Propylene Oxide

Process Technology (including comparison of Sumitomo’s Cumene Hydroperoxide, Hydrogen Peroxide-Based/HPPO, PO/Styrene Monomer, PO/MTBE and Chlorohydrin/CHP Routes), Production Costs (COP), Capacity, Regional Supply/Demand Forecasts.

PERP07/08-6

Report Abstract

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The ChemSystems Process Evaluation/Research Planning (PERP) program is recognized globally as the industry standard source for information relevant to the chemical process and refining industries. PERP reports are available as a subscription program or on a report by report basis.
INTRODUCTION

A continuing trend in the propylene oxide industry is the drive to develop and commercialize process routes that do not produce sizeable co-product quantities and do not use chlorine-based chemistry.

The hydroperoxidation routes to propylene oxide that co-produce styrene monomer (POSM) and \( t \)-butyl alcohol (POTBA) are responsible for the majority of current global production as seen in the figure below. However, they require relatively large capital investments and present difficulties in balancing the markets for propylene oxide and the co-products, leading to considerable volatility in the economic performance of the operations over time. Existing hydroperoxidation plants continue to be operated and incrementally improved, but new installations are more likely in less-developed regions. Although significant propylene oxide capacity is also based on the chlorohydrin process (CHPO), this route suffers from environmental liabilities and large capital investment requirements. Also, inexpensive electric power must be available for the integrated chlor-alkali facility.

![Propylene Oxide Capacity Share by Technology, 2008](Q408_0008100008.4106_Chart/F2.1)

Sumitomo Chemical has developed and commercialized a co-product free hydroperoxidation route to propylene oxide based on the use of cumene hydroperoxide (CHP) as the oxidant. Cumene hydroperoxidation technology is well known from the process for producing phenol and acetone. The Sumitomo process avoids producing any co-product along with propylene oxide by hydrogenating the cumyl alcohol from the oxidation of propylene back to cumene for recycle.
Several companies have been developing technologies for the production of propylene oxide (PO) from propylene and hydrogen peroxide (H₂O₂). Dow acquired its hydrogen peroxide technology from its 2001 purchase of EniChem's polyurethane business. EniChem had been developing the process since the early 1980s. BASF had been exploring hydrogen peroxide-based routes to PO since the mid-1990s. The companies started examining each other's processes in 2002 and began collaboration about a year later. A commercial scale hydrogen peroxide-based propylene oxide (HPPO) plant employing this technology is planned for BASF’s site in Antwerp. In addition to Antwerp, BASF says it is planning an HPPO unit in Geismar, LA, by 2009. Siam Cement and Dow are building a HPPO plant in Thailand.

Degussa AG together with Uhde GmbH, have developed a similar process for producing propylene oxide from hydrogen peroxide, referred to as the Degussa-Uhde HPPO process. SK Corp. has acquired a license and started-up a plant at Ulsan, South Korea in 2008.

Both the CHP and HPPO processes claim lower capital investment costs compared to the other established routes, to be environmentally friendly, and to have no significant quantities of by-products when compared to either the chlorohydrin (salt) or the POSM (styrene) processes.

Much new development has occurred in this subject in the last five years. As evidenced by an extensive number of new patents’ applications in the USA, Lyondell has been involved with more of these than any other company followed by Shell, BASF, Sumitomo and Degussa. Developments during this period are discussed in section 3 of this ChemSystems PERP report.

CHEMISTRY & PROCESS TECHNOLOGIES

Chlorohydrin process (CHPO)

Formation of propylene oxide via chlorohydrin technology is a multi-step process that proceeds via addition of hypochlorous acid to propylene to form a chlorohydrin intermediate, which is subsequently dehydrochlorininated to the epoxide.

\[
\begin{align*}
\text{Cl}_2 + \text{H}_2\text{O} & \rightarrow \text{HOCl} + \text{HCl} \\
\text{CH}_2\text{CH} = \text{CH}_2 + \text{HOCl} & \rightarrow \text{CH}_2\text{CH}_2\text{Cl} + \text{CH}_3\text{CH}_2\text{OH} \\
\text{OH} & \rightarrow \text{Cl} \\
\text{CH}_3\text{CH}_2\text{Cl} + \text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{CH} = \text{CH}_2 + \text{Salt}
\end{align*}
\]

Section 2.2 gives detailed descriptions of the chemistry and process technology for the chlorohydrin route integrated with a large caustic soda/chlorine plant that provides chlorine for the chlorohydrin reaction and cell liquor (caustic soda) for the dehydrochlorination reaction, and accepts the brine solution produced in the dehydrochlorination reactor.

During periods of high caustic soda demand, integrated producers may consider switching from caustic soda use to lime in the chlorohydrin process in order to sell the caustic soda externally, resulting in an essentially stand-alone propylene oxide chlorohydrin plant – the non-integrated chlorohydrin process is discussed in section 2.3. Economics shown herein represent a
chloralkali/propylene oxide producer that can sell caustic soda during periods of high demand, rather than consume it in propylene oxide production or a producer with a plant designed specifically for lime use. Off-site capital costs include more extensive effluent treatment to handle the large dilute calcium chloride brine waste stream.

**Ethylbenzene hydroperoxide with styrene co-product (POSM)**

In propylene oxide and styrene co-production via an ethylbenzene hydroperoxide intermediate, the hydroperoxide is made by direct air oxidation of ethylbenzene. The hydroperoxide is subsequently converted to an alcohol in the epoxidation reaction with propylene, and the alcohol is then dehydrated to styrene.

