

Abstract
Process Economics Program Report 284
BIO-BASED ADIPIC ACID
(December 2012)

Global adipic acid (ADA) demand is estimated at 2.3 million metric tons in 2012 and is growing at 3–5% per year. Nylon 66 accounts for about 85% of the total adipic acid demand. The other applications are polyurethanes (5%), adipic esters (4%), and others (6%). Major global producers of ADA include Invista, Ascend, Honeywell, BASF, Radici, China Shenma, and PetroChina. The average price has been \$1,600/mt in 2012. High-purity fiber-grade adipic acid is used to make nylon 66, while lower purity adipic acid is used primarily to produce polyurethanes.

The purpose of this report is to evaluate the process engineering and corresponding economics for producing ADA from the conventional cyclohexane oxidation process, and compare the results to emerging bio-chemical routes for the purpose of determining 1) the competitive cost position of bio-routes compared to the conventional process, and 2) identifying the areas of bio-chemical processing in which meaningful technology advances can substantially improve cost competitiveness.

Recently, start-up companies such as Rennovia, Verdezyne, BioAmber, Celexion, and Genomatica have developed bio-based routes to produce adipic acid, aiming at creating 100% bio-based nylon; some have reached advanced pilot or demonstration scales. There are two basic motivations for considering alternative ‘green’ feedstock sources for making ADA: 1) in the long term, they could be less expensive to produce than conventional methods using crude oil derivative cyclohexane and 2) societal demands for producing industrial chemicals via ‘sustainable’ methods may create artificial incentives (green mandates, price subsidies, loan guarantees, government sponsored technology development) or technology-specific market demand that results in requirements for producing ADA from bio-chemical resources.

Adipic acid has traditionally been produced from various petroleum-based feedstocks (e.g., phenol, benzene, and cyclohexane), but shifts in the hydrocarbon market have resulted in the virtual elimination of phenol as a feedstock. In recent years, cyclohexane-based processes have accounted for about 93% of global production capacity. Two steps are involved in ADA production: 1) oxidation of cyclohexane to produce KA oil (cyclohexanone and cyclohexanol) and 2) nitric acid oxidation of KA oil to produce adipic acid.

This report reviews and compares the conventional DuPont/Invista cyclohexane-based process to bio-based processes developed by 1) Verdezyne using genetically modified enzymes to ferment glucose to adipic acid, and 2) Rennovia for using air oxidation to convert glucose to glucaric acid, followed by hydrodeoxygenation to convert glucaric acid to adipic acid.

We find that the Rennovia process has a high potential to be cost competitive with the conventional cyclohexane oxidation process, while the Verdezyne process has the potential to be cost competitive. The advantage of both bio-routes is their use of \$300/mt glucose feedstock, compared to the conventional process using cyclohexane having a market price of \$1,250/mt in 2012. However, significant challenges affect both alternative processes in their ability to achieve high feedstock selectivity and catalyst productivity (in the case of Rennovia), and high enzyme turnover rates and satisfactory kinetics for the Verdezyne enzyme fermentation route.



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BIO-BASED ADIPIC ACID

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CONTENTS

GLOSSARY.....	XXIV
1 INTRODUCTION	1-1
2 SUMMARY	2-1
PROCESS TECHNOLOGY DESCRIPTIONS.....	2-1
Conventional Adipic Acid Production Technology from Cyclohexane	2-1
Adipic Acid Production Technology from Glucose via Verdezyne Fermentation	2-3
Adipic Acid Production Technology from Glucose via Rennovia Industrial Catalysis	2-4
PRODUCTION ECONOMICS.....	2-5
Capital Cost Comparison.....	2-6
Variable Production Cost Comparison	2-6
Total Production Cost Comparison	2-7
3 ADIPIC ACID INDUSTRY STATUS.....	3-1
ADIPIC ACID MARKET USES	3-1
ADIPIC ACID DEMAND AND DEMAND GROWTH.....	3-5
Chinese Demand for Adipic Acid.....	3-6
BUSINESS DRIVERS FOR ADIPIC ACID	3-7
MATERIAL SUBSTITUTION BETWEEN NYLON 66 AND NYLON 6.....	3-8
POLYMER INTERMATERIAL SUBSTITUTION.....	3-8
Industry Capacity Utilization	3-10
ENVIRONMENTAL DRIVERS.....	3-11
COMMERCIAL CAPACITY ADIPIC ACID PRODUCERS	3-11
2012 Adipic Acid Nameplate Production Capacity.....	3-11
ADIPIC ACID PRODUCING COMPANIES	3-14
Announced Adipic Acid Production Capacity Increases	3-17
Adipic Acid Capacity Shutdowns	3-18
Caprolactam Capacity Additions	3-18
ADIPIC ACID PRODUCT GRADES AND COMPOSITION	3-19
TECHNOLOGY LICENSORS AND DEVELOPERS	3-20
BIO-BASED ADIPIC ACID PROCESS DEVELOPERS	3-22

CONTENTS (Continued)

ADIPIC ACID PRICE AND MARGIN HISTORY	3-23
Historical Annual Prices for Adipic Acid	3-23
Short-Term Prices for Adipic Acid	3-25
Nylon 66 versus Adipic Acid Margins	3-26
4 TECHNOLOGY OF CONVENTIONAL ADIPIC ACID PRODUCTION.....	4-1
NOMENCLATURE	4-1
MOLECULAR STRUCTURE	4-1
PROCESS SAFETY AND DESIGN IMPLICATIONS	4-2
Chronic Health Effects.....	4-2
Combustion	4-3
Dust Explosion Potential.....	4-3
Exposure and Personal Protective Equipment.....	4-4
Operational Safety Issues	4-4
Spark Reducing Packaging	4-5
ADIPIC ACID PROPERTIES.....	4-5
Physical Properties.....	4-5
Thermodynamic Properties	4-7
Solution Properties	4-8
COMMERCIAL ADIPIC ACID PRODUCTION BY-PRODUCTS.....	4-10
COMMERCIAL MANUFACTURING TECHNOLOGY OPTIONS.....	4-14
CONVENTIONAL TWO-STAGE CYCLOHEXANE OXIDATION PROCESS	4-17
First-Stage Air Oxidation of Cyclohexane to KA Oil	4-18
Air Oxidation Enhanced with Boric Acid	4-21
Second-Stage Nitric Acid Oxidation of KA Oil to Adipic Acid	4-26
NO _x Bleaching with Hot Air	4-31
Nitric Acid Absorber.....	4-32
Adipic Acid Concentrator	4-32
Adipic Acid Crystallization from Nitric Acid Mother Liquor	4-35
Adipic Acid Crystallization from Aqueous Solution.....	4-36
Residual Aqueous Liquor Recovery	4-37
Recycle Processing of Nitric Acid Mother Liquor	4-38

CONTENTS (Continued)

ONE-STEP AIR OXIDATION OF CYCLOHEXANE TO ADIPIC ACID	4-42
SCIENTIFIC DESIGN AIR OXIDATION PROCESS	4-42
KA OIL MANUFACTURING FROM PHENOL.....	4-42
CYCLOHEXANOL FROM CYCLOHEXENE	4-44
ADIPIC ACID FROM BUTADIENE.....	4-45
CHEMISTRY OF COMMERCIAL ADIPIC ACID PRODUCTION.....	4-48
Integrated Chemistry Product Chain	4-48
Chemistry for Producing Cyclohexane from Benzene	4-49
Chemistry for Producing KA Oil from Cyclohexane	4-51
Chemistry for Oxidizing KA Oil to Adipic Acid Using Aqueous Nitric Acid	4-53
Role of Vanadium Catalyst.....	4-54
Chemistry for Producing KA Oil from Phenol	4-55
Asahi Chemistry for Producing Cyclohexanol from Cyclohexene	4-56
Chemistry of Butadiene-Based Adipic Acid.....	4-57
Hydrogen Peroxide Chemistry for Producing Adipic Acid	4-57
5 TECHNOLOGY FOR NON-COMMERCIAL BIO-BASED ROUTES TO ADIPIC ACID	5-1
DRATHS' FERMENTATION PROCESS USING MUCONIC ACID	5-1
BIOAMBER/CELEXION PROCESS.....	5-5
GENOMATICA FERMENTATION PROCESS FOR ADIPIC ACID.....	5-9
RENNOVIA INDUSTRIAL CHEMISTRY PROCESS FOR ADIPIC ACID PRODUCTION	5-13
Rennovia Glucaric Acid Route	5-14
Rennovia Furan Route to Adipic Acid	5-16
VERDEZYNE FERMENTATION FOR PRODUCING ADIPIC ACID.....	5-18
6 DESIGN BASIS FOR ADIPIC ACID PRODUCTION.....	6-1
BUSINESS OBJECTIVES	6-1
SCOPE OF PROJECT	6-2
DESIGN PHILOSOPHY	6-3
DESIGN PRIORITIES	6-3
Process Safety	6-4

CONTENTS (Continued)

Operating Reliability	6-4
Consistency in Producing On-Spec Adipic Acid.....	6-4
Environmental Emission Conformance	6-5
Hazardous Waste Incineration	6-6
Flexibility for Economic Optimization.....	6-6
Ease of Operations and Maintenance	6-6
Scheduled Plant Turnarounds	6-7
Reciprocating Machinery Drivers	6-7
Maximum return on investment	6-7
Buildings	6-8
Security and Vulnerability Analysis	6-8
Production Design Criteria.....	6-9
PLANT LOCATION FACTOR.....	6-9
PEPCOST FACTOR.....	6-10
REGULATORY ENVIRONMENT AND EHS STANDARDS.....	6-11
CONSTRUCTION METHODOLOGY	6-11
OFFSITE FACILITIES	6-12
Black Start Capability	6-13
PROCESS CONTROL PHILOSOPHY.....	6-13
Project to Provide Machine Condition Monitoring Instrumentation	6-13
MATERIALS OF CONSTRUCTION	6-13
ENGINEERING AND DESIGN STANDARDS.....	6-14
SITE-SPECIFIC DESIGN CONDITIONS	6-14
CAPITAL AND OPERATING COST BASES.....	6-15
Capital Investment.....	6-15
Project Construction Timing	6-16
Available Utilities	6-16
Production Cost Factors	6-17
Feedstock, Product, and Energy Pricing	6-17
Effect of Operating Level on Production Costs	6-18
Project Design Capacity	6-19

CONTENTS (Continued)

FEEDSTOCK AND PRODUCT SPECIFICATIONS	6-19
Adipic Acid Product	6-19
Cyclohexane Feedstock	6-20
Glucose Feedstock.....	6-20
ADIPIC ACID PRODUCT PACKAGING AND SHIPPING SPECIFICATIONS.....	6-21
7 ADIPIC ACID FROM CYCLOHEXANE VIA CONVENTIONAL TWO-STAGE OXIDATION PROCESS	7-1
CYCLOHEXANE PROPERTIES AND DESIGN ISSUES	7-1
Cyclohexane Sourcing and Specifications	7-1
Physical Properties of Cyclohexane and Design Implications	7-2
Thermodynamic Properties of Cyclohexane and Design Implications	7-5
Cyclohexane Bulk Storage Considerations	7-5
Cyclohexane Feedstock Specification.....	7-6
PROCESS DESCRIPTION	7-7
Section 100—Air Oxidation of Cyclohexane to Crude KA Oil	7-9
Cyclohexane Scrubbing.....	7-9
Activated Carbon Polishing Beds	7-10
Cobalt Naphthenate Catalyst Addition	7-11
Boric Acid Addition	7-12
Cyclohexane Air Oxidation Reaction to KA Oil.....	7-14
Cyclohexyl Hydroperoxide (CHHP) Converter	7-16
Section 200—Purification of Crude KA Oil.....	7-22
Cyclohexane Recovery Column	7-22
KA Oil Purification Column	7-24
Boric Acid Recovery and Recycle	7-24
Section 300—Nitric Acid Oxidation of KA Oil to Crude Adipic Acid	7-27
Overall Processing Scheme	7-27
Wetted Materials Considerations for Nitric Acid	7-30
Nitric Acid Storage Day Tanks.....	7-30
Copper Vanadate Catalyst Composition and Use	7-31
Nitric Acid Oxidation Reactors Design	7-33
Nitric Acid Bleacher Design	7-34
Adipic Acid Concentrator Design.....	7-34
Nitric Acid Absorber.....	7-35

CONTENTS (Continued)

Section 400—Adipic Acid Crystallization.....	7-35
Crude Acid Suspension Crystallization Using Oslo Crystallizer.....	7-36
Crystal Separation Using Pusher Centrifuge.....	7-39
Crude Adipic Acid Crystallization in Nitric Acid	7-40
Adipic Acid 1st-Stage Aqueous Crystallization.....	7-42
Adipic Acid 2nd-Stage Aqueous Crystallization	7-42
Section 500—Adipic Acid Drying and Packaging.....	7-43
Adipic Acid Explosion Potential during Drying and Solids Transport	7-43
Proposed Adipic Acid Rotary Vacuum Drying System.....	7-43
Addition of Adipic Acid Flow Improver.....	7-45
Section 600—By-Product Recovery to Methyl Esters.....	7-46
NVR Composition and Source.....	7-46
NVR Processing Options.....	7-46
Conversion of NVR to Methyl Esters.....	7-47
Invista NVR Processing Scheme.....	7-48
Mixed Ester Production Process Description	7-50
Witco Approach for Converting Non-Volatile Residue (NVR) Directly to Polyester Polyols	7-53
Design Approach for this Project.....	7-53
Section 700—AGS By-Product Production	7-53
Nitric Acid Mother Liquor Purge Stream from Crystallization	7-53
Evaporation of Nitric Acid and Water from the Purge Stream.....	7-55
Recovery of Vanadium and Copper Catalyst Metals.....	7-56
AGS Aqueous Crystallization and Centrifuging.....	7-56
AGS Crystal Drying	7-57
Section 800—Nitrous Oxide Destruction.....	7-57
Rationale for Nitrous Oxide (N_2O) Destruction.....	7-58
NITROUS OXIDE DESTRUCTION TECHNOLOGIES	7-59
Thermal Reduction of Nitrous Oxide	7-59
Lanxess Thermal Decomposition of N_2O	7-60
Catalytic Reduction of Nitrous Oxide.....	7-61
DuPont Canada Experience in Nitrous Oxide Reduction.....	7-61
BASF Approach to Nitrous Oxide Destruction.....	7-62
Invista N_2O Abatement Technology	7-64
Performance of N_2O Destruction Systems	7-67

CONTENTS (Continued)

UOP Pressure Swing Absorption	7-69
BASF Ammonia-Based N ₂ O Destruction Process	7-69
Proposed N ₂ O Destruction Processing Design	7-70
PROCESS FLOW DIAGRAMS	7-71
MATERIAL BALANCE	7-71
EQUIPMENT LIST.....	7-88
Itemized Capital Cost Estimate	7-95
Segmentation of Itemized Capital Costs	7-103
TOTAL FIXED CAPITAL COST ESTIMATE	7-106
PRODUCTION COST ESTIMATE	7-108
Variable Cost of Adipic Acid Production via Cyclohexane	7-108
Total Cost of Adipic Acid Production via Cyclohexane	7-109
8 VERDEZYNE FERMENTATION PROCESS FOR MAKING ADIPIC ACID FROM GLUCOSE.....	8-1
VERDEZYNE TECHNOLOGY	8-1
Verdezyne Metabolic Pathway (USPA 2012 0156761).....	8-3
PROCESS YIELD AND SELECTIVITY	8-4
COMMERCIAL DESIGN CONSIDERATIONS.....	8-5
Fermentation Conditions	8-5
Requirement for Aqueous Crystallization.....	8-6
By-Product Monetization	8-6
Direct Formation of Diammonium Adipate Salt	8-7
Salt Splitting to Recover Adipic Acid from Diammonium Salt	8-8
DSM Alternative Approach to Salt Formation.....	8-12
Water Solution Purification and Recycle	8-12
Enzyme Catalyst Recycle.....	8-12
Continuous versus Batch Fermentation	8-14
FEEDSTOCK GLUCOSE PROPERTIES.....	8-14
Open and Cyclic Molecular Structure.....	8-15
PROPOSED COMMERCIAL PROCESS SEQUENCE AND DESCRIPTION	8-16
Section 100—Enzyme Preparation	8-17

CONTENTS (Continued)

