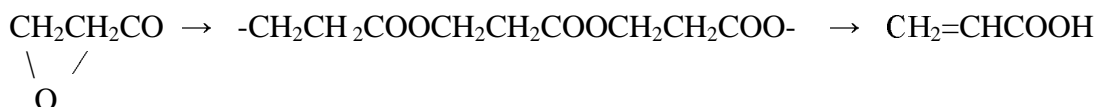


VARIOUS COMMERCIAL PROCESSES

Ethylene Cyanohydrin Method: This process involves the acidic hydrolysis and dehydration of ethylene cyanohydrin (from ethylene oxide and hydrogen cyanide) and the removal of the product from the reaction mixture by distillation. Like all other preparation of polymerizable monomers, care must be exercised to remove the product from the reaction mixture and either inhibit or appropriately cool it before uncontrolled polymerization can ensue .

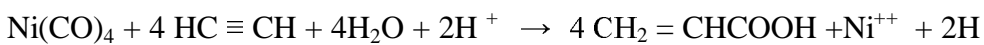


β- Propiolactone Method: This commercial method is based on the polymerization of β-propiolactone and the destructive distillation of this polymer to form acrylic acid

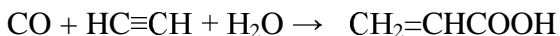


Carbonyl Reaction: Basic raw materials in the preparation of acrylic acid by the carbonyl reaction are acetylene carbon monoxide (supplied as such or in the form of nickel carbonyl) , and water . Three distinct methods are known.

Stoichiometric Carbonyl Reaction: The reaction is very rapid at atmospheric pressure and at mild temperature . The hydrogen shown in the accompanying equation does not appear in gaseous form but is consumed by side reactions

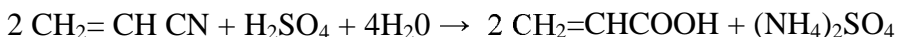


Catalytic Carbonyl reaction: The catalytic reaction requires elevated temperature and superatmospheric pressures. Nickel salts or complexes thereof are used as catalysts.



Semicatalytic Carbonyl Reaction: The catalytic reaction (catalytic as regards nickel carbonyl) of acetylene, carbon monoxide and water is superimposed upon the stoichiometric reaction of nickel carbonyl , acetylene , water and acid. In this way the very mild conditions characteristic of the stoichiometric reaction can be used , with a large proportion of the total CO being supplied as carbon monoxide gas, the remainder being supplied in the form of nickel carbonyl.

Acrylonitrile Method: Care must be exercised in this acid hydrolysis since both the starting Acrylonitrile and the product acrylic acid are polymerizable. The Acrylonitrile should remain in the reaction zone and, hence, must be well inhibited. A major advantage of this method is the increase in molecular weight on hydrolysis from 53 to 72, which provides a definite yield improvement.

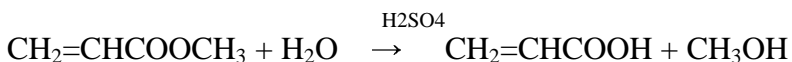


Propylene Method: This recently developed process involves the oxidation of propylene to hydroxypropionic acid: oxides of nitrogen or nitric acid act as catalyst for the reaction. Subsequent dehydration yields acrylic acid. The stepwise representation can be shown as follows:

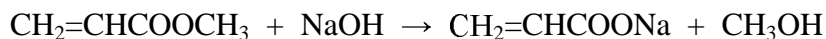


An alternative route is the catalytic oxidation to acrolein, CH_2CHCHO , and then to acrylic acid with oxygen and certain metallic catalyst such as Mo, Co, or Ce.

Acrylic Ester Method: This method is hampered by the ready polymerisability of the starting material, and the low boiling points of the most available esters and the formed alcohols as compared with that of the product, acrylic acid.



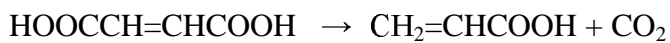
It is generally preferable to saponify the ester to form the corresponding salt.



The salt can then be converted to the acid by:

- Neutralizing the calcium salt with sulphuric acid, removing precipitated calcium sulfate by a difficult filtration procedure, and obtaining the formed acrylic acid in aqueous concentrate.
- Treating an aqueous solution of sodium salt with ion-exchange resin to remove sodium ions, removing the resin by filtration, and obtaining an aqueous concentrate of acrylic acid.

Maleic Acid Method: This patented method involves the decarboxylation of maleic acid to form the desired acrylic acid



Potassium Vinyl Method : The low temperature conversion of vinyl chloride with potassium metal and a subsequent treatment of the cold vinyl potassium with dry ice is reported to give potassium acrylate in 70% conversion . Customary methods produce acrylic acid.



