

PERP Program – Hydrogen Peroxide-Based Propylene Oxide New Report Alert

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Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a report, ***Hydrogen Peroxide-Based Propylene Oxide (06/07S2)***. To view the table of contents or order this report, please click on the link below: <http://www.chemsystems.com/reports/index.cfm?catID=2>

Introduction

Technologies for propylene oxide (PO) production are undergoing a flurry of activity. Since the commercialization of Sumitomo Chemical's PO-only route in 2003, other companies have declared their intentions of developing PO-only technologies. These new methods generally fall into four categories:

- Cumene hydroperoxide-based propylene oxidation with cumene recycle (i.e., the Sumitomo process)
- Hydrogen peroxide-based propylene oxidation
- Direct propylene oxidation with oxygen
- Direct propylene hydro-oxidation with oxygen and hydrogen

The second method noted above is the subject of this report.

H₂O₂ Based PO Technology

Several companies have been developing technologies for the production of propylene oxide (PO) from propylene and hydrogen peroxide. 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. The BASF-Dow HPPO plant will have a capacity of 300 kta. In addition to Antwerp, BASF says it is planning an HPPO unit in Geismar, Louisiana, by 2009. More recently Dow and BASF have announced that they are advancing negotiations for the construction of a world-scale, 390 kta HPPO manufacturing facility in Map Ta Phut, 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. SKC has acquired a license and has plans to build a 100 kta plant at Ulsan, South Korea starting-up in 2008.

The preferred hydrogen peroxide solution concentration is greater than or equal to 35 weight percent. The patent states that the molar ratio of olefin to hydrogen peroxide is not critical, but the preference is between 6:1 and 1:1.

The epoxidation reaction may be carried out in one or more solvents that are liquid at the epoxidation temperature, that are compatible with hydrogen peroxide and that are capable of dissolving the olefin and the olefinic oxide produced. Typically solvents of polar nature are used such as alcohols (e.g., methanol, ethanol, isopropyl alcohol, *t*-butyl alcohol and cyclohexanol), aqueous-alcoholic mixtures, ketones (e.g., acetone, methyl ethyl ketone and acetophenone), ethers (e.g., tetrahydrofuran and butyl ether), esters, aliphatic, cycloaliphatic or aromatic hydrocarbons, halogenated hydrocarbons or mixtures thereof. Dow's preference is methanol and this was used in the cost of production estimate in this report.

A buffer is chosen from aqueous ammonia, ammonium acetate, ammonium formate or a system comprising a nitrogenous base and a salt thereof with an organic or mineral acid.

The epoxidation catalyst is chosen from those generally known as titanium silicalites and may be used in the form of powder, pellets, microspheres, an extrudate or other suitable physical forms. The amount of catalyst is not critical; however, it is chosen so as to allow the epoxidation reaction to proceed to completion in the shortest possible time. Typically, the preferred amount of catalyst is between 4 and 10 weight percent relative to the reaction mixture. The reaction temperature is between 55°C and 90°C (131°F and 194°F). The operating pressure is that which allows the olefin to be maintained in the liquid phase at the chosen reaction temperature.

The reactor used in the epoxidation reaction may be any reactor capable of operating continuously and achieving efficient contact between the components and the catalyst. The patent example employs continuous stirred tank reactors (CSTRs), while recent press releases show a simplified flow diagram with packed bed (up flow) reactors. The patents do not discuss catalyst life and regeneration capabilities.

Economics

The economics of the production of propylene oxide have been developed for a 200 thousand metric ton per year (440 million pounds per year) plant on the U.S. Gulf Coast for the first quarter of 2007. The following PO processes were assessed and compared:

- Dow hydrogen peroxide-based process
- Chlorohydrin process
- Propylene Oxide/Styrene co-product process (PO/SM)
- Sumitomo PO only cumene-based process

For the emerging Dow process, the cost of hydrogen peroxide has been estimated assuming that the price is equivalent to the cost of production employing the anthraquinone auto-oxidation process and including a 10 percent return on investment (a mega-scale 330 kta H₂O₂ plant was assumed).

As stated earlier, both the BASF-Dow and Degussa/Uhde hydrogen peroxide-based processes claim to have low capital investment costs, to be environmentally friendly, and have no significant quantities of byproducts when compared to either the chlorohydrin or the PO/SM processes. Based on the analysis presented in the report, these claims seem to be borne out. While the cash cost of production of the hydrogen peroxide-based routes may be higher than the other routes, due mostly to the cost of hydrogen peroxide, the cost plus return is competitive, if not better, than the other proven routes to PO. What is certain, however, is the freedom from co-production of styrene (or *t*-butyl alcohol) or salt will continue to push PO producers towards the co-product free routes. Besides not having to manage the ups and downs of the co-product markets, the hydrogen peroxide-based routes are also significantly less capital intensive.

Commercial Analysis

After several years of oversupply, the North American propylene oxide market tightened sharply in 2005 and is expected to remain tight over the next few years. Canada and Mexico do not currently produce propylene oxide, and capacity is not expected to develop in the foreseeable outlook. Exports from the United States are expected to remain at the historical level or lower as new capacity comes online in China. BASF may go ahead with a new complex in the United States using a byproduct free process (i.e., HPPO) around 2009-2010.

Despite the major capacity addition at Maasvlakte in Rotterdam in 2004, and the expansions at Stade in 2004 and the new plant at Tarragona in 2006, the supply/demand balance in Western Europe remains firm, following sustained demand growth. Supplies are expected to remain tight until the commissioning of the Dow and BASF joint venture HPPO plant in 2008. Most of this addition will be absorbed by the region in order to meet demand growth. However, with tight global supplies, a temporary spike in exports is also expected.

Asia Pacific has historically been a net importer of PO. This trend is expected to continue for the foreseeable future. In the next few years, the region is expected to be approximately balanced, but imports are likely to grow thereafter. After several years of oversupply, PO operating rates are expected to remain elevated for the next several years.

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