Section 200—Product Fermentation	8-19
Section 300—Salt Splitting of Diammonium Adipate and Monoammonium Adipate.....	8-20
Section 400—Two-Stage Aqueous Crystallization of Adipic Acid.....	8-21
Section 500—Adipic Acid Crystal Drying and Product Packaging.....	8-22
Section 600—Methyl Ester Production.....	8-23
STREAM-BY-STREAM MATERIAL BALANCE	8-24
EQUIPMENT LIST.....	8-34
ITEMIZED CAPITAL COST ESTIMATE.....	8-39
TOTAL FIXED CAPITAL COST	8-46
PRODUCTION COST ESTIMATE	8-48
9 RENNOVIA PROCESS FOR MAKING ADIPIC ACID	9-1
FEEDSTOCK AND PRODUCT MOLECULAR STRUCTURE	9-1
RENNOVIA TECHNOLOGY APPROACH	9-2
RENNOVIA PATENT PORTFOLIO.....	9-3
Overall Process Yield and Feedstock Consumption	9-4
Rennovia 1st-Stage Oxidation of Glucose to Glucaric Acid.....	9-5
Glucose Oxidation Intermediate Products.....	9-8
Glucose Oxidation By-Products	9-9
Rennovia 2nd-Stage Hydrodeoxygenation of Glucaric Acid to Adipic Acid	9-11
COMMERCIAL PLANT DESIGN BASIS	9-14
COMMERCIAL PROCESS DESIGN.....	9-15
PROCESS DESCRIPTION	9-17
Section 100—Glucose Oxidation with Air.....	9-18
Section 200—Glucaric Acid Hydrodeoxygenation to Adipic Acid.....	9-23
Section 300—Adipic Acid Crystallization.....	9-24
Section 400—Adipic Acid Drying and Packaging.....	9-27
Section 500—Acetic Acid Recovery	9-28
Section 600—Mixed Methyl Ester Production	9-29
MATERIAL BALANCE	9-31
EQUIPMENT LIST.....	9-44

CONTENTS (Concluded)

ITEMIZED CAPITAL COST ESTIMATE.....	9-49
TOTAL FIXED CAPITAL COST ESTIMATE	9-58
PRODUCTION COST ESTIMATE	9-60
Variable Production Cost Estimate.....	9-60
Total Production Cost Estimate.....	9-61
APPENDIX A PATENT SUMMARY TABLES	A-1
APPENDIX B CITED REFERENCES	B-1
APPENDIX C PROCESS FLOW DIAGRAMS.....	C-1

FIGURES

1.1	Adipic Acid Molecular Structure.....	1-1
1.2	Adipic Acid Integrated Product Chain.....	1-2
2.1	Oxidation of Cyclohexane to KA Oil	2-2
2.2	Nitric Acid Oxidation of KA Oil to Adipic Acid	2-2
2.3	Verdezyne Pathway to Adipic Acid from Glucose (USPA 2012 0156761).....	2-3
2.4	Verdezyne Fermentation Process Block Flow Diagram.....	2-4
2.5	Glucaric Acid Molecular Structure	2-4
2.6	Rennovia Process Block Flow Diagram	2-5
2.7	Adipic Acid Capital Cost Process Comparison.....	2-6
2.8	Adipic Acid Variable Cost Process Comparison.....	2-7
2.9	Adipic Acid Total Production Cost Process Comparison	2-8
3.1	Nylon Fiber and Resin Demand	3-1
3.2	Forecast Nylon Demand Growth Rate	3-2
3.3	Global End-Use Demand Distribution for Adipic Acid in 2012	3-5
3.4	Global Geographic Demand Distribution for Adipic Acid in 2011	3-6
3.5	Chinese Adipic Acid Capacity, Production, Consumption, and Exports/Imports ..	3-6
3.6	Trends in Materials for Tire Cord.....	3-9
3.7	Historic and Forecast Global Adipic Acid Capacity	3-12
3.8	2012 Adipic Acid Capacity by Geographical Region	3-13
3.9	2013 Adipic Acid Capacity Share by Producer.....	3-15
3.10	Historical US Export Price of Adipic Acid	3-24
3.11	Regional Adipic Acid Prices 2000–2011	3-24
3.12	Exchange Rates (US\$/RMB) Early 2012	3-25
3.13	Nylon 66 Raw Material Prices (27-Jan-2012).....	3-26
3.14	Long-Term Nylon 66 Product Chain Prices.....	3-27
4.1	Adipic Acid Molecular Structure.....	4-2
4.2	Adipic Acid Boiling Point Curve	4-7
4.3	Adipic Acid—Water Solubility Relationship with Temperature	4-9
4.4	Adipic Acid Hydrocarbon Solubility with Temperature.....	4-9
4.5	Crystallization Curve for AGS Mixtures (Monsanto USP 4254283, 3-Mar-1981) .	4-13
4.6	Monsanto High-Purity Crystallization Process (USP 4254283, 3-Mar-1981).....	4-14
4.7	Conventional Process Routes to Adipic Acid	4-15

FIGURES (Continued)

4.8	Alternative Process Routes to Adipic Acid	4-15
4.9	Global Distribution of Adipic Acid Capacity by Technology.....	4-16
4.10	Cyclohexane to KA Oil Block Flow Diagram	4-19
4.11	Basic Stamicarbon KA Oil Process Flow Diagram.....	4-20
4.12	Nypro Chemcial (Flixborough) KA Oil Process Process Flow Diagram.....	4-21
4.13	Halcon Air Oxidation Process Patent (USP 3932513, 13-Jan-1976)	4-23
4.14	Air Oxidation Improvement Using Boric Acid (Halcon USP 3243449)	4-24
4.15	Boric Acid Recovery via Esso USP 3232704	4-25
4.16	Boric Acid Recovery Crystallization Process (Halcon USP 3475500)	4-26
4.17	DuPont 1967 Adipic Acid Process (USP 3359308).....	4-27
4.18	Adipic Acid from KA Oil via Nitric Acid Oxidation Block Flow Diagram.....	4-28
4.19	Adipic Acid from KA Oil via Nitric Acid Oxidation Simplified Process Flow Diagram	4-29
4.20	Forced Circulation Crystallization System.....	4-30
4.21	Nitric Acid Solution Boiling Point Curve.....	4-34
4.22	Water Boiling Temperature under Vacuum Conditions	4-34
4.23	Schematic of Oslo Crystallizer.....	4-35
4.24	Early Monsanto Adipic Acid Crystallizer (USP 3102908, 3-Sep-1963)	4-36
4.25	Adipic Acid Solubility Curve in Water	4-37
4.26	Nitric Acid Purge Liquid Processing (BASF USP 5210297, 11-May-1993).....	4-40
4.27	Two-Stage Oxidation of Cyclohexane to Adipic Acid Block Flow Diagram	4-41
4.28	Phenol Hydrogenation to Cyclohexanol Process Flow Diagram.....	4-43
4.29	Asahi Kasei Cyclohexene Process.....	4-45
4.30	Butadiene Routes to Adipic Acid	4-46
4.31	Butadiene Enzyme Pathways to Adipic Acid.....	4-48
4.32	Integrated Chemistry for Producing Adipic Acid.....	4-48
4.33	Molecular Structure of Cyclohexanol and Cyclohexanone.....	4-49
4.34	Nylon 66 from ADA + HMDA	4-49
4.35	Axens Cyclohexane Block Flow Diagram.....	4-50
4.36	Toray Cyclohexane Process Flow Diagram	4-51
4.37	Dehydrogenation of Cyclohexanol to Cyclohexanone	4-52
4.38	Peroxy Intermediates for Oxidizing Cyclohexane to KA Oil	4-52

FIGURES (Continued)

4.39	Nitric Acid Oxidation of KA Oil to Adipic Acid	4-53
4.40	Chemical Pathways to Adipic Acid Form KA Oil	4-54
4.41	Role of Vanadium and Copper Catalysts in Nitric Acid Oxidation.....	4-55
4.42	Sequential Reduction and Reoxidation of HNO ₃	4-55
4.43	Chemistry for Converting Phenol to KA Oil	4-56
4.44	Chemical Pathway to ADA from Cyclohexene Using H ₂ O ₂	4-58
5.1	Bio-Based Six Carbon Molecules	5-1
5.2	Muconic Acid Platform.....	5-2
5.3	Draths Muconic Acid Fermentation Pathway to Adipic Acid (USP 5798236)	5-3
5.4	Detailed Pathway for Draths Fermentation Synthesis of ADA—Initial Steps (USP 5616496).....	5-4
5.5	Detailed Pathway for Draths Fermentation Synthesis of ADA—Final Steps (USP 5616496).....	5-5
5.6	Celexion Fermentation Pathways to Adipic Acid (WO 2010/068944 A2, USP 8133704)	5-6
5.7	BioAmber Patent for Succinic Acid Processing (USP 8084626).....	5-8
5.8	Succinic Acid Solubility (BioAmber USP 8084626)	5-9
5.9	Succinic Acid Solubility as Function of pH	5-9
5.10	Genomatica Hydroxy Pathway from C ₄ + C ₂ Fragments to Adipic Acid (USP 8088607)	5-11
5.11	Genomatica Oxo Pathway from C ₄ + C ₂ Fragments to Adipic Acid (USP 8088607)	5-12
5.12	Genomatica Muconic Acid Pathway from D-Glucose to Adipic Acid (USP 8088607)	5-13
5.13	Rennovia Approach to Biochemicals Production	5-13
5.14	Rennovia Pathway from Glucose to Glucaric Acid.....	5-14
5.15	Structure of Hydroxy Dicarboxylic Acid	5-14
5.16	Rennovia Pathway from Glucaric Acid to Adipic Acid	5-15
5.17	Rennovia Oxidation of Glucose to Glucaric Acid (USPA 20100317823)	5-16
5.18	Rennovia Hydrodeoxygenation of Glucaric Acid to Adipic Acid (USPA 20100317823)	5-16
5.19	Rennovia Furan Intermediate Product from Carbohydrate	5-17
5.20	Rennovia HMF Production from Carbohydrates	5-17
5.21	Rennovia Adipic Acid Production from HMF	5-18

FIGURES (Continued)

5.22	Verdezyne Pathway to Adipic Acid from Glucose (USPA 2012 0156761).....	5-20
5.23	Verdezyne Alternative Pathway to Adipic Acid via Fatty Acid (USPA 2012 0156761)	5-21
5.24	Verdezyne Pathway to Adipic Acid from Sugars and Triglycerides (USPA 2012 0156761)	5-22
5.25	Verdezyne Intermediates Products to Adipic Acid from Sugar	5-23
5.26	Verdezyne Adipic Acid from Fats and Oils	5-24
5.27	Verdezyne Adipic Acid from Paraffins	5-25
5.28	Verdezyne Carbon Number Selectivity for Strain H43	5-26
5.29	Verdezyne Carbon Number Selectivity for Strain H53	5-27
6.1	Project Scope of Work.....	6-2
6.2	Historical Location Factors for Germany and Japan	6-10
6.3	Historical Values of US PEP Cost Index	6-11
7.1	Physical Structure of Cyclohexane Molecule	7-1
7.2	Cyclohexane Boiling Point Curve	7-4
7.3	Cyclohexane Phase Diagram.....	7-4
7.4	Air Oxidation of Cylohexane to KA Oil Block Flow Diagram	7-7
7.5	Two-Stage Scrubbing of Air Oxidation Reactor Vapors	7-10
7.6	Molecular Structure of Cobalt(II) Naphthenate.....	7-11
7.7	Boric Acid Solubility Curve in Water.....	7-14
7.8	Air Oxidation Reaction Diagram	7-15
7.9	Rhone-Poulenc Process for CHHP Conversion (USP 3927105)	7-18
7.10	DuPont Cyclohexane Oxidation and CHHP Conversion Approach (USP 6703529, 9-Mar-2004)	7-21
7.11	CHHP Decomposition Reactor Section.....	7-21
7.12	KA Oil Conventional Purification Scheme (DuPont USP 3365490)	7-22
7.13	KA Oil Purification Scheme	7-23
7.14	Cyclohexanol Boiling Curve.....	7-24
7.15	Boric Acid Recovery and Recycle Approach (Monsanto USP 3895067)	7-26
7.16	Proposed Boric Acid Recovery System.....	7-27
7.17	Oxidizing Cyclohexanone to Adipic Acid via Nitric Acid	7-28
7.18	KA Oil Nitric Acid Oxidation Block Flow Diagram (DuPont USP 3365490, 23-Jan-1968)	7-28

FIGURES (Continued)

7.19	Nitric Acid Oxidation Current Processing Scheme	7-29
7.20	Recommended Materials in Nitric Acid Service	7-30
7.21	Nitric Acid in Water Boiling Curve.....	7-31
7.22	Role of Vanadium and Copper Catalyst	7-32
7.23	Nitric Acid Oxidation Reactor Process Flow Diagram	7-34
7.24	Proposed Adipic Acid Purification Block Flow Diagram	7-36
7.25	Evaporative Crystallization Mechanism (DuPont USP 5471001, 28-Nov-1995)...	7-37
7.26	Forced Circulation (Oslo) Crystallizer.....	7-38
7.27	Nozzle Locations for Oslo Crystallizer (Draft Tube)	7-39
7.28	Nitric Acid Crystallizer and Centrifuge for Crude Adipic Acid.....	7-41
7.29	Invista 2-Stage Adipic Acid Drying (USP 6946571, 20-Sep-2005)	7-44
7.30	Rotary Dryer Temperature Profile	7-44
7.31	Adipic Acid 2-Stage Rotary Vacuum Drying.....	7-45
7.32	DuPont NVR Processing Scheme (USP 6703529)	7-47
7.33	By-Product Recovery via Esterification Block Flow Diagram	7-50
7.34	Methanol: Water Distillation Curve (284051)—Methanol Mol Fraction versus Temperature (°C).....	7-51
7.35	By-Product Recovery Process Flow Diagram	7-52
7.36	AGS Recovery Block Flow Diagram.....	7-55
7.37	Nitric Acid Mother Liquor Purge Treatment Process Flow Diagram.....	7-57
7.38	Thermal Reduction of Nitrous Oxide Block Flow Diagram (284052).....	7-60
7.39	Lanxess Thermal Decomposition of N ₂ O at Leverkusen.....	7-60
7.40	DuPont Canada N ₂ O Destruction Schematic	7-62
7.41	BASF N ₂ O Destruction Facility in Germany (284056)	7-64
7.42	Invista N ₂ O Thermal Destruction System	7-65
7.43	Invista N ₂ O Catalytic Destruction System	7-66
7.44	Invista N ₂ O to NO Catalytic Oxidation System.....	7-67
7.45	Status of N ₂ O Abatement at Adipic Acid Plants	7-68
7.46	BASF N ₂ O Destruction via NH ₃ Reaction over Zeolite (USP 7951742)	7-70
7.47	N ₂ O Conversion to Nitrogen Oxide Process Flow Diagram	7-71
7.48	Adipic Acid from Cyclohexane via Conventional Two-Stage Oxidation Process Process Flow Diagram	C-3
8.1	Verdezyne Pathway to Adipic Acid from Glucose (USPA 2012 0156761).....	8-3

FIGURES (Continued)

8.2	Verdezyne Glucose Pathway to Adipic Acid (USPA 2012 0156761)	8-4
8.3	Oxygen Saturated in Fresh and Sea Water	8-5
8.4	Cargill USP 7186856 Producing Ammonium Salt of Produced Acid.....	8-7
8.5	BioAmber ADA Recovery from DAA and MAA (USPA 2011/0266133 A1).....	8-8
8.6	Monoammonium Adipate Solubility (USPA 2011/0266133 A1)	8-10
8.7	BioAmber Adipic Acid Purification from DAA and MAA (USPA 2011/0266133 A1)	8-11
8.8	BioAmber Solubility Curve for Adipic Acid in Water (USPA 2011/0269993).....	8-12
8.9	Enzyme Recycling Requirement for Bio-Lactic Acid	8-13
8.10	Enzyme Recovery via Amine Extraction	8-13
8.11	Glucose Chemical Structure.....	8-14
8.12	Ring Structure of Glucose	8-15
8.13	Stressed Three-Dimensional Configuration of Ringed Glucose Structure	8-16
8.14	Verdezyne Fermentation Process Block Flow Diagram.....	8-16
8.15	Section 100—Enzyme Preparation	8-19
8.16	Section 200—Glucose Fermentation	8-20
8.17	Section 300—Salt Splitting and Concentration	8-21
8.18	Section 400—Aqueous Crystallization	8-22
8.19	Section 500—ADA Drying and Packaging	8-23
8.20	Section 600—By-Product Esterification Section	8-24
8.21	Verdezyne Fermentation Process for Making Adipic Acid from Glucose Process Flow Diagram	C-19
9.1	Glucose Molecular Structure	9-1
9.2	Adipic Acid Molecular Structure.....	9-2
9.3	Glucaric Acid Molecular Structure	9-2
9.4	Rennovia Two-Stage Oxidation Chemistry	9-2
9.5	Rennovia Feed Consumption versus Yield	9-5
9.6	Rennovia Oxidation of Glucose to Glucaric Acid.....	9-5
9.7	Oxygen Solubility in Water	9-6
9.8	Gluconic Acid Molecular Structure	9-8
9.9	Glucuronic Acid Molecular Structure	9-8
9.10	Rennovia High Throughput Screening Results	9-12
9.11	Structure of Intermediate C ₆ Oxidized Product.....	9-13

