ADIPIC ACID

1. Introduction

Adipic acid, hexanedioic acid, 1,4-butanedicarboxylic acid, mol wt 146.14, $HOOCCH_2CH_2CH_2CH_2COOH$ [124-04-9], is a white crystalline solid with a melting point of ~152°C. Little of this dicarboxylic acid occurs naturally, but it is produced on a very large scale at several locations around the world. The majority of this material is used in the manufacture of nylon-6,6 polyamide [32131-17-2], which is prepared by reaction with 1,6-hexanediamine [124-09-4]. W. H. Carothers' research team at the Du Pont Company discovered nylon in the early 1930s (1), and the 50th anniversary of its commercial introduction was celebrated in 1989. Growth has been strong and steady during this period, resulting in an adipic acid demand of nearly 2 billion metric tons per year worldwide in 1999. The large scale availability, coupled with the high purity demanded by the polyamide process, has led to the discovery of a wide variety of applications for the acid.

2. Chemical and Physical Properties

Adipic acid is a colorless, odorless, sour tasting crystalline solid. Its fundamental chemical and physical properties are listed in Table 1. Further information may be obtained by referring to studies of infrared and Raman spectroscopy of adipic acid crystals (11,12), ultraviolet spectra of solutions (13), and specialized thermodynamic properties (4,14). Solubility and solution properties are described in Table 2. The crystal morphology is monoclinic prisms strongly influenced by impurities (21). Both process parameters (22) and additives (21) profoundly affect crystal morphology in the crystallization of adipic acid, an industrially significant process. Aqueous solutions of the acid are corrosive and their effect on various steel alloys have been tested (23). Generally, austenitic stainless steels containing nickel and molybdenum and >18% chromium are resistant. Data on 20 metals were summarized in one survey (24). Bulk and handling properties of adipic acid are summarized in Table 3.

Table 1. **Physical and Chemical Properties of Adipic Acid**

Property	Value	References
molecular formula	$C_6H_{10}O_4$	
molecular weight	146.14	
melting point, °C	152.1 ± 0.3	2
specific gravity	1.344 at 18°C (sol)	3
	1.07 at 170°C (liq)	4
coefficient of cubical expansion, K^{-1}	4.0×10^{-4} at 35–150°C (sol)	4
	10.3×10^{-4} at 155–168°C (liq)	5
vapor density, air = 1	5.04	
vapor pressure, Pa[a]		
solid at °C		6
18.5	9.7	
32.7	19.3	
47.0	38.0	
liquid at °C		7
205.5	1,300	
216.5	2,000	
244.5	6,700	
265.0	13,300	
specific heat, kJ/kg K[b]	1.590 (solid state)	8
	2.253 (liquid state)	9,8
	1.680 (vapor, 300°C)	
heat of fusion, kJ/kg[b]	115	
entropy of fusion, J/mol K[b]	79.8	4,10
heat of vaporization, kJ/kg[b]	549	
melt viscosity, mPa s(= cP)	4.54 at 160°C	
	2.64 at 193°C	
heat of combustion, kJ/mol[b]	2,800	10

[a] To convert Pa to mm Hg divide by 133.3.
[b] To convert J to cal divide by 4.184.

3. Chemical Reactions

Adipic acid undergoes the usual reactions of carboxylic acids, including esterification, amidation, reduction, halogenation, salt formation, and dehydration. Because of its bifunctional nature, it also undergoes several industrially significant polymerization reactions.

Esters and polyesters comprise the second most important class of adipic acid derivatives, next to polyamides. The acid readily reacts with alcohols to form either the mono- or diester. Although the reaction usually is acid catalyzed, conversion may be enhanced by removal of water as it is produced. The methyl ester is an industrially important material, because it is a distillable derivative which provides a means of separating or purifying acid mixtures. Recent modifications of adipic acid manufacturing processes have included methanol esterification of the dicarboxylic acid by-product mixture. Thus glutaric acid [110-94-1] and succinic acid [110-15-6] can be recovered upon hydrolysis, or disposed of as the esters (28). Monomethyl adipate can be electrolyzed as the salt to give dimethyl sebacate [106-79-6] (Kolbe synthesis) (29), an important 10-carbon

Table 2. **Solution Properties of Adipic Acid**

Property	Value	References
heat of solution in H_2O, kJ/kg[a]	214 at 10–20°C 241 at 90–100°C	15
dissociation constant in H_2O	$K_1 K_2$	16,17
at 25°C	3.7×10^{-5} 3.86×10^{-6}	
at 50°C	3.29×10^{-5} 3.22×10^{-6}	
at 74°C	2.90×10^{-5} 2.55×10^{-6}	
solubility in H_2O, g/100 g H_2O		18
at 15°C	1.42	
at 40°C	4.5	
at 60°C	18.2	
at 80°C	73	
at 100°C	290	
pH of aqueous solutions		19
0.1 wt %	3.2	
0.4 wt %	3.0	
1.2 wt %	2.8	
2.5 wt %	2.7	
solubility in organic solvents at 25°C		
very soluble in	methanol, ethanol	
soluble in	acetone, ethyl acetate	
very slightly soluble in	cyclohexane, benzene	
distribution coefficient		
organic solvents vs H_2O	$D, \frac{\text{wt \% in H}_2\text{O}}{\text{wt \% in solvent}}$	
CCl_4, $CHCl_3$, C_6H_6	>10	20
disopropyl ketone	4.8	
butyl acetate	2.9	
ethyl ether	2.2	
methyl isobutyl ketone	1.2	
ethyl acetate	0.91	
methyl propyl ketone	0.55	
methyl ethyl ketone	0.50	
cyclohexanone	0.32	
n-butanol	0.31	

[a] To convert kJ to kcal divide by 4.184.

Table 3. **Bulk Phase Handling Properties of Adipic Acid**

Property	Value	References
bulk density[a], kg/m^3	640–800	19
flash point, Cleveland open cup, °C	210	5
flash point, closed cup, °C	196	
autoignition temperature, °C	420	5
dust cloud ignition temperature, °C	550	
minimum explosive concentration (dust in air), kg/m^3	0.035	25,26
minimum dust cloud ignition energy, J[b]	6.0×10^{-2}	27
maximum rate of pressure rise, MPa[c]/s	18.6	

[a] A function of particle size.

[b] To convert J to cal divide by 4.184.

[c] To convert MPa to psi multiply by 145.

Table 4. **Esters of Adipic Acid**

Ester	CAS Registry Number	Pressure, kPa[a]	Boiling point, °C
monomethyl	[627-91-8]	1.3	158
dimethyl	[627-93-0]	1.7	115
monoethyl	[626-86-8]	0.9	160
diethyl	[141-28-6]	1.7	127
di-*n*-propyl	[106-19-4]	1.5	151
di-*n*-butyl	[105-99-7]	1.3	165
di-2-ethylhexyl	[103-23-1]	0.67	214
di-*n*-nonyl	[151-32-6]	0.67	230
di-*n*-decyl	[105-97-5]	0.67	244
di-tridecyl	[16958-92-2]	101.3	349
octyl decyl	[110-29-2]	0.67	235
di-(2-butoxyethyl)	[141-18-4]	0.53	215

[a] To convert kPa to mm Hg multiply by 7.5.

diacid. Diesters from moderately long-chain (8 or 10 carbon) alcohols are also an important group, finding use as plasticizers, eg, for poly(vinyl chloride) (PVC) resins. Table 4 lists the boiling points of several representative adipate esters. Reactions with diols (especially ethylene glycol) give polyesters, also important as plasticizers in special applications. In another important use of adipate esters, low molecular weight polyesters terminated in hydroxyl groups react with polyisocyanates to give polyurethane resins. Polyurethanes consumed ~48% of adipic acid production in the United States in 1999 (30).

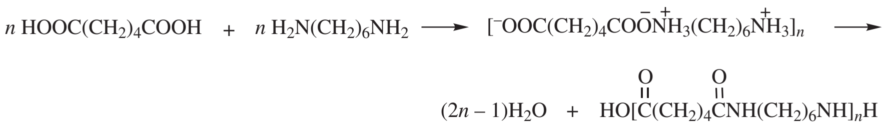
Salt-forming reactions of adipic acid are those typical of carboxylic acids. Alkali metal salts and ammonium salts are water soluble; alkaline earth metal salts have limited solubility (see Table 5). Salt formation with amines and diamines is discussed in the next section.

Heating of the diammonium salt or reaction of the dimethyl ester with concentrated ammonium hydroxide gives adipamide [628-94-4], mp 228°C, which is relatively insoluble in cold water. Substituted amides are readily formed when amines are used. The most industrially significant reaction of adipic acid is its reaction with diamines, specifically 1,6-hexanediamine. A water-soluble polymeric salt is formed initially upon mixing solutions of the two materials; then heating with removal of water produces the polyamide, nylon-6,6. This reaction

Table 5. **Solubility of Adipic Acid Salts**

Salt	CAS Registry Number	Temperature,°C	Solubility, g/100 g H_2O
disodium (hemihydrate)	[7486-38-6]	14	59
dipotassium	[19147-16-1]	15	65
diammonium	[3385-41-9]	14	40
calcium			
(monohydrate)	[18850-78-7]	13	4
(anhydrous)	[22322-28-7]	100	1
barium			
(monohydrate)		12	12
(anhydrous)	[60178-88-0]	100	7

has been studied extensively, and the literature contains hundreds of references to it and to polyamide product properties (31).



$$n\,\mathrm{HOOC(CH_2)_4COOH} + n\,\mathrm{H_2N(CH_2)_6NH_2} \longrightarrow [^{-}\mathrm{OOC(CH_2)_4CO\overset{-}{O}\overset{+}{N}H_3(CH_2)_6\overset{+}{N}H_3}]_n \longrightarrow (2n-1)\mathrm{H_2O} + \mathrm{HO[\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}NH(CH_2)_6NH]_nH}$$

Hydrogenation of dimethyl adipate over Raney-promoted copper chromite at 200°C and 10 MPa produces 1,6-hexanediol [629-11-8], an important chemical intermediate (32). Promoted cobalt catalysts (33) and nickel catalysts (34) are examples of other patented processes for this reaction. An earlier process, which is no longer in use, for the manufacture of the 1,6-hexanediamine from adipic acid involved hydrogenation of the acid (as its ester) to the diol, followed by ammonolysis to the diamine (35).

Heating above the melting point results in elimination of water and formation of a linear or polymeric anhydride [2035-75-8], not the cyclic anhydride as produced in the case of glutaric anhydride [108-55-4] and succinic anhydride [108-30-5]. Decarboxylation occurs at temperatures >230–250°C, leaving cyclopentanone [120-92-3] as the chief product, bp 131°C. This reaction is catalyzed by metals such as calcium (36) or barium (37). Behavior of adipic acid upon Curie-point pyrolysis has been reviewed; mass spectroscopy was used to analyze the anhydrides, cyclic ketones, and rearranged fragments (38). Cyclization of the esters is accomplished by standard condensation chemistry with basic reagents. For example, cyclization via the acyloin condensation occurs in the presence of sodium metal, producing 2-hydroxycyclohexanone [533-60-8] (39).

Conversion of the acid to the acid chloride is accomplished using standard laboratory techniques. The resulting acid chloride frequently is used in subsequent synthesis reactions. An example is the laboratory synthesis of nylon-6,6 via the nylon rope trick, in which the diamine reacts with adipoyl chloride [111-50-2] in a two-phase system. Polyamide produced at the interface may be pulled continuously from the open vessel in a startling demonstration of polymerization chemistry (40). The acid–nitrile interchange is another unique reaction, in which a mixture of adipic acid and adiponitrile [111-69-3] are heated together, producing an equilibrium mixture containing significant amounts of 5-cyanopentanoic acid [5264-33-5]. This material is a precursor to caprolactam [105-60-2] and may be isolated from the reaction mixture by a number of methods, including esterification and hydrogenation (41).

