

PERP Program - Caprolactam New Report Alert

July 2006

Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, *Caprolactam (04/05-3)*. 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 market for caprolactam, the monomer used in production of nylon 6, reached nearly 4 million metric tons per year by the end of 2004. Although the global market is forecast to grow on average at less than global GDP rates, global demand is nonetheless expected to reach around 5 million metric tons per year by 2015. Explosive demand growth in China is expected to account for 20 percent of the global market by that time.

Caprolactam suffers from cyclical profitability for several reasons, including:

- Volatile feedstock pricing
- Variable ammonium sulfate credit in the fertilizer industry, and
- Inter-polymer competition of nylon 6 with other materials, principally nylon 66 and polyesters.

In recent years, technology developments have mainly focused on the reduction or elimination of ammonium sulfate by-product. Large quantities of ammonium sulfate, ranging from 1.4 up to 4.5 tons per ton of caprolactam, are produced by most processes based on aromatic feedstocks. The exception is a process developed by Sumitomo that utilizes a fluidized-bed reactor with hydrogen peroxide as the oxidizing agent.

Figure 1 illustrates the various known routes to caprolactam, from both aromatic and non-aromatic feedstocks. Modern caprolactam manufacture starts with the synthesis of cyclohexanone from either cyclohexane (via catalytic oxidation) or phenol (via catalytic hydrogenation).

The next stage of the process is the conversion of cyclohexanone into cyclohexanone oxime by reaction with hydroxylamine. Portions of the total ammonium sulfate by-product are made in the hydroxylamine preparation and oximation steps. By-product formation in preparation of hydroxylamine can be reduced by the nitric oxide (NO) reduction process and the phosphate oxime (HPO/HPO+) processes developed by DSM.





Figure 1 Different Routes to Caprolactam



Recently, Sumitomo has commercialized a process dubbed ammoximation wherein no by-product accompanies oxime formation. Capital is reduced by elimination of the hydroxylamine formation step, but advantaged hydrogen peroxide pricing requires large-scale production of that feed.

Toray has bypassed the need for the cyclohexanone or oximation steps by commercializing a photochemical process to convert cyclohexane into cyclohexanone oxime by reaction with nitrosyl chloride and hydrogen peroxide. Substantial cost savings result from the elimination of process steps. However, the process requires low-cost electric power to be cost effective, and large-scale photochemical reactors are difficult to design and maintain.

The final step of conventional caprolactam synthesis is the so-called Beckmann rearrangement. This highly exothermic reaction takes place in the presence of oleum, which is subsequently neutralized with ammonia, resulting in ammonium sulfate production. Sumitomo has successfully commercialized a fluid-bed Beckmann rearrangement reactor that does not use oleum or produce ammonium sulfate. Cost of the fluid-bed reactor is offset by savings elsewhere in the overall process.

A combination of ammoximation to obtain the oxime and fluid-bed Beckmann rearrangement of the oxime to give caprolactam provides zero ammonium sulfate by-product. While in some situations this is highly desirable, it should be noted that in regions where there is appreciable local demand for fertilizer (e.g., Spain and Thailand) the by-product may be welcome and command an attractive price.

Caprolactam can also be manufactured from non-aromatic feedstocks such as butadiene or adiponitrile. Adiponitrile, in turn, can be manufactured from butadiene and hydrogen cyanide (a process used by DuPont/Invista and Butachemie) and from the electrolysis of acrylonitrile (a process used by BASF, Solutia, and Asahi). Acrylonitrile is derived from the ammoxidation of propylene.

Two families of processes have been developed based on non-aromatic feedstocks. One approach came from a DSM-DuPont collaboration and is called the ALTAM process. BASF also holds patents taking this same general approach. In the first step, butadiene is catalytically carbonylated at high pressure, in the presence of methanol, to give methyl pentenoates. These esters are then subjected to catalytic hydroformylation with 1:1 synthesis gas at elevated temperature and pressure, resulting in a formyl valerate intermediate. The valerate ester is subsequently subjected to catalytic reductive amination at moderate temperature and pressure to give the methyl ester of 6-aminocaproic



acid. This intermediate is then finally cyclized into caprolactam by heating in a suitable inert medium and inert atmosphere.

The alternative approach, developed separately by BASF in collaboration with DuPont (now Invista, a unit of Koch Industries) and by Rhodia, uses adiponitrile as feedstock. This approach involves the catalytic hydrogenation of adiponitrile to make 6-aminocapronitrile, with a co-product of hexamethylene diamine (HMDA). Liquid- or gas-phase catalytic hydrolysis can be used to convert the 6-aminocapronitrile into caprolactam. By varying process parameters, it is possible to somewhat vary the proportion of 6-aminocapronitrile, which leads to caprolactam and nylon 6, and the proportion of HMDA, which (together with adipic acid) leads to nylon 66.

Commercial Technologies

The classical route for caprolactam production is still the one employed for most of the world's production today. The reaction sequence consists of four distinct steps:

- Manufacture of cyclohexanone
- Manufacture of hydroxylamine
- Production of cyclohexanone oxime from the above intermediates
- Rearrangement of the oxime with sulfuric acid to give caprolactam

The most widely used technologies are those licensed by DSM and Polimex/Polservice (Capropol®). Honeywell (formerly AlliedSignal) has a version that is representative of the original process and also offers it for license. In addition, the processes of SNIA Viscosa and Toray, two distinctly different processes, are also offered for license. The various steps in the commercial routes to caprolactam manufacture are shown graphically in Figure 2. These technologies have been reviewed in terms of chemistry and process flow scheme in previous PERP Reports, and are incorporated in summary form in this report.

The figure includes EniChem's hydrogen peroxide-based ammoximation process and Sumitomo's heterogeneous fluid bed process for the conversion of cyclohexanone oxime into caprolactam.