FIGURES (Concluded)

9.12	Input/Output Diagram for Rennovia Process.....	9-14
9.13	Rennovia Adipic Acid Block Flow Diagram	9-16
9.14	Glucose Air Oxidation Process Flow Diagram	9-18
9.15	Glucose Solubility in Water.....	9-21
9.16	Glucose and Fructose Molecular Structure	9-21
9.17	Glucose Viscosity in Water.....	9-22
9.18	Glucaric Acid Hydrodeoxygenation Process Flow Diagram.....	9-23
9.19	Adipic Acid Crystallization Process Flow Diagram.....	9-24
9.20	Adipic Acid Solubility in Acetic Acid.....	9-26
9.21	Adipic Acid Drying and Packaging Process Flow Diagram.....	9-27
9.22	Acetic Acid Recovery Process Flow Diagram	9-28
9.23	Heterogeneous Extractive Distillation.....	9-29
9.24	Mixed Methyl Ester Production Process Flow Diagram	9-30
9.25	Rennovia Process for Making Adipic Acid Process Flow Diagram	C-31

TABLES

1.1	Status of Bio-Based Adipic Acid Developers.....	1-3
3.1	Nylon 66 End Uses.....	3-2
3.2	Chemical Formulations Containing Adipic Acid.....	3-3
3.3	End-Use Products Containing Adipic Acid	3-4
3.4	Market Drivers for Bio-Based Adipic Acid Commercial Success	3-7
3.5	Solvay/Rhodia Forecast of Nylon End-Use Market Demand Growth.....	3-7
3.6	Production Integration for Nylon 66 and Nylon 6.....	3-8
3.7	Competing Engineering Plastics.....	3-10
3.8	Adipic Acid Capacity by Country to 2011	3-12
3.9	Forecast Adipic Acid Capacity by Country 2012–2016	3-14
3.10	2013 Adipic Acid Capacity Share by Producer.....	3-15
3.11	2012 Adipic Acid Capacity by Plant Site	3-16
3.12	Adipic Acid Capacity Additions	3-18
3.13	Adipic Acid Capacity Eliminations	3-18
3.14	Caprolactam Capacity Additions	3-19
3.15	Invista Fiber-Grade Adipic Acid Specification	3-19
3.16	Radici Fiber-Grade Adipic Acid Specification.....	3-20
3.17	Adipic Acid Active Process Licensors	3-21
3.18	ADA Technology Developer/Operating Company Partnerships	3-22
3.19	Bio-Based Adipic Acid Technology Summary.....	3-23
3.20	Alibaba Offering Prices for Chinese Adipic Acid (January 2012)	3-25
3.21	Nylon Raw Material Margins (27-Jan-2012).....	3-26
4.1	Adipic Acid Alternate Names	4-1
4.2	Adipic Acid Nomenclature	4-1
4.3	Adipic Acid Summary Hazards Table	4-2
4.4	Adipic Acid Hazard Parameters.....	4-4
4.5	Adipic Acid Physical Properties	4-6
4.6	Other Adipic Acid Physical Properties	4-7
4.7	Adipic Acid Thermodynamic Properties	4-8
4.8	Adipic Acid Solution Properties	4-10
4.9	KA Oil Basic Physical Properties.....	4-10
4.10	Adipic Acid Yields	4-11

TABLES (Continued)

4.11	Ascend Materials AGS Product Composition.....	4-11
4.12	Invista Dibasic Acid Composition	4-11
4.13	Physical Properties of Adipic, Glutaric, and Succinic Acid.....	4-12
4.14	Status of Hydrocarbon Process Routes to Adipic Acid	4-16
4.15	Unit Feedstock Consumption for Conventional Adipic Acid Processes	4-17
4.16	Unit Energy Consumption for Conventional Adipic Acid Processes	4-17
4.17	Boric Acid Enhancement US Patents.....	4-22
4.18	Typical Operating Conditions for Nitric Acid Oxidation Reactors	4-31
4.19	Operating Conditions for Adipic Acid Concentrator.....	4-32
4.20	Boiling Point of Acid Concentrator Components	4-33
4.21	Representative Water-Rich Crystallization Liquor Composition (Monsanto USP 4254283)	4-38
4.22	Typical Nitric Acid Mother Liquor Composition (BASF USP 5210297, 11-May-1993)	4-39
4.23	Amberlyst 40Wet Ion Exchange Resin Specifications.....	4-41
4.24	Asahi Kasei US Patents for Its Cyclohexene Process	4-44
5.1	Relevant US Patents on Draths Process	5-3
5.2	BioAmber US Patents.....	5-6
5.3	BioAmber US Patent Applications.....	5-7
5.4	Genomatica US Patents Involving Adipic Acid.....	5-10
5.5	Genomatica US Patent Applications Involving Adipic Acid	5-10
5.6	Typical Rennovia Hydrodeoxygenation Reactor Conditions	5-15
5.7	Rennovia US Patent Applications for Adipic Acid	5-15
5.8	Verdezyne Patents and Applications.....	5-19
5.9	Verdezyne Adipic Acid Performance Claims.....	5-20
6.1	Construction Cost Location Factors	6-10
6.2	IHS Offsite Capital Cost Components	6-12
6.3	Relevant Project Standards Setting Organizations	6-14
6.4	Temperature Design Considerations.....	6-15
6.5	Project Utility Unit Costs	6-18
6.6	Project Feedstock Unit Costs	6-18
6.7	Adipic Acid Fiber-Grade Product Specification	6-20
6.8	Cyclohexane Feedstock Specification.....	6-20

TABLES (Continued)

6.9	Glucose Feedstock Specification	6-21
7.1	Major Cyclohexane Producers	7-2
7.2	Chevron-Phillips Cyclohexane Sales Specification	7-2
7.3	Physical Properties of Cyclohexane	7-3
7.4	Thermodynamic Properties of Cyclohexane	7-5
7.5	Cyclohexane Prior Cargo Restrictions	7-6
7.6	Project Cyclohexane Feedstock Specification	7-7
7.7	Cyclohexane to Adipic Acid—Overall Design Basis.....	7-8
7.8	Design Basis-Air Oxidation of Cyclohexane to KA Oil	7-9
7.9	Cobalt(II) Naphthenate Properties.....	7-12
7.10	Typical Boric Acid Commercial Specification	7-13
7.11	Properties of Boric Acid	7-13
7.12	Foundation Patents for CHHP Oxidation.....	7-16
7.13	Subsequent US Patents for CHHP Oxidation	7-17
7.14	Relevant CHHP Follow-up US Patents	7-20
7.15	CHHP Converter Design Basis.....	7-22
7.16	Approaches to Boric Acid Recovery	7-26
7.17	Ammonium Metavanadate Commercial Specification.....	7-32
7.18	Copper Nitrate Generic Commercial Specification.....	7-33
7.19	Applications for Ferrum Pusher Centrifuges	7-40
7.20	Crystallizer Feed Concentration	7-41
7.21	Solubility in Water of AGS Components at 30°C.....	7-42
7.22	Adipic Acid Flow Improver Approaches.....	7-46
7.23	Polymers Soluble in Methyl Esters.....	7-48
7.24	Methyl Esters Produced from NVR (Invista USPA 20120101009).....	7-48
7.25	NVR Processing Steps to Methyl Esters	7-49
7.26	Boiling Point of Primary Monoester Components.....	7-51
7.27	Invista Methyl Ester Product Composition (Invista USPA 20120064252).....	7-52
7.28	Adipic Acid By-Product End-Use Applications (Invista USPA 2012/0064252)	7-53
7.29	Typical Mother Liquor Composition after Crude Adipic Acid Crystallization	7-54
7.30	US EPA Estimate of N ₂ O Destruction Economics.....	7-58
7.31	Environmental Impact of N ₂ O Destruction Technologies	7-59

TABLES (Continued)

7.32	Adipic Acid and N ₂ O Production at BASF Ludwigshafen Plant (284056)	7-63
7.33	DuPont N ₂ O Catalytic Destruction US Patents	7-66
7.34	IPCC Tabulation of N ₂ O Destruction Performance	7-67
7.35	N ₂ O Abatement Performance at Three European Adipic Acid Plants.....	7-69
7.36	Material Balance Sumary	7-72
7.37	Stream-by-Stream Material Balance	7-73
7.38	Equipment List with Duty Specifications.....	7-89
7.39	Itemized Capital Cost Estimate	7-96
7.40	Itemized Capital Cost Segmentation by FOB and Installation Cost	7-104
7.41	Itemized Capital Cost Segmentation by FOB Equipment Type	7-105
7.42	Itemized Capital Cost Segmented by Section of Plant.....	7-106
7.43	Adipic Acid via Two-Stage Oxidation of Cyclohexane—Total Fixed Capital Cost	7-107
7.44	Variable Cost of Adipic Acid Production via Cyclohexane	7-108
7.45	Adipic Acid Total Production Cost Estimate from Cyclohexane	7-110
7.46	Section 7 Appendix: Global Cyclohexane Producers.....	7-111
8.1	Verdezyne Major Patents	8-2
8.2	Fermentation Broth Growth Promoters	8-6
8.3	Diammonium Adipate Properties.....	8-9
8.4	Glucose Properties	8-15
8.5	Adipic Acid via Verdezyne Fermentation Design Basis	8-17
8.6	Materials Supply to Enzyme Preparation Fermenters.....	8-18
8.7	Typical Production Fermenter Broth Composition (WO 2010/003728).....	8-20
8.8	Unit Feedstock and By-Product Consumption	8-24
8.9	Stream-by-Stream Material Balance	8-25
8.10	Equipment List with Duty Specifications.....	8-35
8.11	Itemized Capital Cost Index.....	8-39
8.12	Segmented Tagged Equipment Capex by Type of Equipment	8-45
8.13	Segmented Tagged Equipment Capex by Section of Plant	8-46
8.14	Total Fixed Capital Cost Estimate	8-47
8.15	Adipic Acid via Verdezyne Fermentation Variable Cost Estimate	8-48

TABLES (Concluded)

8.16	Adipic Acid via Verdezyne Fermentation Production Cost Estimate	8-50
9.1	Properties of Rennovia Feed, Intermediate and Final Product	9-3
9.2	Rennovia Patents and Applications.....	9-4
9.3	Theoretical Yields of Glucose Oxidation Reaction	9-6
9.4	Rennovia USPA 2011/0306790 Partial Yield Table	9-7
9.5	Expected Glucose Oxidation Yield Pattern	9-9
9.6	Expected Mass Yield for Glucaric Acid Production from Glucaric Acid Air via Oxidation.....	9-10
9.7	Rennovia USPA 2011/0306790 Temperature and Residence Time Results	9-10
9.8	Theoretical Yields of Glucaric Acid Hydrodeoxygenation Reaction	9-11
9.9	Theoretical Yields of Overall Glucose to Adipic Acid Reaction	9-12
9.10	Rennovia Conversion of Glucaric Acid to Adipic Acid (USPA 2011/0218318)	9-13
9.11	Expected Commercial Yield for Glucaric Acid Hydrogenation	9-14
9.12	Expected Mass Yield for Adipic Acid Production from Glucaric Acid via Hydrodeoxygenation.....	9-14
9.13	Rennovia Design Basis	9-15
9.14	Cargill Glucose Syrup Specification	9-19
9.15	Commercial Feedstock Components	9-20
9.16	Adipic Acid Solubility in Common Solvents	9-25
9.17	Rennovia Process Material Balance Summary.....	9-31
9.18	Rennovia Process Material Balance	9-32
9.19	Rennovia Process Equipment List	9-45
9.20	Rennovia Itemized Capital Cost Estimate	9-50
9.21	Rennovia Segmented Itemized Capital Cost Estimate.....	9-56
9.22	Rennovia Itemized Capex Segmented by Equipment Type.....	9-57
9.23	Rennovia Itemized Capex Segmented by Plant Section.....	9-57
9.24	Rennovia Total Fixed Capital Cost Estimate.....	9-59
9.25	Factored Total Fixed Capital Cost Estimates	9-60
9.26	Rennovia Process Variable Production Cost Estimate	9-61
9.27	Rennovia Process Total Production Cost Estimate.....	9-62

GLOSSARY

Symbol or Term	Definition
°C	Temperature, degrees Celsius
°F	Temperature, degrees Fahrenheit
304SS	Grade 304 stainless steel
316L SS	Grade 316L stainless steel
3PA	3-Pentenoic acid
ADA	Adipic acid
AGS	A mixture of adipic, glutaric, and succinic acids
Alcohol	A class of organic molecules with a terminal or internal carbon atom containing a hydroxyl (O-HO) group
Aldaric acid	A group of sugar acids characterized by the formula HOOC-(CHOH) _n -COOH. Arabinaric, galactaric (mucic), glucaric (saccharic), mannaric, ribaric and xylaric acids are all aldaric acids
Aliphatic	Any non-aromatic organic compound having an open chain structure
Alkali	A classification of substances that liberate hydroxide ions in water, to form caustic and corrosive solutions which turn litmus paper blue, with a pH higher than 7, for example sodium Hydroxide. A compound that reacts with or neutralizes hydrogen ions
Alkylate	A gasoline blending component composed of isobutane and propylene or butylene
Anhydrous	Without water, dry. Liquids and solids (powders) are sold as "anhydrous" when they have been processed to remove water from the end product. Transesterification of biodiesel must be an anhydrous process or funny things happen. Water in the vegetable oil causes either no reaction or cloudy biodiesel, and water in lye or methanol renders it less useful or even useless, depending on how much water is present. Either let your vegetable oil settle for 2–3 days before using and drain the water off the bottom, or heat the oil and boil off the water. Store lye and methanol in (separate) air-tight containers
ANSI	American National Standards Institute
API	American Petroleum Institute
API gravity	An American Petroleum Institute measure of specific gravity
APM	22% Cr, 6.0% Al alloy
Arabinarates	A salt or ester derivative of arabinaric acid
Arabinaric acid	A five carbon aldaric acid derived from the simple sugar, arabinose
Aromatic	Any organic compound containing de-localized electrons in a ring structure—e.g., benzene, benzoic acid
As	Arsenic
ASTM	American Society for Testing and Materials, an international voluntary standards organization that develops and produces technical standards for materials, products, systems and services
Atm	Atmospheres
B	Boron
Bar	Unit of pressure
Barge	A vessel carrying oil usually on rivers containing between 8,000 to 50,000 bbl or weighing 1,000 to 10,000 mt
Barrel	A volumetric unit of measure for crude oil and petroleum products. One barrel equals 42 US gallons

GLOSSARY (Continued)

Symbol or Term	Definition
Base	A classification of substances which when combined with an acid will form a salt plus water, usually producing hydroxide ions when dissolved
Battery	Equipment to process or store crude oil from one or more wells
bbl	Barrels of petroleum
Benchmarking measures	Data and information used as a point of reference against which industry performance is measured
Benzene	A light aromatic hydrocarbon, which occurs naturally as a part of oil and natural gas activity. It's considered to be a non-threshold carcinogen and is an occupational and public health concern
BFW	Boiler feedwater
BLI	Battery limits investment
bn	Billions
BP	British Petroleum PLC
bpd	Barrels of petroleum per day
bpsd	Barrels per stream day
BTU	British Thermal Unit
BTX	Benzene, toluene + xylene
BTX extraction	The process for removing benzene, toluene and xylene from reformate or pyrolysis gasoline
Capacity factor	The ratio of the electrical energy produced by a generating unit for the period of time considered to the electrical energy that could have been produced at continuous full-power operation during the same period
Capital cost	The cost of field development and plant construction and the equipment required for the generation of electricity
Carbohydrate chemistry	A subdiscipline of chemistry primarily concerned with the synthesis, structure, and function of carbohydrate molecules
Carbon chain	The atomic structure of hydrocarbons in which a series of carbon atoms, saturated by hydrogen atoms, form a chain. Volatile oils have shorter chains. Fats have longer chain lengths, and waxes have extremely long chains
Carboxyl	Carboxylic, the uni-valent acid radical (-COOH), present in most organic acids, this making them biodegradable
Carboxylic acids	Organic acids characterized by the presence of a carboxyl group, which has the formula -C(=O)OH, usually written -COOH or -CO ₂ H
Catalyst	A substance which without itself undergoing any permanent chemical change, facilitates or enables a reaction between other substances
Cd	Cadmium
Centrifugal pump	A rotating pump, commonly used for large-volume oil and natural gas pipelines, that takes in fluids near the center and accelerates them as they move to the outlet on the outer rim
cfd	Standard cubic feet per day flow rate
CFPP	Cold filter plugging point
CH ₄	Methane
CHHP	Cyclohexyl hydroperoxide
CHO	Cyclohexene oxide
CIF	Cost, insurance + freight
cm ²	Square centimeter
CO	Carbon monoxide

