

## Acrylic Acid

Acrylic acid has traditionally been used as the raw material for acrylic esters – methyl acrylate, ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate. These bulk acrylates are used to produce solvent-based acrylic resins and water-based acrylics. Applications for water-based acrylics are primarily in decorative, masonry and industrial coatings but other uses include adhesives, paper and leather coatings, polishes, carpet backing compounds and tablet coatings. Another major use for acrylic acid is the manufacture of polyacrylates which are used as thickeners, dispersants and rheology controllers. Acrylic acid is also employed as a comonomer with acrylamide in anionic polyacrylamide and to produce hydroxyacrylates for use in industrial coating formulations. It is also used in the manufacture of plastics, molding powder for signs, construction units, decorative emblems and insignias, polymer solutions for coatings applications, emulsion polymers, paints formulations, leather finishing's, and paper coatings, detergents (Detergent polymers are essentially homopolymer polyacrylates and copolymers of polyacrylic acid and maleic anhydride that can be used with both zeolites and phosphates in washing powder formulations), wastewater treatment chemicals and super absorbent polymers (SAPs)[ SAPs are cross-linked polyacrylates with the ability to absorb and retain more than 100 times their own weight in liquid]

Acrylic acid ( $\text{CH}_2=\text{CHCOOH}$  bp  $141.0\text{ }^\circ\text{C}$  @101.3 kPa, mp  $13.5\text{ }^\circ\text{C}$ ) is a moderately strong carboxylic acid. it forms crystalline needles in the solid state. It is flammable, volatile, mildly toxic, colorless liquid. Hydroquinone or its monomethyl ether is usually added to commercial preparations to inhibit polymerization.

### Production:

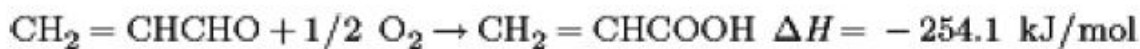
#### Propene oxidation:

Propene oxidation involves heterogeneous catalytic oxidation of propene in the vapor phase with air and steam to give acrylic acid. Generally the product leaving the reactor is absorbed in water, extracted with an appropriate solvent, and then distilled to give technical grade glacial acrylic acid. The two methods for the heterogeneously catalyzed gas-phase oxidation of propene are single-step and two-step processes.

#### Single-step process:



#### Two-step process:



The yield in the single-step process is at best approximately 50 – 60 %. Another drawback is limited lifetime of the catalyst, which is a multicomponent system composed of polyvalent oxides with molybdenum oxide as the main component and tellurium oxide as the promoter. The life of the catalyst is short because of the tendency of tellurium oxide to sublime.

The two-step reaction requires different reaction conditions and different catalysts to produce optimum conversion and selectivity in each step. Research has focused on this process, in which the oxidation of propene to acrolein and the oxidation of acrolein to acrylic acid employ separate catalysts. The steps are operated at different temperatures to permit high overall efficiency.

Catalysts more selective for the oxidation of propylene to acrolein and acrolein to acrylic acid were prepared from bismuth, cobalt, iron, nickel, tin salts, and molybdic, molybdic phosphoric, and molybdic silicic acids. Preferred second-stage catalysts generally are complex oxides containing molybdenum and vanadium. Other

components, such as tungsten, copper, tellurium, and arsenic oxides, have been incorporated to increase low temperature activity and productivity.

The oxidation reactors are of the fixed-bed shell-and-tube type (about 3–5 m long and 2.5 cm in diameter) with a molten salt coolant on the shell side. The tubes are packed with catalyst, a small amount of inert material at the top serving as a preheater section for the feed gases. Vaporized propylene is mixed with steam and air and fed to the first-stage reactor. The feed composition is typically 5–7% propylene, 10–30% steam, and the remainder air (or a mixture of air and absorber off-gas).

The preheated gases react exothermically over the first-stage catalyst with the peak temperature in the range of 330 - 430°C, depending on conditions and catalyst selectivity. The conversion of propylene to waste gas (carbon dioxide and carbon monoxide) is more exothermic than its conversion to acrolein. At the end of the catalyst bed the temperature of the mixture drops toward that of the molten salt coolant.

If necessary, first-stage reactor effluent may be further cooled to 200 - 250°C by an interstage cooler to prevent homogeneous and unselective oxidation of acrolein taking place in the pipes leading to the second-stage reactor. The acrolein-rich gaseous mixture containing some acrylic acid is then passed to the second-stage reactor, which is similar to the first-stage reactor, but packed with a catalyst designed for selective conversion of acrolein to acrylic acid. Here, the temperature peaks in the range of 280 - 360°C, again depending on conditions. The temperature of the effluent from the second-stage reactor again approximates that of the salt coolant. The heat of reaction is recovered as steam in external waste-heat boilers.

