

PERP Program – New Report Alert

January 2004

Nexant's ChemSystems Process Evaluation/Research Planning program has published a report, *Propylene Oxide (02/03-8)*.

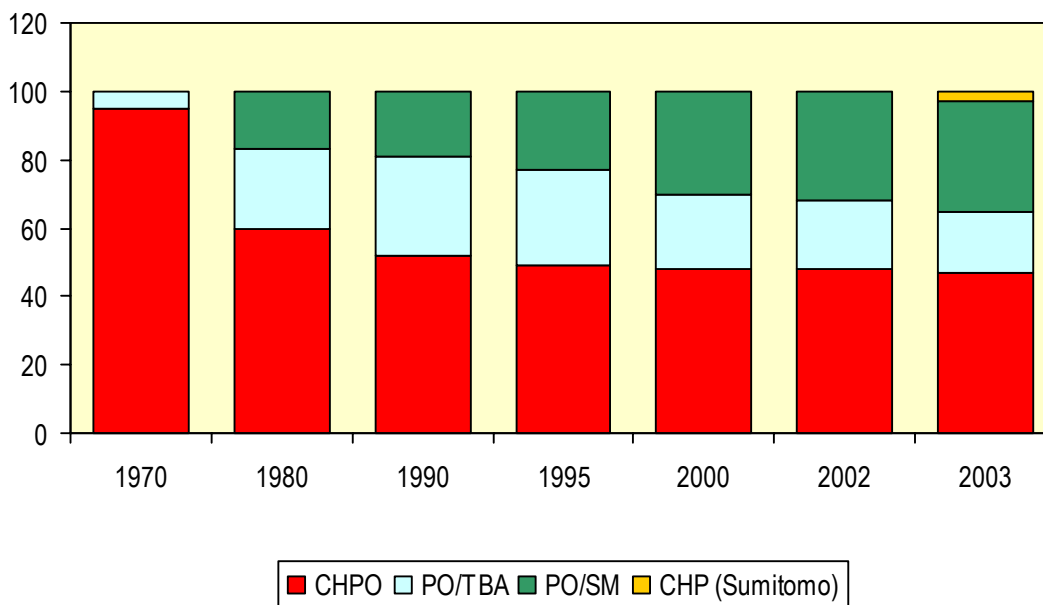
Background

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 (PO/SM) and t-butyl alcohol (PO/TBA) are responsible for the majority of current global production as seen in Figure 1. 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; however, new installations may be limited in the future.

Although significant propylene oxide capacity is based on the chlorohydrin process (CHPO), this route suffers from environmental liabilities and large capital investment requirements.

Figure 1
Percent Propylene Oxide Capacity Share by Process, 1970-2003



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 dehydrating and hydrogenating the cumyl alcohol from the oxidation of propylene back to cumene for recycle.

Much attention has recently been directed to process approaches based on epoxidation of propylene using hydrogen peroxide as the oxidant (HPPO) or the oxidation of propylene with an oxygen-containing gas. The former approach can take the form of direct use of commercial strength hydrogen peroxide or the use of dilute hydrogen peroxide produced in an integrated facility by combination of hydrogen and oxygen or oxidation of a hydrocarbon substrate. Likewise, the oxidation of propylene with an oxygen-containing gas can be performed with or without the presence of hydrogen in the reaction zone. Without hydrogen, the process is referred to as direct oxidation (DOPO) and with hydrogen, the term is hydro-oxidation (HOPO).

It appears that the next PO technology to be commercialized will be based on commercially prepared hydrogen peroxide as oxidant. In-situ production of dilute hydrogen peroxide may follow later.

Hydro-oxidation technology, while somewhat further back on the commercialization time line, is likely to be the next technology commercialized, due to high selectivity to propylene oxide. The chemistry, process technology, production economics, and markets for propylene oxide are covered in this report.

Commercial PO Routes:

- Chlorohydrin with integrated chlor-alkali
- Ethylbenzene hydroperoxidation/styrene co-product (PO/SM)
- Cumene hydroperoxidation/no co-product