GLOSSARY (Continued)

Symbol or Term	Definition
CO ₂	Carbon dioxide
Condensate	Hydrocarbons, usually produced with natural gas, which are liquid at normal pressure and temperature
CST	Centistokes. A way of measuring viscosity similar to seconds
CSTR	Constant composition tank reactor
CTW	Cooling tower water
CUM	Cubic meters
De-icing	The practice of applying chemicals to roadways or other surfaces to remove previously formed frost or ice
Density	The heaviness of crude oil, indicating the proportion of large, carbon-rich molecules, generally measured in kilograms per cubic meter (kg/m ³) or degrees on the American Petroleum Institute (API) gravity scale; in Western Canada oil up to 900 kg/m ³ is considered light to medium crude—oil above this density is deemed as heavy oil or bitumen scale
Desulphurization	The process of removing sulphur and sulphur compounds from gases or liquid hydrocarbon mixes
Detergent builder	Chemical additive used to extend or improve the cleaning properties of detergent surfactants. The primary function of builders is to soften water by sequestering metal cations, thus preventing soap scum formation
dm ²	Square decimeters
DMAD	Dimethyl adipate
DME	Dimethyl ether
DMFC	Direct methanol fuel cells
DMT	Dimethyl terephthalate
DOE	US Department of Energy
Downstream sector	The refining and marketing sector of the petroleum industry
EC	European Commission
EHS	Environmental, Health & Safety
Emulsion	A usually unstable dispersion of two liquids which do not normally mix (they are immiscible). Emulsions can be formed either by mechanical agitation, or by chemical processes. Unstable emulsions will separate over time or temperature, stable emulsions will not separate
Enhanced oil recovery (EOR)	Any method that increases oil production by using techniques or materials that are not part of normal pressure maintenance or water flooding operations. For example, natural gas can be injected into a reservoir to “enhance” or increase oil production
EPA	US Environmental Protection Agency
EPC	Engineer, procure and construct
Ester	A classification of organic compounds occurring naturally as oils and fats, produced by replacing the hydrogen of an acid by an alkyl, aryl, radical. A compound of an organic acid bonded via an ester bond to an alcohol. Any of a large group of organic compounds formed when an acid and alcohol is mixed. CH ₃ COOCH ₃ (Methyl acetate) is the simplest ester. Biodiesel is often described as a fatty acid methyl ester (FAME)
EU	European Union
Exfoliant	A mechanical or chemical agent that is applied to the skin to remove dead cells from the surface

GLOSSARY (Continued)

Symbol or Term	Definition
FEED	Front end engineering design
Flash point	The lowest temperature under very specific conditions at which a combustible liquid will give off sufficient vapor to form a flammable mixture with air in a standardized vessel
Flow line	Pipe, usually buried, through which oil or gas travels from the well to a processing facility
FOB	Free on board
FOR	Free on rail
Free fatty acids	Fatty acid hydrocarbon chains detached from other molecules, like glycerol
g	Gram
G&A	General and administrative costs
G/L	Grams per liter
gal	Gallon
GC	Gas chromatograph instrument
GDP	Gross domestic product
Glucarate	A salt or ester derivative of glucaric (saccharic) acid
Glucaric acid	A six carbon aldaric acid derived from the simple sugar, glucose
Gluconate	A salt or ester of gluconic acid
Gluconic acid	A sugar acid produced from the oxidation of the simple sugar, glucose. Gluconic acid differs from glucaric acid in that gluconic acid has only one carboxylic acid group whereas glucaric acid has two
Glucuronidation	The coupling of glucuronic acid with other substances to increase the water solubility of that substance for safe elimination from the human body
Glycol dehydrator	Field equipment used to remove water from natural gas by using triethylene glycol or diethylene glycol
H	Hydrogen
H ₂	Hydrogen
H ₂ O	Water
HAZOP	Hazardous operations review
HHV	Higher heating value
HMDA	Hexamethylenediamine
HO	Heating oil
HS	High sulfur content
HSFO	Heavy sulfur fuel oil
HX	Heat exchanger
Hydrocarbon	A compound of hydrogen and carbon, often occurring as long atomic chains in which each carbon atom is attached to two hydrogen atoms forming a long chain. They store a great deal of energy
Hydrogenation	A chemical reaction in which unsaturated bonds between carbon atoms are reduced by attachment of a hydrogen atom to each carbon. When the process is carried to completion it converts unsaturated fatty acids to saturated ones. Changing the degree of saturation of the fat changes important physical properties such as melting point, which is why the liquids become semi-solid. Since partially hydrogenated vegetable oils are much less expensive than most other fats with similar characteristics, and because they have other desirable characteristics leading to longer shelf life, they are the predominant fat used in most commercial baked goods

GLOSSARY (Continued)

Symbol or Term	Definition
Hydrotransport	Oil sand from the mine operation is mixed with hot water and caustic and the oil sand slurry is then transported by pipeline to the extraction plant where it feeds directly into the Primary Separation Vessel
Hydrotreater	A unit which removes sulphur and nitrogen from the components of crude oil by the catalytic addition of hydrogen
Hydroxycarboxylic acids	A group of organic compounds containing both carboxyl (-COOH) and hydroxyl (-OH) groups. Citric acid, gluconic acid, and glucaric acid are all examples of hydroxycarboxylic acids
Hygroscopic	The tendency of something to absorb water (usually from humidity in the air). Biodiesel absorbs water to about 1200 parts per million (PPM). Methanol and NaOH are also hygroscopic. Keep containers closed
IBP	Initial boiling point
ICE	Internal combustion engine
ID	Inside diameter
IEA	International Energy Agency
IEEE	Institute of Electrical & Electronic Engineers
IP	Intellectual property
IPCC	Inter-governmental panel on climate control
IRR	internal rate of return
ISO	International Standards Organization
Isomerate	A gasoline blendstock made in an isomerization unit
k	Thousands
KA oil	Cyclohexanone and cyclohexanol
kg	Kilogram
KO	Knock out (drum)
KT	Kilo tons
kty	kilo tons per year
kW	Kilowatt, Unit of power (1,000 watts)
kWh	Kilowatt-hours. A unit of energy equal to that produced or consumed by one kilowatt of capacity in one hour of operation
LNG	Liquefied natural gas
LPG	Liquefied petroleum gas
LPS	Low-pressure steam
LS	Low sulfur
LSD	Low sulfur diesel fuel
LSFO	Low sulfur fuel oil
LSTK	Lump sum turn key
LSWR	Low sulfur waxy residual fuel oil
m	Meter
m ²	Square meter
M2P	Methyl-2-pentenoates
M3CP	Methyl 3-cis-pentenoate
M3P	Methyl-3-pentenoates
M3TP	Methyl 3-trans-pentenoate
M4P	Methyl-4-pentenoate
M5FV	Methyl-5-formylvalerate
Mannarate	A salt or ester derivative of mannaric acid

GLOSSARY (Continued)

Symbol or Term	Definition
Mannaric acid	A six carbon diacid derived from the simple sugar mannose
Medium crude oil	Liquid petroleum with a density between that of light and heavy crude oil
MEK	methyl ethyl ketone
Methane	The principal constituent of natural gas; the simplest hydrocarbon molecule, containing one carbon atom and four hydrogen atoms
Methanol	CH^3OH —a volatile colorless alcohol, derived originally as wood alcohol, used as a racing fuel and as a solvent. Also called methyl alcohol. Lethal if consumed. Used to make methoxide in biodiesel production. Methanol absorbs water from the air, so keep the container closed tightly, and purchase methanol which is known to be dry (anhydrous) or is 99.9% pure
mm	Millimeter
MM	Millions
MMA	Methyl methacrylate
MOGAS	Motor gasoline
MON	Motor octane number
MP	Melting point (temperature of melting)
MP	Methyl pentenoate
MPS	Medium-pressure steam
MSDS	Material safety data sheet
MT	Metric ton
MTBE	Methyl tertiary butyl ether
MW	Megawatt (million watts)
MWH	Megawatt hours
MWp	Megawatt peak or Million watt peak
NGL	Natural gas liquids
NIST	National Institute of Standards & Technology
NOx	Nitrogen oxides
NPRA	National Petrochemicals and Refiners Association
NVR	Non-volatile residue
O&M	Operations and maintenance cost
O&M cost	Operating expenses are associated with operating a facility (i.e., supervising and engineering expenses). Maintenance expenses are that portion of expenses consisting of labor, materials, and other direct and indirect expenses incurred for preserving the operating efficiency or physical condition of utility plants that are used for power production, transmission, and distribution of energy
OD	Outside diameter
OEM	Original equipment manufacturer
Operator	The company or individual responsible for managing an exploration, development or production operation
Organic	Compounds that contain carbon, which are often created as a result of a life process
Organic acid	A class of organic molecules with a terminal chain carbon atom containing one hydrogen atom, and others containing a hydroxyl ($\text{O}-\text{H}$) group
OSI	Offsites investment
Overburden	Layer of rocky, clay like material that lies under muskeg

GLOSSARY (Continued)

Symbol or Term	Definition
Oxidation	Burning in oxygen, normally highly exothermic (heat releasing), but also any increase in oxidization state, (i.e. loss of electrons). Results in the formation of an oxide, rusting or corroding. Various materials, such as copper and brass, may oxidize in the presence of vegetable oil or biodiesel
Oxygenate	Oxygen-containing blend stocks favored for their octane and their clean burning quality
Ozone	Ground level ozone is a colorless gas that forms just above the earth's surface
P	Phosphorus
PET	Polyethylene terephthalate
Petroleum	A naturally occurring mixture composed predominantly of hydrocarbons in the gaseous, liquid or solid phase
pH	A measure of acidity and alkalinity of a solution on a scale with 7 representing neutrality. Lower numbers indicate increasing acidity, and higher numbers increasing alkalinity. Each unit of change represents a tenfold change in acidity or alkalinity. pH is mathematically found by taking the negative logarithm of the effective hydrogen-ion concentration or hydrogen-ion activity. The units are gram equivalents per liter of the solution
PN	Pentenenitrile
Polyglucaramides	Nylon-type polymers produced from combining glucaric acid with a diamine
ppm	Parts per million concentration
ppma	Parts per million atomic
PPMV	Parts per million by volume
ppmw	Parts per million by weight
PPMW	Parts per million by weight
psi	Pounds per square inch
psia	Pounds per square inch absolute
PTA	Purified terephthalic acid
ROI	Return on investment
Saccharic acid	A synonym for D-glucaric acid
Sandstone	A compacted sedimentary rock composed mainly of quartz or feldspar; a common rock in which oil, natural gas and/or water accumulate
Saponification	The reaction of an ester with a metallic base and water. The making of soap. This happens sometimes when you use too much lye in a biodiesel reaction. No worries—you can re-react the resulting top layer of unreacted liquid, and if you wish you can turn the semi-solid bottom layer into soap by adding more lye (make sure you know how much to add...)
scf	Standard cubic feet per day flow rate
scfm	Standard cubic feet per minute
Sodium hydroxide	NaOH, lye, caustic soda (Red Devil Drain Cleaner). A metallic base. Strongly alkaline and extremely corrosive. Mixing with fluids usually causes heat, and can create enough heat to ignite flammables (such as methanol), so add slowly. For biodiesel, this is one of the main reactants. Make sure you are purchasing “anhydrous sodium hydroxide.” Anhydrous means it’s dry, and water turns biodiesel into soap. Store this product in an airtight container to prevent NaOH from absorbing water and CO ₂ from the air. Store separately
SS	Stainless steel

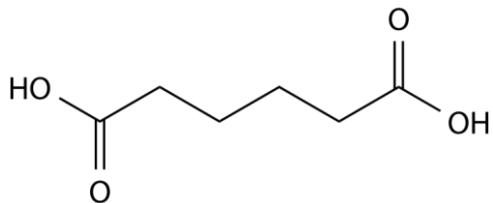
GLOSSARY (Concluded)

Symbol or Term	Definition
TFC	Total fixed capital cost
USAC	US Atlantic Coast
USGC	United States Gulf Coast
VFD	Variable-frequency drive
Viscosity	The ability of a fluid to respond to movement. A high viscosity will resist movement, and a low viscosity will flow quickly. This is not necessarily the same as density. Viscosity is normally measured comparatively by the time a given volume of liquid will pass through a pipe of fixed diameter. Methanol has a low viscosity, while vegetable oil has a high viscosity
VOC	Volatile organic compound. Gases and vapors, such as benzene, released by petroleum refineries, petrochemical plants, plastics manufacturing and the distribution and use of gasoline; VOCs include carcinogens and chemicals which react with sunlight and nitrogen oxides to form ground-level ozone, a component of smog
W	Watts

1 INTRODUCTION

Adipic Acid (CAS 124-04-9: also called ADA, hexanedioic acid, 1,4-butanedicarboxylic acid, 1,6-hexanedioic acid, and adipinic acid) is a white, crystalline solid consisting of a C₆ straight-chain hydrocarbon with two carboxylic acid radicals on the terminal carbon atoms. Adipic acid is slightly soluble in water and highly soluble in alcohol and acetone. Annual global consumption in 2012 is estimated to be 2.6 MM metric tons. Adipic acid's molecular structure is shown below.

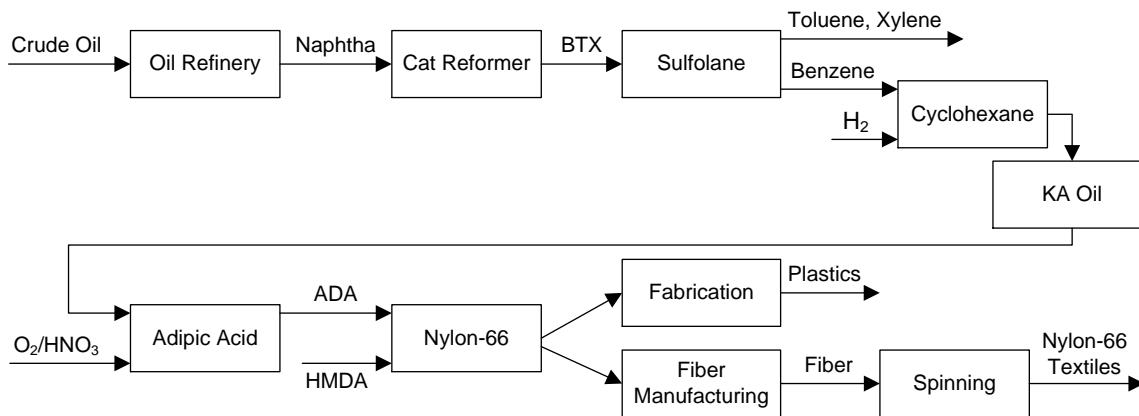
Figure 1.1
ADIPIC ACID MOLECULAR STRUCTURE



Adipic acid is one of the two components used to manufacture nylon 66. The other component is hexamethylenediamine (HMDA). Nearly two-thirds of all the adipic acid made globally is consumed in nylon 66 production for textile fibers and as an engineering resin. Other end uses for adipic acid are in polyols used to make rigid and flexible foam polyurethane products (footwear, bedding, thermal insulation, furniture, auto seating), as a plasticizer component to produce flexible PVC used in wire and cable insulation, and for automotive interiors.

The adipic acid integrated product chain starts with crude oil, which has increased in price significantly over the past 20 years. Developers of bio-based chemical technologies believe that they will be able to create commercial scale manufacturing technology to produce adipic acid at a much lower cost using nonfood agricultural feedstocks that are much lower in cost than hydrocarbon-based feedstocks.

Figure 1.2
ADIPIC ACID INTEGRATED PRODUCT CHAIN



Beside the normal greenhouse gas concerns associated with using any fossil fuel source as a feedstock, the conventional commercial process produces nitrous oxide (N_2O) as a reactor by-product, which exerts an enormous greenhouse gas effect. Due to its long atmospheric lifetime (approximately 120 years) and heat trapping effects—about 310 times more powerful than carbon dioxide on a per molecule basis— N_2O is an important greenhouse gas (US EPA, “Nitrous Oxide—Climate Change,” 22-Jun-2010). Most adipic acid producers in industrial countries have voluntarily installed process equipment to destroy N_2O . Most adipic acid producers in developing countries have not.

Bio-based manufacturing technology has the potential to eliminate both the greenhouse gas impacts associated with using fossil fuels, and the specific greenhouse gas impacts associated with discharging nitrous oxide to the atmosphere.

Alternative process technology is widely practiced to make nylon 6 from caprolactam, which is also derived from crude oil. Nylon-6 and nylon-66 are nearly interchangeable for most commercial end uses, but nylon-66 has superior high-temperature properties for applications such as automotive engine components.

