

Note: This is a reference cited in AP 42, *Compilation of Air Pollutant Emission Factors, Volume I Stationary Point and Area Sources*. AP42 is located on the EPA web site at [www.epa.gov/ttn/chief/ap42/](http://www.epa.gov/ttn/chief/ap42/)

The file name refers to the reference number, the AP42 chapter and section. The file name "ref02\_c01s02.pdf" would mean the reference is from AP42 chapter 1 section 2. The reference may be from a previous version of the section and no longer cited. The primary source should always be checked.

## 2.0 SUMMARY

The purpose of this document is to provide technical information that State and local agencies can use to develop strategies for reducing NO<sub>x</sub> emissions from nitric and adipic acid manufacturing plants. This section presents a summary of the information contained in this document, including uncontrolled and controlled NO<sub>x</sub> emissions data, ACT's, capital and annual costs, and cost effectiveness. Section 2.1 presents a summary of the information relating to nitric acid plants. Section 2.2 presents a summary of the information relating to adipic acid plants.

### 2.1 SUMMARY FOR NITRIC ACID PLANTS

Approximately 65 plants in the United States produce nitric acid. The ammonia-oxidation process is the most commonly used process for producing weak (50 to 70 percent) nitric acid. The absorption tower, common to all ammonia-oxidation nitric acid production facilities, is the primary source of NO<sub>x</sub> emissions. Three control techniques are predominantly used to reduce the level of NO<sub>x</sub> emissions in the absorber tail gas: (1) extended absorption, (2) nonselective catalytic reduction (NSCR), and (3) selective catalytic reduction (SCR). This section presents a summary of NO<sub>x</sub> control performance, control cost data, and environmental impacts for each of the three control techniques applied to each of three model plants.

Table 2-1 is a summary of NO<sub>x</sub> emissions and a cost comparison of the three alternative NO<sub>x</sub> control techniques used in model plants sized at 200, 500, and 1,000 tons of nitric acid

nitration in explosives manufacturing, but nitric acid nitration is also used extensively in producing chemical intermediates such as nitrobenzene and dinitrotoluenes.

In 1990 there were 67 nitric acid production facilities in the United States, including government-owned munitions plants. Twenty-four of these plants had a capacity of at least 180,000 tons per year, as compared to only 13 plants with such capacity in 1984. Total plant capacity was about 11.3 million tons of nitric acid as of January 1990.<sup>4,5</sup> Actual production has remained steady from 1984 to 1988, with an average annual production of about 7.5 million tons of acid.<sup>6</sup>

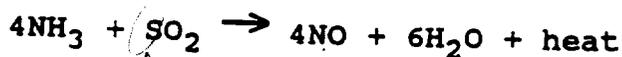
Since a principal use of nitric acid is to produce ammonium nitrate for fertilizer, the heaviest concentrations of nitric acid production facilities are located in agricultural regions, primarily in the Midwest, the South Central, and the Gulf States.

### 3.1.2 Production Process

Nitric acid is commercially available in two forms: weak (50 to 70 percent nitric acid) and concentrated (greater than 95 percent nitric acid). Different processes are required to produce these two forms of acid. For its many uses, weak nitric acid is produced in far greater quantities than is the concentrated form. Concentrated nitric acid production is discussed in Section 3.1.4.

Virtually all commercial production of weak nitric acid in the United States utilizes three common steps: (1) catalytic oxidation of ammonia (NH<sub>3</sub>) to nitric oxide (NO), (2) oxidation of nitric oxide with air to nitrogen dioxide (NO<sub>2</sub>), and (3) absorption of nitrogen dioxide in water to produce "weak" nitric acid.<sup>2</sup> The basic process is shown in Figure 3-1.

