6.2 Adipic Acid

6.2.1 General[1,3-5]

Adipic acid, $HOOC(CH_2)_4COOH$, is a white crystalline solid used primarily in the manufacture of nylon-6,6 polyamide and is produced in 4 facilities in the U. S. Worldwide demand for adipic acid in 1989 was nearly 2 billion megagrams (Mg) (2 billion tons), with growth continuing at a steady rate.

Adipic acid historically has been manufactured from either cyclohexane or phenol, but shifts in hydrocarbon markets have nearly resulted in the elimination of phenol as a feedstock in the U. S. This has resulted in experimentation with alternative feedstocks, which may have commercial ramifications.

6.2.2 Process Description[1,4-5]

Adipic acid is manufactured from cyclohexane in two major reactions. The first step, shown in Figure 6.2-1, is the oxidation of cyclohexane to produce cyclohexanone (a ketone) and cyclohexanol (an alcohol). This ketone-alcohol (KA) mixture is then converted to adipic acid by oxidation with nitric acid in the second reaction, as shown in Figure 6.2-2. Following these 2 reaction stages, the wet adipic acid crystals are separated from water and nitric acid. The product is dried and cooled before packaging and shipping. Dibasic acids (DBA) may be recovered from the nitric acid solution and sold as a coproduct. The remaining nitric acid is then recycled to the second reactor.

The predominant method of cyclohexane oxidation is metal-catalyzed oxidation, which employs a small amount of cobalt, chromium, and/or copper, with moderate temperatures and pressures. Air, catalyst, cyclohexane, and in some cases small quantities of benzene are fed into either a multiple-stage column reactor or a series of stirred tank reactors, with a low conversion rate from feedstock to oxidized product. This low rate of conversion necessitates effective recovery and recycling of unreacted cyclohexane through distillation of the oxidizer effluent.

The conversion of the intermediates cyclohexanol and cyclohexanone to adipic acid uses the same fundamental technology as that developed and used since the early 1940s. It entails oxidation with 45 to 55 percent nitric acid in the presence of copper and vanadium catalysts. This results in a very high yield of adipic acid. The reaction is exothermic, and can reach an autocatalytic runaway state if temperatures exceed 150°C (300°F). Process control is achieved by using large amounts of nitric acid. Nitrogen oxides (NO_x) are removed by bleaching with air, water is removed by vacuum distillation, and the adipic acid is separated from the nitric acid by crystallization. Further refining, typically recrystallization from water, is needed to achieve polymer-grade material.

6.2.3 Emissions And Controls[1-2,4-7]

Emissions from the manufacture of adipic acid consist primarily of organic compounds and carbon monoxide (CO) from the first reaction, NO_x from the second reaction, and particulate matter from product cooling, drying, storage, and loading. Tables 6.2-1 and 6.2-2 present emission factors for the processes in Figure 6.2-1 and Figure 6.6-2, respectively. Emissions estimation of in-process

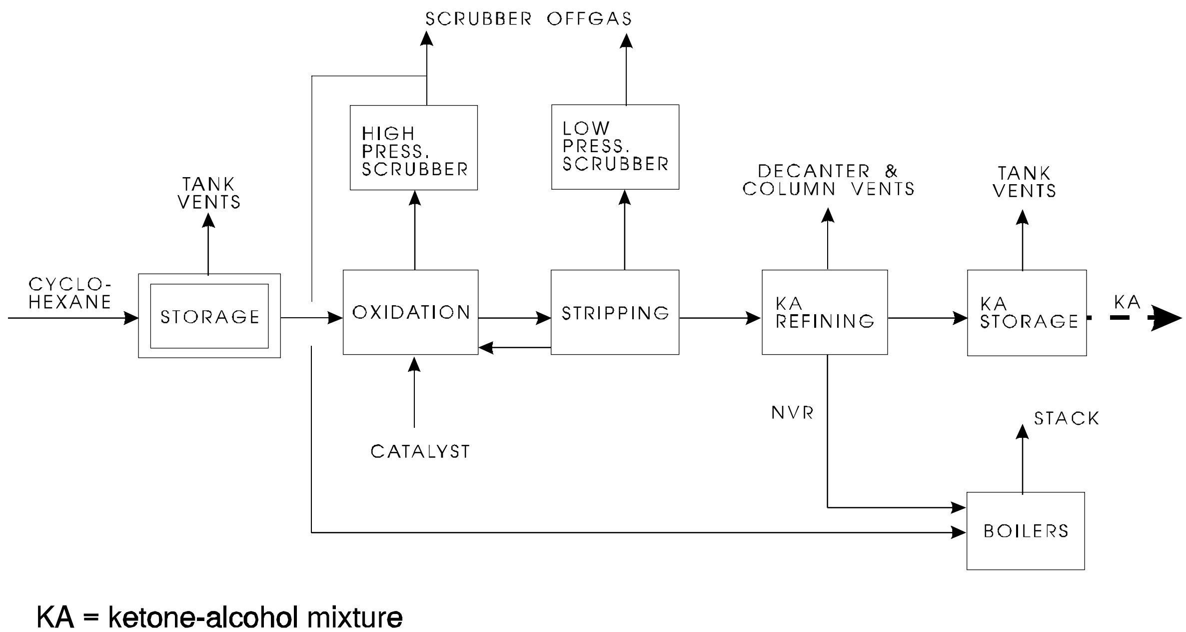

Figure 6.2-1. Adipic acid manufacturing process: Oxidation of cyclohexane.

combustion products, fractional distillation evaporation losses, oxidizer effluent streams, and storage of volatile raw or intermediate materials, is addressed in Chapter 12, "Metallurgical Industry".