4. Manufacture and Processing

Several general reviews of adipic acid manufacturing processes have been published since it became of commercial importance in the 1940s (42–46), including a very thorough report based on patent studies (47). Adipic acid historically has been manufactured predominantly from cyclohexane [110-82-7] and, to a lesser extent, phenol [108-95-2]. During the 1970s and 1980s, however, much research has been directed to alternative feedstocks, especially butadiene [106-99-0] and cyclohexene [110-83-8], as dictated by shifts in hydrocarbon pricing. All current industrial processes use nitric acid [7697-37-2] in the final oxidation stage. Growing concern with air quality may exert further pressure for alternative routes as manufacturers seek to avoid NO_x abatement costs, a necessary part of processes that use nitric acid.

Since adipic acid has been produced in commercial quantities for almost 50 years, it is not surprising that many variations and improvements have been made to the basic cyclohexane process. In general, however, the commercially important processes still employ two major reaction stages. The first reaction stage is the production of the intermediates cyclohexanone [108-94-1] and cyclohexanol [108-93-0], usually abbreviated as KA, KA oil, ol-one, or anone-anol. The KA (ketone, alcohol), after separation from unreacted cyclohexane (which is recycled) and reaction by-products, is then converted to adipic acid by oxidation with nitric acid. An important alternative to this use of KA is its use as an intermediate in the manufacture of caprolactam, the monomer for production of nylon-6 [25038-54-4]. The latter use of KA predominates by a substantial margin on a worldwide basis, but not in the United States.

4.1. Preparation of KA by Oxidation of Cyclohexane.

There are three main variations to the basic cyclohexane oxidation process pioneered by Du Pont in the 1940s. The first, which can be termed metal-catalyzed oxidation, is the oldest process still in use and forms the base for the other two. It employs a cyclohexane-soluble catalyst, usually cobalt naphthenate [61789-51-3] or cobalt octoate [136-52-7], and moderate temperatures (150–175°C) and pressures (800–1200 kPa). Air is fed to each of a series of stirred tank reactors or to a column reactor that contains numerous reaction stages, along with cyclohexane. The catalyst, at 0.3–3 ppm based on cyclohexane feed, is usually premixed by injection into the feed stream, though it is not uncommon to divide the catalyst stream into many separate additions to each of the series reactors. The conversion of cyclohexane to oxidized products is 3–8 mol %, which is quite low compared to most important industrial processes. There are claims of commercial processes operating as low as 1 mol% conversion (48), which translates to 99% of the feed material being recovered and recycled to the oxidation reactors. Low conversion is the major factor in achieving high selectivities to ketone (K) and alcohol (A) (and to cyclohexylhydroperoxide [766-07-4] discussed below). This is so because the intermediates of interest (K, A, and cyclohexylhydroperoxide) are all much more easily oxidized than is cyclohexane (49,50). Selectivities vary inversely and linearly with conversion, ranging from ~90 mol% at 1–2 mol% conversion to 65–70 mol% at 8 mol% conversion. Table 6 illustrates the range of reaction conditions to be found in the patent literature.

Because the process operates at such low conversion of cyclohexane per pass through the oxidation reactors, large quantities of unreacted cyclohexane must be recovered by distillation of the oxidizer effluent. This, and the increase in energy prices in the 1970s, has resulted in considerable attention being given to the energy conservation schemes employed in recovering the cyclohexane. Examples of techniques used in energy conservation are process–process heat interchange, high efficiency packed distillation columns, and use of the “pinch-point” technique in designing recovery steps. Contacting the final crude KA oil with water or solutions of caustic soda, or both, for removal of mono- and dibasic

Table 6. **Reaction Conditions for Air Oxidation of Cyclohexane**

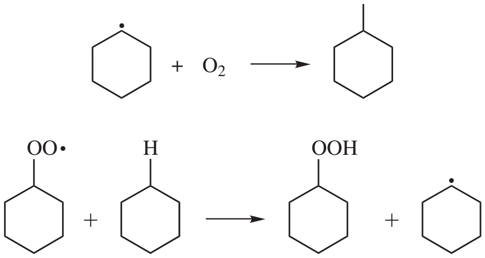
Process and company	Temperature, °C	Pressure, MPa[a]	Catalyst or additive	Reactor type	Cyclohexane conversion, mol %	KA yield, mol %	References
Metal-catalyzed							
Du Pont	170	1.1	Co	column	6	76	51
Stamicarbon	155	0.9	Co	tank	4	77	52
High peroxide							
BASF							
oxidation	145	1.1	none	tank	3	83	53–55
deperoxidation	125		Co/NaOH				
Du Pont							
oxidation	160	1.0	Co	column	4	82	56–58
deperoxidation	120		Co, Cr				
Rhône Poulenc							
oxidation	175	1.8	none	tank	4	84	59–62
deperoxidation	115		Cr, V, Mo				
Stamicarbon							
oxidation	160	1.3	none	tank	3	86	48,63,64
deperoxidation	100		Co/NaOH				
Boric acid							
Halcon	165	1.0	H_3BO_3	tank	3	87	65,66
ICI	165	1.0	H_3BO_3	tank	5	85	67
IFP	165	1.2	H_3BO_3		12	85	68,69
Solutia (formerly Monsanto)	165	1.0	H_3BO_3	tank	4	87	70

[a] To convert MPa to psi multiply by 145.

acid impurities also can be considered an energy conservation technique since this treatment can eliminate the final steam stripper often used to purify the crude KA oil.

Regardless of the techniques used to purify the KA oil, several waste streams are generated during the overall oxidation–separation processes and must be disposed of. The spent oxidation gas stream must be scrubbed to remove residual cyclohexane, but afterwards will still contain CO, CO_2, and volatile hydrocarbons (especially propane, butane, and pentane). This gas stream is either burned and the energy recovered, or it is catalytically abated. There are usually several aqueous waste streams arising from both water generated by the oxidation reactions and wash water. The principal hydrocarbon constituents of these aqueous wastes are the C_1–C_6 mono- and dibasic acids, but also present are butanol [71-36-3], pentanol [71-41-0], ε-hydroxycaproic acid [1191-25-9], and various lactones and diols (71,72). The spent caustic streams contain similar components in addition to the caustic values. These streams can be burned for recovery of sodium carbonate or sold directly as a by-product for use in the paper industry. The most concentrated waste stream is one often called still bottoms, heavy ends, or nonvolatile residue. It comes from the final distillation column in which the KA oil is steam-stripped overhead. The tails stream from this column contains most of the nonvolatile by-products, as well as metals and residues from the catalysts and from corrosion. Both the metals and acid content may be high enough to dictate that this stream be classified as a hazardous waste. It usually is burned and the energy used to generate steam (73). Much effort has gone into recovering valuable materials from it over the years, including adipic acid, which may be present in as much as 3–4% of the cyclohexane oxidized (74). It has potential as a feedstock in the production of monobasic acids, polyester polyols, butanediol, and maleic acid (75,76). The frequency of fugitive emissions from cyclohexane oxidation plants has been reviewed (77).

An alternative to maximizing selectivity to KA in the cyclohexane oxidation step is a process which seeks to maximize cyclohexylhydroperoxide, also called P or CHHP. This peroxide is one of the first intermediates produced in the oxidation of cyclohexane. It is produced when a cyclohexyl radical reacts with an oxygen molecule (78) to form the cyclohexylhydroperoxy radical. This radical can extract a hydrogen atom from a cyclohexane molecule, to produce CHHP and another cyclohexyl radical, which extends the free-radical reaction chain.



The peroxide can be converted to KA easily, and in high yield, in a number of ways; thus maximization of CHHP, at high yield, gives a process with high

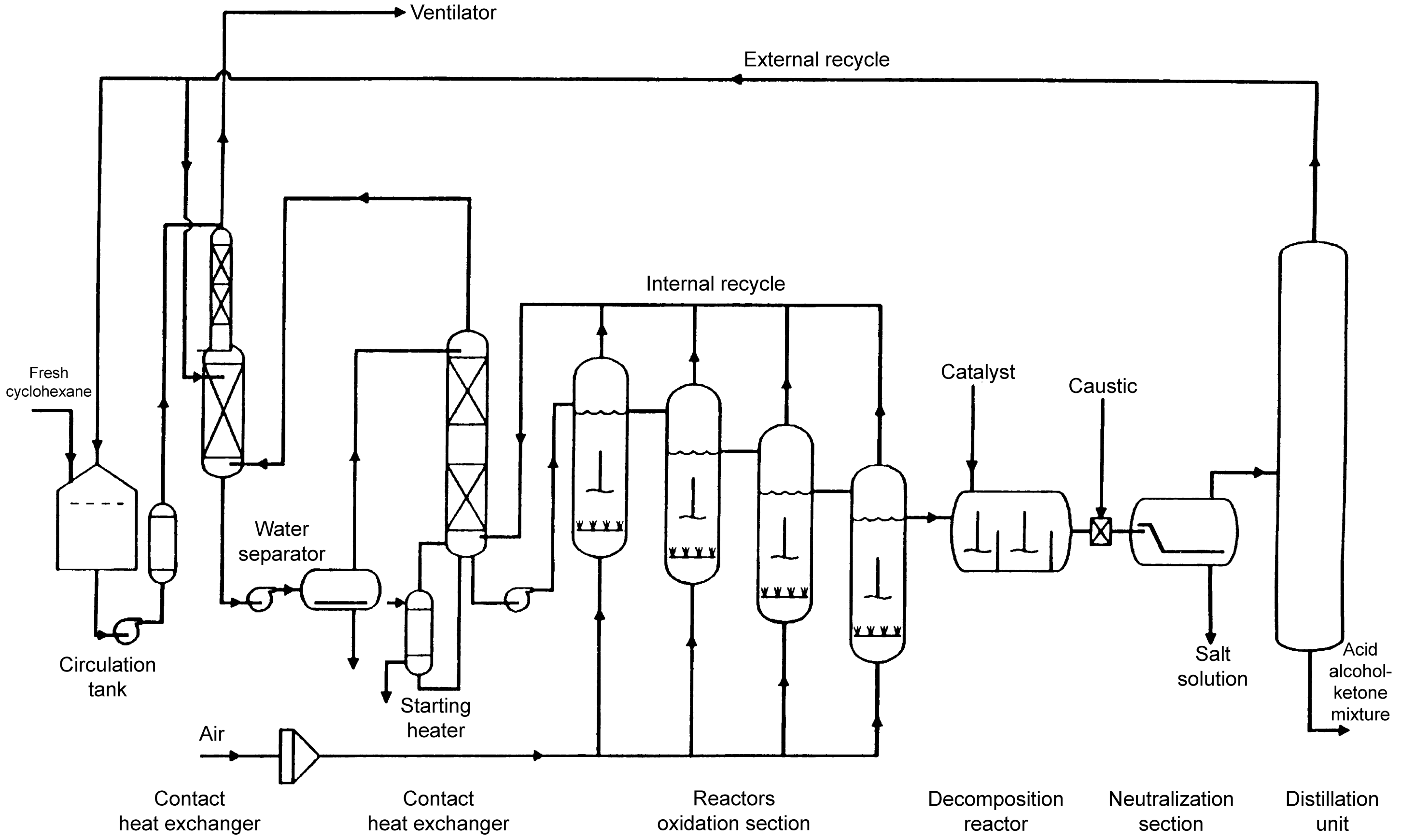


Fig. 1. Stamicarbon cyclohexane oxidation process.

yield to KA. Techniques employed to produce high CHHP yield include drastically cutting or eliminating metal catalysts in the oxidation step, minimizing cyclohexane conversion, passivating reactor walls, lowering reaction temperature (to as low as 140°C), adding water to the reaction mix to extract acid catalysts from the cyclohexane phase, and adding metal-chelating agents to the reaction mix. Optimization of this process can produce CHHP in a proportion as high as 75% of the reaction products (59). The CHHP then can be converted to KA by any of the following methods: decomposing it with homogeneous or heterogeneous catalysts from the group Co, Cr, Mo, V, Cu, or Ru; dehydrating it by treatment with caustic soda (which preferentially gives K); or hydrogenating it (which preferentially gives A). KA is separated from the reaction mixture in a manner similar to the conventional process. It may be possible, however, to avoid a final steam distillation of the KA overhead if the tails stream from the distillation train is sufficiently clean. This could result from a high yield process that employs thorough water and caustic washing. Figure 1 illustrates schematically the high peroxide process practiced by Stamicarbon (60).