The conventional industrial process for making adipic acid uses the air oxidation of cyclohexane to produce a combination of cyclohexanol and cyclohexanone (called KA oil) as an intermediate product. KA oil is further oxidized to crude adipic acid using nitric acid oxidation. Crude adipic acid is purified to fiber-grade specifications using three stages of crystallization, most often using Oslo suspension crystallizers in combination with pusher centrifuges. The leading producers of conventional adipic acid are Invista, Ascend, BASF, Radici, Rhodia, China Shenma, and PetroChina.

Food-based bio-feedstocks used to make first generation fuels such as bio-ethanol and biodiesel have received scrutiny for driving up the price of food, and thereby contributing to starvation in poor parts of the world. As a result, most developmental activities for second-generation bio-chemicals and bio-fuels are focused on nonfood bio-source feedstocks such as sugar, waste agricultural products, grasses, algae, and non-edible fast growing species like jatropha.

The leading developers of bio-based adipic acid process technology are BioAmber, Draths, Genomatica, Rennovia, and Verdezyne (284001). The development status of these organizations, as of mid-2012, is listed in the table below.

Table 1.1
STATUS OF BIO-BASED ADIPIC ACID DEVELOPERS

Bio-Developer	HQ Location	Feedstock	Technology	2012 Commercialization Status
BioAmber	Plymouth, MN, USA	Carbohydrates	Fermentation via genetically modified enzymes. Advanced purification scheme	Dedicated lab built in Plymouth, Mn USA for ADA purification
Celexion	Cambridge, MA, USA	Carbohydrates	Modified bacteria (<i>Escherichia coli</i>) applied to C ₆ substrates	Modifying its commercial succinic acid fermentation know-how to ADA
Draths/Amyris	Lansing, MI, USA	Muconic acid	Produces commercial C ₆ -based nylon precursors (ADA, HMDA, Capro)	Acquired by Amyris, who is developing higher performance fermentation organisms
Genomatica	San Diego, CA, USA	Sugar	Genetically modified bacteria applied in direct fermentation	Bio-ADA patent filed in 2010
Rennovia	Menlo Park, CA, USA	Glucose	Catalytic hydrogenation and oxidation	Continuous pilot plant operating and making KG quantities. Design of demonstration unit initiated. Targets commercial production in 2015
Verdezyne	Carlsbad, CA, USA	Sugars, fatty acids and esters	Fermentation using genetically modified bacteria	Pilot plant start-up in 2011. Commercial plant expected in 2014
DSM	Heerlen, Netherlands	Glucose	Fermentation	Patents filed. Plans to commercialize at 100 kty by 2017. Invested in Verdezyne
Novozymes	Waltham, MA, USA	Glucaric acid	Fermentation of sugars using genetically modified enzymes	Developing lab scale product in partnership with Cargill and BASF

This report presents Class-3 process engineering designs and the corresponding production economics for three routes to adipic acid. The conventional route is our understanding of the current version of the Invista/DuPont two-stage oxidation of cyclohexane. This process includes crystallization recovery of high-purity AGS by-product, recovery of miscellaneous carboxylic acids to commercial product via esterification with methanol, and nitrous oxide destruction.

Two bio-based routes for making commercial quantities of adipic acid are evaluated. The first is our understanding of the Verdezyne fermentation process using genetically modified enzymes and a glucose substrate. Verdezyne is also developing adipic acid technology using other feedstock platforms, including hexane and vegetable oils.

The second bio-based route is our understanding of Rennovia's catalytic process for converting glucose to adipic acid using novel precious metal catalyst complexes developed via

Symyx high-throughput screening technology. The first step is oxidizing an aqueous glucose solution to glucaric acid using air as the oxidant and a gold/platinum/palladium/tungsten nano-dispersed catalyst on titanium oxide substrate. This chemistry converts the C₆ terminal carbon atoms (one saturated, one an aldehyde) to carboxylic acid groups without affecting the internal carbon atoms. The second step uses hydrogen at high pressure to hydrogenate the four internal carbon atoms containing hydroxyl groups (OH-) of glucaric acid (in acetic acid solvent promoted with hydrogen bromide) such that they become saturated with hydrogen, forming adipic acid. The hydrogenation step is conducted over a platinum/rhodium catalyst dispersed on a silicon oxide substrate.

Conclusions are drawn about the potential economic competitiveness of the bio-based routes with the conventional cyclohexane process, and the major hurdles that will have to be overcome for the bio-based routes to be able to compete on cost with conventional commercial technology.

This report is the fourth IHS Process Economics Program (PEP) report on adipic acid since the original PEP report was prepared in 1965. Other relevant IHS publications include an IHS Chemical Economics Handbook (CEH) report on adipic acid, and a Safe and Sustainable report entitled, "Chemical Building Blocks from Renewables."

2 SUMMARY

Over 90% of the global production of adipic acid (ADA) is made via the two-stage oxidation of cyclohexane, which is derived from crude oil production. The first stage oxidizes cyclohexane with air to produce a combination of cyclohexanone (ketone) plus cyclohexanol (alcohol) termed 'KA oil,' while the second stage oxidizes KA oil to adipic acid in concentrated nitric acid. Purification to fiber specification ADA is accomplished with three stages of suspension crystallization (one-stage crude crystallization, two stages of aqueous crystallization) using Oslo crystallizers and pusher centrifuges.

There are significant efforts being made to develop alternative bio-based processes to produce adipic acid from potentially lower cost and sustainable biomass derived feedstocks, either using fermentation or using industrial catalytic processes. For this study, we have evaluated the production of adipic acid using 1) Verdezyne Corporation's fermentation technology employing genetically modified enzymes to convert glucose to adipic acid, and 2) Rennovia Corporation's catalytic technology to convert glucose first to glucaric acid in water using air oxidation, and then converting glucaric acid into adipic acid via trickle bed hydrodeoxygenation with hydrogen.

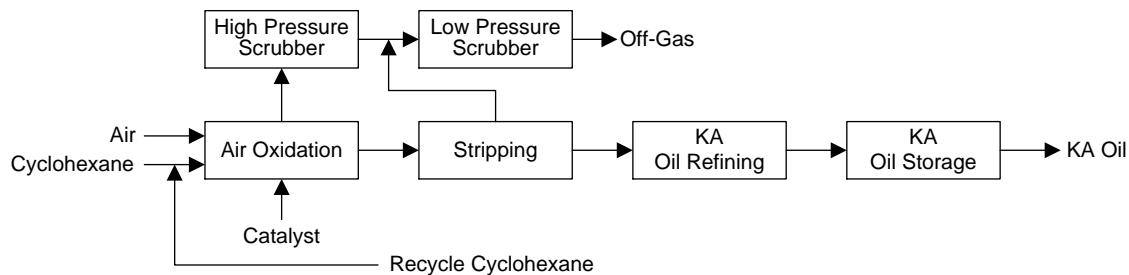
As a benchmark for comparison, we have updated our previous reports on conventional adipic acid production from cyclohexane, using trade and patent literature from DuPont and Invista.

PROCESS TECHNOLOGY DESCRIPTIONS

Conventional Adipic Acid Production Technology from Cyclohexane

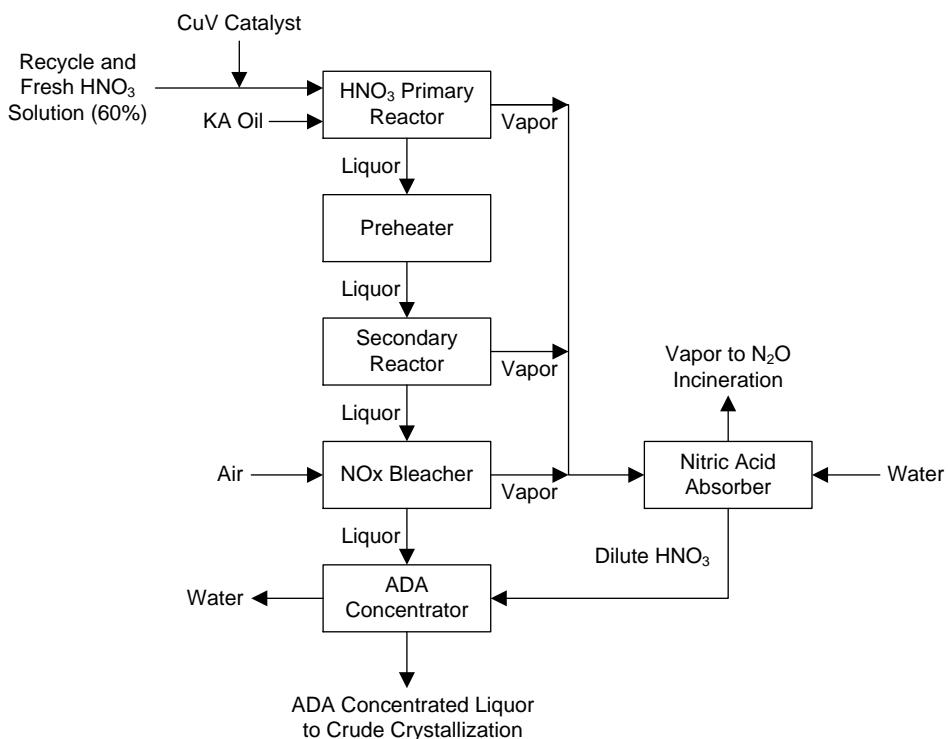
Cyclohexane from heated storage (to prevent freezing) is oxidized to KA oil using air in a series of autoclave constant composition tank reactor (CSTR) liquid reactors using compressed air. The catalyst is homogenous cobalt naphthenate enhanced with boric acid. Conversion per stage is maintained at a low 12% in order to maximize selectivity to KA oil. The air-rich off-gas is first scrubbed with fresh cyclohexane feedstock to recover hydrocarbons, and subsequently scrubbed with caustic soda to remove residual acidic contaminants. The exothermic heat of reaction is removed by jacketing the autoclave reactors with cooling water coils. A significant portion of the cyclohexane is converted to intermediate product cyclohexyl hydroperoxide, which is oxidized in an on-purpose reactor to KA oil using chromium oxide catalyst. Due to the low conversion per pass of reaction, the reactor product liquid is distilled for the purpose of recovering and recycling unconverted cyclohexane.

Figure 2.1
OXIDATION OF CYCLOHEXANE TO KA OIL



KA oil is further oxidized to crude adipic acid using two stages of nitric acid reactors in series, and a mixture of copper and vanadium homogeneous catalyst. The first reactor is designed as a shell-and-tube reactor packed with catalyst, while the second reactor in series operates as a CSTR reactor. The exothermic heat of reaction is removed on the shell side of the reactor by producing saturated steam.

Figure 2.2
NITRIC ACID OXIDATION OF KA OIL TO ADIPIC ACID



Crude adipic acid product dissolved in nitric acid mother liquor is recovered via three consecutive stages of suspension crystallization. Due to the high rate of production of by-products succinic acid and glutaric acid, a separate on-purpose crystallization unit is provided to

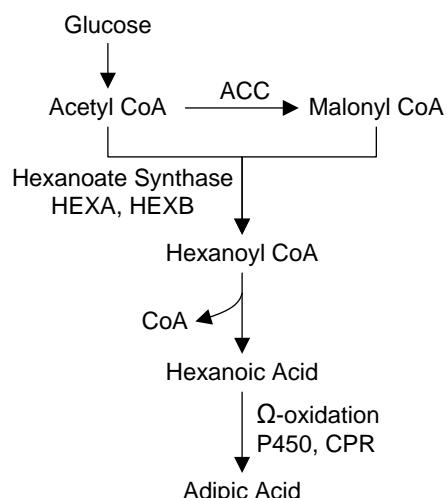
recover a combination of adipic acid, succinic acid, and glutaric acid (termed AGS) as a commercial product. Miscellaneous mono- and dicarboxylic acids are also recovered as a commercial product by reacting them with methanol to produce the corresponding methyl esters, and then recovering and purifying the methyl esters via conventional fractional distillation.

A third process unit is employed to destroy nitrous oxide, which has an enormous greenhouse gas potential. Several commercially offered technologies are available to either reduce N₂O back to molecular nitrogen, or to oxidize N₂O back to dilute nitric acid for recycle to the process. We have selected in our design the nitric acid regeneration technology offered by Invista.

Adipic Acid Production Technology from Glucose via Verdezyne Fermentation

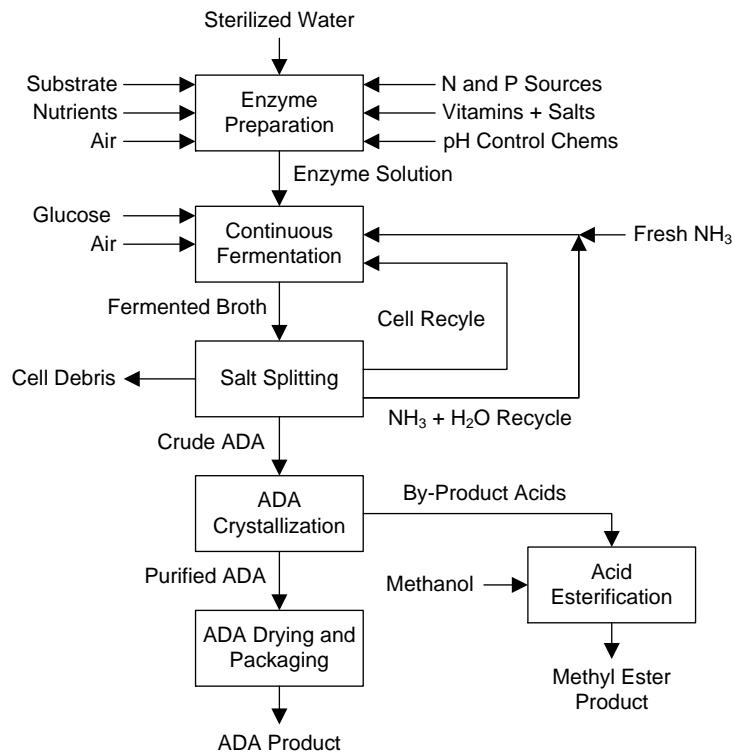
Verdezyne Corporation has developed a patent estate for producing adipic acid from a variety of biomass feedstocks using genetically modified enzyme catalysts (forms of candida yeast). The Verdezyne pathway from glucose to adipic acid appears to be hexanoate synthesis, in which hexanoic acid is the intermediate product (see pathway diagram below). Hexanoic acid is then preferentially oxidized to adipic acid.

**Figure 2.3
VERDEZYNE PATHWAY TO ADIPIC ACID FROM GLUCOSE (USPA 2012 0156761)**



To prevent the enzyme yeast from becoming poisoned by the production of crude adipic acid, which progressively reduces the pH of the aqueous fermentation broth, a chemical has to be continuously added to the broth to convert the acid to a non-toxic form. The conventional approach is for ammonia to be injected constantly into the broth to convert produced adipic acid to the corresponding diammonium salt, which remains dissolved in the broth. The broth is subsequently processed through a liquid-liquid extraction unit to selectively remove the ammonium salt, which is then back split to recover the adipic acid by heating. For our design, however, we have chosen a patented approach by BioAmber to first convert the diammonium salt to monoammonium salt, and then to distill the monoammonium salt in solution to re-form ammonia and dilute adipic acid. The dilute adipic acid is purified by suspension crystallization. The overall Verdezyne process for converting glucose to adipic acid is presented in the block flow diagram shown below.

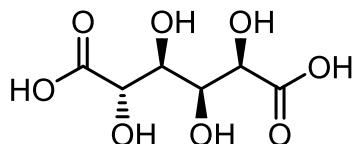
Figure 2.4
VERDEZYNE FERMENTATION PROCESS BLOCK FLOW DIAGRAM



Adipic Acid Production Technology from Glucose via Rennovia Industrial Catalysis

Rennovia Corporation has developed a two-stage process for producing adipic acid from glucose using industrial catalytic chemistry. In the first stage, a glucose solution in water is oxidized with air to produce primarily glucaric acid using nano-dispersed gold and platinum catalyst on a titania substrate. Glucaric acid is a linear C₆ dicarboxylic acid with acid groups on the terminal carbon atoms, while the four internal carbon atoms each contain one hydroxyl (OH-) group.

