brazil, South Africa and probably Argentina.

Although the capacity utilization varied between 60-70% but the growth of the industry was fairly rapid. In 1976 butanol production in USA was 248,100 MT while the world production was 540,000 MT and the corresponding figures for 1984 was 700,000 MT and 1,200,000 MT respectively. Compared to this, butanol industry growth rate in India is insignificant. In the international arena the R&D efforts, in most of the cases have been directed towards improvement of catalyst, leading to improvement in operating conditions with respect to lowering of pressure and conversion of raw material to finished product and conservation of energy.

10. R&D EFFORTS, TECHNOLOGY ABSORPTION AND GAPS

In the area of oxo synthesis (hydroformylation), NCL, Pune has considerable expertise. PDIL and NCL have expertise in the field of catalyst. A good number of industrial catalysts have been developed by them and are in commercial use. There are other catalyst manufacturers also who manufacture practically whole range of catalyst for butanol industry. With active involvement of Indian industry, NCL is in a position to undertake development of indigenous oxo technology. Some of the national laboratories and industrial houses have considerable R&D work to their credit in the field of fermentation, more so for the production of ethanol, both potable and industrial.

11. THRUST AREA

No major improvement have taken place in the ethanol based technology for butanol in the world as well as in India. This can be attributed to the fact that oxo process is

the predominant process in the world. In India though alcohol is available yet because of various constraints with respect to allocation, pricing and other factors, industry efforts in utilising alcohol for value added products did not materialise extensively.

Industry using alcohol as a feed stock for various chemicals, continued to sustain their activities without much investment in terms of modernisation and upgradation of technology. Therefore, alcohol route needs a thrust to make it economically competitive with oxo process that what it is today. Fermentation process for the manufacture of butanol along with other valuable co-products like acetone, ethanol, carbondioxide, hydrogen, riboflavin and livestock feed is another very promising area where adequate thrust would bring about substantial benefit to a tropical country like India.

12. RECOMMENDATIONS

- In Indian context ethanol based route having long term prospect may be further improved through sponsored R&D in terms of the process technology and conservation of energy.
- Renewable resource like ethanol based route may be given preference over oxo process, because of India's dominant position with respect to sugar/molasses/ethanol instead of exporting ethanol or molasses even as short term measures.
- Fermentation technology may be utilised for butanol and other valued co-products, since India has some expertise in this field.
- To improve competitiveness of oxo technology, one new plant may be allowed to import Rhodium catalyst based technology.
- R&D in fermentation process/technology may be undertaken for production of butanol along with other valuable co-products by Institutes like National Chemical Laboratory, Pune, Institute of Microbial Technology, Chandigarh and Bio-technology Department of IIT, Delhi.