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Hydrogen Peroxide

Process Technology, Production Costs (including Economic Comparison of Solvay's Mega-Scale Technology, Emerging Direct Synthesis and Conventional Anthraquinone Routes), and Regional Supply/Demand Forecasts are presented.

PERP07/08-3

Report Abstract

May 2009

Nexant

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INTRODUCTION

At one time, most hydrogen peroxide was produced by electrolysis of ammonium bisulfate. However, nowadays virtually all production is based on a process featuring catalytic hydrogenation followed by auto-oxidation of a suitable organic carrier molecule, predominantly an alkylated anthraquinone. Although most hydrogen peroxide producers closely hold the technology and expertise involved in operating this complex process, the technology has been made available in recent years by several engineering companies - Chematur Peroxide AB (Sweden), and Ericsson Industries (Sweden). Producers such as Evonik, EKA Chemicals, FMC, and Solvay may grant licenses in certain instances, primarily for projects in which they participate with other firms.

The production of hydrogen peroxide by the oxidation of isopropyl alcohol (IPA) was practiced commercially by Shell Chemical from 1957-1980. The acetone co-product can either be sold or hydrogenated back to isopropyl alcohol for recycle. Several plants operating on this principle were built in the former Soviet Union. Although IPA oxidation technology is not being actively licensed by Shell or western engineering companies, it may be available from sources in the former Soviet Union.

Another version of the oxidation of a secondary alcohol to hydrogen peroxide and a ketone is the work by Lyondell (ARCO) Chemical, using methylbenzyl alcohol as hydrogen carrier. This material is an intermediate in its propylene oxide/styrene process. The oxidation co-product, acetophenone, is hydrogenated back to methylbenzyl alcohol in a step that has also been proven as part of the Lyondell styrene technology.

An electrochemical process for the production of alkaline hydrogen peroxide has been developed by H-D Tech Inc., formerly a joint venture of Huron Technologies Inc. and Dow Chemical of Canada, but now wholly owned by Dow. The process employs a monopolar cell to achieve an electrolytic reduction of oxygen in a dilute sodium hydroxide solution.

Evonik Headwaters, a joint venture between Evonik and Headwaters, is developing a direct synthesis process based on reaction of hydrogen and oxygen in methanol solvent over a catalyst comprised of minute (nanometer sized) phase-controlled noble metal crystal particles on carbon or silica support.

A hydrogen peroxide to propylene oxide (HPPO) complex owned by SK Chemicals (Seoul) was started in July 2008 at Ulsan (Korea). The HPPO technology was developed by Evonik and Uhde industries.

Solvay has announced the development of its so-called high-yield (high-productivity) process, based on an optimized distribution of anthraquinone and related species. The process was first implemented at Solvay Chemicals (Finland) AB (formerly Finnish Peroxides). This technology is being used to supply hydrogen peroxide at another HPPO facility at Zandvliet, Antwerp (Belgium). This HPPO facility is a joint venture with Dow and BASF. The hydrogen peroxide portion of the facility was opened in July 2008, and the propylene oxide portion of the plant was started in October 2008. Another HPPO joint venture, between Solvay and, Dow and Siam Cement is being built at Map Ta Phut (Thailand). The facility is scheduled to come on-stream in 2011.

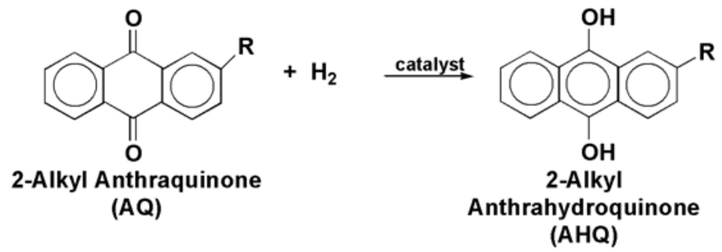
ChemSystems has completed a new report that discusses these commercial, developing and non-commercial processes. Detailed economic analysis comparing the conventional anthraquione process, Solvay's new "mega-scale" plants based on its high productivity/yield process technology and the developing direct synthesis process are given in the report. Commercial applications and regional supply/demand are estimated.