The waste gas stream from cyclohexane oxidation, after removal of most of the valuable unreacted cyclohexane by 1 or more scrubbers, will still contain CO, carbon dioxide (CO_2), and organic compounds. In addition, the most concentrated waste stream, which comes from the final distillation column (sometimes called the "nonvolatile residue"), will contain metals, residues from catalysts, and volatile and nonvolatile organic compounds. Both the scrubbed gas stream and the nonvolatile residue may be used as fuel in process heating units. If a caustic soda solution is used as a final purification step for the KA, the spent caustic waste can be burned or sold as a recovered byproduct. Analyses of gaseous effluent streams at 2 plants indicate that compounds containing cobalt and chromium, in addition to normal products of combustion, are emitted when nonvolatile residue is burned. Caproic, valeric, butyric, and succinic acids are emitted from tanks storing the nonvolatile residue. Cyclohexanone, cyclohexanol, and hexanol are among the organic compounds emitted from the cyclohexane recovery equipment (such as decanters and distillation columns.)

The nitric acid oxidation of the KA results in 2 main streams. The liquid effluent, which contains primarily water, nitric acid, and adipic acid, contains significant quantities of NO_x, which are considered part of the process stream with recoverable economic value. These NO_x are stripped

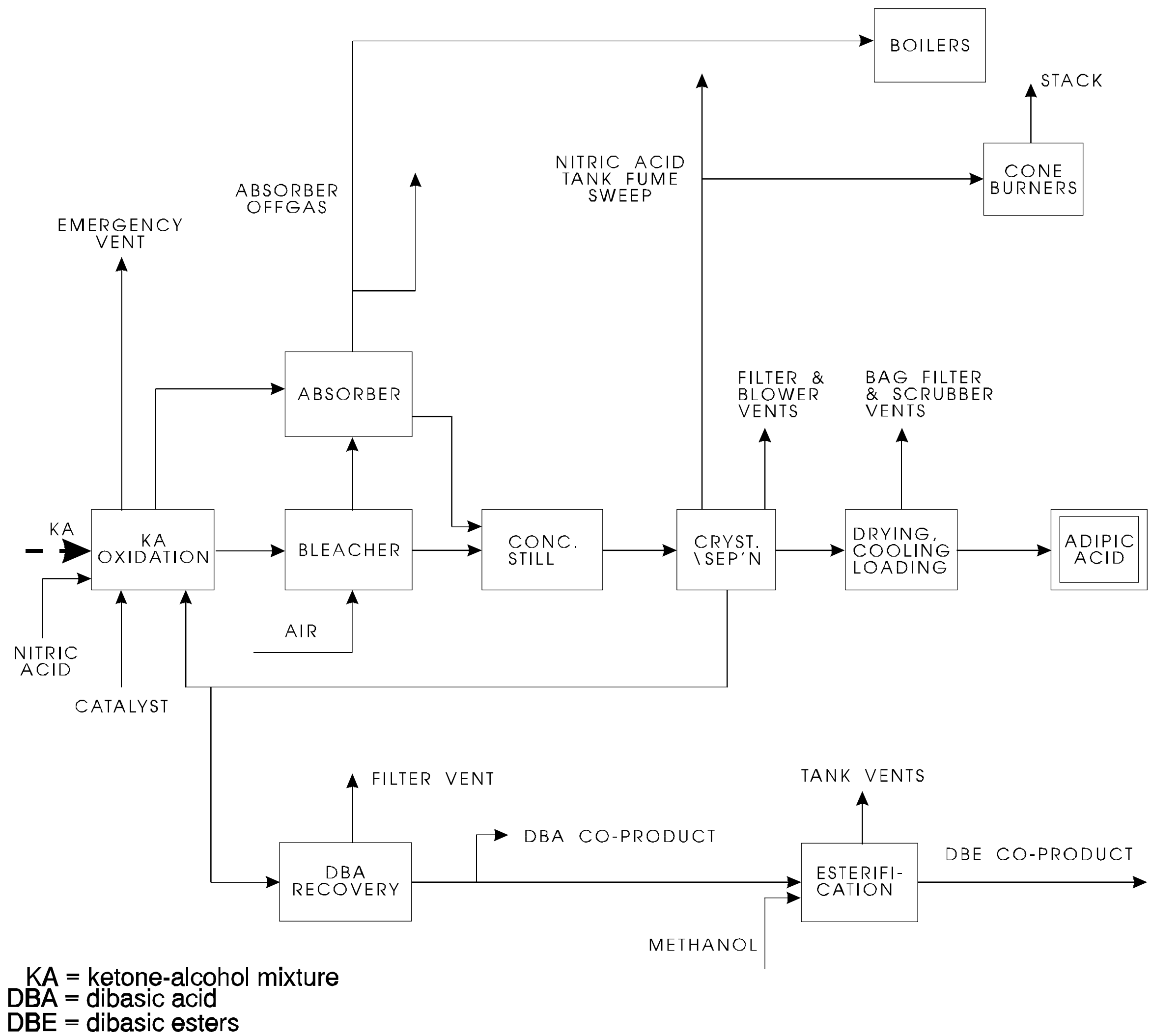

Figure 6.2-2. Adipic acid manufacturing process: Nitric acid oxidation of ketone-alcohol mixture.

