ACRYLONITRILE BY THE AMMOXIDATION OF PROPANE
Aspen Model Documentation

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Process Summary

This Aspen Plus model simulates the process for the production of acrylonitrile by the ammoxidation of propane. Our concept of the process closely follows the guidelines for the Sohio (Standard Oil Company of Ohio, now part of British Petroleum or BP America). The base capacity is 400 million lb/yr (181,000 t/yr), which is similar to the major world sized plants.
About This Process

Acrylonitrile is currently the second largest outlet for propylene (after polypropylene) with principal applications in the production of acrylic fibers, ABS (acrylonitrile-butadiene-styrene) resins, and SAN (styrene-acrylonitrile) resins. Other significant uses for acrylonitrile include acrylamide, adiponitrile, and nitrile elastomers. The manufacture of acrylonitrile is today almost exclusively based on the ammoxidation of propylene. The older acetylene hydrocyanation process, which was dominant until the early 1960s, is now obsolete. Standard Oil Company of Ohio, better known as Sohio (acquired by British Petroleum Company of the U.K. in 1989 and now renamed BP America), which pioneered the development of the propylene ammoxidation route, is now the exclusive licensor of this process technology. Rival processes, such as those developed by Montecatini-Universal Oil Products, Snamprogetti, and Ugine Kuhlmann-Distillers, are now dormant. Nitto Chemical Industry of Japan is an active licensor of its proprietary ammoxidation catalyst.

Current world capacity (early 1991 basis) is about 9,400 million lb/yr (4.3 million t/yr) - with the United States, Western Europe, and Japan accounting for 32.4%, 25.5%, and 13.7%, respectively. From the mid to late 1980s, four of the five U.S. producers (American Cyanamid, BP America, Monsanto, and Sterling Chemical) - all except the fifth (Du Pont) - completed capacity expansions. In Western Europe some minor debottlenecking was carried out by EC Erdolchemie, Germany and Repsol Quimica, Spain, but this was more than offset by the closure of the Chemie Linz plant in Austria, the BP plant in the U.K., and the Norsolor plant in France (the last two of which used the outdated fixed bed technology of Ugine Kuhlmann-Distillers). Japan, likewise, reduced its production capacity as a result of plant closures by Asahi Chemical Industry, Nitto Chemical Industry, and Sumitomo Chemical Company. Competition from imports was the rationale behind the Japanese closures; most imports came from regions (mainly the United States) having excess capacity and access to cheaper propylene.

SRI estimates that the 1990 world consumption of acrylonitrile was approximately 8,700 million lb (4 million metric tons), with the United States (15.6%), Western Europe (32.3%), and Japan (16.7%) taking a combined 64.6% of the aggregate. Compared with the United States, both Western Europe and Japan consume a larger proportion of their acrylonitrile for acrylic fibers. This trend results from a greater substitution of wool in knitwear and carpets. In addition, the Japanese combined consumption of ABS and SAN resins exceeds that in each of the other two regions, both in actual volume and as a proportion of its total consumption. This is because these resins are used in automotive components and Japan’s special position as an automobile exporter.

Of the three developed world regions, the United States is a large exporter of acrylonitrile and the other two regions are net importers. Besides Western Europe and Japan, other principal destinations of U.S. exports are Mexico, Taiwan, and South Korea. Between 1984 and 1990, U.S. exports expanded at an average annual growth rate (AAGR) of 7.5%. SRI forecasts that exports will continue to grow through the mid-1990s, albeit at a slower AAGR of slightly under 4%.
Process Definition

The process can be divided into two sections:
- Propane ammoxidation
- Acrylonitrile separation.

Propane Ammoxidation

The ammoxidation reaction is carried out in a fluidized bed reaction system (R-101A&B), comprising two units in parallel. Propylene (chemical grade) and ammonia (fertilizer grade) feedstocks are transferred from their respective liquid storage tanks (T-101A-D and T-102A&B) and vaporized in E-101 and E-102 against the condensate from the downstream evaporators, described below. The feedstocks are then preheated in exchangers E-103 and E-104, to 173°C (280°F) by 150 psia medium pressure (MP) steam, before being mixed and fed to the reactors. Air is adiabatically compressed in a centrifugal compressor (K-101A&B) that is driven by a high pressure (HP) steam turbine and is introduced at the bottom of the reactors.

The hot reactor product is cooled to 232°C (450°F) in an exchanger (E-105), which generates 150 psia MP steam. Further cooling is carried out in a direct contact quench cooler (C-101), which is a column packed with 1 inch pall rings. The quench water is fed at the top and the hot gases are introduced at the bottom. Sulfuric acid is blended into the quench water to remove the unreacted ammonia as ammonium sulfate; a slight excess of acid (about 10%) is used to ensure nearly complete removal of ammonia. The aqueous stream from the column leaves at 66°C (150°F) and is sent to waste treatment. The vapor stream from the column, at 82°C (180°F), is cooled down to 43°C (110°F) against cooling water in exchanger E-106 before being contacted with water in the absorber column (C-102).

