

PERP Program

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Chem Systems' Process Evaluation/Research Planning program has published a new report, ***Acrylic Acid (00/01-7)***.

The Reppe process to acrylates and acrylic acid production in which carbon monoxide and water (or an alcohol) are added to acetylene became unattractive because of the following reasons:

- The toxicity and corrosive nature of the nickel carbonyl catalyst
- The cost and availability of acetylene

Propylene is a much more commercially attractive starting material due to availability and price. Consequently, various methods for the production of acrylic acid from propylene were investigated in the late 1950s.

The oxidation of propylene to acrylic acid occurs in two stages:

- Oxidation of propylene to acrolein
- Oxidation of acrolein to acrylic acid

Processes were and continue to be developed in which propylene is directly converted to acrylic acid or in which acrolein is first formed and further oxidized to acrylic acid.

A two stage propylene oxidation process is now operated by every major producer of acrylic acid because of the improved overall acrylic acid yield and improved catalyst selectivity.

The overall yield obtained from the two stage process, using present day catalysts, is approximately 90 percent. The major improvement is related to catalyst selectivity since conditions and catalysts required for optimization of the oxidation of propylene to acrolein are different from those used for the oxidation of acrolein to acrylic acid. By forming acrolein and directly feeding the crude material into the next reactor, yields are optimized and, in practice, the process becomes equivalent to a one step reaction.

One of the impurities present in significant quantities in the propylene oxidation process and difficult to remove from the product is furfural. Most acrylic acid contains furfural at a level of 2 ppm, although levels of up to 20 ppm may be found. The furfural may arise by

a hetero Diels-Alder-type reaction between ethylene (feed impurity) and acrolein, followed by rearrangement. Oxidation of the resulting 2-methylfuran gives furfural. The other major impurity of the process, acetic acid, is readily removed by distillation.

The two step process is a continuous operation with propylene, air, and steam fed into the first step and acrylic acid, as a 30-60 percent aqueous solution, isolated from the second step. Due to the reactions' highly exothermic nature, the heat that is generated is utilized to preheat the incoming propylene, air, and steam to the required reaction temperature.

The original catalyst for the first oxidation stage, propylene to acrolein, consisted of cuprous oxide, but this was soon replaced by bismuth molybdate systems that were, however, hindered by slow conversion. More recently developed catalysts consist of a multicomponent mixture in which molybdenum predominates.

The catalysts now in use have a lifetime of about three years. Operating temperatures are 300°C-350°C with contact time of a few seconds. Propylene concentrations are 5 to 10 percent and pressure is 20 to 30 psia. Although quite selective for acrolein, small quantities of acrylic acid (3-16 percent) are, nonetheless, formed by overoxidation.

The second stage reaction, oxidation of acrolein to acrylic acid, proceeds at a much lower temperature than the first stage, and the gases exiting from the first stage must be cooled to the optimal operating temperature of the second stage catalyst.

The first catalysts employed in acrolein oxidation were molybdenum/cobalt based. Since these gave both low yield and low conversions, they were replaced by molybdenum/vanadium based catalysts. The catalyst system was further improved by adding other metals such that lower operating temperatures and greater yield and conversion resulted. Contact times for the oxidation are similar to the first stage, a matter of a few seconds. Lifetimes of the catalysts may be on the order of seven years under optimal operating conditions.