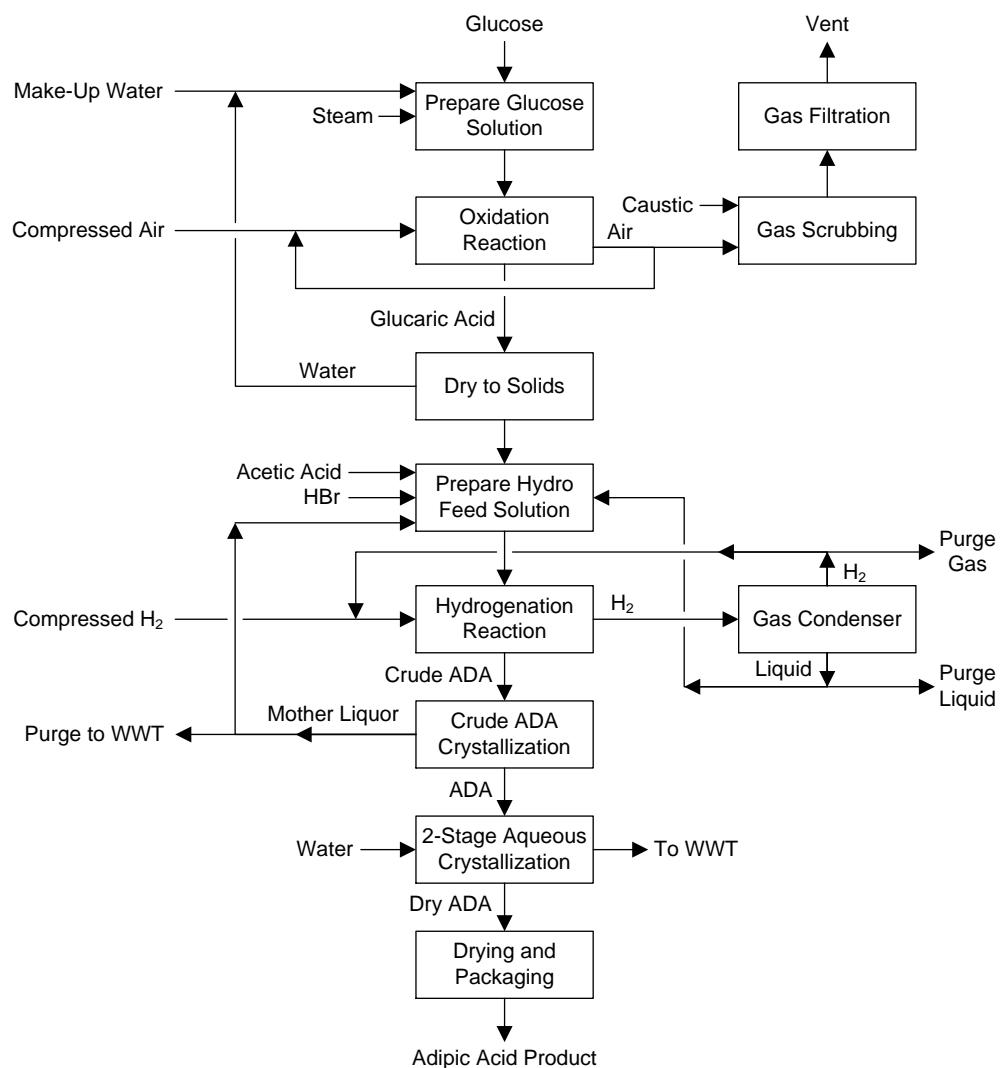
Figure 2.5
GLUCARIC ACID MOLECULAR STRUCTURE



The glucaric acid solution produced by the air oxidation reaction is completely dried to remove water, and subsequently redissolved in a solution of acetic acid containing a small quantity of hydrogen bromide promoter. The acetic acid solution is directed to a trickle bed hydrogenation reactor, in which the hydrogen atoms strip the oxygen atoms from the internal

carbon atom hydroxyl groups (forming water), resulting in a molecule in which the internal atoms are fully saturated with hydrogen. The terminal carbon atoms containing carboxylic acid groups are unaffected by the hydrogenation reaction. The catalyst used in the trickle bed reactor is a combination of platinum and rhodium on a silica substrate. The product of this reaction is crude adipic acid, which is purified by conventional multi-stage suspension crystallization. A block flow diagram of the proposed Rennovia process is shown below.

Figure 2.6
RENNOVIA PROCESS BLOCK FLOW DIAGRAM



PRODUCTION ECONOMICS

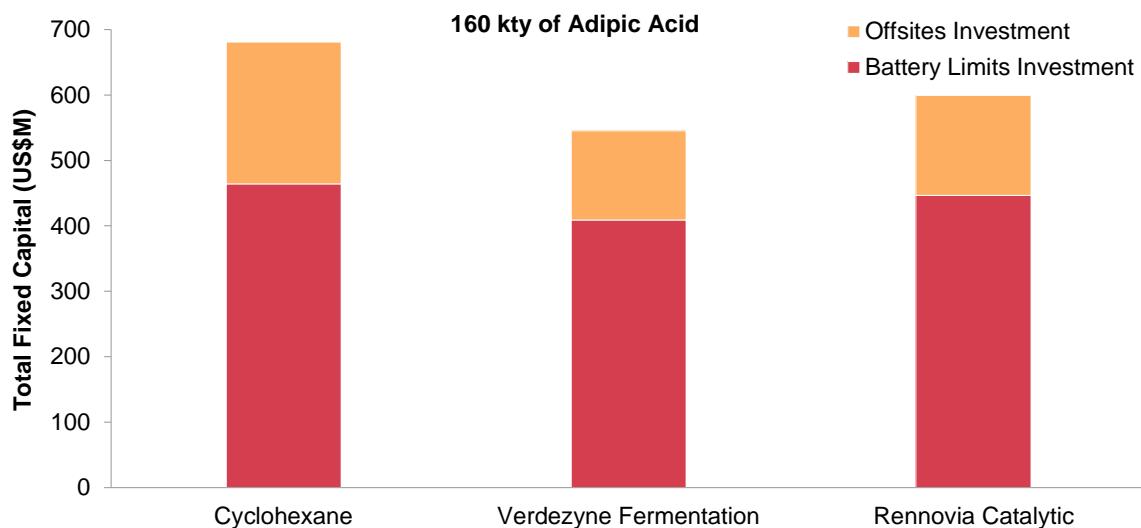
We have prepared a series of process flow diagrams (PFDs) for each of the three adipic acid processes, developed stream-by-stream material balances, and produced a tagged process equipment list with duty specifications for major equipment. From the equipment list we prepared

both an itemized capital cost estimate for the ISBL process equipment, and a total fixed capital cost estimate for each process. Our design was based on a single process train, 160 kty production plant on a grassroots basis.

Capital Cost Comparison

Our estimated total fixed capital cost for each process is presented in the figure below, segmented by inside battery limits investment and offsites battery limits investment. The capital cost estimate for the conventional cyclohexane-based process has the highest capital cost, as a result of the combination of process complexity (producing three commercial products, and destroying nitrous oxide), and the use of expensive alloys when processing the nitric acid solution for the oxidation of KA oil to crude adipic acid. Both biomass-based process capital costs are lower than the conventional process because they are simpler, and do not require expensive alloys.

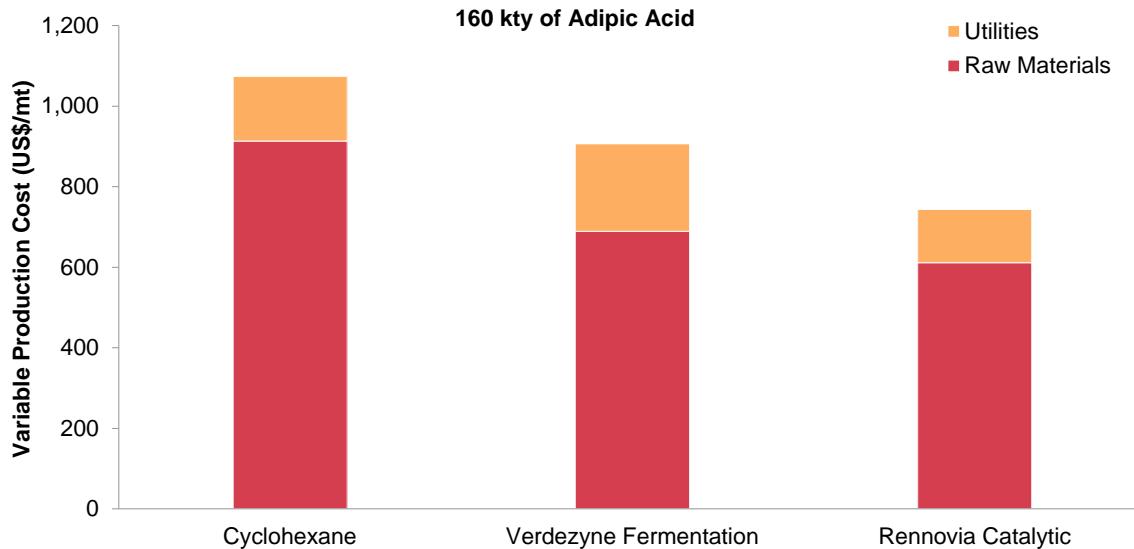
Figure 2.7
ADIPIC ACID CAPITAL COST PROCESS COMPARISON



Variable Production Cost Comparison

A comparison of the unit costs of raw materials and utilities is presented in the figure below. The conventional process using cyclohexane feedstock requires the most expensive feedstock, but the biomass-based processes using glucose feedstock require significantly more glucose to produce each metric ton of adipic acid. Utility costs are similar, but the Verdezyne fermentation process requires more process steam to concentrate, purify, and recycle the very dilute aqueous solution of feedstock and nutrients used to produce adipic acid via fermentation.

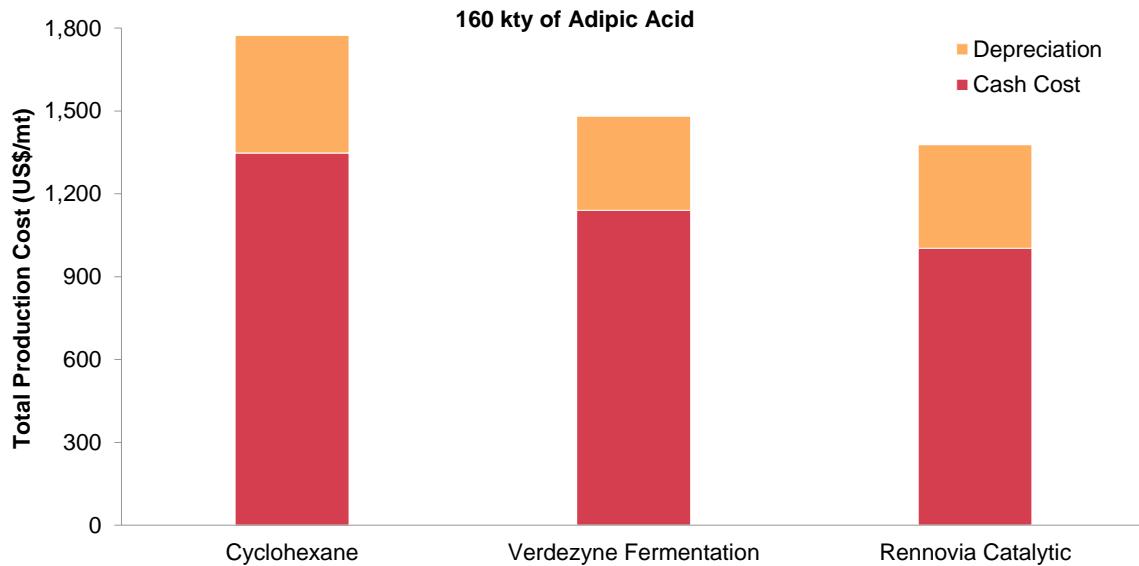
Figure 2.8
ADIPIC ACID VARIABLE COST PROCESS COMPARISON



Total Production Cost Comparison

A comparison of the total production cost of to produce adipic acid using each process is presented in the figure below. The conventional process and Verdezyne fermentation process have similar cash costs and total production costs, while the Rennovia process has measurably lower cash and total production costs due to its relatively low capital cost, and relatively high yield of adipic acid from glucose.

Figure 2.9
ADIPIC ACID TOTAL PRODUCTION COST PROCESS COMPARISON



Since the development of our production economics for the non-commercial bio-based processes is based on patent and trade data, a number of important assumptions were made in the development of the process designs and production economics. These assumptions may or not be valid when the lab and pilot scale data used in our analysis is scaled up to industrial capacity. The key assumptions that will affect actual production economics at industrial scale include:

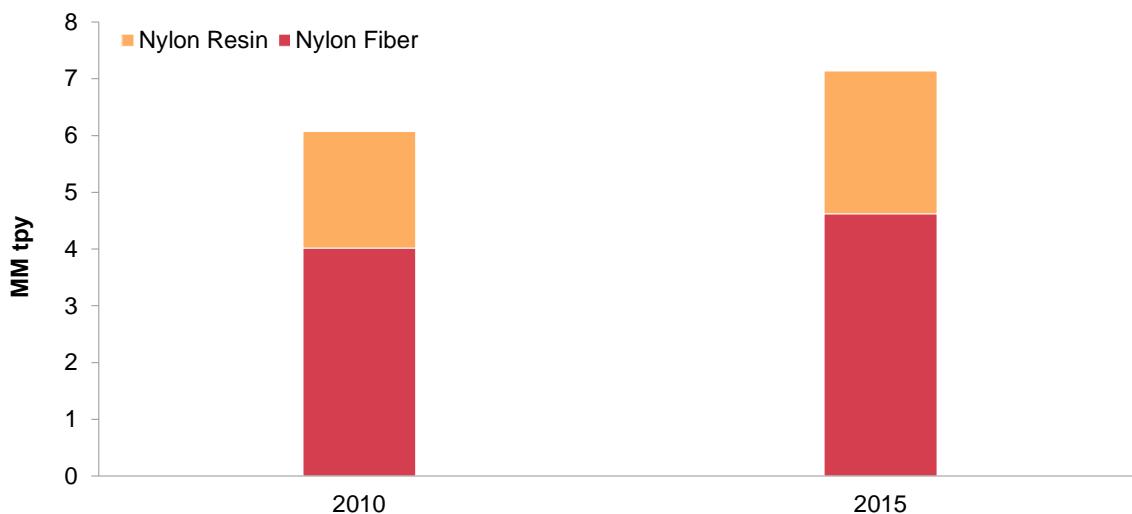
- The ability of glucose conversion reactions to scale-up while retaining competitive conversion and selectivity
- The ability of the Verdezyne enzyme catalyst to be recovered and recycled sufficient times to assure adequate commercial productivity (metric tons of product per metric ton of enzyme)
- The ability of the Rennovia precious metal catalysts to be manufactured at industrial scale at reasonable production cost, provide adequate catalyst productivity and yield, avoid in-process losses, and be recovered through conventional precious metal processing.

3 ADIPIC ACID INDUSTRY STATUS

ADIPIC ACID MARKET USES

Adipic acid is used primarily as a co-feedstock with HMDA (hexamethylenediamine) to produce nylon 66 fiber (mostly for carpets) and nylon 66 resin (mostly for automotive engine tubing and cast part applications). Nylon 66 is composed by weight of 66% adipic acid, and 34% HMDA. The 2010 and 2015 IHS forecast global demand for nylon fiber and resin is shown in the figure below.

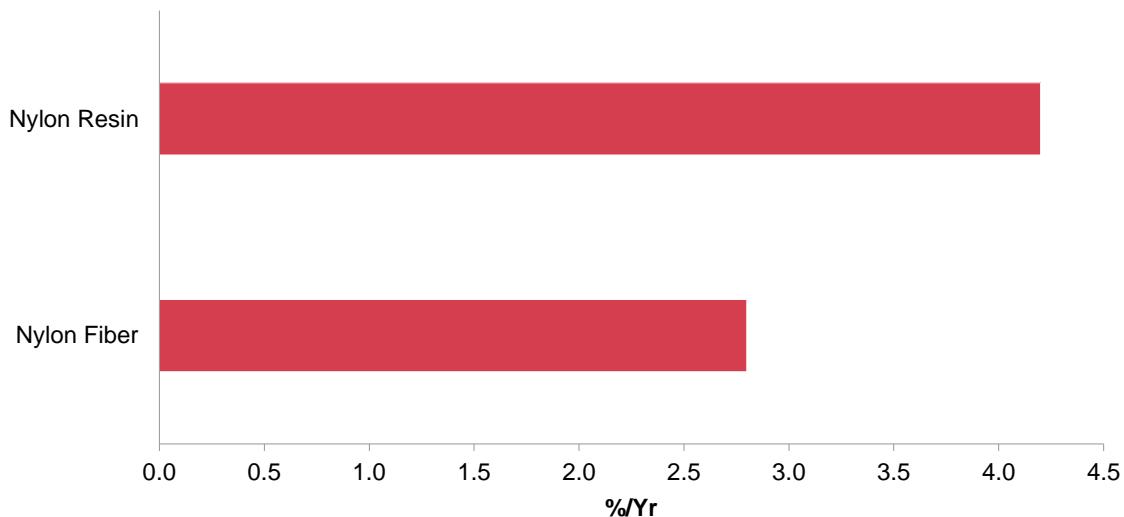
Figure 3.1
NYLON FIBER AND RESIN DEMAND



Source: IHS Chemical CEH

The anticipated annual global demand growth for nylon between 2010 and 2015 is presented in the graph below.