The absorber is also a packed column with 1 inch pall rings; however, this column differs from the quench cooler column because the packing is divided into two sections. The vapor is fed at the base of the column and the water for absorption is fed to the top via an interchanger (E-108) and a refrigerated cooler (E-107), which reduce the water temperature to 4°C (40°F). The interchanger cools the water against the extract stream that leaves at the base of the column. A part of the liquid stream from the base of the column is circulated to the lower packed section through a refrigerated interstage cooler (E-109), which removes the heat of absorption and maintains the base temperature at 10°C (50°F). The aqueous extract from the column is fed to the acrylonitrile purification section via a surge vessel [V-101A (or B), one on line at any time]; the unabsorbed gases (stream 8) are disposed of by combustion in an incinerator (S-102, not shown on the flow diagram).

The quench cooler and absorber combination are designed to operate at conditions that minimize the loss of valuable acrylonitrile in the quench liquid effluent to waste treatment (stream 20) and the absorber vapor effluent to incineration (stream 8). Although, heavy end impurities (cyanohydrins and polymers) form throughout the process, we have made the simplifying assumption that all such materials are generated in the reactors and eventually disposed of in stream 31, which combines the quench effluent (stream 20) with the downstream distillation acrylonitrile column bottoms (stream 19).
Acrylonitrile Separation

The water extract from V-101A (or B) is mixed with inhibitors from T-201A & B and preheated to 82°C (180°F) in E-201 against the extractant before being fed to an extractive distillation column (C-201). As discussed in Section 4, the use of water as an entrainer (or extractive solvent) facilitates the separation of acrylonitrile from acetonitrile. Additionally, inhibitors are employed to minimize polymerization and cyanohydrin decomposition reactions. Although the inhibitors used in actual practice are not known, we have assumed, for the purpose of this evaluation, that a pyrogallol-oxalic acid mixture (as discussed in Section 4) is used. A crude acrylonitrile stream is separated overhead as a vapor phase and acetonitrile is removed as an aqueous sidestream below the feed tray. The extractive water to the column consists of a recirculating stream that is withdrawn a few trays from the bottom and returned back to the top of the column via the exchanger (E-201, referred to above) and a surge vessel (V-201). Thus, the feed to the column is heated against the recirculating water stream; as a result, the extractive water is cooled to 54°C (130°F).

The aqueous sidestream is fractionated in column C-202 to produce an enriched acetonitrile stream overhead and a bottoms product that is essentially water. The enriched acetonitrile stream is cooled in E-212 and sent to waste treatment via off-site tanks, T-251 A&B, and the bottoms stream (mostly water) is recycled to C-201 at a point between the exit of the recirculating water and the base of the column. The bottoms product from the extractive distillation column consists of a dilute aqueous mixture of heavy-end impurities and the inhibitors. The reboil energy for the two linked columns (C-201 and C-202) is provided by 150 psia MP steam in E-202 and E-204, respectively.

The crude acrylonitrile vapor product from C-201 (stream 11) is fed to the HCN column (C-203), which is the first of a three column fractionation train that produces by-product HCN overhead for transfer to storage tanks T-252A&B. As in the case of the upstream extractive distillation column, inhibitors are added to the HCN column feed. The second column in the train (C-204) performs the function of removing light ends overhead and separating most of the water via a sidestream below the feed tray. The light ends are sent to waste treatment via off-site storage tanks, T-253A&B. To minimize acrylonitrile carryover, the sidestream is cooled in E-209 and decanted in V-205, and the organic layer is recycled back to the column. The aqueous layer (stream 18) is added to the absorber (C-102) water feed, as described later.

The final column in the train (C-205) produces specification grade acrylonitrile overhead and rejects the inhibitors in the bottoms product along with some water and acetonitrile. The acrylonitrile product is cooled against cooling water in E-213 and transferred to the off-site storage system consisting of T-254A&B via on-site rundown tanks T-202A&B. The bottoms product (stream 19) is combined with the quench column liquid effluent (stream 20, referred to above) and sent to waste treatment via a surge vessel (V-209). Storage tanks T-255A&B provide greater holding time for the combined effluent stream, in case of a temporary shutdown of the waste treatment step.

The bottoms product (stream 21) from the extractive distillation column (C-201) is processed in a multiple effect evaporator system (S-201A-D) to produce a concentrate (stream 5) that is used as the quench column aqueous feed and a condensate mixture (stream 23) for recycle to the absorber column. The evaporator system comprises four stages that operate at progressively decreasing pressures of 60, 40, 25, and 15 psia, where 150 psia MP steam is the thermal energy source in the first stage. To prevent the buildup of impurities, a purge (stream 27) is drawn from the condensate stream, and fresh process water is used to make up the deficit. Both
the condensate and concentrate streams are transferred via surge vessels V-207 and V-208, respectively.
Process Conditions

Table 1 below shows the design basis and process conditions.