Another alternative to the basic cyclohexane oxidation process is one which maximizes only the yield of A. This process uses boric acid as an additive to the cyclohexane stream as both a promoter and an esterifying agent for the A that is produced. Metaboric acid [10043-35-3] is fed to the first series oxidizer as a slurry in cyclohexane to give a molar ratio of boron:cyclohexane of around 1.5:100. No other metal catalyst is used. Esterifying the A effectively shields it from overoxidation and thus allows the attainment of very high yields ($\sim$90%) (65). The ratio A : K in the final product can exceed 10:1. The process was developed in the mid-1960s by a number of companies, including Halcon/Scientific Design (79,80), Institute Francais Petrole (68,81), and Stamicarbon (82). The process was licensed and commercialized by several companies in the decade following its development, including Solutia (formerly Monsanto), ICI, and Bayer. The major drawback to the process is the need to hydrolyze the borate ester in order to recover A. This is an energy-intensive step and can be quite a mechanical nuisance because of the requirement for handling boric acid solids. Without careful attention to energy conservation and engineering, the savings that accrue from the high yield can be more than offset. The process does, because of its high yield, offer advantages in waste minimization and product purity. It does, however, introduce boron into the waste streams.

4.2. Preparation of KA From Phenol.

In past years, economics has dictated against the preparation of KA from phenol [108-95-2] because of the relatively high cost of this material compared to cyclohexane. However, given new routes to phenol and occasional periods of overcapacity for this commodity chemical, such technology has been revisited.

For example, the Solutia Benzene to Phenol process (83) has been touted as a step-change in adipic acid manufacturing technology. As shown in Figure 2, the reaction between benzene and nitrous oxide over an Fe- ZSM-5 catalyst (84) produces phenol in high yield and selectivity. Here, the nitrous oxide is obtained from removing the NO_x, oxygen and low-level organic compounds from the adipic acid offgas (85). Rather than destroying the N_2O (see Section 8 under N_2O Abatement Technology), the benzene to phenol process converts it to a value-added product which also serves as an adipic acid intermediate per the phenol to KA

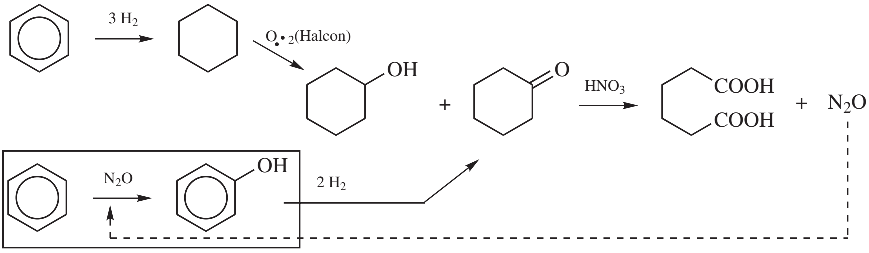


Fig. 2. Solutia benzene to phenol technology.

process, discussed below. The reaction runs at 3 atm and 300–500°C. Since it takes place in the gas phase with N_2O levels maintained below the minimum oxidant concentration (86), it is inherently safer than the high pressure, liquid phase cyclohexane to KA operation, which has a potential for flammable vapor cloud release. A moving bed design is used to provide a continuous operation and extend catalyst life.

Downstream, the vapor phase hydrogenation of phenol to KA is used. Its primary selling points over cyclohexane to KA routes include a lower benzene usage and a 99% KA yield (87,88). The catalyst is Pd/Al_2O_3. Reaction conditions are 130–160°C, 165 kPa (15 psi), and 4 H_2/phenol. A three-step distillation separates the product KA from the light ends, high boiler by-products (eg, cyclohexenyl and cyclohexanone) and unreacted phenol. Steam generated in the tubular isothermal reactor provides the energy required by the distillation section.

The liquid phase hydrogenation of phenol to KA also gives a very high yield, typically 97–99% (89). Just as in the vapor phase process, high KA yield leads to a simple purification section, consisting of an ion exchange step to remove the unreacted phenol (90). Typical reaction conditions are 140°C and 400 kPa (58 psi) using a heterogeneous nickel on silica catalyst (89).

In both liquid- and vapor-phase phenol to KA processes, one can obtain varying ratios of K to A. If the desired product is to be further oxidized with nitric acid to make adipic acid, then there is an optimal concentration of K that maximizes the tradeoff between adipic yield (91) and nitric acid usage. If the desired product is caprolactam, then a high K concentration would be required.

Cyclohexanol (A) can be manufactured from cyclohexene using a process developed and commercialized by Asahi (92,93). This process, illustrated in Figure 3 involves a selective partial hydrogenation of benzene to cyclohexene

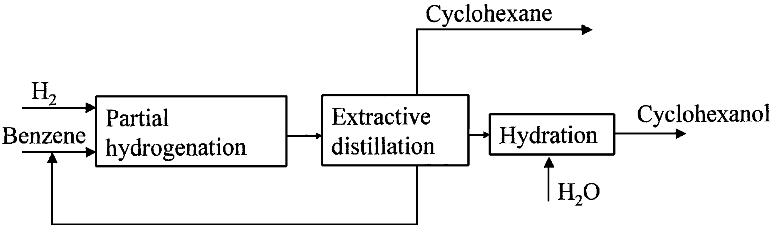


Fig. 3. Asahi cyclohexene process for KA.

using an aqueous ruthenium catalyst system containing metal oxide dispersants (eg, Al_2O_3) and zinc compound promoters (94). Reaction conditions of 120–180°C and 30–100 atm give a benzene conversion of 50–60% and a cyclohexene selectivity of 80%. Cyclohexane is the primary byproduct. The reactor contents are well agitated in order to create adequate mixing between gas (hydrogen), oil (benzene raw material and cyclohexene;cyclohexane products), and water (catalyst) phases. After hydrogenation, the oil (disperse phase) is separated from the water (continuous phase). Next, the unreacted benzene is recovered via extractive distillation using a polar solvent such as dimethylacetamide (95,96). The cyclohexene is then hydrolyzed in the presence of a ZSM-5 zeolite (97) suspended in water. The conversion is 10–15% and the cyclohexanol selectivity is 99%. This result is based on the nature of the extractive reaction step. Here, the cyclohexene is adsorbed on the catalyst introduced in the process as an aqueous phase slurry. Cyclohexanol, once formed, separates from the reaction medium and disperses back to the organic phase. Using proprietary multistep extractive distillation process, the cyclohexanol is separated from unreacted cyclohexene and purified (98). Provided that one has a use for the cyclohexane byproduct, this low waste process is an attractive alternative to other more traditional technology.

ARCO has developed a coproduct process that produces KA along with propylene oxide [75-56-9] (99–101). Cyclohexane is oxidized as in the high peroxide process to maximize the quantity of CHHP. The reactor effluent then is concentrated to about 20% CHHP by distilling off unreacted cyclohexane and cosolvent *tert*-butyl alcohol [75-65-0]. This concentrate then is contacted with propylene [115-07-1] in another reactor in which the propylene is epoxidized with CHHP to form propylene oxide and KA. A molybdenum catalyst is employed. The product ratio is ~2.5 kg of KA per kilogram of propylene oxide.

4.3. Nitric Acid Oxidation of Cyclohexanol(One). Although many variations of the cyclohexane oxidation step have been developed or evaluated, technology for conversion of the intermediate ketone–alcohol mixture to adipic acid is fundamentally the same as originally developed by Du Pont in the early 1940s (102,103). This step is accomplished by oxidation with 40–60% nitric acid in the presence of copper and vanadium catalysts. The reaction proceeds at high rate, and is quite exothermic. Yield of adipic acid is 92–96%, the major byproducts being the shorter chain dicarboxylic acids, glutaric and succinic acids, and CO_2. Nitric acid is reduced to a combination of NO_2, NO, N_2O, and N_2. The trace impurities patterns are similar in the products of most manufacturers since essentially all commercial adipic acid production uses this nitric acid oxidation process.

Papers addressing the mechanism of nitric acid oxidation began appearing in the mid-1950s (104). Then, a series of reports beginning in 1962 described the mechanism of the oxidation in considerable detail (105–109). The reaction pathway diagram shown in Figure 4 is based on these and other studies of nitric acid oxidation chemistry. A key intermediate in the reaction sequence is 2-oximinocyclohexanone [24858-28-4], produced via nitrosation of cyclohexanone. Nitrous acid [7782-77-6] is produced during the conversion of cyclohexanol to the ketone, and also upon oxidation of aldehyde and alcohol impurities usually accompanying the KA and arising in the cyclohexane oxidation step. The nitric acid oxidation chemistry is controlled by nitrous acid, which is in equilibrium with NO, NO_2, HNO_3, and H_2O in the reacting mixture. Total inhibition of reaction can be achieved by incorporating a small amount of urea [57-13-6], which effectively scavenges (110) nitrous acid from the mixture. Further nitration leads to 2-nitro-2-nitrosocyclohexanone [23195-89-3], which is converted via hydrolytic cleavage of the ring to 6-nitro-6-hydroximinohexanoic acid (nitrolic acid) [1069-46-1]). Of all the intermediates shown in Figure 4, the nitrolic acid is the only one of sufficient stability to be isolable under very mild conditions. It is hydrolyzed to adipic acid in one of the slowest steps in the sequence. Nitrous oxide (N_2O) is formed by further reaction of the nitrogen-containing products of nitrolic acid hydrolysis. The NO and NO_2 are reabsorbed and converted back to nitric acid, but N_2O cannot be recovered in this manner, and thus is the major nitric acid derived by-product of the process.

About 60–70% of the reaction occurs as in path 1 in Figure 4, the remainder by other pathways. About 20% of the reaction occurs by the vanadium oxidation of 1,2-dioxygenated intermediates (path 2 in Fig. 4). This chemistry has been discussed in detail (108,109). This path is noteworthy since it does not produce the nonrecoverable nitrous oxide. The other reactions shown in Figure 4 occur to varying degrees, depending on either an excess or deficiency of nitrous acid, arising from variations in reaction conditions. These lead to varying yields of the lower dicarboxylic acids. Yield of monobasic and dibasic acid by-products also is a function of the purity of the KA feed. A distinguishing characteristic for several of the commercial processes is the degree to which the intermediate KA is refined, prior to feeding it to nitric acid oxidation.

In a typical industrial adipic acid plant, as schematically illustrated in Figure 3, the KA mixture reacts in reactor A with 45–55% nitric acid containing copper (0.1–0.5%) and vanadium (0.02–0.1%) catalyst (111,112). Design of the oxidation reactor for optimum yield and heat removal has been the subject of considerable research and development over the years of use of this process (113). The reaction occurs at 60–90°C and 0.1-0.4 MPa (14–58 psi). It is very exothermic (6280 kJ/kg = 1500 kcal/kg), and can reach an autocatalytic runaway state at temperatures above ~150°C. Control is achieved by limiting the KA feed to a large excess of nitric acid in a stirred tank or circulating loop reactor. Two stages of oxidation are sometimes employed to achieve improved product quality (114). Oxides of nitrogen are removed by bleaching with air in column C, then water is removed by vacuum distillation in column E.

The concentrated stream, nominally adipic acid and lower dibasic acid coproducts in 35–50% HNO_3 (organic-free basis), is then cooled and crystallized (F). Crude adipic acid product is removed via filtration or centrifugation (G), and the mother liquor is returned to the oxidizer. Further refining is required to achieve polymer grade material, usually by recrystallization from water. Residual lower dibasic acids, nitrogen-containing impurities, and metals are removed in this step. Additional purification steps occasionally are employed, including slurry washing, further recrystallization, and charcoal treatment. The bleacher off-gas, containing NO and NO_2, is combined with air and absorbed in water generating nitric acid for reuse (D).