COMMERCIAL PROCESSES

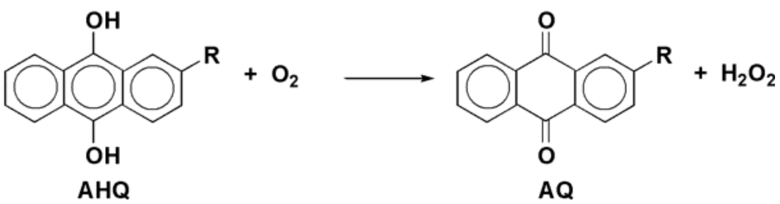
Anthraquinone Auto-Oxidation

Anthraquinone auto-oxidation processes are discussed in this section, including a brief overview of the differences between the Solvay process that enables construction of much larger mega scale plants compared with the conventional process. In addition to the basic process flow diagram and description, other aspects that are highlighted are primary (see figure below) and secondary reactions, reversion, solvents, recovery/purification, working solution treatment, explosion risks.

Alkyl Anthraquinone Hydrogenation:



Hydrogen Peroxide Production:



Dow Electrochemical

Process flow diagram and description of Dow's electrochemical production technology are given. The anode and cathode reactions are given below, along with the overall reaction.

At the anode	$2OH^-$	$\longrightarrow$	$H_2O + \frac{1}{2}O_2 + 2e^-$
At the cathode	$H_2O + O_2 + 2e^-$	$\longrightarrow$	$HO^-_2 + OH^-$
Overall	$NaOH + \frac{1}{2}O_2$	$\longrightarrow$	HO_2Na

DEVELOPING AND NON-COMMERCIAL PROCESSES

Direct Synthesis

A process for the direct reaction of hydrogen and oxygen represents considerable challenges in catalysis and process design. The reaction is accomplished with oxygen rather than air and noble metal catalysts in an acidic solution, usually containing halide. Developments in direct synthesis processes in methanol and aqueous reaction media are described, as well as other new developments such as nanocatalysts, and gold/palladium catalysts. Conceptual process flow diagrams are provided.

Historical Lyondell Methyl Benzyl Alcohol Oxidation

Process flow diagram and description of Lyondell's methyl benzyl alcohol oxidation technology is given.

Historical Shell Isopropanol Oxidation

From 1957 to 1980, Shell Chemical operated a hydrogen peroxide plant at its Norco, Louisiana, complex that was based on the liquid phase oxidation of isopropanol. Acetone was obtained as a co-product, as shown in the following equation:

$$\underset{\text{Isopropanol}}{CH_3CH(OH)CH_3} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Acetone}}{CH_3COCH_3} + \underset{\text{Hydrogen Peroxide}}{H_2O_2}$$

Q109_00101.0008.4103-1.cdx

This process is briefly described in the report.

ECONOMIC ANALYSIS

In the economic analyses that are given, all the costs for hydrogen peroxide quoted in the discussion and production tables are on a 100 percent basis.

Economics for various plant sizes were carried out. The economics are discussed in detail. The specific cost of production tables that have been evaluated are as follows:

- Ethyl Anthraquinone (EAQ) Standard Productivity Technology at production capacities deemed to be indicative of an average-sized plant for the regions considered in the commercial section and the largest single train capacity estimated for this technology. Production of 43 and 70 weight percent solution of hydrogen peroxide have been estimated
- Amyl Anthraquinone High Productivity Technology at three production capacities – averaged-sized and large plant for comparison with EAQ technology and for the much larger, Solvay Single-Train "Mega" Plant. Production of 40 and 70 weight percent solution of hydrogen peroxide have been estimated

