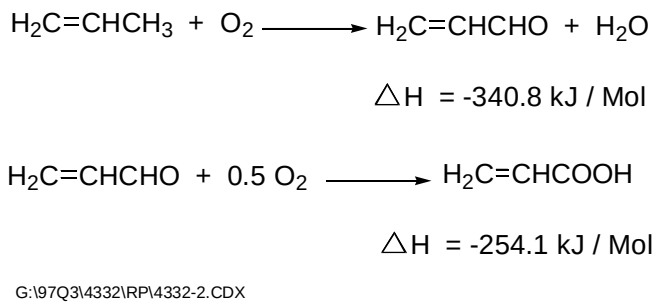
Acrylic Acid/Acrylates (96/97-8)

Acrylic acid and acrylates were initially produced by the Reppe process in which carbon monoxide and water or an alcohol are added to acetylene. The cost and availability of acetylene, and the corrosivity and toxicity of the nickel carbonyl catalyst system, caused this route to fall into disfavor.

Acrylic acid is now made chiefly by the two stage air oxidation of propylene, a much less expensive route and more readily available raw material. First stage oxidation to give the intermediate acrolein is conducted at about 325°C over catalysts whose main constituents are molybdenum and cobalt or bismuth. The second stage oxidation of acrolein to acrylic acid is conducted at 220-240°C over catalysts based mainly on molybdenum and vanadium.

TWO STEP PROPYLENE OXIDATION TO ACRYLIC ACID



The overall yield obtained from the two stage process, using present day catalysts, is approximately 90 percent. The 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.

The original catalyst for the first oxidation stage, propylene to acrolein, consisted of cuprous oxide, but 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.

Crude acrylic acid is recovered from the solution by solvent extraction. If the oxidation is conducted at high propylene and low steam concentrations, the result is a more highly concentrated acrylic acid solution that may be azeotropically dried in lieu of the solvent extraction step.

To remove light and heavy impurities, the crude acid is subjected to a series of distillations conducted under reduced pressure; hydroquinone methyl ether is added to the tops of the columns to prevent polymerization. The major losses in this process result from dimerization during the distillation process, and some to aqueous streams that exit the process. Dimer can be cracked to acrylic acid to improve overall process yield.

The semipurified acrylic acid is greater than 99 percent pure and suitable for use in producing acrylic esters. A further purification to afford glacial acrylic acid is necessary to give material suitable for superabsorbent polymers and polyacrylic acid manufacture. Some producers operate purification processes based on distillation; others prefer crystallization. Crystallization is claimed to provide a higher purity (reduced water content) product suitable for all end uses. Having a single product grade could reduce inventory quantities, but there is potential to give away quality in less stringent applications.