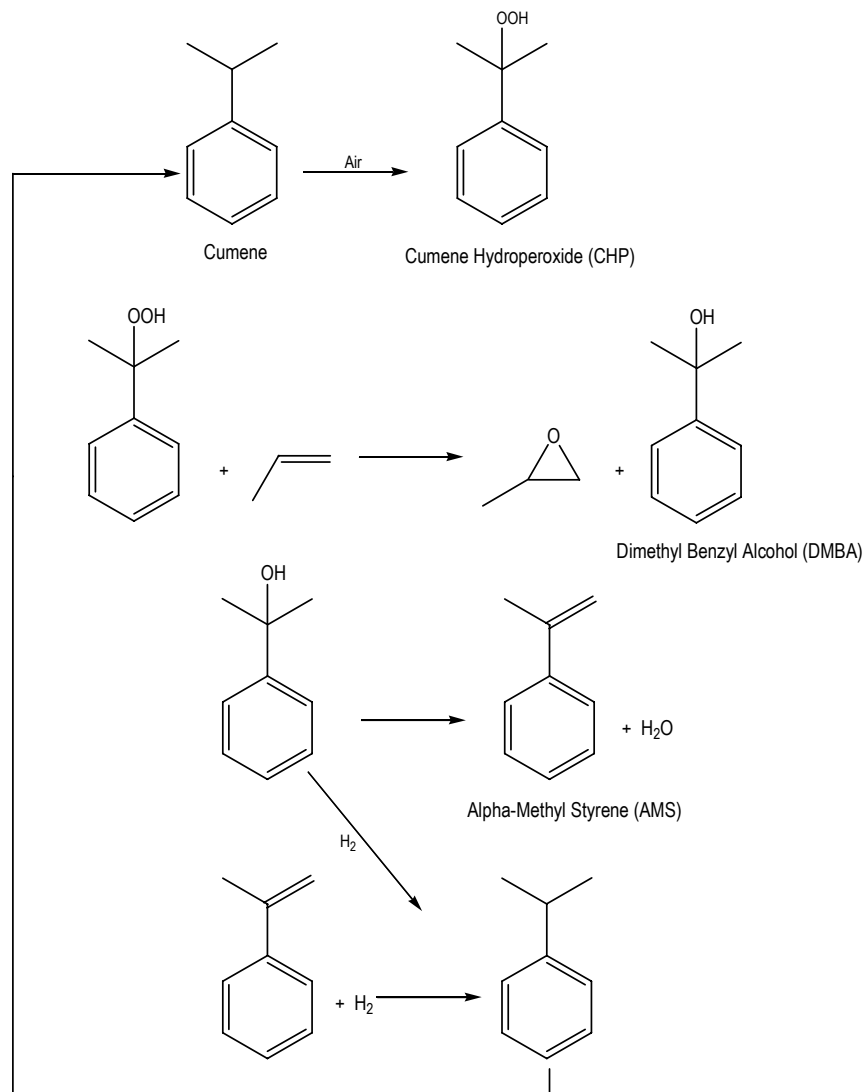
Developing PO Routes:

- Epoxidation with in-situ hydrogen peroxide
- Epoxidation with purchased hydrogen peroxide
- Direct oxidation of propylene with oxygen
- Hydro-oxidation of propylene with oxygen and hydrogen

Sumitomo Process

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 alpha-methyl styrene (AMS) which can be, in

turn, hydrogenated back to cumene for recycle. The dehydration and hydrogenation steps can be combined into a single hydrogenolysis step. The chemistry for such an approach is shown below. The liquid phase oxidation of cumene proceeds according to a free radical chain mechanism; the sodium salt of CHP can be used as an oxidation catalyst.



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Selectivity of cumene to CHP is about 95-98 percent.

The use of cumene hydroperoxide (CHP) to epoxidize propylene has potential advantages over the analogous use of ethylbenzene hydroperoxide (EBHP). Cumene hydroperoxidation is more facile,

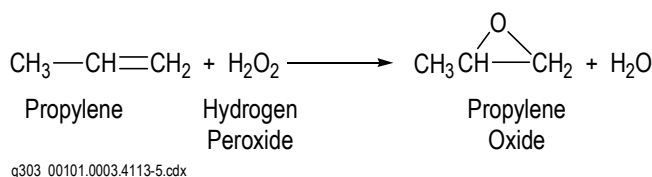
selective, and stable than EB hydroperoxidation. The stability of CHP allows safe concentration to levels five times those of EBHP. These factors translate into smaller and simpler equipment, with attendant capital cost reductions.

In the epoxidation, a molar ratio of propylene to CHP of 10:1 is used at a reaction temperature of 60°C and sufficient pressure to maintain propylene in the liquid phase. The reaction is catalyzed by a proprietary silylated titanium-containing silicon oxide catalyst. Conversion of CHP of 99 percent is attained. Selectivity to PO based on CHP is 95 percent, whereas selectivity to PO based on propylene is about 99 percent.

The cumyl alcohol co-product is subjected to hydrogenolysis over multiple beds of (e.g.) copper-chromium oxide catalyst. Hydrogenolysis temperature is preferably 30-400°C and the pressure is preferably 100-10,000 KPa (14.5-1450 psi).