Vinyl Grignard Method : This interesting synthesis involves the use of the well known carboxylation of a Grignard reagent to form the acid.



CHOICE OF PROCESS

Various methods for the manufacture of acrylic acid are mentioned above. For a route to be commercially attractive the raw material costs and utilization must be low, plant investment and operating cost not excessive, and waste disposal charges minimal.

A lead time of several years for development and plant construction is important in a period where availability of hydrocarbon raw materials are changing rapidly and significantly. Natural gas costs are expected to increase steadily while the supply is decreasing. Acetylene should be in short supply with rising costs in the next decade unless new technology based on coal is developed. Hence, acrylic acid manufacture by acetylene routes will be increasingly uneconomical. Ethylene cost, dependent on crude oil are expected to increase, but not sharply. Propylene may be considered a byproduct from the large volume manufacture of ethylene from heavy petroleum feed stocks. New ethylene facilities, based on naphtha and other heavy feed stocks will ensure a large supply of coproducts including propylene. Propylene requirements for acrylic acid will be small, compared to other chemical uses (polypropylene, Acrylonitrile, propylene oxide, isopropanol and cumene for acetone and phenol). Hence, although the cost of propylene is expected to rise, this should be at a slower rate than the increases for any of the other raw materials. The favourable supply and cost projection for propylene suggest that all new acrylic acid plants will employ propylene oxidation technology for at least the next two decades.

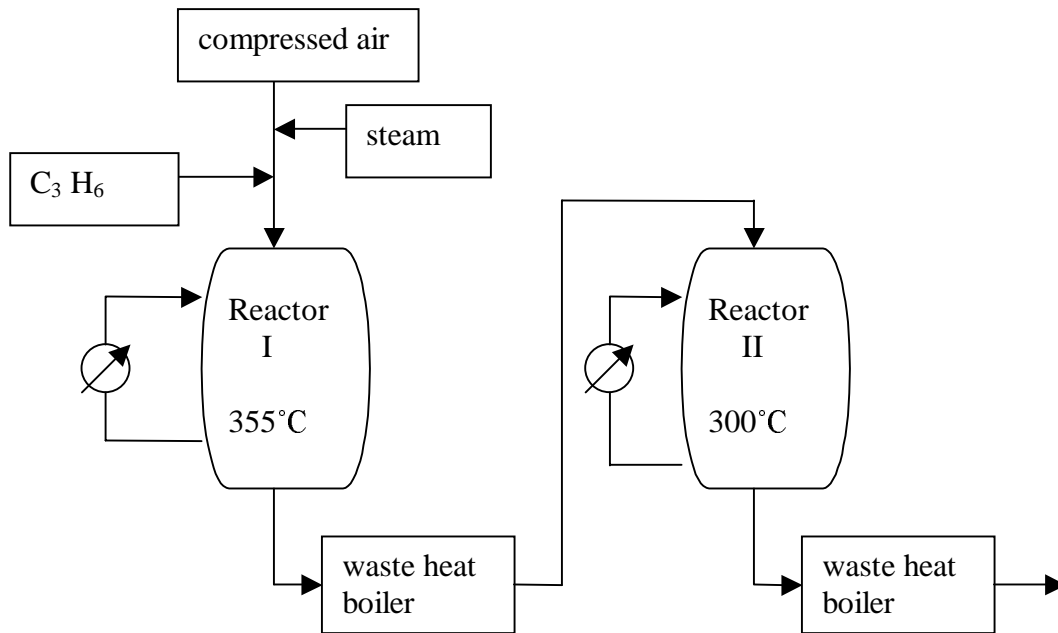
The most economical process for the manufacture of acrylic acid is based on the two stage vapour phase oxidation of propylene to acrylic acid.

Process based on acetylene - the high pressure Reppe process (BASF), the modified Reppe process (Rohm Haas) - or on Acrylonitrile are still being used for the production of acrylic acid. A ketone and an ethylene cyanohydrin process were once commercially important, but are no longer used.