The epoxidation of propylene with the hydroperoxide is the heart of the process. Catalysts used in this reaction are compounds of metals with variable valences. These are capable of coordinating the unshared electron pairs of the hydroperoxide with vacant 4-orbitals of the metal.

Section 2.4 gives detailed descriptions of the chemistry and process technology for the POSM route.

**Cumene hydroperoxide process (CHP)**

Sumitomo has patented the use of cumene hydroperoxide (CHP) for the epoxidation of propylene. The CHP is obtained by oxidation of cumene (isopropyl benzene) with air. On giving up oxygen to propylene, the CHP is converted to cumyl alcohol (also referred to as dimethylbenzyl alcohol or DMBA). The cumyl alcohol can be dehydrated to alphamethyl styrene (AMS) which can be, in turn, hydrogenated back to cumene for recycle. According to the cited Sumitomo patent, the dehydration and hydrogenation steps can be combined into a single hydrogenolysis step.

Section 2.5 gives the chemistry and process technology for the speculative Sumitomo propylene oxide process consisting of four main steps: oxidation, epoxidation, PO recovery/purification, and hydrogenolysis.

**Epoxidation with hydrogen peroxide (HPPO)**

The greatest attraction of the direct hydrogen peroxide process for producing propylene oxide is its apparent simplicity.

\[
\begin{align*}
\text{Propylene} + \text{H}_2\text{O}_2 & \rightarrow \text{Propylene Oxide} \\
\text{Hydrogen Peroxide} & \\
\end{align*}
\]

The reaction is relatively straightforward, with few by-products and no sizeable co-products which must be marketed. The co-product water can be subjected to nominal treating and discharged. No chlorine is used in the process, so that the production of chlorinated by-products and copious amounts of wastewater is avoided.

Although reaction conditions are mild, the presence of water and possibly alcohol as a solvent can result in product loss to secondary ring-opening reactions.
Section 2.6 expands upon the chemistry involved in this process, coupled with evaluations of the speculative technologies used by Dow/BASF and Degussa/UHDE.

ECONOMIC ANALYSIS

Economics for the production of propylene oxide by various routes discussed in this report have been developed in section 4. Comparisons of the cost of production estimate (based on a plant of world-scale capacity) for the following processes have been detailed and calculated in the report:

- BASF-DOW HPPO
- Chlorohydin (Integrated with Chloro-alkali)
- Chlorohydin (Non-integrated with Chloro-alkali)
- POSM
- Sumitomo Cumene Hydroperoxide

Various sensitivities have been explored to illustrate the effects of variations in certain parameters on the base case economics presented in the previous section. These results can also be used to make approximate comparisons between cases for which detailed economics have not been provided by adjusting for capacity differences, alternative feedstock valuations, etc. The sensitivities examined include the cost of key material prices including propylene, hydrogen peroxide and styrene, capital investment, and economy of scale.

It is important to note that the economics presented in this section are in essence a “snapshot” in time and are not necessarily representative of the recent historical cost of production. An analysis of the sensitivity of the economics to overall pricing is shown comparing the full cost of production economics for the first quarter of 2008 with the 5-year average economics for 2003-2007. The rankings of the technologies change slightly under this scenario.

To explore the sensitivity of the cost of production to the plant capacity, the economics have been developed over a range of plant capacities for each technology discussed herein. The sensitivity of the propylene oxide economics to economy of scale is discussed. While the economics provided herein are for a world scale plant with a capacity, some regional plants are being built at smaller capacities. The results of this sensitivity show the impact of plant capacity on the cost of production including capital charges depending on the technology employed.

COMMERCIAL ANALYSIS

Propylene oxide (PO) is a chemical intermediate predominantly used in the production of polyether polyols and propylene glycol.

Consumption of PO has been strong dominated by the largest end use, polyols, and driven by the housing industry. Polyols are reacted with an isocyanate to form polyurethanes. Polyurethane end uses include flexible foams for the furniture and automotive industries; rigid foams for appliance and building insulation; and various non-foam applications including coatings, adhesives, sealants, and elastomers. Sectors of the polyurethanes markets such as furnishing are maturing, but other such as automotive and insulation have better growth potential.
Consumption of mono propylene glycol (MPG) is for the manufacture of unsaturated polyester resins. Another major use for MPG is in de-icers, notably aircraft de-icing fluids where it has achieved good market penetration compared with mono ethylene glycol (MEG) due to its lower toxicity (primarily environmental concerns). MPG is a high cost product than MEG and its penetration of the automotive market has been less successful thus far. Other significant uses of MPG are in foods, pharmaceuticals, detergents, and cosmetics. Major applications for di-propylene glycol include plasticizers, unsaturated polyester resins, and cosmetics (fragrance carrier). Tri-propylene glycol’s major uses include urethane elastomers, adhesives, and radiation curable coatings.

Propylene glycol ethers (PGE) are used in applications analogous to ethylene glycol ethers (EGE), namely, solvents in coating, inks, and cleaner formulations. As a class, PGE solvents characteristically exhibit lower toxicological effects than their EGE counterparts, although they are higher cost than the EGE products.

Other uses for PO are the production of isopropanolamines, production of allyl alcohol, modified starches/cellulosic polymers, and propylene carbonate.

Detailed Supply/Demand and Trade for USA, Western Europe and Asia Pacific are also given in this section.
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