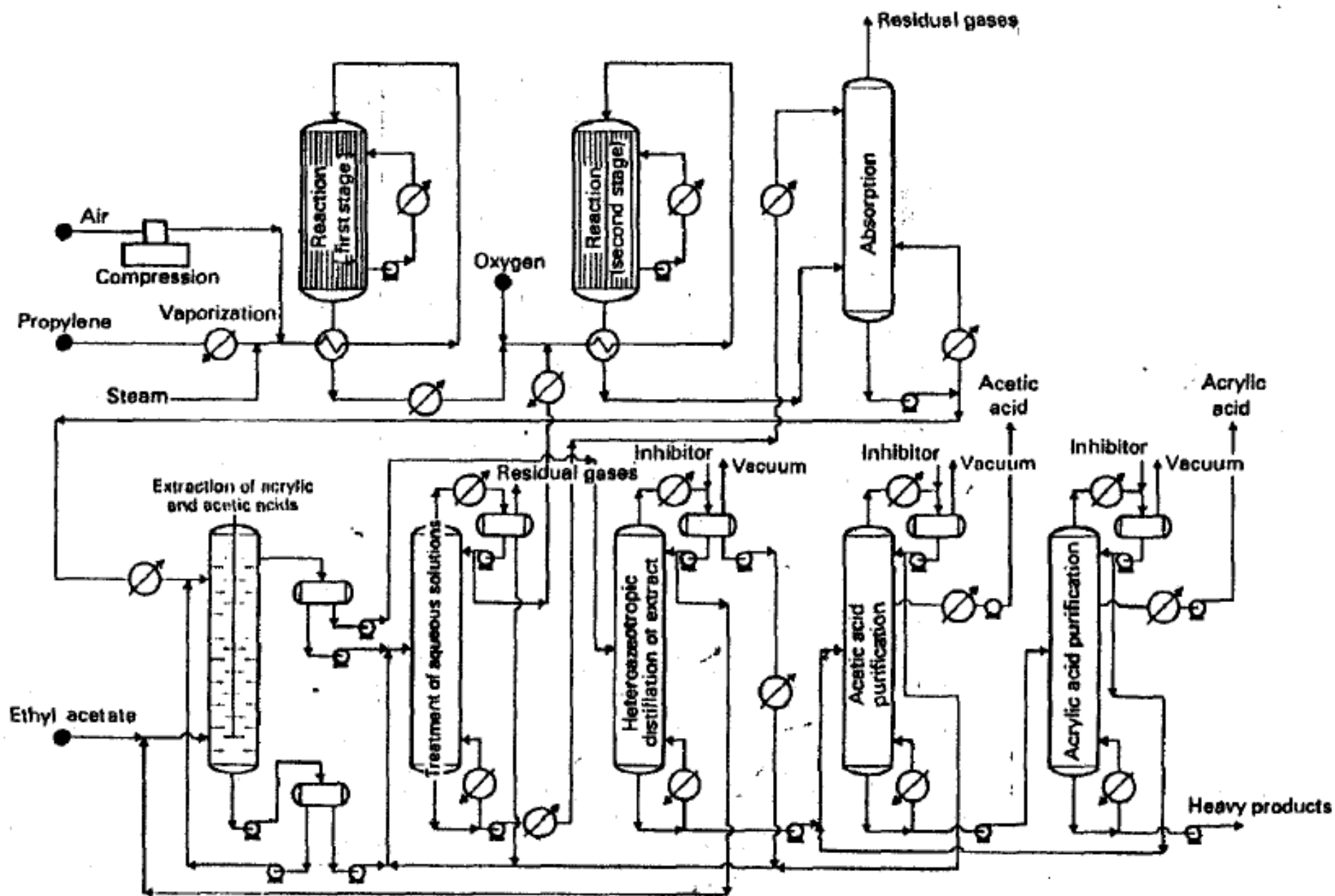
The effluent gas from the second-stage multi-tube reactor is cooled to about 200 °C and then fed to the absorbing column to be scrubbed with water. Because the effluent gas contains a large amount of steam, acrylic acid usually is obtained as an aqueous solution of 20 to 70 wt %. Alternatively, the acid may be absorbed by an organic solvent such as biphenyl, diphenyl ether, or a carboxylic ester with a boiling point higher than 160 °C. Then the steam in the reaction gas does not condense in the absorbing column, but is discharged with other gases from the column top. This method reduces energy consumption in the subsequent purification step, but it also increases the loss of acrylic acid and solvent from the column top.