3.1.2.1 Oxidation of Ammonia. The first step of the acid production process involves oxidizing anhydrous ammonia over a platinum-rhodium gauze catalyst to produce nitric oxide and water. The exothermic reaction occurs as follows:<sup>8</sup>



This extremely rapid reaction proceeds almost to completion, evolving 906 kilojoules per mole (kJ/mole) (859 British thermal units per mole [Btu/mole]) of heat. Typical ammonia conversion efficiency ranges from 93 to 98 percent with good reactor design.<sup>8</sup>

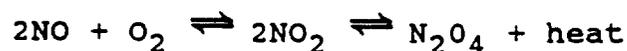
Air is compressed, filtered, and preheated by passing through a heat exchanger. The air is mixed with vaporized anhydrous ammonia and passed to the converter. Since the explosive limit of ammonia is approached at concentrations greater than 12 mole percent, plant operation is normally maintained at 9.5 to 10.5 mole percent.<sup>9</sup> In the converter, the ammonia-air mixture is catalytically converted to nitric oxide and excess air. The most common catalyst consists of 90 percent platinum and 10 percent rhodium gauze constructed from squares of fine wire.<sup>9</sup> Up to 5 percent palladium is used to reduce costs.<sup>2</sup>

Operating temperature and pressure in the converter have been shown to have an influence on ammonia conversion efficiency.<sup>8</sup> Generally, reaction efficiency increases with gauze temperature. Oxidation temperatures typically range from 750° to 900°C (1380° to 1650°F). Higher catalyst temperatures increase reaction selectivity toward NO production, while lower catalyst temperatures are more selective toward less useful nitrogen (N<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O).<sup>9</sup> The high-temperature advantage is offset by the increased loss of the precious metal catalyst. Industrial experience has demonstrated and the industry has generally accepted conversion efficiency values of 98 percent for atmospheric pressure plants at 850°C (1560°F) and 96 percent for plants operating at 0.8 megapascals (MPa) (8 atmospheres [atm]) and 900°C (1650°F).<sup>2</sup>

As mentioned earlier, the ammonia oxidation reaction is highly exothermic. In a well-designed plant, the heat byproduct is usually recovered and utilized for steam generation in a waste heat boiler. The steam can be used for liquid ammonia evaporation and air preheat in addition to nonprocess plant requirements.

As higher temperatures are used, it becomes necessary to capture platinum lost from the catalyst. Consequently, a platinum recovery unit is frequently installed on the cold side of the waste heat boiler. The recovery unit, composed of ceramic-fiber filters, is capable of capturing 50 to 75 percent of the lost platinum.<sup>10</sup>

3.1.2.2 Oxidation of Nitric Oxide. The nitric oxide formed during the ammonia oxidation process is cooled in the cooler/condenser apparatus, where it reacts noncatalytically with oxygen to form nitrogen dioxide and its liquid dimer, dinitrogen tetroxide.<sup>4</sup> The exothermic reaction, evolving 113 kJ/mole (107 Btu/mole), proceeds as follows:<sup>3</sup>



This slow, homogeneous reaction is highly temperature- and pressure-dependent. Lower temperatures, below 38°C (100°F), and higher pressures, up to 800 kilopascals (kPa) (8 atm), ensure maximum production of NO<sub>2</sub> and minimum reaction time.<sup>4</sup>

Furthermore, lower temperatures and higher pressures shift the reaction to the production of N<sub>2</sub>O<sub>4</sub>, preventing the reverse reaction (dissociation to NO and O<sub>2</sub>) from occurring.<sup>2</sup>

3.1.2.3 Absorption of Nitrogen Dioxide. The final step for producing weak nitric acid involves the absorption of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> in water to form nitric acid (as N<sub>2</sub>O<sub>4</sub> is absorbed, it releases gaseous NO). The rate of this reaction is controlled by three steps: (1) the oxidation of nitrogen oxide to NO<sub>2</sub> in the gas phase, (2) the physical diffusion of the reacting oxides from the gas phase to the liquid phase, and (3) the chemical reaction in the liquid phase.<sup>7</sup> The exothermic reaction, evolving 135 kJ/mole (128 Btu/mole), proceeds as follows:<sup>2</sup>



