

PERP Program - Acrylonitrile New Report Alert

November 2006

Nexant's *ChemSystems* Process Evaluation/Research Planning (PERP) program has published a new report, *Acrylonitrile (05/06-2)*. 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

Technology

Acrylonitrile is a clear, colorless or pale yellow flammable liquid with a sweet, pungent, irritating odor. Acrylonitrile is soluble in organic solvents such as ethanol, acetone, ethyl acetate, carbon tetrachloride, and benzene, but is only partially soluble in water. Due to the presence of both a carbon-carbon double bond and a carbon-nitrogen triple bond in the same molecule, acrylonitrile is very reactive. Violent polymerization can occur in the presence of alkalis, peroxides, or exposure to light.

Conventional Propylene-based Process

Both Sohio and Distillers simultaneously developed processes involving the heterogeneous vapor phase catalytic oxidation of ammonia and propylene. Distillers made use of a fixed bed reactor in its process, and Sohio used a fluid bed reactor. Both companies were ultimately bought by BP (thus settling any legal disputes over technology ownership). The Sohio process prevailed over the Distillers process and has been licensed extensively. Almost all of the acrylonitrile produced worldwide is now made using the BP (Sohio) process. BP split out its olefins and derivatives businesses into Innovene, and Innovene was subsequently sold to INEOS in December 2005.

The INEOS/BP (Sohio) process to produce acrylonitrile involves the catalytic oxidative reaction of propylene with ammonia in the vapor phase. Approximately stoichiometric amounts of propylene and ammonia, combined with air, are passed through the reactor in a single pass operation with a residence time of just a few seconds.

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The reaction is highly exothermic, and the heat of reaction is generally used to make high pressure steam which is then utilized downstream in separation and purification operations.

The main by-products produced are hydrogen cyanide, used primarily in the manufacture of methyl methacrylate, and acetonitrile, used as an industrial solvent. Unreacted ammonia in the reactor effluent is neutralized with sulfuric acid. The resulting ammonium sulfate can be recovered for use as a fertilizer.

Chemical grade propylene (average propylene content of 92-94 percent) and fertilizer grade ammonia and air are fed with a molar ratio of approximately 1.0:1.2:10 to a fluid bed catalytic reactor. The reactor is operated at temperatures of 400 to 500°C and pressures of 5 to 30 psig. Contact time in the reactor is 10 seconds or less. A high conversion of propylene is obtained in a single pass, so as to obviate the need for recycle.

Oxygen enrichment is sometimes used to increase the oxygen concentration in the oxidizing gas from 21 mol percent to 25-26 mol percent. This increases the productivity of a given size reactor. Acrylonitrile yield on propylene is assumed at 77 mol percent. The reaction is highly exothermic, releasing about one third more energy than theoretical due to partial combustion of the propylene. Any unreacted ammonia must be removed from the reactor effluent before acrylonitrile separation to avoid the formation of by-products and resins.

The first step in the purification process is the separation of the acetonitrile from the product stream. This is complicated by proximity of the boiling points of acrylonitrile and acetonitrile (77°C and 81°C, respectively). Extractive distillation with water is typically used to accomplish this separation. The extractive distillation column overheads product is fed to a hydrogen cyanide stripper where hydrogen cyanide is removed overhead as a pure product. The bottoms product is fed to an acrylonitrile stripper. The acrylonitrile is recovered from its water azeotrope. The acrylonitrile is sent to the product column where pure acrylonitrile is taken as the overhead product.

The need to dispose of process by-products in a cost effective and environmentally acceptable manner has increased in importance. Although process offgases are typically incinerated, methods for dealing with liquid effluents include deep well disposal, wet air oxidation, ammonium sulfate separation, and biological treatment. Since deep well disposal as an available option is declining steeply, integrated treatment schemes combining wet air oxidation, ammonium sulfate recovery, and biological treatment have been developed.



Developing Propane-based Processes

Over the last 20 years, much research on propane ammoxidation has been performed by several companies worldwide, including BP, Asahi Chemical, and Mitsubishi Chemical.

Over the last ten years or so, BP had indicated that their next acrylonitrile plant could very well be propane-based. However, with the split out of BP's olefins and derivatives businesses into Innovene, and the subsequent sale of Innovene to INEOS in December 2005, the development plans for this technology is unclear. There have been no recent announcements, and the INEOS and Innovene websites are silent on developments in this technology.

Mitsubishi appears to not be advancing their version of propane-to-acrylonitrile technology, since there have been no recent announcements and their website is silent on this technology.

However, Asahi Kasei Chemicals Corp. appears to be advancing propane-to-acrylonitrile technology to commercialization in the near future. Recent contact with Asahi Kasei confirmed its intention to build a new acrylonitrile plant based on its propane ammoxidation technology in Thailand, with a capacity of 200 KTPA and expected completion in mid-2009. Asahi claims that its proprietary catalyst will require only minor modification of existing propylene-based acrylonitrile plants, as the flow sheet layout is unchanged in switching from propylene to propane feedstock.