In order to control the concentration of lower dibasic acid by-products in the system, a portion of the mother liquor stream is diverted to a purge treatment

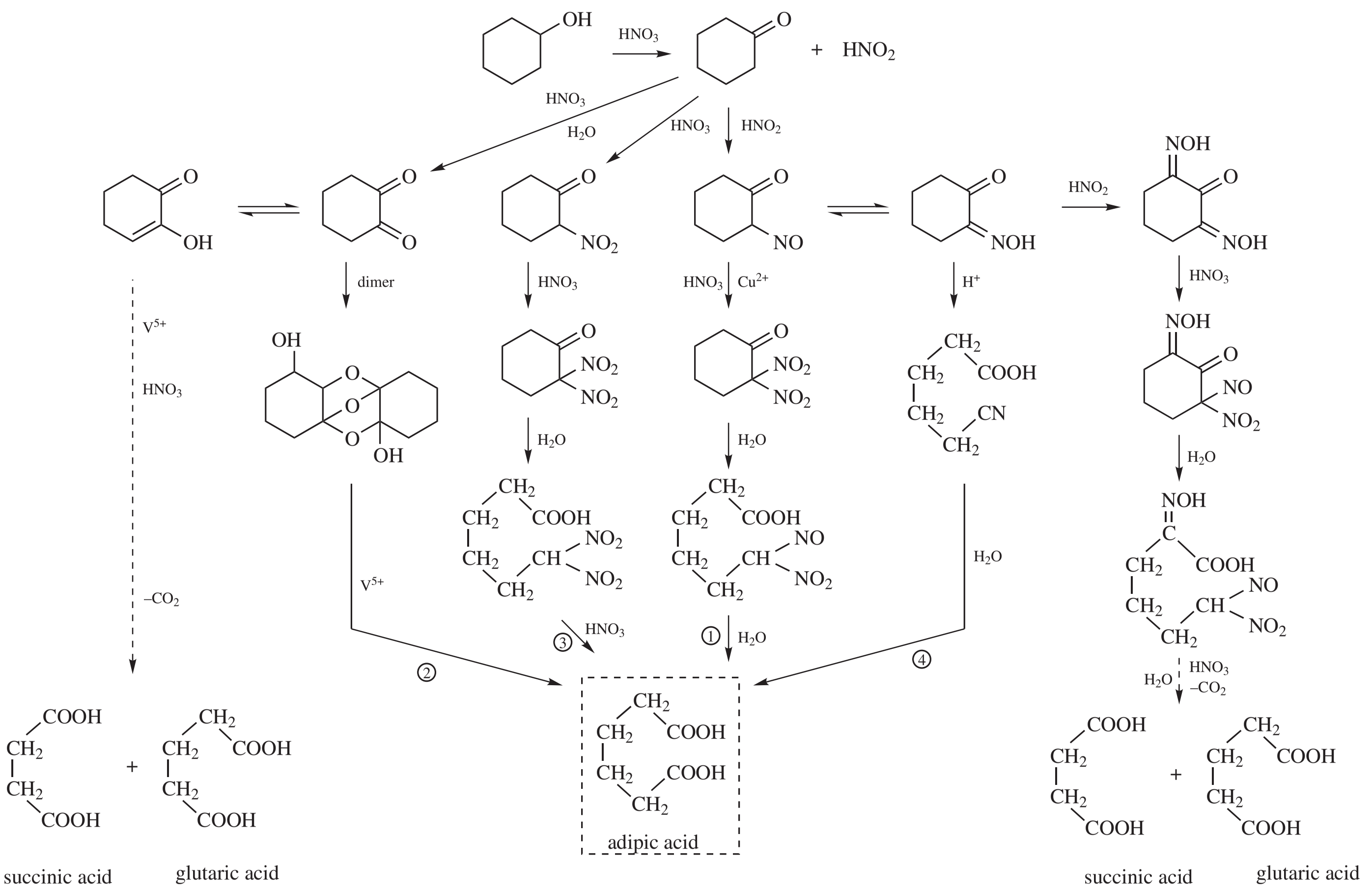


Fig. 4. Reaction paths to adipic acid. Encircled numbers label the pathways discussed in the text.

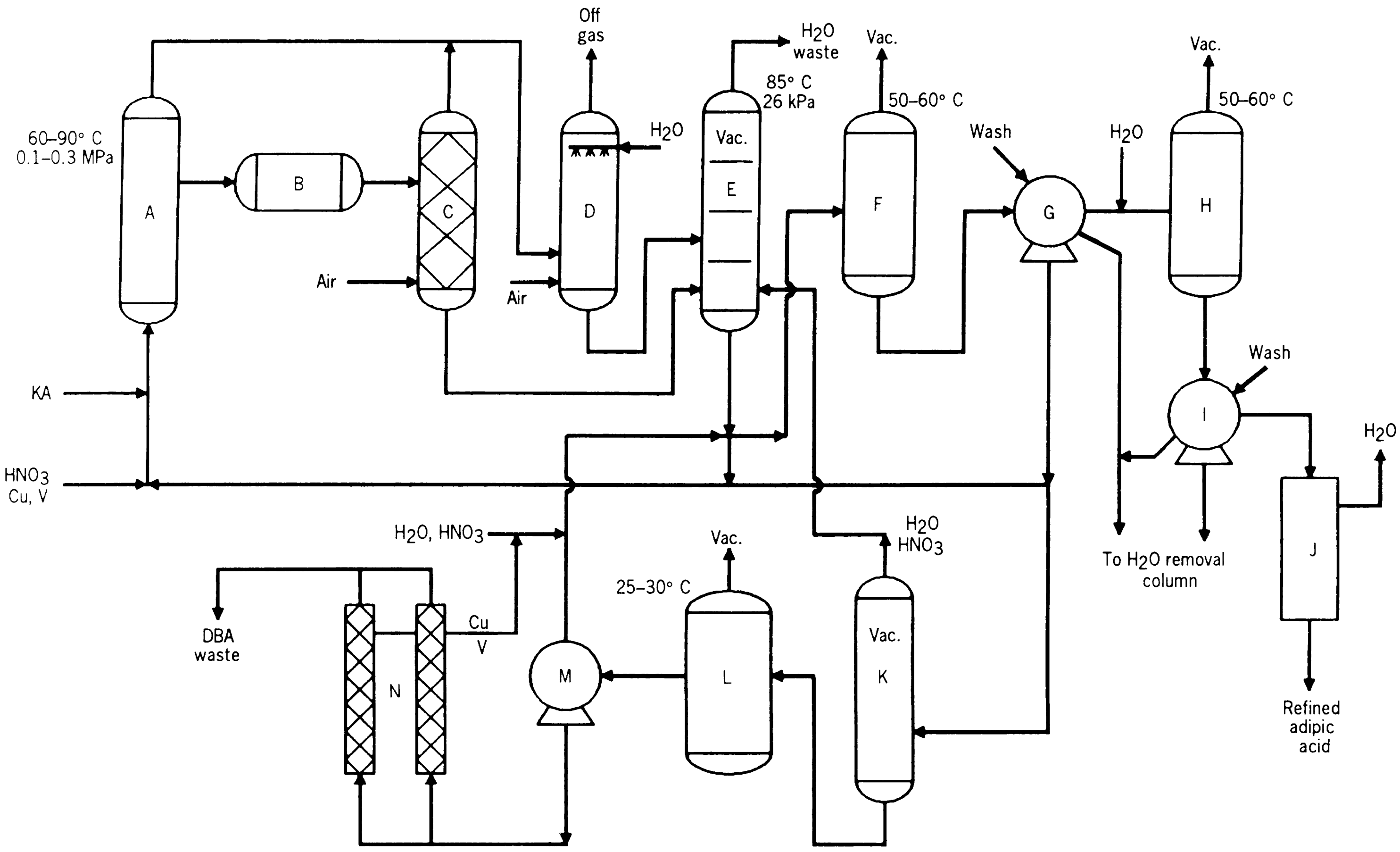


Fig. 5. Typical nitric acid oxidation process. A, reactor; B, optional cleanup reactor; C, bleacher; D, NO_x absorber; E, concentrating still; F, crude crystallizer; G, centrifuge or filter; H, refined crystallizer; I, centrifuge or filter; J, dryer; K, purge evaporator; L, purge crystallizer; M, centrifuge or filter; N, ion-exchange beds; DBA = dibasic acids.

process. Following removal of nitric acid by distillation (Fig. 5, K), copper and vanadium catalyst are recovered by ion-exchange treatment (Fig. 5, N). This area of the process has received considerable attention in recent years as companies strive to improve efficiency and reduce waste. Patents have appeared describing addition of SO_2 to improve ion-exchange recovery of vanadium (115), improved separation of glutaric and succinic acids by dehydration and distillation of anhydrides (116), formation of imides (117), improved nitric acid removal prior to dibasic acid recovery (118), and other claims (119).

Because of the highly corrosive nature of the nitric acid streams, adipic acid plants are constructed of stainless steel, or titanium in the more corrosive areas, and thus have high investment costs.

Nitric acid oxidation may be used to recover value from waste streams generated in the cyclohexane oxidation portion of the process, such as the water wash (120) and nonvolatile residue (76) streams. The nitric acid oxidation step produces three major waste streams: an off-gas containing oxides of nitrogen and CO_2; water containing traces of nitric acid and organics from the water removal column; and a dibasic acid purge stream containing adipic, glutaric, and succinic acids. The off-gas usually is passed through a reducing-flame burner to the atmosphere, or it may be oxidized back to NO_x at 1000–1300°C and recovered as nitric acid, as claimed in a patent (121). The overhead water stream usually is treated (eg, neutralization, biotreatment) and reused. This stream can also be burned or disposed of by deepwell injection or biotreatment along with the waste dibasic acids. However, as more uses for these acids are discovered, the necessity for their disposal diminishes. The principal emissions of concern from these processes are related to nitric acid, either as the various oxides of nitrogen or as a very dilute solution of the acid itself. The fate of these waste streams varies widely, subject to the usually very complex environmental and regulatory situations at each individual manufacturing site. These issues are now a prime consideration, equal to economics, in the design of chemical processing systems in the petrochemical industry (122).

4.4. Other Routes to Adipic Acid. A number of adipic acid processes rely on feedstocks other than cyclohexane and phenol and produce neither K nor A as intermediates. Although these have been investigated, none has been employed at a commercial scale. A one-step air oxidation process, first researched by Halcon (123,124) and Gulf (125) in the 1960s, and developed by Asahi and others (126–130) in the 1970s, uses an acetic acid [64-19-7] solvent for the cyclohexane. High concentrations of soluble cobalt catalyst (60–300 ppm) are used, along with cyclohexanone or acetaldehyde [75-07-0] promoter. Yields to adipic acid of 70–75% are reported at cyclohexane conversions of 50–75%. Reaction temperature is a moderate 70–100°C. References to air oxidation processes have continued to appear through the 1990s (131–136).

It has been known since the early 1950s that butadiene reacts with CO to form aldehydes and ketones that could be treated further to give adipic acid (137). Processes for producing adipic acid from butadiene and carbon monoxide [630-08-0] have been explored since around 1970 by a number of companies, especially ARCO, Asahi, BASF, British Petroleum, Du Pont, Monsanto, and Shell. BASF has developed a process sufficiently advanced to consider commercialization (138). There are two main variations, one a carboalkoxylation and the other a hydrocarboxylation. These differ in whether an alcohol, such as methanol [67-56-1], is used to produce intermediate pentenoates (139), or water is used for the production of intermediate pentenoic acids (140). The former is a two-step process which uses high pressure, >31 MPa (306 atm), and moderate temperatures (100–150°C) (138–141). Butadiene, CO, and methanol react in the first step in the presence of cobalt carbonyl catalyst and pyridine [110-86-1] to produce methyl pentenoates. A similar second step, but at lower pressure and higher temperature with rhodium catalyst, produces dimethyl adipate [627-93-0]. This is then hydrolyzed to give adipic acid and methanol (141), which is recovered for recycle. Many variations to this basic process exist. Examples are ARCOs palladium/copper-catalyzed oxycarbonylation process (142–144), and Monsanto's palladium and quinone [106-51-4] process, which uses oxygen to reoxidize the by-product hydroquinone [123-31-9] to quinone (145).

Other processes explored, but not commercialized, include the direct nitric acid oxidation of cyclohexane to adipic acid (146–149), carbonylation of 1,4-butanediol [110-63-4] (150), and oxidation of cyclohexane with ozone [10028-15-5] (151–154) or hydrogen peroxide [7722-84-1] (155–156). Production of adipic acid as a by-product of biological reactions has been explored in recent years (157–162).