The combination of the EniChem and Sumitomo approaches eliminates the ammonium sulfate coproduct. While there is a continued move to eliminate ammonium sulfate due to its perceived low value, if a local market is available for ammonium sulfate then it is a useful by-product to have. In essence, the licensee or producer now has more flexibility and choice of technology for different market situations.



Non-Commercial Technology

This section of the report focuses on the more recent developments of technologies based on butadiene and adiponitrile. There are two approaches to making caprolactam from these feedstocks.

- The collaborative effort of DSM, DuPont, and, more recently, Shell provides a multi-step process starting from butadiene and carbon monoxide. BASF also owns patents covering this approach.
- BASF, in collaboration with DuPont, developed a process for the co-production of caprolactam and hexamethylene diamine (HMDA) from adiponitrile. Subsequently, Rhodia has also developed a similar and so-claimed improved process.

Adiponitrile itself can be manufactured from three sources, namely:

- butadiene (addition of hydrogen cyanide)
- acrylonitrile (electrochemical dimerization)
- cyclohexane (via adipic acid)

ICI developed and operated the adipic acid to adiponitrile/HMDA process at Wilton in the United Kingdom, and it proved a means of deriving nylon 6 and nylon 6,6 feedstocks from one source, namely cyclohexane. Unfortunately, the value of adipic acid rose steeply over time, making such an approach uneconomic.

Adiponitrile is still manufactured from acrylonitrile by BASF at Seal Sands in the U.K. and Solutia in the United States. A unique electrochemical dimerization process is involved.

Butachimie, a DuPont-Rhodia joint venture, operates adiponitrile production at Chalampe in France. This process is based on the addition of hydrogen cyanide to butadiene. DuPont operates similar technology in the United States.

In a previous PERP report, 96/97S8, the adiponitrile-based process was considered only from the point of view of butadiene, i.e. an integrated butadiene to caprolactam process with a HMDA coproduct. While this view has been updated, Nexant has also considered splitting out adiponitrile to permit the development of feedstock sensitivity in respect of the process being butadiene based or propylene/acrylonitrile based.



A key feature of the adiponitrile to caprolactam process is the co-production of HMDA. There may be a commercial situation whereby only caprolactam is needed with no HMDA. The revised approach here examines the potential for process flexibility and subsequent economic consequences.

Chemistry and process descriptions for these two routes to caprolactam from butadiene are detailed in the report.

Economics

Cost of production analyses of the following caprolactam processes are given in the report:

- Conventional process from cyclohexane (high ammonium sulfate make)
- DSM HPO process from cyclohexane (low ammonium sulfate make)
- Sumitomo hydrogen peroxide based process (fluid bed)
- Toray Photochemical process
- SNIA route from toluene
- Phenol based
- Butadiene via aminocaproic acid
- Butadiene based (HMDA co-product) Dupont/BASF

One must bear in mind that the butadiene-based processes are at a much earlier stage of development and have not achieved commercialization as yet. Thus, they may be more susceptible to costs creeping upwards as the requirements of the commercial processes become better defined.

Having made that point, it does appear from these comparisons that the butadiene-based routes have a reasonably good prospect of ultimately being commercialized, although this development may still be five or more years in the future. Success for butadiene-based routes will require that a feedstock cost advantage exist, and persist, relative to cyclohexane (hence benzene).

The body of the report includes extensive sensitivity analysis, exploring the effects of:

- Plant capacity
- Cyclohexane/toluene feedstock prices
- Ammonium sulfate credit
- HMDA credit



Commercial Analysis

Caprolactam is the monomer used to produce nylon 6. Nylon 6 fiber and filament constitute the bulk of the caprolactam market, accounting for around 80 percent of global demand. Nylon fibers are used in carpeting, textiles, hosiery, and tire cords. Carpeting is the highest volume segment. The other key application is nylon 6 engineering resins; this segment is driven by under-the-hood automotive components. In addition to nylon 6 fibers and resins, a small volume of caprolactam is used globally in a variety of small tonnage fine and specialty chemicals. The distribution of global caprolactam demand by end use is shown in Figure 2.



Figure 2 Global Caprolactam Demand by End Use, 2005

The global demand for caprolactam is about 3.9 million tons for the year 2005. This represents an average annual growth rate of 0.3 percent between 2000 and 2005. Asia has experienced the most rapid demand growth. Over the short to medium term, demand growth overall will be in the 2.8 percent per year range to bring global demand up to the 4.5 million tons level by 2010. As Figure 3 illustrates, East Asia is likely to dominate future demand growth, and by 2010 it could account for about 42 percent of total global demand.





Figure 3 Global Caprolactam Demand by Region, 2000-2010

Q405_00101.0005.4113_charts.xls

Global operating capacity for caprolactam is currently around 4.6 million tons per year, and total utilization stands at about 85 percent.

The body of the report contains supply, demand, and supply/demand balance data for North America, Western Europe, Japan, Latin America, and East Asia.

Nexant, Inc. (<u>www.nexant.com</u>) is a leading management consultancy to the global energy, chemical, and related industries. For over 38 years, Nexant's *ChemSystems Solutions* has helped clients increase business value through assistance in all aspects of business strategy, including business intelligence, project feasibility and implementation, operational improvement, portfolio planning, and growth through M&A activities. Nexant has its main offices in San Francisco (California), White Plains (New York), and London (UK), and satellite offices worldwide.

These reports are for the exclusive use of the purchasing company or its subsidiaries, from Nexant, Inc., 44 South Broadway, 5th Floor, White Plains, New York 10601-4425 U.S.A. For further information about these reports contact Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: <u>jplotkin@nexant.com</u>; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: <u>hcoleman@nexant.com</u>, Website: <u>http://www.nexant.com</u>.