Table 6.2-1 (Metric And English Units). UNCONTROLLED EMISSION FACTORS FOR PRIMARY OXIDATION ADIPIC ACID MANUFACTURE[a]

EMISSION FACTOR RATING: D

Source (Cyclohexane → KA)	TNMOC[b]		CO		CO_2		CH_4	
	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton
High-pressure scrubber	7.0[c]	14[b]	25	49	14	28	0.08	0.17
Low-pressure scrubber	1.4[d]	2.8[c]	9.0	18	3.7	7.4	0.05	0.09

[a] Factors are kilograms per megagram (kg/Mg) and pounds per ton (lb/ton) of adipic acid. KA = ketone-alcohol mixture. TNMOC = total nonmethane organic compounds.
[b] One TNMOC composition analysis at a third plant utilizing only 1 scrubber yielded the following speciation: 46% butane, 16% pentane, 33% cyclohexane, 5% other; this test not used in total TNMOC emission factor calculation.
[c] Multiple TNMOC composition analyses from 2 reactors within 1 plant yielded the following average speciation: 1.6% ethane, 1.2% ethylene, 6.7% propane, 63% butane, 16% pentane, 11% cyclohexane.
[d] Multiple TNMOC composition analyses from 2 reactors within 1 plant yielded the following average speciation: 2.3% ethane, 1.7% ethylene, 5.2% propane, 54% butane, 10% pentane, 26% cyclohexane.

from the stream in a bleaching column using air. The gaseous effluent from oxidation contains NO_x, CO_2, CO, nitrous oxide (N_2O), and DBAs. The gaseous effluent from both the bleacher and the oxidation reactor typically is passed through an absorption tower to recover most of the NO_x, but this process does not significantly reduce the concentration of N_2O in the stream. The absorber offgases and the fumes from tanks storing solutions high in nitric acid content are controlled by extended absorption at 1 of the 3 plants utilizing cyclohexane oxidation, and by thermal reduction at the remaining 2. Extended absorption is accomplished by simply increasing the volume of the absorber, by extending the residence time of the NO_x-laden gases with the absorbing water, and by providing sufficient cooling to remove the heat released by the absorption process. Thermal reduction involves reacting the NO_x with excess fuel in a reducing atmosphere, which is less economical than extended absorption.

Both scrubbers and bag filters are used commonly to control adipic acid dust particulate emissions from product drying, cooling, storage, and loading operations. Nitric acid emissions occur from the product blowers and from the centrifuges and/or filters used to recover adipic acid crystals from the effluent stream leaving the second reactor. When chlorine is added to product cooling towers, all of it can typically be assumed to be emitted to the atmosphere. If DBA are recovered from the nitric acid solution and converted to dibasic esters (DBE) using methanol, methanol emissions will also occur.

Table 6.2-2 (Metric And English Units). UNCONTROLLED EMISSION FACTORS FOR SECONDARY OXIDATION ADIPIC ACID MANUFACTURE[a]

EMISSION FACTOR RATING: E (except as noted)

Source (KA —> Adipic Acid)	TNMOC		CO		CO_2		N_2O		NO_x		PM	
	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton	kg/Mg	lb/ton
Oxidation reactor[b,c]	0.28	0.55	0.25	0.49	60	120	290	590	7.0	14	NA	NA
Nitric acid tank fume sweep[d]	0.007	0.014	0.14	0.28	2.6	5.2	1.3	2.6	0.81	1.6	NA	NA
Adipic acid refining[e]	0.3	0.5	0	0	NA	NA	NA	NA	0.3	0.6	0.1[f]	0.1[f]
Adipic acid drying/cooling/ storage	0	0	0	0	NA	NA	NA	NA	0	0	0.4[f]	0.8[f]

[a] Factors are kilograms per megagram (kg/Mg) and pounds per ton (lb/ton) of adipic acid. KA = ketone-alcohol mixture. TNMOC = total nonmethane organic compounds. NA = not applicable.
[b] EMISSION FACTOR RATING: D
[c] Derived from multiple gas-stream composition analyses at 2 plants, 1 of which can use extended absorption to lower NO_x emissions to 3.2 lb/ton adipic acid.
[d] Derived from gas-stream composition analysis during 1 stack test.
[e] Includes chilling, crystallization, and centrifuging.
[f] Factors are after baghouse control device, no efficiency given.

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