PERP Program – Acrylic Acid

New Report Alert

July 2006

Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, ***Acrylic Acid (04/05-6)***. To view the table of contents or order this report, please click on the link below:
http://www.nexant.com/products/csreports/index.asp?body=http://www.chemsystems.com/reports/show_cat.cfm?catID=2

Introduction

The global crude acrylic acid market reached around 3.2 million tons by the end of 2005. Forecast global demand growth lies in the range of average global GDP at around 3.4 percent. Glacial acrylic acid grades account for around 44 percent of global demand. Commodity acrylates as a whole account for 52 percent of global acrylic acid demand, while butyl acrylate alone accounts for 30 percent. The demand distribution for acrylate polymers in waterborne and solvent-borne systems is highly fragmented, but led predominantly by the coatings and adhesives sectors.

In terms of geographic region, current crude acrylic acid demand is centered in the United States and Western Europe, which account for 36 percent and 27 percent of global demand, respectively. However, the future major investments in acrylic acid/acrylate complexes will be made in developing economies. China is seeing continued investment in intermediate-sized complexes from local companies, with technology developed locally, in conjunction with large investments from the major international producers, e.g. BASF. Given strong forecast double digit demand growth in Asia, particularly China, Asian demand for crude acrylic acid will outstrip that in developed economies, moving from only 21 percent of global demand in 2005 to around 38 percent in 2015. However, several factors could have a dramatic effect on future acrylic acid demand, e.g., whether (super absorbent polymer containing) diapers can further penetrate Chinese and Indian markets.

Global commodity acrylate ester demand reached 2.8 million tons in 2005. The market is forecast to grow at rates aligned with average global GDP. The growth in higher acrylates into emulsions and dispersions is much stronger than light acrylates. Butyl acrylate dominates commodity acrylate demand at nearly 60 percent of total demand. Continued focus on water-based coatings and dispersion systems will positively influence 2-ethylhexyl acrylate demand in developing economies, while substitution in many applications in developed economies has already occurred.

In terms of regional acrylates demand East Asia has already overtaken the United States and Western Europe, accounting for around 31 percent of global demand. By 2015, this share will rise to around 37 percent as the region will lead future global demand.

Nexant estimates that global demand for glacial acrylic acid reached around 1.4 million tons in 2005 with reasonable forecast demand growth as a base case. SAP dominates the market at around 76 percent of total demand. Demand growth could accelerate, but this depends not only on innovations in the diaper business but also social and cultural developments in new target markets for diaper manufacturers. Strong and successful penetration into China and India could dramatically change the SAP and glacial acrylic acid market outlook. At present infant diaper uptake is limited in these countries despite their demographics. Making SAP-based diapers more affordable in these markets would have a major impact on demand.

With the closure of acetylene-based and acrylonitrile-based plants in the 1990s, the two-stage oxidation of propylene is now virtually the only crude acrylic acid technology in commercial operation. Salt inter-cooled multi-tubular reactors are the heart of the process, with separation approaches using either a water quench/azeotropic system or solvent quench/absorber/desorber system. The design of acrylic acid and acrylate plants vary enormously by site and company. A world-scale facility has a capacity of 160,000 tons per year.

Looking forward, the oxidative dehydrogenation of propane provides a propylene-containing crude acrylic acid feedstock that could be integrated with designs for existing processes. This approach could, with further development, offer a realistic way forward for a propane-based acrylic acid process. Given the current and forecast tightness in propylene supply, lack of integrated propylene may be an issue in future competitiveness.

Global propylene demand reached around 66 million tons in 2005 and is forecast to grow at an average annual rate of 4.5 percent to 2015. Around 63 percent of all propylene demand is taken by polypropylene. Nexant projects that by 2015 around 68 percent of all propylene demand will be taken by polypropylene.