After the absorption in water, the acrylic acid is purified by extraction with an organic solvent and then distillation. Various solvents can be used for the extraction. The first group (light solvents) includes those with boiling points lower than acrylic acid, such as ethyl acetate, butyl acetate, ethyl acrylate, and 2-butanone, as well as combinations of these. The second group (heavy solvents) has boiling points higher than acrylic acid (e.g., tert-butyl phosphate, isophorone, and aromatic hydrocarbons). Mixtures of these light and heavy solvents form a third group.

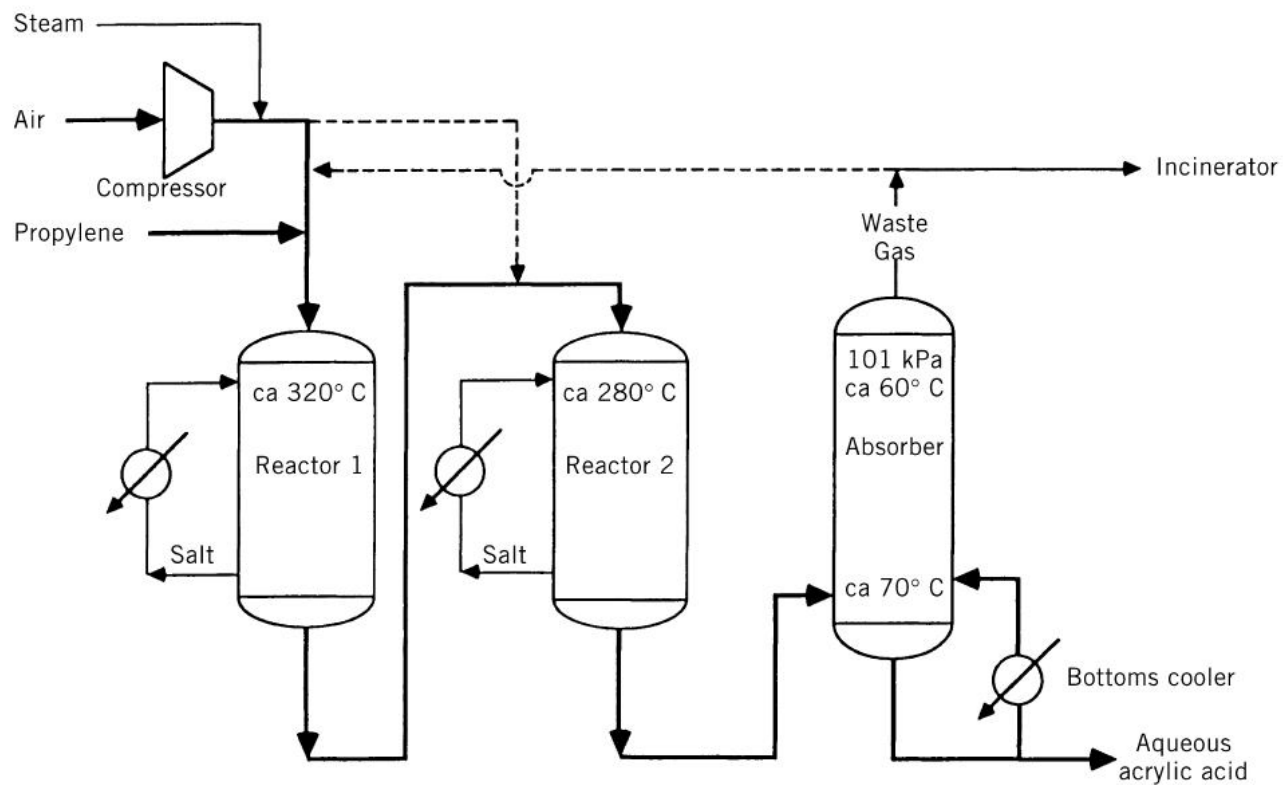
The aqueous acrylic acid from the absorbing column is introduced into the extraction column countercurrent to an organic solvent. The solvent must have a high distribution coefficient for acrylic acid and low solubility in water, and it must form an azeotrope containing a high percentage of water. The extract from the top of the extraction column goes to the solvent-separation column where the solvent and water are distilled overhead and the solvent is separated and recycled to the extraction column.

The bottom stream from the extraction column and the water from the overhead of the solvent-separation column are sent to the raffinate-stripping column, where a small amount of solvent is recovered by distillation. The waste water from the raffinate-stripping column is biologically treated or incinerated.