5. Storage, Handling, and Shipping

When dispersed as a dust, adipic acid is subject to normal dust explosion hazards. See Table 7 for ignition properties of such dust–air mixtures. The material is an irritant, especially upon contact with the mucous membranes. Thus protective goggles or face shields should be worn when handling the material. Prolonged contact with the skin should also be avoided. Eye wash fountains, showers, and washing facilities should be provided in work areas. However, *MSDS Sheet 400* (5) reports that no acute or chronic effects have been observed.

The material should be stored in corrosion-resistant containers, away from alkaline or strong oxidizing materials. In the event of a spill or leak, nonsparking equipment should be used, and dusty conditions should be avoided. Spills should be covered with soda ash, then flushed to drain with large amounts of water (5).

Adipic acid is shipped in quantities ranging from 22.7 kg (50-lb bags) to 90.9 t (200,000-lb hopper cars). Upon long standing, the solid material tends to cake, dependent on such factors as initial particle size and moisture content. Shipping data in the United States are "Adipic Acid," *DOT-ID NA 9077, DOT Hazard Class ORM-E*. It is regulated only in packages of 2.3 t (5000 lb) or more (hopper cars and pressure-differential cars and trucks) (163).

6. Economic Aspects

The continuing pursuit of a wide variety of alternate manufacturing processes indicates an effort by competitors to position themselves to take advantage of potential shifts in petrochemical feedstock prices. A large number of the reports concern the use of C_4 feedstocks, notably butadiene, although several major

Table 7. **Worldwide Adipic Acid Capacities**[a]

Company	Location	Capacity, 10^3 t/year
North America		
Du Pont	Orange, Tex	220
Du Pont	Victoria, Tex	380
Du Pont	Maitland, Canada	190
Inolex Chemical Co. (formerly Allied)	Hopewell, va	30
Solutia, Inc. (formerly Monsanto)	Pensacola, Fla	830
Western Europe		
Rhodia Alsachimie SAS	Chalampe, France	355
BASF Aktiengeschaft	Ludwigshafen, Germany	260
Bayer AG	Leverkusen, Germany	55
Radici Chimica SpA	Zeitz, Germany	80[b]
Radici Chimica SpA	Novara, Italy	60
DuPont (U.K.) Ltd	Wilton, U.K.	260
Asia		
CNP Liaoyanf Petrochemical Fiber Co.	Liaoyang, China	100
Pingdingshan Petrochemical Co.	Pingdingshan, China	37
Taiyuan Chemical Industry Group	Taiyuan, China	2
Asahi Chemical Industry Co., Ltd	Nobeoka, Japan	120
Sumitomo Chemical Co., Ltd	Niihama, Japan	2
Kofran Chemical Co., Ltd (100% owned by Rhodia)	Ulsan, Korea	65
DuPont Singapore Pte. Ltd	Pulau Sakra, Sing	114
Nan Ya Plastics Corp.	Mailiao City, Taiwan	40[c]
Other Regions		
Rhodia S.A.	Paulina, Brazil	67
Remaining		15

[a] See Ref. 167.
[b] Scheduled for startup in 2001.
[c] Scheduled for startup in 2002.

modifications to cyclohexane- or benzene-based processes are included. The continued buildup of capacity in nylon-6,6 intermediates, especially in the Far East, attests to the confidence in continued growth by the major participants. Although the nylon-6 [25038-54-4] market currently is larger in Europe, both markets will share in the growth, especially in the developing areas of the world. The emergence of new polymers for specialized applications may tend to limit growth in certain areas. For example, polypropylene may take a significant share of the lower cost carpet market. Specialized polyamides such as nylon-4,6 [24936-71-8] have now appeared, although this one consumes adipic acid. Adipic acid is a very large volume organic chemical. Worldwide production in 1999 reached 2.1×10^6t (4.6×10^9 lb) (30) and by 2004, it is estimated to reach 2.45×10^6t (Table 7). It is one of the top 50 (164) chemicals produced in the United States in terms of volume, with 1999 production estimated at 918,000 t (165). Although the current economic climate has temporarily slowed the adipic acid growth rate, when these conditions improve, growth in demand in the United States is expected to match the 1996–1999 growth of 2.8%/year (166). Table 7 provides individual capacities for U.S. manufacturers. Western European capacity is essentially equivalent to that in the United States at 685,000 t/year. Demand is highly cyclic (167), reflecting the automotive and housing markets especially.

Prices usually follow the variability in crude oil prices. In 1998, adipic acid for was responsible for >50% of U.S. cyclohexane. In 1999 ~84% of U.S. adipic acid production was used in nylon-6,6 (66% fiber and 18% resin), 7.4% in polyurethanes, 3.5% in plasticizers, 2.7% miscellaneous, and 2.44% net exported (166).

Du Pont plans to expand its North American capacity by 150,000 t as a result of growth in the nylon 6,6, polyureathane and plasticizer markets (168).

7. Specifications and Analysis

Because of the extreme sensitivity of polyamide synthesis to impurities in the ingredients (eg, for molecular-weight control, dye receptivity), adipic acid is one of the purest materials produced on a large scale. In addition to food-additive and polyamide specifications, other special requirements arise from the variety of other applications. Table 8 summarizes the more important specifications. Typical impurities include monobasic acids arising from the air oxidation step in synthesis, and lower dibasic acids and nitrogenous materials from the nitric acid oxidation step. Trace metals, water, color, and oils round out the usual specification lists.

Standard methods for analysis of food-grade adipic acid are described in the Food Chemicals Codex (see Refs. in Table 8). Classical methods are used for assay (titration), trace metals (As, heavy metals as Pb), and total ash. Water is determined by Karl–Fisher titration of a methanol solution of the acid. Determination of color in methanol solution (APHA, Hazen equivalent, max. 10), as well as iron and other metals, are also described elsewhere (170). Other analyses frequently are required for resin-grade acid. For example, total nitrogen content is determined by chemiluminescence. Hydrolyzable nitrogen (NH_3, amides, nitriles, etc) is determined by distillation of ammonia from an alkaline solution. Reducible nitrogen (nitrates and nitroorganics) may then be determined by adding DeVarda's alloy and continuing the distillation. Hydrocarbon oil contaminants may be determined by gas chromatographic analysis.

Table 8. **Quality Specifications**

	Application		
Parameter	Food grade	Other	Page reference[a]
melting range	151.5–154.0°C		519
assay	99.6% min		11
water	0.2% max		552
residue on ignition	20.0 ppm max		11
arsenic (as As)	3.0 ppm max		464
heavy metals (as Pb)	10.0 ppm max		11,513
iron (as Fe)		2.0 ppm	
ICV color		5.0 max	
caproic acid		10.0 ppm	
succinic acid		50.0 ppm	
nitrogen		3 ppm	
hydrocarbon oil		10 ppm	

[a] Refers to pages in Ref. 169.

Monobasic acids are determined by gas chromatographic analysis of the free acids; dibasic acids usually are derivatized by one of several methods prior to chromatographing (171,172). Methyl esters are prepared by treatment of the sample with BF_3–methanol, H_2SO_4–methanol, or tetramethylammonium hydroxide. Gas chromatographic analysis of silylation products also has been used extensively. Liquid chromatographic analysis of free acids or of derivatives also has been used (173). More sophisticated high-performance liquid chromatography (hplc) methods have been developed recently to meet the needs for trace analyses in the environment, in biological fluids, and other sources (174,175). Mass spectral identification of both dibasic and monobasic acids usually is done on gas chromatographically resolved derivatives.

8. Health and Safety Factors

Adipic acid is relatively nontoxic; no OSHA PEL or NIOSH REL have been established for the material. Airborne exposure should be limited to 10 mg/m^3 (total dust), the ACGIH TLV-TWA for an organic nuisance dust (5). Toxicity in laboratory animals based on exposure to adipic acid has been reported (176).

eye, rabbit (eye irritant)	20 mg/24 h (SEV)
oral, rat	LDL_o: 3600 mg/kg
intraperitoneal, rat	LD_{50}: 275 mg/kg
oral, mouse	LD_{50}: 1900 mg/kg
intraperitoneal, mouse	LD_{50}: 275 mg/kg
intravenous, mouse	LD_{50}: 680 mg/kg

Adipic acid is excreted essentially unmetabolized in human urine, based on tests with a series of dicarboxylic acids (177). However, adipic acid may be produced via liver metabolism of longer chain diacids, as observed in a recent study with rats (178). The acid has achieved "generally recognized as safe" (GRAS) status from the U.S. Food and Drug Administration for use as a direct ingredient in food for such uses as acidulant, leavening agent, or pH control agent (179). The sodium salt [23311-84-4] has not achieved GRAS status. Maximum permissible usage of the acid in foods was studied with respect to toxicity and teratological and mutagenicity effects (180). No mutagenic or teratological activity was observed (181). Recommended maximum concentration in water reservoirs is 2 mg/L (5).

Adipic acid is an irritant to the mucous membranes. In case of contact with the eyes, they should be flushed with water. It emits acrid smoke and fumes on heating to decomposition. It can react with oxidizing materials, and the dust can explode in admixture with air (see Table 3). Fires may be extinguished with water, CO_2, foam, or dry chemicals.

Airborne particulate matter (182) and aerosol (183) samples from around the world have been found to contain a variety of organic monocarboxylic and dicarboxylic acids, including adipic acid. Traces of the acid found in southern California air were related both to automobile exhaust emission (184) and, indirectly, to cyclohexene as a secondary aerosol precursor (via ozonolysis) (185). Dibasic acids (eg, succinic acid) have been found even in such unlikely sources as the Murchison meteorite (186). Public health standards for adipic acid contamination of reservoir waters were evaluated with respect to toxicity, odor, taste, transparency, foam, and other criteria (187). Biodegradability of adipic acid solutions was also evaluated with respect to BOD/theoretical oxygen demand ratio, rate, lag time, and other factors (188).

8.1. N_2O Abatement Technology. During the 1990s, the adipic acid industry updated its offgas control technology (189). These process modifications were based on the disclosure that nitrous oxide (N_2O), a gas-phase byproduct of adipic acid manufacture, is the major source of strasospheric nitric oxide (NO) and thus has a global warming potential many times more than CO_2 (190). At 0.15–0.3 tons of N_2O per ton of adipic acid, these emissions were cited as the source of recent measured increases in atmospheric levels.

Reducing flame burner technology represents the high-temperature option to N_2O abatement (1200–1500°C). Here, natural gas reduces N_2O to nitrogen, CO_2 and water. Staged injection of fuel and air abates the N_2O and organics present in the vent gas. Flue gas recycle and/or a convection section provide additional residence time. With these two features, N_2O destruction efficiencies >99% are obtained without an increase in NO_x emissions.

Other options commercially practiced depend on the use of a catalyst. An intermediate temperature process (1000–1500°C) developed by DuPont and Rhone Poulenc is based on the catalytic reaction of N_2O to NO. This product is then followed by an air oxidation forming NO_2 which is subsequently absorbed in water. The final product, nitric acid, is then recycled back to the adipic acid process. The low-temperature catalytic process (400–700°C) is designed to destroy N_2O without the formation of NO_x. Such facilities can be installed with or without heat recovery depending on the value of steam. Since startup in the mid-1990s, they have been reported to achieve N_2O abatement efficiencies of 98% or better (191).

Table 9 lists the major adipic acid manufacturers and the N_2O Abatement Technology practiced at their respective site.

Table 9. **N_2O Abatement Technology Practiced at Major Adipic Acid Production Sites**[a]

Site	Technology	Start-up Date
Dupont Singapore	Thermal	1994
Dupont Orange, Tex	Catalytic	1996
Dupont Maitland, Ontario	Catalytic	1997
Dupont Victoria, Tex	Catalytic	1997
Dupont Wilton, U.K.	Thermal	1998
Asahi	Thermal	1999
BASF	Catalytic	1997
Bayer	Thermal	1993
Rhodia	Conversion to HNO_3	1998
Solutia	Thermal	1972

[a] See Ref. 189.

