

## CHEMICAL MANUFACTURING

### A. PROCESS DESCRIPTION

Due to the broad expanse and complexity of the chemical manufacturing industry, **acrylonitrile manufacturing** has been selected as being representative of it; however, process procedures may vary somewhat between different chemical industries.

Nearly all of the acrylonitrile (ACN) produced in the world today is produced using the SOHIO process for ammoxidation of propylene and ammonia. The overall reaction takes place in the vapor phase in the presence of a catalyst. Exhibit 1 shows a typical simplified process flow diagram for an uncontrolled SOHIO process.

The primary by-products of the process are hydrogen cyanide, acetonitrile, and carbon oxides. The recovery of these by-products depends on such factors as market conditions, plant location, and energy costs. Hydrogen cyanide and acetonitrile, although they carry a market value, are usually incinerated, indicating that the production of these by-products has little effect on the economics of producing ACN.

In the process represented in Exhibit 1, by-product hydrogen cyanide and acetonitrile are routed to an incinerator. Variations within the SOHIO process may provide for purification, storage, and loading facilities for these recoverable by-products. Other variations of the SOHIO process include the recovery of ammonium sulfate from the reactor effluent to allow for biological treatment of a wastewater stream and variations in catalysts and reactor conditions.

In the standard SOHIO process, air, ammonia, and propylene are introduced into a fluid-bed catalytic reactor operating at 5-30 psig and ~400-510°C (750-950°F). Ammonia and air are fed to the reactor in slight excess of stoichiometric proportions because excess ammonia drives the reaction closer to completion and air continually regenerates the catalyst. A significant feature of the process is the high conversion of reactants on a once-through basis with only a few seconds residence time. The heat generated from the exothermic reaction is recovered via a waste-heat-recovery boiler.

The reactor effluent is routed to a water quench tower, where sulfuric acid is introduced to neutralize any unconverted ammonia. The product stream then flows through a countercurrent water absorber-stripper to reject inert gases and recover reaction products. The operation yields a mixture of ACN, acetonitrile, and water and then is sent to a fractionator to remove hydrogen cyanide.

#### **Exhibit 1**

The final two steps involve the drying of the ACN stream and the final distillation to remove heavy ends. The fiber-grade ACN obtained from the process is 99+% pure.

Several fluid-bed catalysts have been used since the inception of the SOHIO ammoxidation

process. Catalyst 49, which represents the fourth major level of improvement, is currently recommended in the process.

Emissions of ACN during start-up are substantially higher than during normal operation. During start-up, the reactor is heated to operating temperature before the reactants (propylene and ammonia) are introduced. Effluent from the reactor during start-up begins as oxygen-rich, then passes through the explosive range before reaching the fuel-rich zone that is maintained during normal plant operation. To prevent explosions in the line to the absorber, the reactor effluent is vented to the atmosphere until the fuel-rich effluent mixture can be achieved. The ACN emissions resulting from this start-up procedure have been estimated to exceed 4500 kg (10,000 lb)/h.

The absorber vent gas contains nitrogen and unconverted oxygen from the air fed to the reactor, propane and unconverted propylene from the propylene feed, product ACN, by-product hydrogen cyanide and acetonitrile, other organics not recovered from the absorber, and some water vapor.

The ACN content of the combined column purge vent gases is relatively high, about 50% of the total VOCs emitted from the recovery, acetonitrile, light ends, and product columns. The rest of the vent gases consist of noncondensibles that are dissolved in the feed to the columns, the VOCs that are not condensed, and, for the columns operating under vacuum, the air that leaks into the column and is removed by the vacuum jet systems.

For the ACN process illustrated in Exhibit 1, by-product hydrogen cyanide and acetonitrile are incinerated along with product column bottoms. The primary pollutant problem related to the incinerator stack is the formation of  $\text{NO}_x$  from the fuel nitrogen of the acetonitrile stream and hydrogen cyanide. Carbon dioxide and lesser amounts of CO are emitted from the incinerator stack gas.

Other emission sources involve the volatilization of hydrocarbons through process leaks (fugitive emissions) and from the deep well ponds, breathing and working losses from product storage tanks, and losses during product loading operations. The fugitive and deep well/pond emissions consist primarily of propane and propylene, while the storage tank and product loading emissions consist primarily of ACN.

## **B. SOURCES OF POLLUTION**

Exhibit 2 presents an emissions profile for sources in an ACN manufacturing facility, along with pollution control options and their efficiencies. Seven points are included:

1. Absorber vent gas
2. Column purge waste gas
3. Fugitive emissions
4. Incinerator stack gas
5. Deep well/pond emissions
6. Storage tank emissions

## 7. Product transport loading facility vent

Wastewater for disposal is generated mainly from the wastewater and acetonitrile columns.