Hydrogen Peroxide Route

The use of hydrogen peroxide to oxidize olefins to epoxides has been known for many years. The direct use of hydrogen peroxide as a reagent in epoxidations is desirable for its mild reaction conditions and few co-products, except for water as shown in the following chemical equation:



However, a hydroxylic solvent such as water or an alcohol generally is needed, and this can result in loss of initially formed propylene oxide due to further reactions that open the epoxide ring.

The cost and shipping hazards of standard grades of hydrogen peroxide can be an impediment to their use in an economically viable epoxidation process. Further, while dilute aqueous solutions of hydrogen peroxide can be used in epoxidations, shipping costs could be prohibitive depending on logistics.

Cost and logistics problems can be mitigated by the use of hydrogen peroxide produced *in-situ* at relatively low concentrations as an epoxidizing agent. Examples of such approaches are the use of methyl benzyl alcohol or isopropanol as oxidizable substrates that generate hydrogen peroxide *in-situ*. The epoxidation process is coupled with the peroxide-producing process without intermediate concentration or purification.

Integrated processes for generating hydrogen peroxide *in-situ* for use in epoxidation have recently trended towards peroxide synthesis from hydrogen and oxygen in an alcoholic or hydro-alcoholic

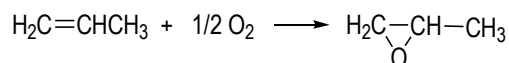
solution. Typically, the reaction solution also contains acid and halide ions. Recent work in this regard has been disclosed by EniChem, BASF, and Hydrocarbon Technologies.

An alternative approach is a large, co-located hydrogen peroxide plant feeding a crude product which has not incurred costs for concentration, purification, and shipping. This would also allow minimization of raw material storage and inventory costs.

Recently, hydrogen peroxide producers have claimed the ability to build anthraquinone-process hydrogen peroxide plants of up to 440 million pound (200,000 metric ton) per year capacity using a single train of equipment. The resulting effect of economy of scale in reducing hydrogen peroxide feedstock costs into propylene oxide manufacture will be an important success factor in the collaborations between BASF and Dow, Dow and Solvay, and Degussa and Krupp-Uhde.

Direct Oxidation of Propylene with Oxygen

In theory, propylene oxide should be attainable by a direct oxidation process analogous to that for ethylene oxide. The challenge in the case of propylene oxidation has been to find a catalyst that gives sufficiently high selectivity to propylene oxide by suppressing the competing combustion reaction.



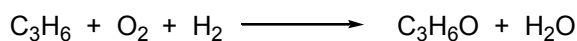
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In a recent patent to ARCO, a silver-based catalyst, using an alkaline earth metal compound as support, is promoted by the addition of tungsten and potassium. The best results were 8.8 percent propylene conversion with 53 percent selectivity of propylene to propylene oxide, giving a propylene oxide yield on propylene of 4.7 percent.

Plant design for direct oxidation of propylene would most likely be based on pure oxygen feed, rather than air, to gain yield advantage and lower battery-limits capital costs. The small purge gas flow in an oxygen based process makes it economically feasible to use a ballast gas (diluent) other than nitrogen.

Hydro-Oxidation of Propylene with Oxygen and Hydrogen

The desired hydro-oxidation reaction involves one mole each of propylene, oxygen, and hydrogen reacting to form one mole each of propylene oxide and water.



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Competing side reactions include propylene hydrogenation to propane and propylene combustion to carbon dioxide and water. Additional hydrogen and oxygen consumption occurs to form water.

Illustrative of work in this area is a Dow patent that describes the preparation of a gold-based catalyst supported on a MFI-structure titanosilicate, with sodium as a promoter. Propylene conversion of 3.2 percent was attained with a selectivity to propylene oxide of 96 percent, resulting in a yield of propylene oxide on propylene of 3.1 percent. As a measure of side losses of hydrogen and oxygen, the molar ratio of water to propylene oxide produced was 5.2 compared to the 1.0 ratio characteristic of the desired primary reaction.

The report compares the economics of the conventional PO routes to the new and emerging processes.

Commercial Aspects

Propylene oxide is the third largest propylene derivative, ranking behind polypropylene and acrylonitrile, and is used primarily as a chemical intermediate. The majority of propylene oxide production is used to manufacture polyether polyols and propylene glycol. The other major uses include alkoxylates and glycol ethers. An overview of the propylene oxide industry is shown on the next page in Figure 2.

The report presents supply/demand analysis for propylene oxide in the United States, Western Europe, and Japan, with forecasts through 2010.

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Figure 2
Propylene Oxide Industry Structure Overview