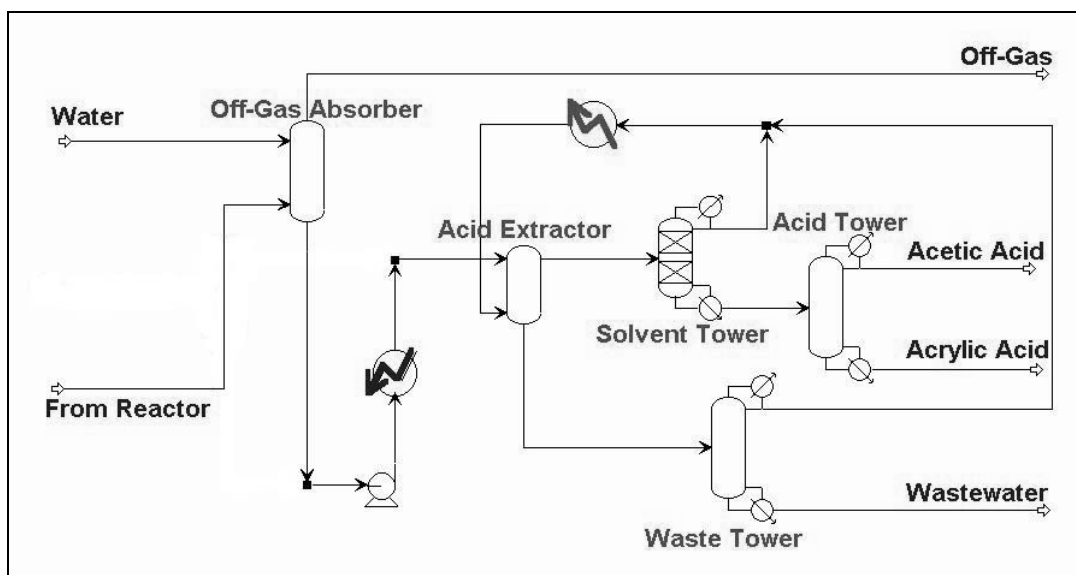
The propylene oxidation process is attractive because of the availability of highly active and selective catalysts and the relatively low cost of propylene.

PROCESS DESCRIPTION : Propylene oxidation process

ACRYLIC ACID PRODUCTION (OXIDATION SECTION)



ACID RECOVERY AND PURIFICATION SECTION



The oxidation process flow sheet shows equipment and typical operating conditions. The reactors are of the fixed-bed shell-and-tube type (about 3-5m long and 2.5cm 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 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. At the end of the catalyst bed, the temperature of the mixture drops toward that of the molten salt coolant.

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 catalyst designed for selective conversion of acrolein to acrylic acid. Here the temperature peaks in the range of 280- 360° C, again depending on condition. 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 boiler.

The process is operated at the lowest temperature consistent with high conversion. Conversion increases with temperature: the selectivity generally decreases only with large increase in temperature. Catalysts are designed to give high performance over a range of operating condition permitting gradual increase of salt temperature over the operating life of the catalysts to maintain productivity and selectivity near the initial levels, thus compensating for gradual loss of catalyst activity.

The first unit the product stream enters is the absorption tower, which quickly lowers the temperature of the entering stream from about 220 °C to less than 80°C. The purpose is to put the acrylic acid into a cool, liquid state that will not readily dimerize. Also, this separates out the gaseous material in the product stream such as nitrogen, carbon dioxide, oxygen, and propylene. These components exit out the top along with some fugitive acrylic and acetic acid that is still in the vapor phase. The gases

entering the gas absorber are absorbed using deionized water. The water absorbs the acrylic and acetic acids and allows the other gases to continue on to an incinerator to be burned. The aqueous effluent from the bottom of the absorber is 20 - 30 % acrylic acid which is sent to the recovery. The overall yield of acrylic acid in the oxidation reaction steps is in the range of 73 - 83 % depending on the catalysts and condition employed.

The acrylic acid is extracted from the absorber effluent with a solvent. The acid extractor is a liquid-liquid extraction column. The acid containing water enters through the bottom feed stream. The top feed stream contains an organic solvent. The two liquid phases flow counter-currently through a liquid-liquid extractor. The acids enter solution with the solvent and exit out the top stream with a fraction of the water, and the water exits out the bottom stream with a very small amount of solvent.

The top stream continues on to the solvent tower, which is a packed distillation column. Because of acrylic acid's ability to dimerize easily at high temperatures, all of the distillation processes are performed in part with vacuum distillation. The solvent and remaining water leave in the distillate stream at 0.12 bar and 13°C. Refrigerated water is used to condense the distillate. Some is refluxed back into the column, but the distillate is then heated up to 40°C and used as a recycle and is re-fed into the acid extractor.

Meanwhile, the acids leave the solvent tower in the bottoms and are fed into the acid tower. The acid tower is a distillation column that again operates in vacuum conditions. The acetic acid leaves the top at 0.07 bar, while the acrylic acid leaves in the bottoms. Both the acrylic and acetic acids are warmed and compressed to normal pressure levels. Both now meet the given requirements. Namely, that acrylic acid must be 99% pure and that acetic acid must be 95% pure.

Only one detail remains. The bottom stream from the acid extractor is nearly completely water save for a small amount of solvent. This stream is fed to another distillation column. Here, the solvent is separated out the top stream and then joins the solvent recycle stream re-entering the acid extractor tower. The bottom stream is sent to wastewater treatment