The principal route to acrylonitrile from propane is believed to proceed through propylene as an intermediate. The limiting factor is the speed of the propylene-to-acrylonitrile step relative to other products, acetonitrile and HCN.

The key reactions can be shown as follows:

(1) $CH_3CH_2CH_3 + 0.5 O_2 \longrightarrow CH_2 = CHCH_3 + H_2O$ (2) $CH_2 = CHCH_3 + 1.5 O_2 + NH_3 \longrightarrow CH_2 = CHCN + 3 H_2O$ Overall: (3) $CH_3CH_2CH_3 + 2 O_2 + NH_3 \longrightarrow CH_2 = CHCN + 4 H_2O$ $C406_00101.0006.4109.CDX$

Economics

The economics of acrylonitrile production is highly influenced by the price of propylene but is also significantly influenced by the credits taken for by-product materials. In this study, hydrogen



cyanide is valued at its cost plus return value for on-purpose production from natural gas and ammonia by the dominant Andrussow process. Due to its high toxicity, HCN is not suited to long distance transport. Most companies consume the material on site or convert it to acetone cyanohydrin, an intermediate in the production of methyl methacrylate, which is more readily shipped.

Acetonitrile by-product has only limited demand as an industrial solvent. Most U.S. acrylonitrile producers recover crude acetonitrile, whereas no companies in Western Europe and a few in Japan do so. When not recovered for sale, acetonitrile must be incinerated at costs that effectively negate any fuel credit for the material. Because it is common for U.S. producers to recover some amount of produced acetonitrile, a by-product value consistent with use as a specialty solvent is used in the economic analysis.

Ammonium sulfate derived from the neutralization of unreacted ammonia can be recovered and sold into the fertilizer market. However, the cost of recovery and purification generally equals or exceeds the revenue obtainable from this outlet and few producers, if any, recover ammonium sulfate for sale. For the purpose of this report, ammonium sulfate is taken to have no net value.

Several scenarios of propane-based processes are also presented in this report. The following detailed cost of production assessments are provided:

- Conventional propylene ammoxidation (270,000 metric tons/yr)
- Conventional propylene ammoxidation with an improved catalyst (270,000 metric tons/yr)
- Developing propane-based process with air (no recycle case)
- Developing propane-based process with oxygen (recycle case)
- Developing propane-based process with air and ammonia recovery

Commercial Analysis

End-Uses

Acrylonitrile (ACN) is used principally as a monomer or comonomer for synthetic fibers, plastics, and elastomers. ACN contributes heat, chemical, solvent, and weathering resistance to polymers. In addition to its use in acrylic and modacrylic fibers, acrylonitrile is used to produce adiponitrile, a nylon intermediate, by electrolytic reduction and dimerization. Adiponitrile is then hydrogenated to hexamethylenediamine, a comonomer with adipic acid in the manufacture of nylon 66 polymers used in fibers and plastics.



Acrylonitrile is an important constituent of high impact strength resins such as acrylonitrile/butadiene/styrene (ABS) and styrene/acrylonitrile (SAN). ABS contains about 25 percent acrylonitrile, and SAN contains about 30 percent acrylonitrile. ABS is used in appliances, business machines, telephones, transportation and recreation equipment, luggage, and construction. SAN is used in appliances, packaging, housewares, and automotive applications.

ABS and SAN resins generally exhibit performance properties intermediate to those of commodity and engineering resins. As such, there is significant competition for ABS from rigid polyvinyl chloride in pipe applications and from high heat polystyrene in appliances, business machines, and construction applications.

Nitrile rubbers, made by copolymerization of acrylonitrile with butadiene, have good resistance to abrasion, heat aging, lubricating oils, and gasoline. They are chiefly used in automotive applications such as fuel lines.

Catalytic hydrolysis of acrylonitrile yields acrylamide, which forms a variety of homopolymers and copolymers. These polymers are used as flocculants in water and waste treatment, as mobility control agents in crude oil recovery, as retention aids in paper making, and in froth flotation processes.

Polyacrylonitrile (PAN) is the precursor for carbon fiber for high strength applications ranging from aircraft parts to sporting equipment. PAN-based carbon fiber is still a low volume specialty material due to its relatively high cost to produce.

Other applications for acrylonitrile include adhesives, corrosion inhibitors, and comonomer with vinyl chloride, vinylidene chloride, vinyl acetate, and/or acrylates in resins for paints and coatings.

Supply

After increases in global acrylonitrile capacity of about 5 percent in 2003 and 4.5 percent in 2004, annual increases have moderated to one percent per year or less. This trend is expected to hold through 2008. Acrylonitrile capacity in Europe/Middle East/Africa and the Americas is expected to be flat to slightly declining after 2005. On the other hand, capacity in Asia Pacific is anticipated to grow by about two percent per year from 2005 to 2008. Figure 1 shows the forecast distribution of global capacity by company in 2010.





INEOS is forecast to have the largest global capacity share at 10 percent, followed by Solutia at 8 percent, Asahi Kasei at 7 percent, and Jilin Chemical at 5 percent. Six other producers are identified as having 4 percent of global capacity each.

Petrochemical 4.2%

4.2%

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