

## ***Hydrogen Peroxide (98/99-8)***

Virtually all hydrogen peroxide production is now based on a process featuring catalytic hydrogenation followed by autoxidation of a suitable organic carrier molecule, predominantly an alkylated anthraquinone.

The hydrogenation step in the cyclic process to produce hydrogen peroxide involves hydrogenating the working solution in the presence of a catalyst such as supported palladium or Raney nickel at temperatures of 40-50°C under a hydrogen partial pressure up to 4 atmospheres. The resulting hydroquinone, still in solution, is oxidized by an oxygen-containing gas, usually air, to produce hydrogen peroxide and regenerate the quinone. Economics and safety considerations favor air over pure oxygen. The oxidation is carried out noncatalytically by bubbling air through the solution at 30-60°C at near atmospheric pressure. Various methods have been proposed for separating crude hydrogen peroxide from the working solution, but the method most generally used involves extraction with water. This crude product, at concentrations of 25 to 45 percent hydrogen peroxide, must be upgraded to meet commercial requirements for purity and concentration.

A novel electrochemical process for the production of alkaline hydrogen peroxide is available from Dow Chemical. The process produces a 4 percent alkaline solution of hydrogen peroxide that is well suited for onsite pulp bleaching. Hydrogen peroxide is synthesized by electrolysis of dilute sodium hydroxide solution in Dow's proprietary electrochemical cell. Alkaline peroxide, nominally in the weight ratio 1.7 NaOH to 1.0 H<sub>2</sub>O<sub>2</sub>, is produced by cathodic reduction of oxygen on a catalytic trickle bed of carbon chips. The basic raw materials are water, oxygen, sodium hydroxide, and tetrasodium EDTA. The alkaline peroxide technology is best utilized for applications where it is not necessary to separate the peroxide from the caustic soda in the product, as in pulp bleaching.

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 coproduct, which could either be sold or hydrogenated back to isopropanol. Oxidation of 2 pounds of isopropanol produces 1 pound of hydrogen peroxide and about 1.8 pounds of acetone.

Another process based on the oxidation of a secondary alcohol has been proposed by Lyondell Chemical (formerly ARCO Chemical). The alcohol in this case is methyl benzyl alcohol (MBA), which is present in large quantities in Lyondell's propylene oxide/styrene plants. Since the Lyondell Chemical propylene oxide/styrene process makes approximately 2.5 pounds of styrene per pound of propylene oxide, some 3 pounds of the alcohol per pound of propylene oxide are processed in the plant. All or part of the alcohol may be noncatalytically oxidized to acetophenone and H<sub>2</sub>O<sub>2</sub> and the acetophenone hydrogenated

back to the alcohol.

A process for the direct reaction of hydrogen and oxygen represents a considerable challenge in catalysis and process design. The reaction is accomplished with oxygen rather than air and platinum group catalysts in an acidic aqueous solution, almost always containing halide. Halide ions give improved hydrogen selectivity and peroxide concentration, but decrease the activity of the platinum group metal. This is an extremely corrosive medium, although it is typically mitigated by the low reaction temperatures (0°C-25°C) employed.

Direct reaction processes proposed by ACP Technologies, Interlox, Mitsubishi Gas Chemical and Princeton Advanced Technology (PAT) are discussed in the report. The economics of the conventional route are compared to the developing Lyondell and direct PAT processes.