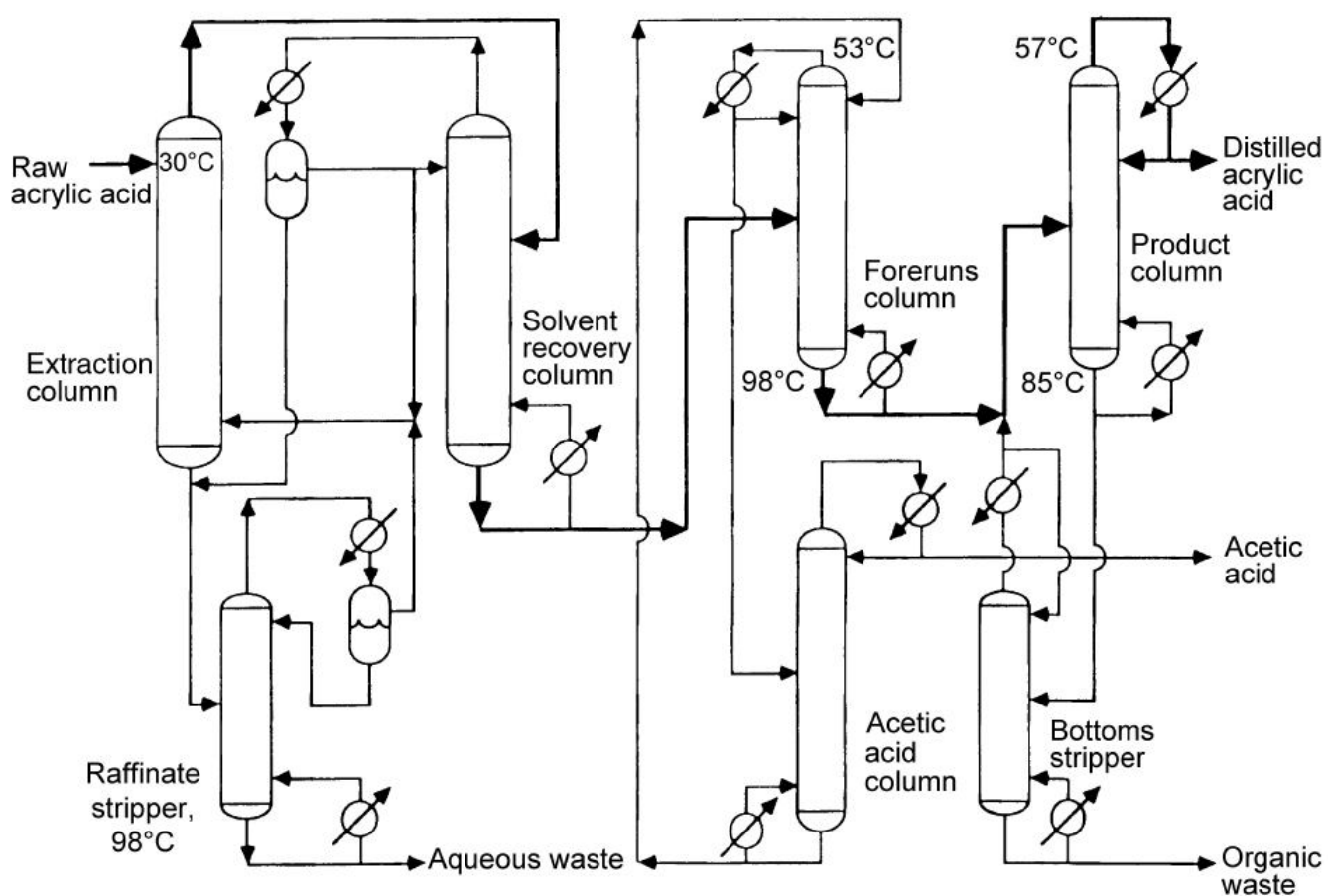
The bottom fraction from the solvent-separation column is fed to the light-ends cut column, where acetic acid is distilled off and, if desired, recovered. The crude acrylic acid from the bottom of the light-ends cut column is sent to the product column, where acrylic acid of high purity is obtained overhead. The material from the bottom of the product column containing acrylic acid dimer is fed to the evaporator, where the dimer is decomposed to the monomer. The evaporator residue, composed of acrylic acid oligomers, polymers, and inhibitors, is withdrawn and burned as waste oil. Because acrylic acid is readily polymerized, distillation columns are operated with an inhibitor, such as hydroquinone or hydroquinone monomethyl ether, in the presence of oxygen, and at reduced pressure to lower the distillation temperature. The purity of acrylic acid produced by this process usually exceeds 99.5 wt %, and the purified yield is about 98 %.



Acrylic acid production by propylene oxidation. Two-stage process.



Oxidation process.



Separations process.