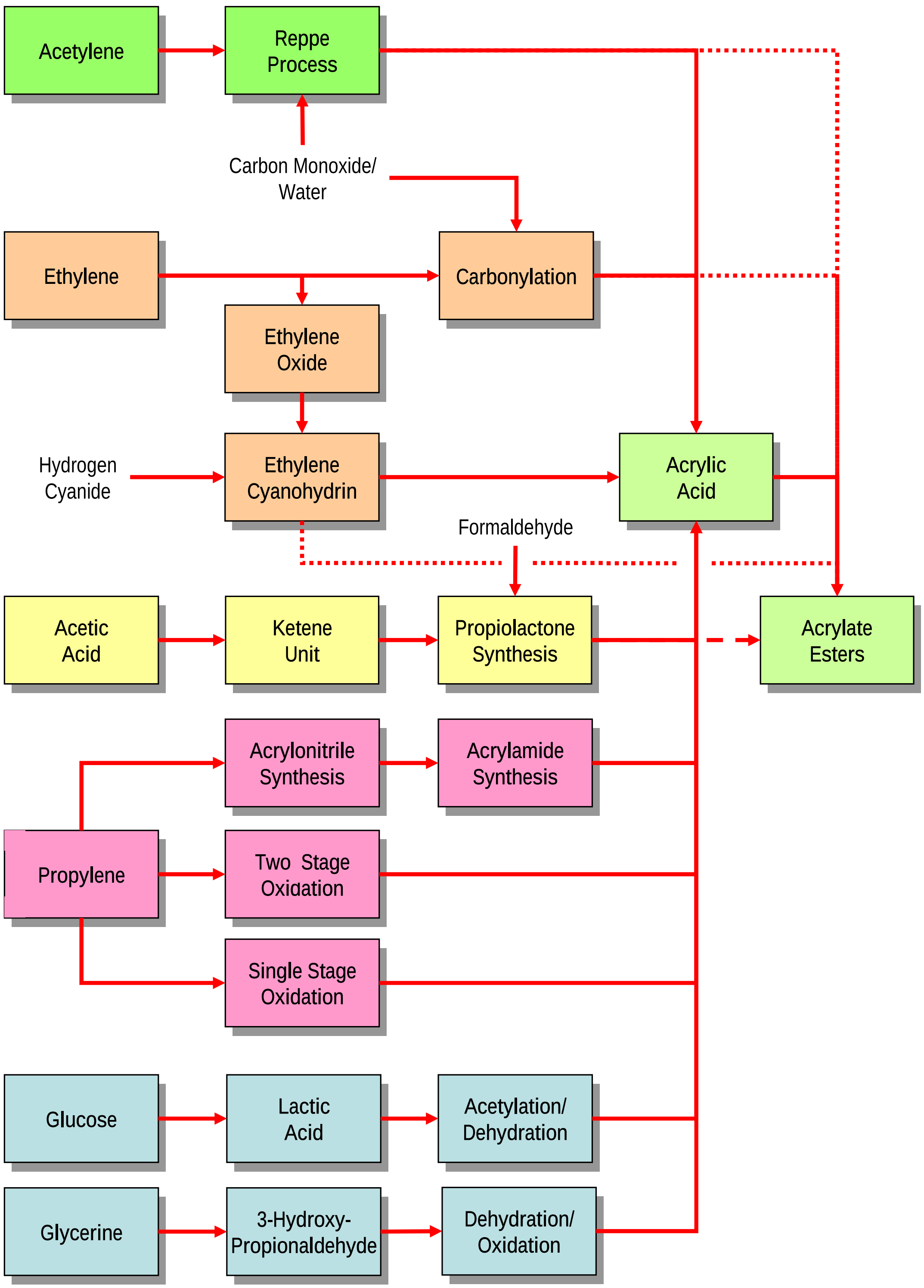
In contrast, acrylic acid accounts for only three percent of global propylene demand and around eight percent of non-polypropylene demand. Given current growth projections, by 2015 the latter figure will be ten percent.

Recent improvements in microorganisms for producing lactic acid from glucose could make a biotransformation route economically viable, with lactic acid converted into acrylic acid via dehydration using an acetylation/cracking approach.

In a continuing high oil price world, any major improvement in corn to glucose to lactic acid economics could make a biotransformation acrylic acid/acrylate process more realistic, adding more petrochemical intermediates to the possibilities for “white” biotechnology.

Acrylic acid synthesis dates back to the mid nineteen century, but only came to prominence as a chemical intermediate in the 1930s when a reliable commercial synthesis became available. Figure 1 summarizes some of the commercial and developmental processes for acrylic acid production.

Figure 1 Chemical Routes to Acrylic Acid/Acrylates



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Commercial Technology

The two stage oxidation of propylene is the approach used today to produce crude acrylic acid. However, there is considerable variation in plant design and even the generations of technology used at major sites.

At the heart of the process are the molten salt inter-cooled shell and tube reactors. Catalysts for the primary oxidation are based on promoted molybdenum-bismuth systems and operate at 350°C ±50°C. Secondary oxidation catalysts are based on promoted molybdenum-vanadium systems and operate at a lower temperature. Catalyst packing and control of catalyst activity throughout the reactor tubes are vital to prevent large exotherms. Reactor design is key in maintaining optimum temperature control in all tubes. Heat of reaction can be recovered as steam for use in the separation train and integrated processes. Reactor design and catalyst performance currently limit acrylic acid capacity to circa 100,000 tons per year in a single line.