- Direct Synthesis process in Aqueous Reaction Medium at two production capacities - averaged-sized and large plant for comparison with above processes. Detailed cost of production tables for production of a 70 weight percent solution of hydrogen peroxide are given, and while cost of production estimates of a 15 weight percent solution are given and discussed (a detailed table is not provided)
- Direct Synthesis in Methanol Reaction Medium at two production capacities - averaged-sized and large plant for comparison with the other processes. Detailed cost of production tables for production of a 9 weight percent solution of hydrogen peroxide are estimated

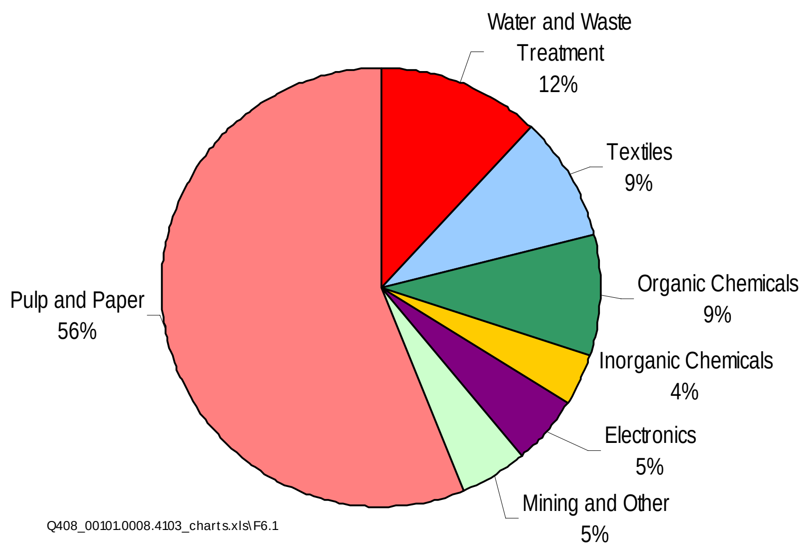
The costs for various scenarios are discussed:

- Economics of Processes Producing Concentrated (70 weight percent) Hydrogen Peroxide
- Economics of Hydrogen Peroxide Processes Suitable for Feeding to a HPPO plant
- Economics of Hydrogen Peroxide Plants with Production Capacities of 50 thousand tonnes per year (which is considered average-sized in this study)

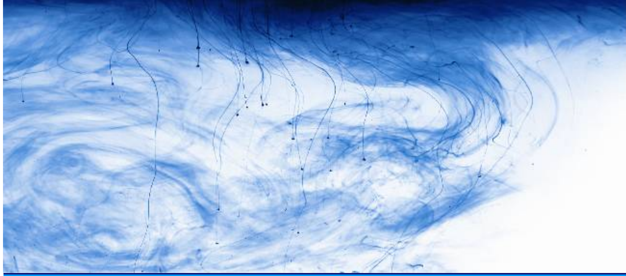
COMMERCIAL ANALYSIS

Hydrogen peroxide is a strong, non-polluting oxidizing agent, and most of its uses and those of its derivatives depend on this property. Hydrogen peroxide is one of the most powerful oxidizers known - stronger than chlorine, chlorine dioxide, and potassium permanganate. Both easy-to-oxidize pollutants (iron and sulfides) and difficult-to-oxidize pollutants (solvents, gasolines, pesticides) can be oxidized by adjusting reaction conditions of pH, temperature, dosage, reaction time, and catalyst. It is even possible to oxidize one pollutant over another, or even to favor different oxidation products from the same pollutant. Applications for hydrogen peroxide are discussed in this section. Major applications of hydrogen peroxide in the U.S. are shown in the figure below.

U.S. Hydrogen Peroxide Demand by Segments, 2008



- U.S. and Western Europe supply and demand data are estimated, including a listing of specific plant capacities in these regions denoted by company, location and annual tonnage produced
- East Asia supply and demand are also estimated, including listings of specific plant capacities in these regions denoted by company, location and annual tonnage produced (except for China and India where composite data are provided).



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