The absorption process takes place in a stainless steel tower containing numerous layers of either bubble cap or sieve trays. The number of trays varies according to pressure, acid strength, gas composition, and operating temperature. Nitrogen dioxide gas from the cooler/condenser effluent is introduced at the bottom of the absorption tower, while the liquid dinitrogen tetroxide enters at a point higher up the tower. Deionized process water is added at the top, and the gas flows countercurrent to both liquids. Oxidation occurs in the free space between the trays, while absorption takes place in the trays. Because of the high order of the oxidation process in absorbers, roughly one-half the volume of the absorber is required to absorb the final 3 percent of nitrogen oxide gas concentration.<sup>9</sup> Because lower temperatures are favorable for maximum absorption, cooling coils are placed in the trays. Nitric acid in concentrations of 55 to 65 percent is withdrawn at the bottom of the tower.

Secondary air is used to improve oxidation in the absorption tower and to bleach remaining nitrogen oxides from the product acid. Absorption efficiency is further increased by utilizing high operating pressure in the absorption process. High-pressure absorption improves efficiency and increases the overall absorption rate.

Absorber tail gas is reheated using recovered process heat and expanded through a power recovery turbine. In a well-designed plant, the exhaust gas turbine can supply all the power needed for air compression with excess steam available for export.<sup>10</sup>

### 3.1.3 Plant Design

Corrosive effects of nitric acid under pressure precluded the use of pressures greater than atmospheric in early plant designs. With the advent of corrosion-resistant materials, nitric acid producers were able to take advantage of the favorable effects of increased pressure in the NO oxidation and absorption processes. All modern plants incorporate increased pressure at some point in the process. Currently, two plant

pressure designs are in use: single-pressure and dual-pressure processes.

3.1.3.1 Single-Pressure Process. The single-pressure process is the most commonly employed method of nitric acid production in the United States. This process uses a single pressure--low (atmospheric), medium (400 to 800 kPa [4 to 8 atm])--or high (800 to 1,400 kPa [8 to 14 atm]) in both the ammonia oxidation and nitrogen oxides absorption phases of production. The majority of new smaller capacity (less than 300 tons per day) nitric acid plants use the high-pressure process. Operating at atmospheric pressure offers advantages over higher-pressure processes: the catalyst lasts longer (6 months) and ammonia conversion efficiency is increased. These advantages are far outweighed, however, by low absorption and NO oxidation rates (prompting the need for several large absorption towers).<sup>8</sup> Atmospheric plants still in existence generally operate in a standby capacity, and no new atmospheric plants are likely to be built.<sup>7</sup> The medium-pressure process utilizes a single higher pressure throughout the process. Though ammonia conversion efficiency and catalyst life are somewhat decreased, the economic benefits of medium pressure downstream are substantial. Single-pressure-type plants require significantly smaller, less expensive equipment for oxidation, heat exchange, and absorption.<sup>7</sup> A simplified single-pressure process flow diagram is shown in Figure 3-2.

3.1.3.2 Dual-Pressure Process. The dual-pressure process combines the attributes of low-pressure ammonia oxidation with high-pressure absorption, thus optimizing the economic benefits of each. Popularized in Europe, this process is finding increasing utility in the United States. A simplified dual-pressure process flow diagram is shown in Figure 3-3.