Figure 3.2
FORECAST NYLON DEMAND GROWTH RATE



Source: IHS Chemical CEH

A table segmenting major end uses for nylon 66 fiber and nylon 66 resin follows.

Table 3.1
NYLON 66 END USES

Nylon 66 Fiber	Nylon 66 Resin
Automotive tires	Auto intake manifolds
Residential carpet	Auto oil pans
Construction materials	Auto radiator end tanks
Recreation apparel	Auto valve train cover
Military apparel	Auto turbo air duct
Fishing line	Auto hybrid brake pedal
Rope and cord	Auto under carriage body panel and hood liner
Mattress pads and bath rugs	Auto engine mounts
Parachutes	Auto seating structure
Camping equipment (tents)	Auto fuel tank
Swim wear	Industrial machinery coatings
Auto airbags	Electric and electronic parts
	Film
	Wire and cable insulation
	Hydraulic hose linings

Source: Solvay/Rhodia

Other end uses for adipic acid are in polyols used to make rigid and flexible foam polyurethane products (bedding, thermal insulation, furniture, auto seating), and as a plasticizer component to produce flexible PVC used in wire and cable insulation, and automotive interiors. Adipic acid is also used as a lubricant formulating chemical, gel additive, acidulant, and solution buffering agent. Adipic acid is reacted with other chemicals to produce derivative chemicals used in flavoring agents, pesticides, textile colorings, fungicides, and pharmaceuticals. Specialty chemical formulations using adipic acid as a component are listed in the table below.

Table 3.2
CHEMICAL FORMULATIONS CONTAINING ADIPIC ACID

Polyamide polymers	Adhesives
Polyurethane systems	Paints
Organic synthesis	Flexible and rigid foams
Plasticizers	Detergents

Some of the major end-use products containing adipic acid are listed in the table below.

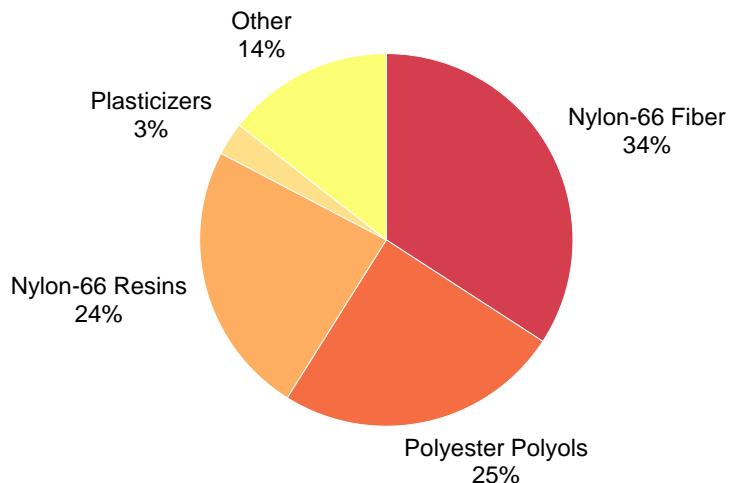
Table 3.3
END-USE PRODUCTS CONTAINING ADIPIC ACID

Agriculture	Manufacturing of plastics
Alkyd resins	Manufacturing of tensides
Carrier for fragrances	Manufacturing of textile dyestuffs
Coal	Manufacturing of textiles dyestuffs
Coating	Paper and board
Dyestuffs, pigments and optical brighteners	Paper manufacture
Energy	Pesticides
Environment protection	Photography
Flavor and fragrances	Plastic and polymers
Gas desulphurization	Plasticizers for polymers
Glues and adhesives	Polyester
Hardener and crosslinking agents for polymers	Polyester resins
Leather	Polymer auxiliaries
Leather auxiliaries	Specialties
Manufacturing of coating	Surface-active substances
Manufacturing of dyestuffs	Synthetic lubricants
Manufacturing of fibers	Tanning agents
Manufacturing of herbicides	Textile dyestuffs
Manufacturing of pharmaceutical agents	Textiles and fibers
Manufacturing of photochemicals	

Source: Lanxess

The distribution of global demand by use for adipic acid in 2012 is shown in the figure below.

Figure 3.3
GLOBAL END-USE DEMAND DISTRIBUTION FOR ADIPIC ACID IN 2012



Source: IHS Chemical CEH

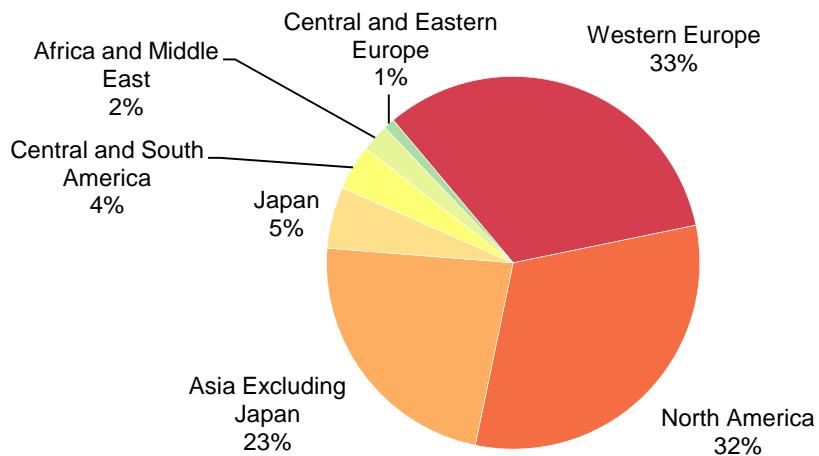
ADIPIC ACID DEMAND AND DEMAND GROWTH

Global consumption of adipic acid was 2.5 MM metric tons per year in 2011, with global demand growth forecasts of 1.5–2.0% per year. After World War II, economic recovery and the economic use of petrochemical feedstocks allowed for the production of nylon synthetic fiber carpets to replace natural fiber carpets (wool and cotton). Adipic acid demand has historically been closely tied with the residential nylon carpet market. Over time, PET-based carpeting replaced nylon in most commercial applications, while polypropylene-based carpet has become the dominant outdoor carpeting material, taking market share away from nylon, and by inference, adipic acid.

Countering the stagnation in nylon carpet demand, high energy prices in the 1970s created a need for more energy efficient automobiles. One of the industry responses to this imperative was the replacement of heavy metal automotive parts with lighter weight plastic parts, including nylon. At the same time, advances in the automotive tire industry resulted in the development of high mileage radial ply tires to replace lower mileage bias ply tires. Radial tires required high strength but flexible tire cord, and nylon became the standard tire cord material.

Demand growth for adipic acid is driven primarily by the demand for nylon in fiber and resin markets. The 2008–2009 economic recession caused a dramatic reduction in the demand for nylon in the housing and automotive industries. As a result, adipic acid consumption dropped during that period, and has only recovered slightly since then. From a geographic perspective, sluggish overall economic recovery from the recession has resulted in relatively flat demand for adipic acid in western economies and Japan, with nearly all demand growth being in China. The 2011 distribution of adipic acid demand by geography is presented in the graph below.

Figure 3.4
GLOBAL GEOGRAPHIC DEMAND DISTRIBUTION FOR ADIPIC ACID IN 2011

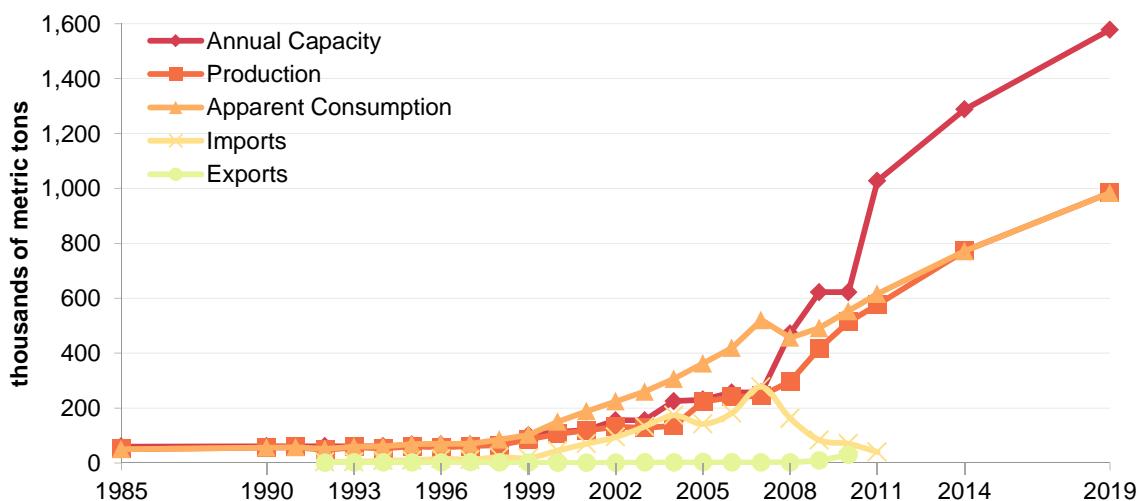


Source: IHS Chemical CEH

Chinese Demand for Adipic Acid

Demand growth for adipic acid in China has been high due to its use as a feedstock for making polyester polyols, rather than as a nylon 66 precursor. Due to the high demand for polyester polyols used in athletic shoes, and the high proportion of the global athletic shoe manufacturing business located in China, nearly all of the ADA capacity announced for the next 5 years, and nearly all of the demand growth globally, is for China. The graph below presents China historical and forecast ADA consumption, production, and nameplate capacity.

Figure 3.5
CHINESE ADIPIC ACID CAPACITY, PRODUCTION, CONSUMPTION, AND EXPORTS/IMPORTS



Source: IHS Chemical China Report, Adipic Acid, 2011 (284002)

BUSINESS DRIVERS FOR ADIPIC ACID

The principal business drivers for success in the adipic acid business, including consideration of bio-based adipic acid, are listed in the table below.

**Table 3.4
MARKET DRIVERS FOR BIO-BASED ADIPIC ACID COMMERCIAL SUCCESS**

Achieving lower production cost (using lower cost bio-based feedstock)
Consistently producing on-spec fiber-grade adipic acid
Managing industry capacity utilization
Less demanding process conditions resulting in lower capital and operating costs
Customer demand for sustainable or bio-based products
Manufacturing with lower greenhouse gas footprint
Avoiding carbon taxes
Reducing use of crude oil derived feedstock from unreliable global suppliers
Creating demand for adipic acid into the polyurethane polyol polyester market

The principal driver for demand growth for adipic acid is the need for nylon 66 in fiber and resin end-use applications. Since nylon 66 is nearly interchangeable with nylon 6 (produced from caprolactam), the relative production economics of nylon 66 and nylon 6 dictate which form of nylon is preferred based on being the low cost option: adipic acid for nylon 66, or caprolactam for nylon 6. Since both feedstocks are derived from crude oil, the direction of crude oil prices affects both forms of nylon equally. Nylon 66 has better high temperature performance than nylon 6.

According to Solvay/Rhodia (284003), the nylon 66 polymer derived from ADA can be segmented into four major end-use markets, with different forecast demand growth rates. The demand growth rate of nylon for each end-use market is shown in the table below.

**Table 3.5
SOLVAY/RHODIA FORECAST OF NYLON END-USE MARKET DEMAND GROWTH**

End-Use Market	Forecast Demand Growth
Engineering Plastics	High
Industrial Yarns	Moderate
Textiles	Flat
Carpet fibers	Flat globally/decreasing in the United States

Source: Solvay/Rhodia

In China, where demand growth is highest and where nearly all the additional adipic acid capacity is planned to be built, the demand growth driver is not the nylon business but the polyurethane business. Much of the athletic shoe manufacturing business is centered in China, and adipic acid demand is rapidly being driven by needs for adipic acid as a feedstock for making polyester polyols that are consumed in polyurethane shoe soles (284004).

MATERIAL SUBSTITUTION BETWEEN NYLON 66 AND NYLON 6

The high volume forms of nylon sold into the commercial market place are nylon 66 and nylon 6. Other forms of nylon (11, 12, 4-6, 6-9, 6-10, 6-12, 6T, M6, etc.) are specialties sold at much higher prices and at much lower volumes.

BASF and Toray are the only major nylon producers that are fully integrated into both feedstocks and products for making both nylon 66 and nylon 6. Other producers make both nylon 66 and nylon 6, but are captive in caprolactam and purchase the ADA and/or HMDA required to also produce nylon 66. Presented below is a table showing the product and feedstock integration of the major global nylon producers.

Table 3.6
PRODUCTION INTEGRATION FOR NYLON 66 AND NYLON 6

Producer	ADA	HMDA	Capro	Nylon 66	Nylon 6
Asahi Kasei	✓	✓		✓	
Ascend	✓	✓		✓	
BASF	✓	✓	✓	✓	✓
China Petrochemical Development Corp				✓	✓
DSM			✓		✓
DuPont				✓	
Honeywell				✓	✓
Hua Long Corporation				✓	✓
Hyosung			✓	✓	✓
Invista	✓	✓		✓	
Kolon Industries				✓	✓
Lanxess				✓	✓
Li Peng Enterprise Co				✓	✓
Mitsubishi Engineering Plastics				✓	✓
Radici	✓	✓		✓	
Rhodia	✓	✓		✓	
Toray Industries	✓	✓		✓	✓
Ube Industries				✓	✓
Xinhua Nylon				✓	✓

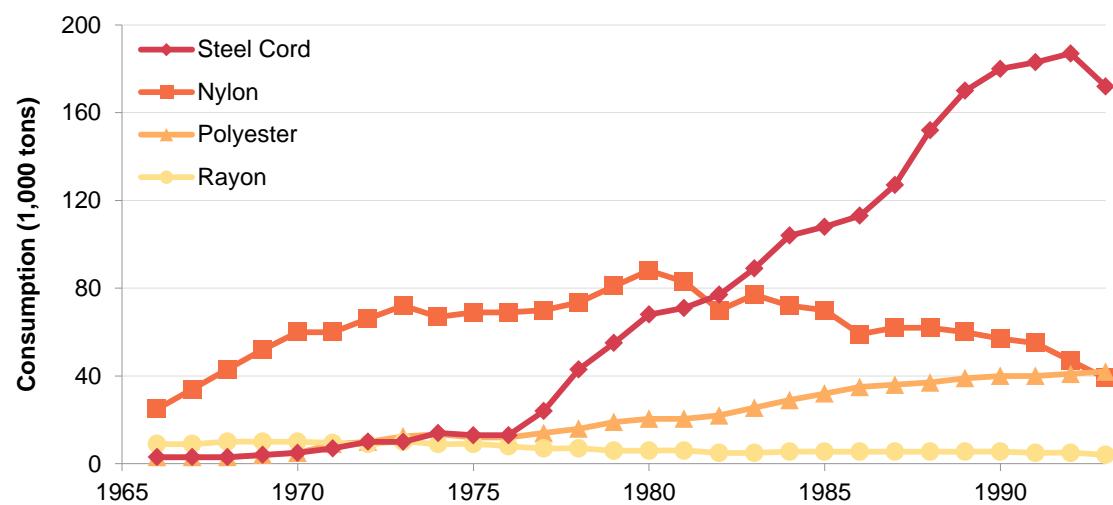
Source: IHS

POLYMER INTERMATERIAL SUBSTITUTION

In many end-use applications, there are intermaterial substitution opportunities between nylon and other synthetic polymers. As mentioned above, nylon fiber replaced natural fibers in carpets and related textiles, and over time has given up market share to synthetic carpeting made from PET and PP.

For automotive tire cord, nylon 66 competes with steel belted tires, polyester cord, rayon cord, and more recently Kevlar cord. Radial tire demand has increased the market share of steel belted material versus other fiber options. The graph below shows that steel cord has replaced polymers for most tire cord applications.

Figure 3.6
TRENDS IN MATERIALS FOR TIRE CORD



Source: Toyo Tires

In resin applications, the chemical industry generally segments products based upon polymer softening temperature. Those that soften below 80°C are largely the commodity thermoplastics such as polyethylene, polypropylene, PVC, and polystyrene. Polymers able to withstand higher temperatures before softening are considered 'engineering plastics,' and many of these are crystalline thermo-setting materials rather than thermo-plastic materials.

Engineering plastics are used mostly in extruded or molded fabricated parts; nylon 66 competes with a variety of other engineering resins where the combination of cost to performance dictates specific choices. Other engineering resins competing with nylon are listed below.