9. Uses

About 86% of U.S. adipic acid production is used captively by the producer, almost totally in the manufacture of nylon-6,6 (192). The remaining 14% is sold in the merchant market for a large number of applications. These have been developed as a result of the large scale availability of this synthetic petrochemical commodity. Prices for 1960–1989 for standard resin-grade material have paralled raw material and energy costs (petroleum and natural gas) growing at a rate of 1.7%/year. In the early 1990s, the price leveled off around 1.37 $/kg. By the late 1990s, it jumped to 1.53 $/kg (193).

In 1999, 66% of U.S. demand for adipic acid was for nylon-6,6 fiber, while 11% was used in nyon-6,6 resins (166). In Western Europe only about 40% was for polyamide. Nylon-6,6 resins were distributed between injection molding (90%) for such applications as automotive and electrical parts.

Less than 5% of the U.S. polyurethanes market in 1999 was derived from the condensation product of polyisocyanates with low molecular weight polyadipates having hydroxyl end groups (166). In 1999 this amounted to 68,000 t, or 84% of total adipic acid consumption. The percentage in Western Europe was closer to 20%. About 90% of these adipic acid containing polyurethanes are used in flexible or semirigid foams and elastomers, with the remainder used in adhesives, coatings, and spandex fibers.

About 4% of U.S. adipic acid consumed in 1999 was used in two basic types of adipic ester based plasticizers (194). Simple adipate esters prepared from C_8–C_{13} alcohols are used especially as PVC plasticizers (qv). For special applications requiring low volatility or extraction resistance, polyester derivatives of diols or polyols are preferred.

1,6-Hexanediamine, the second ingredient in the production of Nylon-6,6 polyamide, is prepared by hydrogenation of adiponitrile [111-69-3]. For many years, the nitrile was produced from adipic acid by dehydration of the ammonium salt (195); however, this process is no longer used in the United States or Western Europe. New processes based on propylene and butadiene have supplanted this technology in the United States. For several years, Du Pont operated a process based on the chlorination and cyanation of butadiene, but this was shut down in 1983 (196,197). Du Pont produces adiponitrile at two large U.S. plants and one French joint venture by direct nickel(0)-catalyzed homogeneous hydrocyanation of butadiene (198). Monsanto/Solutia and Asahi developed and practiced the electrolytic coupling of acrylonitrile process, used in the United States, Western Europe, and Japan (199,200).

About 2.4% of U.S. consumption in 1999 was distributed among several other applications, amounting to several thousand tons each (193). Wet-strength resins based on polyamide–epichlorohydrin products consumed about 16,000–18,000 t in 1998. Unsaturated polyester resins (4000 t in 1998) are used in surface coatings, flexible alkyd resins (qv), coil coatings, and other coatings because of their curing properties. Adipic acid also is used as a food acidulant in jams, jellies, and gelatins. Although it has only 2% of the acidulant market, 3200 t were used for this purpose in 1989 (201). The synthetic lubricant market consumed about 7000 t as the C_{8-13} adipate esters in 1998, for gas turbines, compressors, and military jet engines. An environmentally significant use of the acid, and especially its dibasic acid by-products, is as a buffer in the scrubbing operation of power plant flue gas desulfurization (202–206). Adipoyl chloride is occasionally used as a softening agent for leather.

BIBLIOGRAPHY

"Adipic Acid" under "Acids, Dicarboxylic" in *ECT* 1st ed., Vol. 1, pp. 153–154, by P. F. Bruins, Polytechnic Institute of Brooklyn; "Adipic Acid" in *ECT* 2nd ed., Vol. 1, pp. 405–421, by W. L. Standish and S. V. Abramo, E. I. du Pont Nemours & Co., Inc.; in *ECT* 3rd ed., Vol. 1, pp. 510–531, by D. C. Danly and C. R. Campbell, Monsanto Chemical Intermediates Company; in *ECT* 4th ed., Vol. 1. pp. 466–493, by Darwin D. Davis and Donald R. Kemp, E.I. du Pont de Nemours and Co., Inc.; "Adipic Acid" in *ECT* (online), posting date: December 4, 2000, by Darwin D. Davis and Donald R. Kemp, E. I. Du Pont de Nemours and Co.

CITED PUBLICATIONS

1. E. Bolton, *Ind. Eng. Chem.* **34**, 53 (1942).
2. H. Serwy, *Bull. Soc. Chim. Belg.* **42**, 483 (1933).
3. Armour Research Foundation, *Anal. Chem.* **20**, 385 (1948).
4. S. Khetarpal, L. Krishan, and H. Bhatnager, *Ind. J. Chem., Sect. A.* **19A**, 516 (1986).
5. P. Igoe, D. Wilson, and W. Silverman, *Material Safety Data Sheet No. 400* in *Genum's Reference Collection*, Genum Publishing Corp., Schenectady, N.Y., 1989.
6. A. Granovskaya, *Zh. Fiz. Khim.* **21**, 967 (1947).
7. F. Kraft and H. Noerdlinger, *Ber. Dtsch. Chem. Ges.* **22**, 818 (1889).
8. A. Van Dooren and B. Mueller, *Thermochim. Acta* **54**(1–2), 115 (1982).
9. P. E. Verkade, H. Hartman, and J. Coops, *Recl. Trav. Chim. Pays-Bas* **45**, 380 (1926).
10. I. Contineanu, E. Corlateanu, J. Herscovici, and I. Dumitri, *Rev. Chim. (Bucharest)* **31**, 763 (1980).
11. S. Kahnyakina and G. Puchkovskaya, *Zh. Prikl. Spektrosk.* **34**, 885 (1981).
12. Y. Morechal, *Can. J. Chem.* **63**, 1684 (1985).
13. K. Urano, K. Kawamoto, and K. Hayoshi, *Yosui To Haisui* **23**(2), 196 (1981).
14. A. Babinkov and co-workers, *Termodin. Organ. Sordin. Gor'*kii **1979**(8), 28 (1979).
15. A. Apelblat, *J. Chem. Thermodyn.* **18**, 351 (1986).
16. I. Jones and R. Soper, *J. Chem. Soc.* **1936**, 135 (1936).
17. J. Burgot, *Talanta* **25**, 233 (1978).
18. A. Apelblat and E. Manzurola, *J. Chem. Thermodyn.* **19**, 317 (1987).
19. *Adipic Acid, Product Bulletin E-99079-1*, E. I. du Pont de Nemours & Co., Inc., 1989.
20. C. S. Marvel and J. C. Richards, *Anal. Chem.* **21**, 1480 (1949).
21. K. Chow, J. Go, M. Mehdizadeh, and D. Grant, *Int. J. Pharm.* **20**(1–2), 3 (1984).
22. L. Hus, C. Chang, J. Beddow, and A. Vetter, *Proc. Tech. Prog. Int. Powder and Bulk Solids Handling and Processing, Atlanta, Georgia, May 24–26, 1983*, Books Demand UMI, Ann Arbor, Mich., 1983, pp. 52–66.
23. O. Georgescu, S. Ivascon, and M. Apostolescu, *Rev. Chim. (Bucharest)* **36**, 839 (1985).
24. *Corrosion Data Survey, Metals Section*, 5th and 6th ed., National Association of Corrosion Engineers, Houston, Tex., 1974 and 1985, pp. 6 and 4.
25. G. Lunn, *J. Hazard. Mater.* **17**(2), 207 (1988).
26. E. Scholl and co-workers, *Inst. Explos. Sprengtech. Bergbau-Versuchstrecke FRG, STF-Rep.* **1979**(2), 99 (1979).

27. D. Felstead, R. Rogers, and D. Young, *Conf. Ser.—Inst. Phys. (Electrostatics), ICI, United Kingdom* **66**, 105 (1983).
28. U.S. Pat. 4,375,552 (Mar. 1, 1983), V. Kuceski (to C. P. Hall Co.).
29. M. Seko, A. Yomiyama, and T. Isoya, *Chem. Econ. Eng. Rev.* **11**(9), 48 (1979).
30. R. T. Gerry, "Adipic Acid" in *Chemical Economics Handbook, Marketing Research Report*, SRI International, Menlo Park, Calif., 1987, p. 608.5000A, p. 4.
31. M. I. Kohan, *Nylon Plastics*, John Wiley & Sons, Inc., New York, 1973, pp. 14–73.
32. Ger. Offen. 3,510,876 (Oct. 2, 1986), W. Hoelderich and co-workers (to Badische Anilinund Soda-Fabrik A. G.).
33. Jpn. Kokai Tokkyo Koho 6105,036 (Jan. 10, 1986), K. Tsukada, N. Fukuoka, and I. Kinoshita (to Kao Corp.).
34. Jpn. Kokai Tokkyo Koho 80 04,090 (Jan. 29, 1980), J. Kanetaka and S. Mori (to Mitsubishi Petrochemical Co.).
35. Fr. Pat. 1,509,288 (Jan. 12, 1968), P. Volpe and W. Humphrey (to Celanese Corp.).
36. W. Hentzchel and J. Wislicenus, *Justus Leibigs Ann. Chem.* **275**, 312 (1983).
37. G. Vavon and A. Apchie, *Bull. Soc. Chim. Fr.* **43**, 667 (1928).
38. J. Dullinga, N. Nibbering, and A. Boerboom, *J. Chem. Soc. Perkin Trans.* **2**, 1065 (1984).
39. J. Sheehan, R. O'Neill, and M. White, *J. Am. Chem. Soc.* **72**, 3376 (1950).
40. P. Morgan, *J. Chem. Educ.* **36**(4), 182 (1959).
41. Ger. Offen. 3,235,938 (Apr. 21, 1983), K. Kimura and T. Isoya (to Asahi Chemical Industries, Ltd.).
42. I. V. Berezin, E. T. Denisov, and N. M. Emanuel, *The Oxidation of Cyclohexane*, Pergamon Press, Oxford, England, 1965.
43. S. A. Miller, *Chem. Process Eng.*, **1969**, 63 (June 1969).
44. Tamarapu Sridhar, *Mass Transfer in Cyclohexane Oxidation*, Ph.D. Thesis, Department of Chemical Engineering, Monash Univ., Australia, 1978.
45. V. D. Luedeke, "Adipic Acid", in *Encyclopedia of Chemical Process and Design*, J. McKetta and W. Cunningham, eds. Vol. 2, Marcel Dekker, Inc., New York, 1977, pp. 128–146.
46. A. K. Suresh, T. Shidhar, and O. E. Potter, *AIChE J.* **34** (1), 55 (1988).
47. Y. C. Yen and S. Y. Wu, *Nylon 6,6, PEP Report 54B*, SRI International, Menlo Park, Calif., 1987.
48. U.S. Pat. 4,238,415 (Dec. 9, 1980), W. O. Bryan (to Stamicarbon N. V.).
49. L. Bateman, H. Hughes, and A. L. Morris, *Faraday Discuss. Chem. Soc.* **1953**(14), 190 (1953).
50. D. G. Hendry and co-workers, *J. Org. Chem.* **41**, 2 (1976).
51. U.S. Pat. 3,530,185 (Sept. 22, 1970), K. Pugi (to E. I. du Pont de Nemours & Co., Inc.).
52. *Hydrocarbon Process.* **48**, 163 (1969).
53. U.S. Pat. 4,163,027 (July 31, 1979), P. Magnussen, G. Herrman, and E. Frommer (to Badische Anilin- und Soda-Fabrik A. G.).
54. Ger. Offen. 3,328,771 (Feb. 28, 1985), Stoessel and co-workers (to Badische Anilin- und Soda-Fabrik A. G.).
55. U.S. Pat. 4,704,476 (Nov. 3, 1987), J. Hartig, G. Herrman, and E. Lucas (to Badische Anilin- und Soda-Fabrik A. G.).
56. U.S. Pat. 3,957,876 (May 18, 1976), M. Rapoport and J. O. White (to E. I. du Pont de Nemours & Co., Inc.).
57. U.S. Pat. 3,987,100 (Oct. 19, 1976), W. J. Barnette, D. L. Schmitt, and J. O. White (to E. I. du Pont de Nemours Co., Inc.).
58. U.S. Pat. 4,465,861 (Aug. 14, 1984), J. Hermolin (to E. I. du Pont de Nemours & Co., Inc.).