In the dual-pressure process, ammonia oxidation is usually carried out at pressures from slightly negative to about (400 kPa [4 atm]).<sup>2</sup> This maintains the advantages of high ammonia conversion efficiency and extended catalyst life. The heat of reaction is recovered by the waste heat boiler, which supplies

steam for the turbine-driven compressor. After passing through the cooler/condenser, the gases are compressed to the absorber pressure of 800 to 1,400 kPa (8 to 14 atm). Absorption is further enhanced by internal water cooling, which results in acid concentrations up to 70 percent and absorber efficiency to 96 percent. Nitric acid formed in the absorber is usually routed through an external bleacher where air is used to remove (bleach) dissolved oxides of nitrogen. The bleacher gases are then compressed and passed through the absorber. Using excess ammonia oxidation heat, tail gas is reheated to about 200°C (392°F) and expanded in the power-recovery turbine.<sup>4,7,8</sup>

Atmospheric ammonia conversion is limited (due to low gas loading at atmospheric pressure) to about 100 tons per day of equivalent acid.<sup>2,9</sup> Consequently, for large plants, several ammonia converters and waste heat boilers are required. Moreover, nitrous gas compression requires the use of stainless-steel compressors. These costs require an investment for dual-pressure plants from one and one-half to two times the amount for single-pressure plants. However, these costs are offset by improved ammonia efficiency, reduction of platinum catalyst loss, higher absorption efficiency, and higher power recovery.<sup>2,7</sup>

#### 3.1.4 Concentrated Nitric Acid Process

In some instances, such as organic nitrations, nitric acid concentrations as high as 99 percent are required. Nitric acid forms an azeotrope with water at 68.8 weight percent (simple distillation will not separate the water from the acid). The method most commonly employed in the United States for attaining highly concentrated nitric acid is extractive distillation. Another method, the direct strong nitric process, can produce 95 to 99 percent nitric acid directly from ammonia.<sup>2,8</sup> However, this process has found limited commercial application in the United States.

The extractive distillation method uses concentrated sulphuric acid as a dehydrating agent to produce 98 to 99 percent nitric acid. The process is shown in Figure 3-4. Strong sulfuric acid (typically 60 percent concentration) mixed with 55

to 65 percent nitric acid enters the top of a packed tower and flows countercurrent to ascending vapors. Ninety-nine percent nitric acid vapor containing small amounts of  $\text{NO}_x$  is recovered at the top of the tower. The vapors are then bleached and condensed, leaving weak nitric acid,  $\text{NO}_x$ , and oxygen. The gases are subsequently passed to an absorber, where they are converted to nitric acid and recovered.<sup>2,8</sup>

The direct strong nitric acid process (DSN) produces concentrated nitric acid directly from ammonia. While several DSN processes exist, the Uhde process has demonstrated commercial application in the United States. The Uhde process is shown in Figure 3-5. Air and gaseous ammonia are mixed and reacted. Heat of reaction produces steam in the burner/waste-heat boiler. Upon cooling, the reaction products condense to form weak nitric acid. After separating the liquid nitric acid, the remaining  $\text{NO}$  is oxidized to  $\text{NO}_2$  by passing through two oxidizing columns. The vapors are then compressed and cooled to form liquid dinitrogen tetroxide. At a pressure of 5 MPa (50 atm), the liquid  $\text{N}_2\text{O}_4$  reacts with  $\text{O}_2$  to form strong nitric acid of 95 to 99 percent concentration. Because  $\text{NO}_x$  from the absorber is a valuable raw material, tail gas emissions are scrubbed with water and condensed  $\text{N}_2\text{O}_4$ . The scrubber effluent is then mixed with the concentrated acid from the absorber column. The combined product is oxidized in the reactor vessel, cooled, and bleached, producing concentrated nitric acid.<sup>8</sup>

### 3.2 ADIPIC ACID MANUFACTURING

Adipic acid,  $\text{COOH}-(\text{CH}_2)_3-\text{COOH}$ , was the 48th-highest-volume chemical produced in the United States in 1985 and is considered one of the most important commercially available aliphatic dicarboxylic acids. Typically, it is a white crystalline solid, soluble in alcohol and acetone.<sup>15</sup>

#### 3.2.1 Uses and Industry Characterization

Ninety percent of adipic acid manufactured in the United States is used to produce nylon 6/6 fiber and plastics. Esters used for plasticizers and lubricants are the next largest