**Table 1**

**ACRYLONITRILE BY THE AMMOXIDATION OF PROPANE**

**DESIGN BASES**

<table>
<thead>
<tr>
<th>Process Aspect</th>
<th>Design Features</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ammoxidation</strong></td>
<td></td>
</tr>
<tr>
<td>Reactor type</td>
<td>Fluidized bed with cooling heat transfer surface that generates 600 psia steam.</td>
</tr>
<tr>
<td><strong>Feedstocks</strong></td>
<td></td>
</tr>
<tr>
<td>Fractionated propane, containing 97 wt% propane and 3 wt% paraffins (ethane plus butanes). Fertilizer grade ammonia, containing 99.9 wt% ammonia and the balance mainly water.</td>
<td></td>
</tr>
<tr>
<td><strong>Operating conditions</strong></td>
<td>500_C (932_F) and 30 psia at exit; 5 sec contact time; C₃H₆:NH₃:air molar feed ratio = 1.00:0.62:9.48</td>
</tr>
<tr>
<td><strong>Catalyst system</strong></td>
<td>Supported metal oxide complex based on V, Sb, and W.</td>
</tr>
<tr>
<td><strong>Per pass conversions</strong></td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>67%</td>
</tr>
<tr>
<td>Ammonia</td>
<td>80%</td>
</tr>
<tr>
<td><strong>Per pass molar propane yields (%)</strong></td>
<td></td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>40.00</td>
</tr>
<tr>
<td>HCN</td>
<td>2.54</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.86</td>
</tr>
<tr>
<td>CO</td>
<td>5.05</td>
</tr>
<tr>
<td>CO₂</td>
<td>17.68</td>
</tr>
<tr>
<td>Light ends (mainly acrolein)</td>
<td>0.29</td>
</tr>
<tr>
<td>Heavy ends (polymers &amp; cyanohydrins)</td>
<td>0.58</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>67.00</td>
</tr>
<tr>
<td><strong>Water absorption step</strong></td>
<td></td>
</tr>
<tr>
<td>Gas:Water molar feed ratio</td>
<td>1:1.23</td>
</tr>
<tr>
<td><strong>Top temperature</strong></td>
<td>(4.4_C) 40_F</td>
</tr>
<tr>
<td><strong>Acrylonitrile absorbed</strong></td>
<td>99%</td>
</tr>
<tr>
<td><strong>Extractive distillation</strong></td>
<td></td>
</tr>
<tr>
<td>Feed:water recycle wt ratio</td>
<td>1.2:1.0</td>
</tr>
<tr>
<td><strong>Overall acrylonitrile yield on propane</strong></td>
<td>38.68 mol%</td>
</tr>
</tbody>
</table>
Physical Property Methods and Data

The Aspen Plus simulation uses the NRTL-RK physical property method.
Chemistry/Kinetics

The ammoxidation of propane is represented by:

\[ \text{C}_3\text{H}_8 + \text{NH}_3 + 2\text{O}_2 = \text{CH}_2=\text{CHCN} + 4\text{H}_2\text{O} \]  
\[ \text{DH} = -151.22 \text{ kcal/mol propane} \]  

As discussed below, propane ammoxidation is considered to proceed by a mechanism that consists of prior dehydrogenation of propane to propylene:

\[ \text{C}_3\text{H}_8 = \text{C}_3\text{H}_6 + \text{H}_2 \]  
\[ \text{DH} = +29.70 \text{ kcal/mol propane} \]

Most of the hydrogen formed is oxidized to water:

\[ 2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} \]  
\[ \text{DH} = -57.80 \text{ kcal/mol hydrogen} \]

The overall ammoxidation of propane is exothermic.

Overoxidation reactions include the formation of CO and CO\(_2\):

\[ \text{C}_3\text{H}_8 + 3\text{O}_2 = 3\text{CO} + 3\text{H}_2\text{O} \]  
\[ \text{DH} = -257.54 \text{ kcal/mol propylene} \]  

\[ 2\text{C}_3\text{H}_6 + 9\text{O}_2 = 6\text{CO}_2 + 6\text{H}_2\text{O} \]  
\[ \text{DH} = -460.43 \text{ kcal/mol propylene} \]  

\[ 2\text{C}_3\text{H}_6 + 7\text{O}_2 = 6\text{CO} + 8\text{H}_2\text{O} \]  
\[ \text{DH} = -285.64 \text{ kcal/mol propane} \]

\[ \text{C}_3\text{H}_8 + 5\text{O}_2 = 3\text{CO}_2 + 4\text{H}_2\text{O} \]  
\[ \text{DH} = -488.53 \text{ kcal/mol propane} \]

Other reactions lead to the formation of small amounts of by-products, such as acrolein, acetone, acetaldehyde, propionaldehyde, and relatively less volatile cyanohydrins.
References

This documentation is based on SRI’s PEP report number 17 by Park L. Morse, November, 1966.

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November 1, 1999