### Exhibit 2: VOC and Acrylonitrile Emissions From ACN Manufacturing<sup>a</sup>

Emission Point Control Method Efficiency (%)	Emission Rate (kg/hr)		Control	Efficiency (%)
	Acrylonitrile	Total VOC		
Absorber Vents Catalytic Oxidation 95-97	2.05	2050.00	Thermal Incineration	
Column Vents Storage Tanks	103.00 13.50	205.00 14.80	Flare Double Seal Floating Roof	98-99
Water Scrubber 99	N/A			
Loading <sup>b</sup> Incinerator 99	3.44 98-99	3.98	Flare	
Fugitive Incinerator Stack	9.50	19.50 7.40	Leak Detection/Maintenance N/A	N/A N/A
Deep Well/Pond		267.00	Water Scrubber	N/A

<sup>a</sup> Model plant has an annual ACN capacity of 180 million kg, and is assumed to operate 8760 hours annually

<sup>b</sup> Loading into tank cars; does not include loading into barges

## C. POLLUTANTS AND THEIR CONTROL

### 1. Air Pollution

**Absorber Vent Gas.** The absorber vent gas stream contains nitrogen, oxygen, unreacted propylene, hydrocarbon impurities from the propylene feed stream, CO, CO<sub>2</sub>, water vapor, and small quantities of ACN, acetonitrile, and hydrogen cyanide. Two control methods are used to treat this stream: thermal incineration and catalytic oxidation.

The thermal incineration units have demonstrated VOC destruction efficiencies of 99.9% or greater, while most catalytic units can achieve destruction efficiencies only in the 95-97% range. Destruction efficiencies in the 99% and greater range can be achieved with catalytic oxidizers, but these are not achieved on a long-term basis because of deactivation of the catalyst by a number of causes. The advantage of catalytic oxidation is low fuel usage, but emissions of NO<sub>x</sub> formed in the reactors and not destroyed across the catalyst can pose problems.

**Column Waste Purge Gas.** Waste gas releases from the recovery column, light-ends column, product column, and the acetonitrile column are frequently tied together and vented to a flare. The estimated VOC destruction efficiency of the flare is 98-99% for all streams with a heat content of 300 Btu/scf or greater. The use of a flare is ideally suited for streams that are intermittent and having heating values of 300 Btu/scf.

**Fugitive emissions.** Fugitive emissions from piping, valves, pumps, and compressors are controlled by periodic monitoring by leak checking with a VOC detector and a directed maintenance program.

**Incinerator Stack Gas.** Staged combustion and ammonia injection are used to control the emissions of  $\text{NO}_x$  from the incinerator that treats the absorber off-gas vent, the crude acetonitrile waste gas stream, and the by-product liquid HCN stream. Staged combustion suppresses the formation of  $\text{NO}_x$  by operating under fuel-rich conditions in the flame zone where most of the  $\text{NO}_x$  is formed and oxygen-rich conditions downstream at lower temperatures where  $\text{NO}_x$  is not appreciably formed.

Ammonia injection reduces  $\text{NO}_x$  by selectively reacting ammonia with  $\text{NO}_x$ . The reaction occurs at temperatures in the range of 870-980°C (1600-1800°F) and, as such, the ammonia must be injected in the postflame zone of the combustion chamber. Residence times of 0.5-1.0 second are required for  $\text{NO}_x$  destruction efficiencies in the range of 80%, which is compatible with the residence time required for VOC destruction.

**Deep Well/Pond Emissions.** Emissions of acrolein and other odorous components in vents from wastewater treatment steps are controlled with water scrubbers. In some cases, pond emissions are controlled by adding a layer of a low-vapor-pressure oil on the surface of the pond to limit volatilization.

**Storage Tank Emissions.** Product storage tank emissions are controlled with double-seal floating roofs or, in some cases, water scrubbers. Field experience indicates that a removal efficiency of 99% can be achieved with water scrubbing.

**Product Transport Loading.** Emissions from product transport loading vents are gathered and sent to a flare or incinerator for VOC control. Destruction efficiencies of 98-99% are achieved using the flare and greater than 99% using incineration.

## 2. Solid/Liquid Waste

Wastes include salts of hydrogen cyanide, metal cyanide complexes, and organic cyanides (cyanohydrins) as solutions or solids. The wastewater from the wastewater column contains ammonium sulfate and heavy hydrocarbons, while the wastewater from the acetonitrile column mainly contains heavy bottoms. The wastewater from both these columns is typically discharged to a deep well pond (Exhibit 3). Other methods of waste treatment include alkaline chlorination in a recycle lagoon system, and incineration.

### Exhibit 3: Potentially Hazardous Wastes Generated From Acrylonitrile Production

Waste Source	Pollutant	Amount	Disposal Method
Wastewater Column	Ammonium Sulfate		
Heavy Hydrocarbons			
N/A	Deep well pond		
Acetonitrile Column	Heavy Bottoms	N/A	Deep well pond

## **D. REFERENCES**

1. Wilkinsin, Gary R. The Manufacture and Use of Selected Inorganic Cyanides. Kansas City: Midwest Research Institute (for the U.S.EPA), April 2, 1976.
2. Air and Waste Management Association. Air Pollution Engineering Manual. New York: Van Nostrand Reinhold, 1992.