As the reaction is highly exothermic, heat of reaction is usually dissipated by maintaining a high ratio (40:1) of nitric acid to KA mixture.<sup>19</sup>

Nitric acid (50 to 60 percent) and a copper-vanadium catalyst are reacted with the KA mixture in a reactor vessel at 60° to 80°C and 0.1 to 0.4 MPa. Conversion yields of 92 to 96 percent are attainable when using high-purity KA feedstock. Upon reaction, nitric acid is reduced to nitrogen oxides: NO<sub>2</sub>, NO, N<sub>2</sub>O, and N<sub>2</sub>. The dissolved oxides are stripped from the reaction product using air in a bleaching column and subsequently recovered as nitric acid in an absorption tower.<sup>16,19</sup>

The stripped adipic acid/nitric acid solution is chilled and sent to a crystallizer, where crystals of adipic acid are formed. The crystals are separated from the mother liquor in a centrifuge and transported to the adipic acid drying and/or melting facilities. The mother liquor is separated from the remaining uncrystallized adipic acid in the product still and recycled to the reactors.

### 3.3 REFERENCES FOR CHAPTER 3

1. Keleti, C. (ed.). The History of Nitric Acid. In: Nitric Acid and Fertilizer Nitrates. New York, Marcel Dekker, Inc. 1985. pp. 2, 19-23.
2. Newman, D.J. Nitric Acid. In: Kirk-Othmer Encyclopedia of Chemical Technology. New York, John Wiley & Sons. 1981. pp. 853-871.
3. Control Techniques for Nitrogen Oxides Emissions From Stationary Sources: Revised 2nd Edition. U. S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-450/3-83-002. January 1983. Ch. 6: pp. 35-46.
4. Review of New Source Performance Standards for Nitric Acid Plants. U. S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-450/8-84-011. April 1984. Ch. 2: pp. 1-13.
5. SRI International. Directory of Chemical Producers, United States of America. Menlo Park, CA. 1990. pp. 809-811.

6. Inorganic Fertilizer Materials and Related Products. In: Current Industrial Reports. U.S. Department of Commerce, Bureau of Census. Washington, DC. 1988. 3 pp.
7. Nitric Acid Plant Inspection Guide. Prepared for U. S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-340/1-84-013. August 1984. p. 9.
8. Reference 1, pp. 31-71.
9. Ohsol, E.O. Nitric Acid. In: Encyclopedia of Chemical Processing and Design, J. J. McKetta and W. A. Cunningham (eds.). New York, Marcel Dekker, Inc. 1990. pp. 150-155.
10. Nitric Acid Plant Inspection Guide. U. S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-340/1-84-013. August 1984.
11. Reference 4, p. 7.
12. Reference 4, p. 9.
13. Reference 3, p. 8
14. Reference 3, p. 9.
15. Sax, N.I., and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. New York, Van Nostrand Reinhold Company. 1987. p. 24.
16. Adipic Acid. In: Encyclopedia of Chemical Technology, Kirk-Othmer. New York, John Wiley & Sons. 1978. pp. 513-528.
17. Adipic Acid. In: Synthetic Organic Chemicals, U.S. Sales and Production. U.S. International Trade Commission. Washington, DC. 1989. 1 p.
18. Compilation of Air Pollutant Emission Factors: Volume 1: Stationary Point and Area Sources. U. S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. AP-42. September 1985. p. 5.1-2.
19. Luedeke, V.D. Adipic Acid. In: Encyclopedia of Chemical Processing and Design, J. J. McKetta and W. A. Cunningham (eds.). New York, Marcel Dekker, Inc. 1977. pp. 128-146.
20. Cyclohexanol/Cyclohexanone. In: Organic Chemical Manufacturing: Volume 6: Selected Processes. U. S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-450/3-80-028a. December 1980. pp. III-2-7.