59. U.S. Pat. 3,925,316 (Dec. 9, 1975), J. C. Brunie, N. Creene, and F. Maurel (to Rhône-Poulenc S. A.).
60. Adapted from L. L. van Dierendonck and J. A. de Leeuw den Bouter, *PT/Procestechniek* **39**(3), 44–48 (1984).
61. U.S. Pat. 3,923,895 (Dec. 2, 1975), M. Costantini, N. Creene, M. Jouffret, and J. Nouvel (to Rhône-Poulenc S. A.).
62. U.S. Pat. 3,927,105 (Dec. 16, 1975), J. C. Brunie and N. Creene (to Rhône-Poulenc S. A.).
63. U.S. Pat. 4,326,085 (Apr. 20, 1982), M. De Cooker (to Stamicarbon N. V.).
64. Eur. Pat. 092,867 (Nov. 2, 1983), J. G. Housmans and co-workers (to Stamicarbon N. V.).
65. U.S. Pat. 3,932,513 (Jan. 13, 1976), J. L. Russell (to Halcon International, Inc.).
66. U.S. Pat. 3,796,761 (Aug. 18, 1971), Marcell and co-workers (to Halcon International, Inc.).
67. Brit. Pat. 1,590,958 (June 10, 1981), J. F. Risebury (to Imperial Chemical Industries, Ltd.).
68. J. Alagy and co-workers, *Hydrocarbon Process.* **47**(12), 131 (1968).
69. H. Van Landeghem, *Ind. Eng. Chem. Process. Des. Dev.* **13**, 317 (1974).
70. U.S. Pat. 3,895,067 (Jan. 12, 1973), G. H. Mock and co-workers (to Monsanto Co.).
71. E. F. J. Duynstee and co-workers, *Recl. Trav. Chim. Pays-Bas* **89**, 769 (1970).
72. Ref. (50), pp. 1–5.
73. C. T. Chi and J. H. Lester, *Presentation to MCA Waste Minimization Workshop*, New Orleans, La., Nov. 11–13, 1987.
74. U.S. Pat. 3,260,743 (July 12, 1966), W. B. Hogeman (to Monsanto Co.); U.S. Pat. 3,365,490 (Jan. 23, 1968), W. J. Arthur and L. S. Scott (to E. I. du Pont de Nemours & Co., Inc.); U.S. Pat. 3,969,465 (July 13, 1976), J. K. Brunner (to Badische Anilin- und Soda-Fabrik A. G.); U.S. Pat. 4,105,856 (Aug. 8, 1978), C. A. Newton (to El Paso Products, Co.); K. J. Mehta and co-workers, *Chem. Eng. World* **24**(30), 63 (1989).
75. U.S. Pat. 3,993,691 (Nov. 23, 1976), J. K. Brunner (to Badische Anilin- und Soda-Fabrik A. G.); U.S. Pat. 4,166,056 (Aug. 28, 1979), K. P. Satterly and F. E. Livingston (to Witco Chemical Corp.); U.S. Pat. 4,233,408 (Nov. 11, 1980), K. P. Satterly and F. E. Livingston (to Witco Chemical Corp.).
76. Jpn. Pat. 82-041456-B (Sept. 3, 1982), (to Sumitomo Chemical Co.).
77. B. Harris and B. Tichenor, *Proceedings of 74th Annual Meeting*, Air Pollution Control Association, Pittsburgh, Pa., 1981, Vol. 3, paper 81–41.5.
78. Ref. 43, p. 69.
79. U.S. Pat. 3,243,449 (Mar. 29, 1966), C. N. Winnick (to Halcon International, Inc.).
80. *Eur. Chem. News* **15**, 22 (May 2, 1969).
81. *Eur. Chem. News* **11**, 32 (June 9, 1967).
82. U.S. Pat. 3,287,423 (Nov. 22, 1966), J. Steeman and J. von den Hoff (to Stamicarbon, N. V.).
83. A. Uriarte, M. Rodkin, M. Gross, A. Kharitonov, and G. Panov, *Studies in surface Science and Catalysis* **110**, 857 (1997).
84. G. Panov, G. I. G. Sheveleva, G. A. Kharitonov, A. V. Romannikov, and L. Vostrikova, *Appl. Catal.* **82**(1), 31–6 (1992).
85. J. Oppenheim, *16th North American Catalysis Society Meeting*, Boston, Mass. June 2, 1999.
86. C. Buechler, J. Ebner, M. Gross, W. McGhee, J. Morries, E. Sall, and A. Uriarte, PCT Int. Appl. (1998).
87. I. Dodgson, K. Griffin, G. Barberis, F. Pignataro, and G. Tauszik, *Chem. Ind.* (London) **(24)**, 830–833 (1989).

88. H. Naumann, H. Schaefer, H. Oberender, D. Timm, H. Meye, and G. Pohl, *Chem. Tech.* (Leipzig) **29(1)**, 38 (1977) .
89. U.S. Pat. 2,794,056 (May 28, 1957), L. O. Winstrom (to Allied Chemical Co.).
90. Brit. Pat. 979,268 (Jan. 1, 1965), J. G. Mather and F. G. Webster (to Imperial Chemical Industries, Ltd.).
91. U.S. Pat. 3,987,100, (1976) Barnette, (to E.I. du Pont de Nemours & Co., Inc.).
92. *Jpn. Chem. Week*, 5 (Oct. 29, 1987).
93. *Comline Chemicals and Materials*, Comline News Service, Tokyo 107, Japan, Feb. 22, 1988.
94. Jpn. Pat. 62-205037 (1987) H. Nagahara, M. Konishi (to Asahi Chem. Ind. Co. Ltd).
95. Jpn. Pat. 04-41442 (1992) S. Kodama, K. Nakagawa (to Asahi Chem. Ind. Co. Ltd).
96. Jpn. Pat. 04-41441 (1992) S. Kodama, K. Nakagawa (to Asahi Chem. Ind. Co. Ltd).
97. Jpn. Pat. 01-192.717 (1989) H. Ishida, K. Nakagawa (to Asahi Chem. Ind. Co. Ltd).
98. Jpn. Pat. 04-41448 (1993) S. Kodama, K. Nakagawa (to Asahi Chem. Ind. Co. Ltd).
99. U.S. Pat. 3,987,115 (Oct. 19, 1976), J. G. Zajacek and F. J. Hilbert (to Atlantic Richfield Co.).
100. U.S. Pat. 4,080,387 (Mar. 21, 1978), J. C. Jubin, I. E. Katz, and R. G. Tave (to Atlantic Richfield Co.).
101. T. T. Shih and W. J. Klingebiel, paper presented to *The First Shanghai International Symposium on Technology of Petroleum and Petrochemical Industry*, May 16–20, 1989, Shanghai, China.
102. U.S. Pat. 2,557,282 (1951), C. Hamblett and A. Mac Alevy (to E. I. du Pont de Nemours & Co., Inc.).
103. U.S. Pat. 2,703,331 (1953), M. Goldbeck and F. Johnson (to E. I. du Pont de Nemours & Co., Inc.).
104. H. Godt and J. Quinn, *J. Am. Chem. Soc.* **78**, 1461 (1956).
105. I. Lubyanitski, R. Minati, and M. Furman, *Russ. J. Phys. Chem. (Engl. trans.)*, **32**, 294 (1962).
106. I. Lubyanitski, *Zh. Obshch. Khim.* **36**, 343 (1962).
107. I. Lubyanitski, *Zh. Prikl. Khim. (Leningrad)* **36**, 819 (1963).
108. D. van Asselt and W. van Krevelen, *Chem. Eng. Sci.* **18**, 471 (1963).
109. D. van Asselt and W. van Krevelen, *Recl. Trav. Chim. Pays-Bas* **82**, 51, 429, 438 (1963).
110. U.S. Pat. 3,758,564 (Sept. 11, 1973), D. Davis (to E. I. du Pont de Nemours & Co., Inc.).
111. U.S. Pat. 3,564,051 (1971), E. Haarer and G. Wenner (to Badische Anilin- und Soda-Fabrik A. G.).
112. Brit. Pat. 1,092,603 (1969), G. Riegelbauer, A. Wegerich, A. Kuerzinger, and E. Haarer (to Badische Anilin- und Soda-Fabrik A. G.).
113. T. Hearfield, *Chem. Eng. (London)* **1980** (361), 625 (1980).
114. U.S. Pat. 3,359,308 (Dec. 19, 1967), O. Sampson (to E. I. du Pont de Nemours & Co., Inc.).
115. Eur. Pat. Appl. 122-249A1 (Oct. 17, 1984), C. Hsu and D. Laird (to Monsanto Co.).
116. U.S. Pat. 4,254,283 (Mar. 3, 1981), G. Mock (to Monsanto Co.).
117. Ger. Offen. 3,002,256 (July 30, 1981), W. Rebafka, G. Heilen, and W. Klink (to Badische Anilin- und Soda-Fabrik A. G.).
118. U.S. Pat. 4,014,903 (Mar. 29, 1977), W. Moore (to Allied Chemical Corp.).
119. Brit. Pat. 1,480,480 (July 20, 1977), A. Bowman (to Imperial Chemical Industries, Ltd.).
120. U.S. Pat. 4,227,021 (1980), O. Grosskinsky and co-workers (to Badische Anilin- und Soda-Fabrik A. G.).

121. Jpn. Kokai Tokkyo Koho, JP61-257940 (Nov. 15, 1986), T. Sakamoto, H. Suga, and T. Sakasegawa (to Asahi Chemical Industries Co., Ltd.).
122. S. Fathi-Afshar and J. Yang, *Chem. Eng. Sci.* **40**, 781 (1985).
123. Brit. Pat. 956,779 (Apr. 29, 1964) (to Halcon International, Inc.).
124. Brit. Pat. 956,780 (Apr. 29, 1964) (to Halcon International, Inc.).
125. U.S. Pat. 3,231,608 (Jan. 22, 1966), J. Kollar (to Gulf Research and Development Corp.).
126. Jpn. Pat. 45-16444 (June 8, 1970), G. Inoue and co-workers (to Asahi Chemical Industries, Ltd.).
127. Jpn. Pat. 50-116415 (Sept. 11, 1975), S. Furuhashi (to Asahi Chemical Industries, Ltd.).
128. Jpn. Pat. 51-29427 (Mar. 12, 1976), M. Nishino and co-workers (to Toray Industries).
129. U.S. Pat. 4,032,569 (June 28, 1977), A. Onopchenko and co-workers (to Gulf Research and Development Corp.).
130. K. Tanaka, *Chem. Technol.* **4**(9), 555 (1974).
131. Jpn. Pat. 58-021642 (Feb. 8, 1983), M. Suematsu and K. Nakaoka (to Toray Industries).
132. H. Shen and H. Weng, *Ind. Eng. Chem. Res.* **27**, 2254 (1988).
133. E. Sorribes, J. Navarro, A. Romero, and L. Jodra, *Rev. R. Acad. Cienc. Exactas, Fis. Nat. Madrid* **81**(1), 233 (1987).
134. D. Rao and R. Tirukkoyilur, *Ind. Eng. Chem. Process Des. Dev.* **25**(1), 299 (1986).
135. U.S. Pat. Appl. No.PCT/US97/10830 (2002) Aldrich, M. Sharon; Decoster, C. David; Vassiliou, Eustathious; Dassel, W. Mark; Rostami, M. Ader (RPC Inc., USA).
136. C. Xu, J. Oyloe; Richardson, and E. David, *Single-step synthesis of adipic acid by catalytic oxidation of cyclohexane in air*. 218th ACS National Meeting, New Orleans, August 22–26, 1999.
137. D. Forster and J. F. Roth, eds., *Homogeneous Catalysis II* (Advances in Chemistry Series 132), American Chemical Society, Washington, D.C. 1974; H. Adkins and co-workers, *J. Org. Chem.* **17**,980–987 (1952); U.S. Pat. 2,729,651 (Jan. 3, 1956), W. Reppe (to Badische Anilin-und Soda-Fabrik A. G.); USSR Pat. 198,324 (June 28, 1967), N. S. Imyanitov and co-workers; U.S. Pat. 3,509,209 (Apr. 28, 1970), D. M. Fenton (to Union Oil of California); U.S. Pat. 3,876,695 (Apr. 8, 1975), N. Von Kutepow (to Badische Anilin- und Soda-Fabrik A. G.).
138. *Chem. Eng. News*, 14 (May 25, 1987).
139. S. Hosaka and co-workers, *Tetrahedron* **27**, 3821 (1971); W. E. Billeys and co-workers, *Chem. Commun.* 1067 (1971).
140. Ger. Offen. 2,630,086 (Jan. 12, 1978), H. Schneider and co-workers (to Badische Anilin-und Soda-Fabrik A. G.); U.S. Pat. 4,316,047 (Feb. 16, 1982), R. Kummer and co-workers (to Badische Anilin- und Soda-Fabrik, A. G.).
141. U.S. Pat. 4,169,956 (Oct. 2, 1979), R. Kummer and co-workers (to Badische Anilin-und Soda-Fabrik A. G.); U.S. Pat. 4,171,451 (Oct. 16, 1979), R. Kummer and co-workers (to Badische Anilin- und Soda-Fabrik A. G.); U.S. Pat. 4,360,695 (Nov. 23, 1982), P. Magnussen and co-workers (to Badische Anilin- und Soda-Fabrik A. G.).
142. U.S. Pat. 4,171,450 (Oct. 16, 1979), H. S. Kesling, Jr., and co-workers (to Atlantic Richfield Co.).
143. U.S. Pat. 4,166,913 (Sept. 4, 1979), H. S. Kesling, Jr., and co-workers (to Atlantic Richfield Co.).
144. U.S. Pat. 4,195,184 (Mar. 25, 1980), H. S. Kesling, Jr., and co-workers (to Atlantic Richfield Co.).
145. U.S. Pat. 4,575,562 (Mar. 11, 1986), C. K. Hsu and co-workers (to Monsanto Co.).
146. U.S. Pat. 3,306,932 (Feb. 28, 1967), D. D. Davis (to E. I. du Pont de Nemours & Co., Inc.).