Separation trains fall into two major categories designed around the quench system. A water quench with azeotropic distillation is more common. A solvent quench with an absorber/desorber separation system is also used. Some plants will also upgrade heavy ends via the use of a cracking reactor. A key feature of the process is the need to prevent polymerization of acrylic acid in the separation train. Special measures are employed such as low temperature separation, smooth internal surfaces, special trays, inhibitor injection, etc.

These plants are backed up by an extensive environmental protection system, e.g., separation train off-gases and organic waste liquids are sent to incineration to recover energy.

Although acetylene is no longer used as a feedstock for acrylic acid production, it could prove economic in the appropriate location, i.e., a location with stranded gas, advantageously priced.

Although commodity acrylates are made in most cases via esterification, processes worldwide vary enormously and can also be impacted by other integrated processes at the site. Plants can also operate in swing mode. Typically lighter acrylates, i.e., methyl and ethyl esters, are made in one swing line and heavy acrylates in another.

Purification technologies vary around the world and typically distillation and crystallization are used. Two-stage distillation with the aid of a complexation additive is used by one producer to produce a flocculent grade of glacial acrylic acid. Combinations of static, dynamic and falling film crystallizers are also used.

Emerging Technology

In recent years, there has been considerable research activity in alkane activation to exploit low cost propane for processes like acrylonitrile and acrylic acid. The direct catalytic oxidation of propane provides numerous challenges, and to date catalyst performance has generally resulted in relatively low yields of acrylic acid. This leads to sub-world-scale plants, large recycles and high capital investment which adversely impact economic performance.

However, the approach of propane oxidative dehydrogenation looks promising. Here, a mixture of propane and a propane-rich recycle gas are mixed with a tailored oxygen-nitrogen mixture and reacted over proprietary catalyst to produce an intermediate stream. When this intermediate stream is mixed with more tailored oxygen-nitrogen mixture, the result is a stream suitable for primary oxidation to acrolein similar to current commercial practice in terms of propylene content and propylene/oxygen ratio. The quench tower must be modified, with the off-gas feeding a propane enrichment column to provide the desired recycle stream.

This process looks encouraging, but substantial research and development is still needed to bring this concept to commercialization.

Of the two biotransformation concepts under consideration, the lactic acid approach looks more interesting given the approach to dehydration via acetylation/cracking. Acetylation with acetic acid or preferably acetic anhydride forms 2-acetoxy propionic acid. The cracking of this species produces acrylic acid. A conceptual process based on integrated acetic anhydride production has been proposed and could form the basis for a commercial process after further development. The process could use glacial lactic acid or a 90 percent concentrate.

Economics

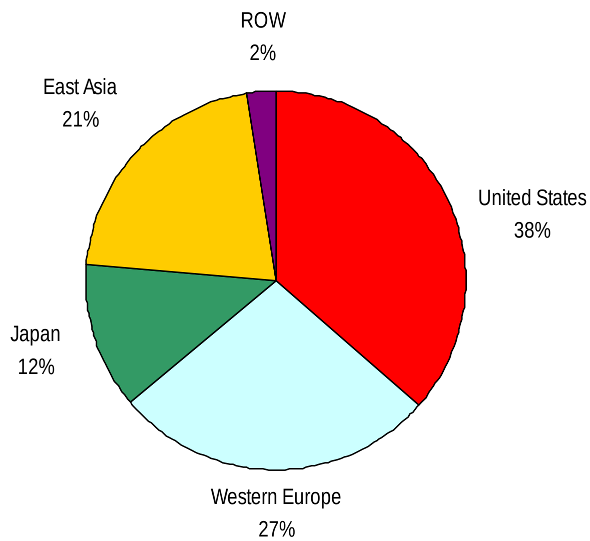
Cost of production analyses for the following processes/products are provided in this report:

- Crude acrylic acid via propylene
- Crude acrylic acid via acetylene
- Glacial acrylic acid via distillation
- Glacial acrylic acid via crystallization
- Ethyl acrylate
- N-Butyl acrylate
- Ethylhexyl acrylate

Commercial

The report provides application, demand, supply, and trade data for crude and purified acrylic acid, as well as commodity and specialty acrylate esters. The United States, Western Europe, and Japan are covered in detail, and a global summary is also presented. Figure 2 presents a breakdown of crude acrylic acid consumption by region.

Figure 2
Regional Breakdown of Crude Acrylic Acid Consumption, 2005



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