147. U.S. Pat. 3,654,355 (Nov. 19, 1969), W. H. Mueller and co-workers (to Monsanto Co.).
148. U.S. Pat. 3,636,100 (Jan. 18, 1972), W. H. Mueller and co-workers (to Monsanto Co.).
149. U.S. Pat. 3,636,101 (Jan. 18, 1972), T. F. Doumani (to Union Oil Co. of California).
150. Brit. Pat. 1,278,353 (June 21, 1972), H. Arnold and co-workers (to Monsanto Co.).
151. Brit. Pat. 1,239,224 (July 14, 1971), C. Gardner (to Imperial Chemical Industries, Ltd.).
152. U.S. Pat. 3,607,926 (Sept. 21, 1971), R. D. Smetana (to Texaco, Inc.).
153. Fr. Add. 96,191 (May 19, 1972), C. Gardner (to Imperial Chemical Industries, Ltd.); Jpn. Pat. 56-5374 (Feb. 4, 1981), S. Miyazaki (to Agency of Industrial Sciences and Technology).
154. Brit. Pat. 1,361,749 (July 31, 1974), S. D. Razumovskii and co-workers (to USSR).
155. Fr. Pat. 2,140,088 (Dec. 1, 1973), O. Grosskinsky, G. Herrmann, and R. Kaiser (to Badische Anilin- und Soda-Fabrik A. G.).
156. Jpn. Pat. 54-135720 (Oct. 22, 1979), Y. Ishii (to Yasutaka).
157. U.S. Pat. 3,912,586 (Oct. 14, 1975), H. Kaneyuki and co-workers (to Mitsui Petrochemical Industries).
158. Jpn. Pat. 57-129694 (Aug. 11, 1982), H. Nakano and co-workers (to Dainippon Ink and Chemicals).
159. U.S. Pat. 4,400,468 (Aug. 23, 1983), M. Faber (to Hydrocarbon Research).
160. Jpn. Pat. 58-149687 (Sept. 6, 1983), T. Minoda, T. Oomori, and H. Narishima (to Nissan Chemical Industries).
161. Eur. Pat. 74,169 (Mar. 16, 1983), P. C. Maxwell (to Celanese Corp.).
162. *Chem. Econ. Eng. Rev.* 35 (Jan./Feb. 1986).
163. Hazardous Materials Table, *Code of Federal Regulations 49CFR 172.101* (revised Nov. 1989).
164. *Chem. Eng. News* **67**(15), 12 (1989).
165. Ref. 30, p. 13.
166. Ref. 30, p. 16.
167. Ref. 30, p. 12, 31, 33, 37, 41, 43.
168. *Chem. Week*, **160**(12), 21 (1 Apr, 1998).
169. *Food Chemicals Codex*, 3rd ed., National Academy of Sciences, National Academy Press, Washington, D.C., 1981.
170. R. Keller in F. Snell and C. Hilton, eds., *Encyclopedia of Industrial Chemicals Analysis*, Vol. 4, Wiley-Interscience, New York, 1967, pp. 408–423.
171. "Chromatography" in R. Freis and J. Lawrence, eds., *Derivatization in Analytical Chemistry*, Vol. 1, Plenum Press, New York, 1981.
172. J. Drozd, *Chemical Derivatization in Gas Chromatography*, Elsevier, Amsterdam, The Netherlands, 1980.
173. R. Schwarzenbach, *J. Chromatogr.* **251**, 339 (1982).
174. M. Gennaro and co-workers, *Ann. Chim. (Rome)* **78**(3–4), 137 (1988).
175. G. Lippe and co-workers, *Clin. Biochem.* **20**(4), 275 (1987).
176. N. Sax, *Dangerous Properties of Industrial Materials*, Van-Nostrand Reinhold Co., New York, 1984, p. 141.
177. J. Svendsen, L. Sydnes, and J. Whist, *Spectrosc. Inst. J.* **3**(4–5), 380 (1984).
178. J. Vamecq, J. Draye, and J. Brison, *Am. J. Physiol.* **256**(4, pt. 1), G680–688 (1989).
179. *Federal Register* **47**(123) (June 25, 1982).
180. Y. Hirayama, *Shokuhin Eisei Kenkyu* **33**, 852 (1983).
181. H. Shimuzu and co-workers, *Sangyo Igaku* **27**, 400–419 (1985); see also D. Guest and co-workers, eds., *Patty*'s Industrial Hygiene and Toxicology, 3rd ed., Vol. 2C, Wiley-Interscience, New York, 1982, p. 4945.
182. Y. Yokouchi and Y. Ambi, *Atmos. Environ.* **20**, 1727 (1986).

183. R. Ferek, A. Lazrus, P. Haagenson, and J. Winchester, *Environ. Sci. Technol.* **17**, 315 (1983).
184. K. Kawamura and I. Kaplan, *Environ. Sci. Technol.* **21**, 105 (1987).
185. B. Appel and co-workers, *Environ. Sci. Technol.* **13**, 98 (1979).
186. E. Pelzer, J. Bada, G. Schlesinger, and S. Miller, *Adv. Space. Res.* **4**(12), 69 (1984).
187. Y. Novikov and co-workers, *Gig. Sanit.* **1983**(9), 72 (1983).
188. K. Urano and Z. Kato, *J. Hazard Mater.* **13**(2), 147 (1986).
189. R. Reimer, C. Slaten, M. Seapan, T. Koch, and V. Triner, *Proceedings of the International Symposium, 2nd, Noordwijkerhout, Netherlands, September 8–10, 1999 (2000), Meeting Date 1999, 347–358.*
190. M. Thiemens, and W. Trogler, *Science*, **251**, 932 (1991).
191. Seapan et al, Proceedings of the AlChE Annual Meeting. Los Angeles. Calif. (nov. 1997). *Proceedings of the AlChE Annual Meeting. Los Angeles, Ca (Nov. 1997).*
192. Ref. 30, p. 6.
193. Ref. 30, p. 27.
194. Ref. 30, p. 23.
195. Ref. 30, p. 24.
196. J. Szymanowski and A. Sobczynska, *Przem. Chem.* **66**, 373 (1987).
197. U.S. Pat. 2,680,761 (1952), R. Halliwell (to E. I. du Pont de Nemours & Co., Inc.).
198. U.S. Pat. 2,518,608 (1947), M. Farlow (to E. I. du Pont de Nemours & Co., Inc.).
199. *Eur. Chem. News* **23**(2), 17 (1973); U.S. Pats. 3,496,217; 3,496,218; 3,766,237; 3,526,654; 3,542,847; 3,536,748; W. Drinkard and co-workers (to E. I. du Pont de Nemours & Co., Inc.).
200. M. M. Baizer and D. E. Danly, *Chem. Technol.* **10**(10), 161, 302 (1980).
201. Ref. 30, p. 26.
202. M. Kato, *Nikkakyo Geppo* **26**, 561 (1973).
203. *CPI Purchasing*, 31 (Aug. 1989).
204. U.S. Pat. 4,423,018 (Dec. 27, 1983), D. Danly and J. Lester (to Monsanto Co., now dedicated to the public).
205. S. Litherland and co-workers, *Energy Research Abstr.* **10**(8), Abstr. No. 12145 (1985).
206. C. Chi and J. Lester, Jr., *CHEMTECH*, 308 (May 1990).

GENERAL REFERENCES

Y. C. Yen and S. Y. Wu, *Nylon-6,6, Report No. 54B, Process Economics Program*, SRI International, Menlo Park, Calif., Jan. 1987, pp. 1–148.

V. D. Luedeke, “Adipic Acid” in *Encyclopedia of Chemical Processing and Design*, J. McKetta and W. Cunningham, eds., Vol. 2, Marcel Dekker, Inc., New York, 1977, 128–146.

Jpn. Pat. 59184138 (Oct. 19, 1984), O. Mitsui and Y. Fukuoka (to Asahi Chemical Industry, Ltd.).

Jpn. Pat. 59186929 (Oct. 23, 1984), O. Mitsui and Y. Fukuoka (to Asahi Chemical Industry, Ltd.).

Jpn. Pat. 61050930 (Mar. 13, 1986), H. Nagahara and Y. Fukuoka (to Asahi Chemical Industry, Ltd.).

Jpn. Pat. 62045541 (Feb. 27, 1987), H. Nagahara and M. Konishi (to Asahi Chemical Industry, Ltd.).

Jpn. Pat. 60104029 (June 8, 1985), Y. Fukuoka and O. Mitsui (to Asahi Chemical Industry, Ltd.).

Fr. Pat. 2,554,440 (May 10, 1985), O. Mitsui and Y. Fukuoka (to Asahi Chemical Industry, Ltd.).

Eur. Pat. 162,475 (Nov. 11, 1985), M. Tojo and Y. Fukuoka (to Asahi Chemical Industry, Ltd.).
Ger. Offen. 3,441,072 (May 23, 1985), O. Mitsui and Y. Fukuoka (to Asahi Chemical Industry, Ltd.).
Ref. 30, pp. 12, 33, 37, 41, 43.
Chem. Mark. Rep. **236**(15), 54 (1989).
Chem. Mark. Rep. **236**(17), 50 (1989).
Chem. Econ. Eng. Rev. **17**(6), 45 (1985).
Eur. Chem. News **50**(1329), 25 (1988).
Eur. Chem. News **52**(1370), 10 (1989).
Chem. Eng. News **65**(21), 14 (1987).
Chem. Week **142**(2), 11 (1990).
Agence Economique and Financiere, 7 (Nov. 1, 1987).
Chem. Eng. News **67**(49), 15 (1989).
Jpn. Chem. Week 2 (April 27, 1989).
Eur. Chem. News **50**(1329), 4 (1988).
U.S. Exports, EM546, U.S. Dept. of Commerce, Bureau of Census, data for 1986.
Ref. (30), p. 608.5031A.
Food Chemicals Codex, 3rd ed., National Academy of Sciences, National Academy Press, Washington, D.C., 1981.
Chem. Mark. Rep. **230**(14), 58 (1989).
Koon-Ling Ring, “Adipic Acid”, in Chemical Economics Handbook, Marketing Research Report, SRI International, Menlo Park, Calif., 200 608.5001 G, p 6.

JUDITH P. OPPENHEIM
GARY L. DICKERSON
Solutia Inc.