Table 3.7
COMPETING ENGINEERING PLASTICS

Acrylonitrile butadiene styrene (ABS)
Polycarbonates (PC)
Specialty Polyamides (PA)
Polybutylene terephthalate (PBT)
Polyethylene terephthalate (PET)
Polyphenylene oxide (PPO)
Polysulphone (PSU)
Polyetherketone (PEK)
Polyetheretherketone (PEEK)
Polyimides
Polyphenylene sulfide (PPS)
Polyoxymethylene plastic (POM)

Beside performance, cost is a primary determinant of engineering plastic success in the market place. As the cost of crude oil and derivatives continues to climb faster than the cost of inflation, process developers are seeking alternative materials that are not derived from crude oil. Bio-based materials are one family of alternative feedstocks, although commercial experience using food as chemical or fuel feedstock (corn, soybean oil, rapeseed oil) suggests that over most time periods food will remain more costly than fuel.

Industry Capacity Utilization

One of the major factors affecting economic success in the commercial adipic acid business is the degree to which industry demand and industry capacity remain in balance. As the balance periodically tightens, profit margins increase. As industry excess capacity increases, profit margins erode, and in some cases disappear. Intermediate chemicals like adipic acid usually require industry capacity utilization factors above 85% to maintain acceptable profitability.

For the particular case of adipic acid, and its close ties with the nylon business, profit margins have historically been erratic. The two historically largest adipic acid producers in the United States (DuPont and Monsanto) sold their nylon 66 businesses (adipic acid, HMDA, nylon 66 chips and fibers) to Invista and Solutia/Ascend, respectively, due to poor profitability across the economic business cycle.

A large proportion of nylon sales are into the housing and automotive sectors, which are volatile and change quickly with macroeconomic conditions such as national and global 'gross domestic product (GDP). During economic recessions, demand for nylon into these sectors of the economy nearly evaporates. For the year 2012, estimated global demand for adipic acid was 2.6 MM tpy, while global capacity for adipic acid was 3.7 MM tpy, resulting in an industry capacity utilization of only 70%. It is believed that this level of industry capacity utilization does not generate sufficient profits to justify new grassroots capacity investment.

ENVIRONMENTAL DRIVERS

The principal environmental drivers for most chemical products are reduced greenhouse gas footprint, perceived sustainability, and recycling of plastics. In the particular case of adipic acid, discarded nylon carpet has drawn attention to recycling efforts, either by recycling the fiber, or by depolymerizing the polymer back to its base monomer constituents for use as feedstock. These efforts have been technically successful, but the economic incentive for nylon carpet recycling has been disappointing to most practitioners.

Using a bio-based, nonfood agricultural feedstock for make adipic acid would result in a significant improvement in the adipic acid carbon footprint, when compared to the conventional commercial technology derived from crude oil through naphtha, benzene, and cyclohexane.

The reaction chemistry for oxidizing KA oil (cyclohexanone + cyclohexanol) to adipic acid uses nitric acid as the oxidant. This results in the production of by-product gas nitrous oxide (N_2O), which has historically been vented to the atmosphere. One ton of vented nitrous oxide has the same greenhouse gas impact as 310 tons of carbon dioxide (284005). For the conventional cyclohexane process, one ton of adipic acid production results in the production of 0.3 tons of nitrous oxide.

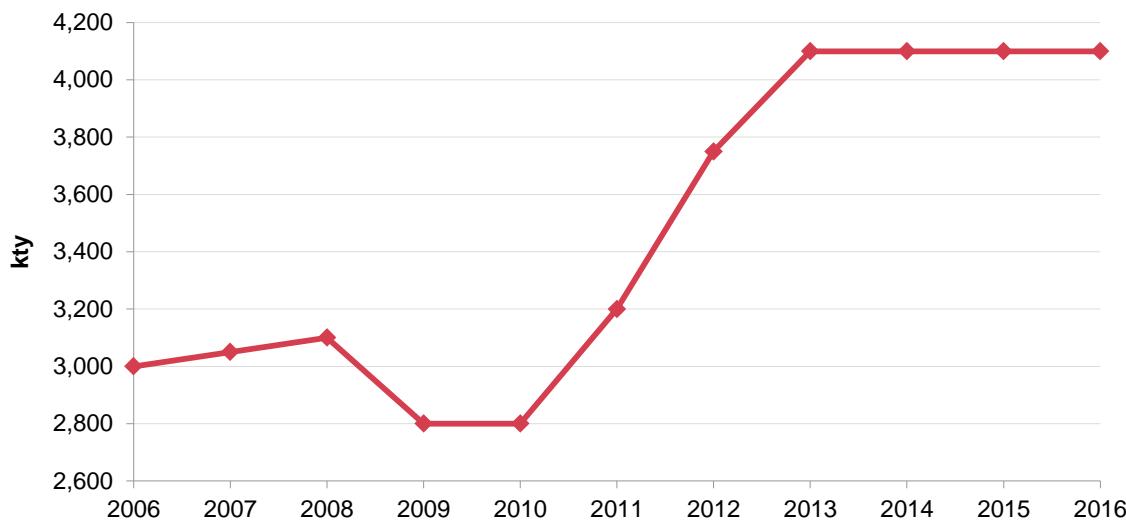
Many western producers of adipic acid have installed process units to destroy nitrous oxide. Nitrous oxide exerts an enormous greenhouse gas liability. An alternative chemistry that did not produce nitrous oxide would have significant greenhouse gas benefits.

COMMERCIAL CAPACITY ADIPIC ACID PRODUCERS

2012 Adipic Acid Nameplate Production Capacity

Historic and forecast adipic acid production capacity, on a global basis, is presented in the figure below. For many years, demand growth was flat with capacity at approximately 3 MM tpy, and subsequently no significant capacity was added. Between 2010 and 2013, significant new capacity was added, all in China, primarily for the purpose of producing polyester polyols from adipic acid, for the footwear industry.

Figure 3.7
HISTORIC AND FORECAST GLOBAL ADIPIC ACID CAPACITY



Source: IHS Chemical

The distribution of current (as of 2012) adipic acid capacity by country is presented in the table below.

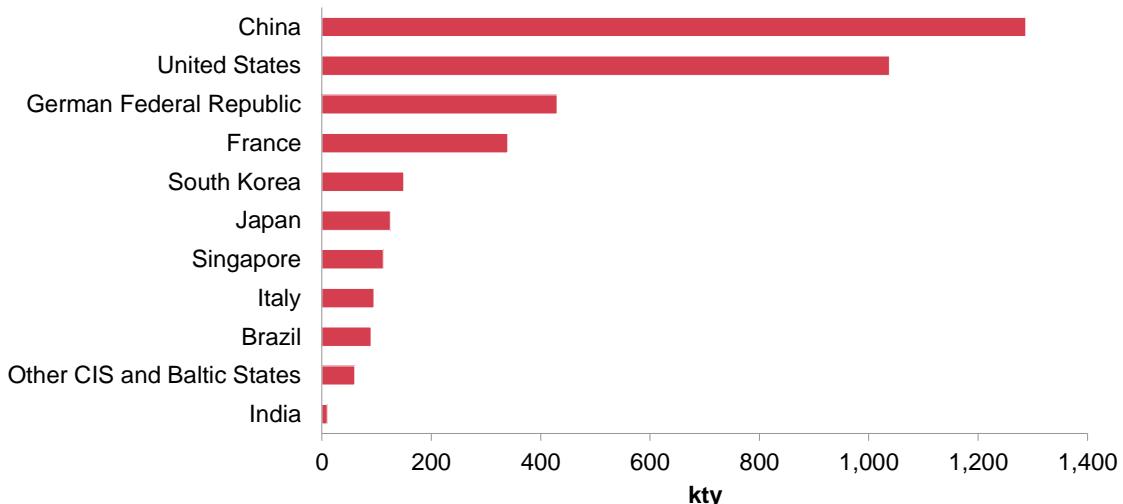
Table 3.8
ADIPIC ACID CAPACITY BY COUNTRY TO 2011

	2006	2007	2008	2009	2010	2011
Canada	201	201	201	83	0	0
United States	1,010	1,010	950	795	825	1,040
Brazil	90	90	90	90	90	90
France	340	340	340	340	340	340
Germany	403	403	407	427	427	427
Italy	63	92	92	92	92	92
United Kingdom	270	270	270	65	0	0
CIS and Baltic States	58	58	30	30	58	58
India	1	1	1	1	1	1
China	197	197	360	512	605	737
Japan	124	124	124	124	124	124
South Korea	135	135	150	150	150	150
Singapore	110	110	110	110	110	110
World	3,002	3,031	3,125	2,819	2,822	3,169

Source: IHS Chemical

The 2012 distribution of adipic acid capacity by country is shown in the figure below. China and the United States are the most significant adipic acid producers, with US capacity remaining flat while Chinese capacity is growing quickly.

Figure 3.8
2012 ADIPIC ACID CAPACITY BY GEOGRAPHICAL REGION



Source: IHS Chemical

Based upon publicly announced capacity expansions, IHS has forecast the adipic acid capacity by country between 2012 and 2016. This information is presented in the table below.

Table 3.9
FORECAST ADIPIC ACID CAPACITY BY COUNTRY 2012–2016

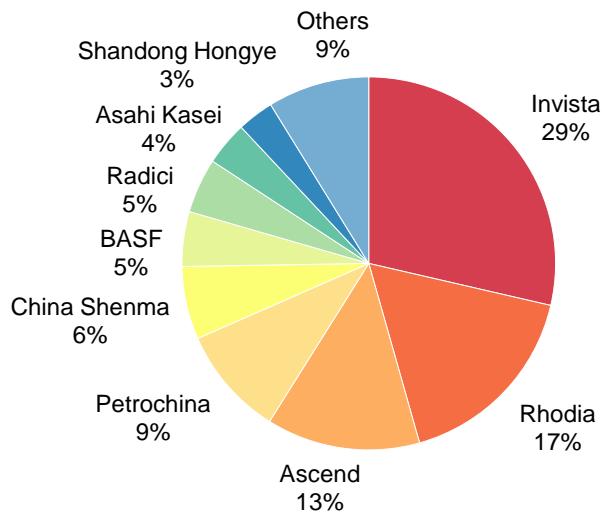
	2012	2013	2014	2015	2016
Canada	0	0	0	0	0
United States	1,040	1,040	1,040	1,040	1,040
Brazil	90	90	90	90	90
France	340	340	340	340	340
Germany	427	427	427	427	427
Italy	92	92	92	92	92
United Kingdom	0	0	0	0	0
CIS and Baltic States	58	58	58	58	58
India	1	1	1	1	1
China	1,289	1,657	1,657	1,657	1,657
Japan	124	124	124	124	124
South Korea	150	150	150	150	150
Singapore	110	110	110	110	110
World	3,721	4,089	4,089	4,089	4,089

Source: IHS Chemical

ADIPIC ACID PRODUCING COMPANIES

The major commercial volume producers of adipic acid are Invista (USA), Rhodia (France), Ascend (USA), BASF (Germany), and Radici (Italy). The top 9 producers command approximately 90% capacity share globally, and are shown in the graph below. Only four producers (Invista, Rhodia, Radici, Shandong Haili) operate more than one adipic acid manufacturing plant.

Figure 3.9
2013 ADIPIC ACID CAPACITY SHARE BY PRODUCER



The forecast change in capacity by the producers above, between 2009 and 2013, are presented in the table below. Companies reducing capacity are Invista and BASF. Companies increasing capacity are China Shenma and PetroChina.

Table 3.10
2013 ADIPIC ACID CAPACITY SHARE BY PRODUCER

	2013	2009
Invista	904	1,174
Rhodia	537	537
Ascend	420	420
BASF	150	260
Radici	150	150
China Shenma	200	140
PetroChina	300	140
Asahi Kasei	120	120
Shandong Hongye	100	100
Others	278	278

A plant-by-plant listing of adipic acid capacity for 2012 is presented in the table below.

Table 3.11
2012 ADIPIC ACID CAPACITY BY PLANT SITE

Company and Plant Location (kty)	2012	Raw Material
INVISTA		
Orange and Victoria, Texas, United States	590	Cyclohexane
Maitland, Ontario, Canada	0	Shut down in 2009
Wilton, United Kingdom	0	Shut down in 2009
Pulau Sakra, Singapore	110	Cyclohexane
Total	700	
Rhodia		
Chalampe, France	340	Cyclohexane
Onsan, Kyongsangnam-do, Republic of Korea	150	KA oil
Sao Paulo, Sao Paulo, Brazil	90	Phenol
Total	580	
Ascend Performance Materials		
Cantonment, Florida, United States	450	Cyclohexane
BASF		
Ludwigshafen, Germany	240	Cyclohexane
Radici Chimica Deutschland		
Novara, Italy	92	KA oil
Tröglitz, Germany	97	Phenol
Total	189	
China Shenma Chemical Co. Ltd.		
Pingdingshan, Henan, China	215	KA oil
PetroChina Liaoyang Petrochemical Co.		
Liaoyang, Liaoning, China	145	Cyclohexane
Huafeng Group		
Chongqing, Sichuan China	120	Cyclohexane
Hualu Hengsheng		
Dezhou, Shandong	112	Cyclohexene/Cyclohexanol
Kailuan Energy Chemical		
Tangshan, Hebei China	25	Cyclohexene/Cyclohexanol

Table 3.11 (Concluded)
2012 ADIPIC ACID CAPACITY BY PLANT SITE

Company and Plant Location (kty)	2012	Raw Material
Shanxi Tianji Group		
Lucheng, Shanxi China	35	Cyclohexene/Cyclohexanol
Taiyuan		
Taiyuan, Shanxi China	2	Cyclohexane
Ganesh Benzoplast		
Tarapur, India	1	Cyclohexane
Asahi Kasei Chemical Corp.		
Nobeoka, Miyazaki, Japan	120	Cyclohexene/Cyclohexanol
Shandong, Hongye Chemical Industries		
Dongming, Shandong, China	235	Cyclohexane
Shandong Haili Chemicals		
Zibo, Shandong, China	225	Cyclohexane
Yancheng, Jiangsu China	100	Cyclohexane
Total	325	
Xinjiang Dushanzi Tianli High and New Tech. Co. Ltd.		
Dushanzi, Xinjiang, China	75	Cyclohexane
Lanxess		
Krefeld, Germany	90	Cyclohexane
Aznot Rivnea		
Rovno, Ukraine	28	Cyclohexane
SSME Obedeninie Azot		
Severodnetsk, Ukraine	30	Cyclohexane
Taiyuan Chemical Industry Inc.		
Taiyuan, Shanxi, China	3	Cyclohexane
Sumitomo Chemical		
Niihama, Ehime, Japan	4	Caprolactam by-product
Total	3,724	

Announced Adipic Acid Production Capacity Increases

Several adipic acid producers have announced ADA capacity additions post-2012. All the announced capacity increases are by Chinese companies in China, and they are all scheduled to start up in 2013. The aggregate increase in capacity is 318 kty, or 9% of aggregate global capacity. The capacity additions are listed below with announced capacity and expected start-up year.

Table 3.12
ADIPIC ACID CAPACITY ADDITIONS

ADA Producer and Location	Capacity (kty)	Start-Up Year
Huafeng Group, China	40	2013
Hualu Hengsheng, China	38	2013
Kailuan Energy Chem, China	125	2013
Shandong Hongye, China	45	2013
Shanxi Tianji Group, China	35	2013
Shenma Chemical, China	35	2013
Shandong Haili, China	50	2013
BASF, Antwerp, Belgium	50 (KA oil)	2013
Total	418	

Adipic Acid Capacity Shutdowns

Invista shut down adipic acid capacity in 2009 in Canada and the UK by 470 kty. The affected plants are listed below.

Table 3.13
ADIPIC ACID CAPACITY ELIMINATIONS

ADA Producer and Location	Capacity (kty)	Shut-Down Year
Invista, Canada	200	2009
Invista, United Kingdom	270	2009

Caprolactam Capacity Additions

In order to obtain insight as to whether the bulk of new nylon capacity is likely to be nylon 66 (based on ADA + HMDA) or nylon 6 (based on caprolactam), we prepared the table below of announced capacity additions for caprolactam between 2013 and 2016. The announced capacity increase is 1,195 kty, which is much larger than the announced capacity increase of 318 for adipic acid, suggesting that project proponents intend to build much more new nylon 6 capacity than new nylon 66 capacity.

Table 3.14
CAPROLACTAM CAPACITY ADDITIONS

Caprolactam Producer and Location	Capacity (kty)
Judon, Yugoslavia	5
Baling, China	190
CNCEC, China	100
DNCC, China	200
Dongli, China	75
Hangshon, China	400
Hengyi, China	100
Shandong Haili, China	100
CPDC, Taiwan	25
Total	1,195

ADIPIC ACID PRODUCT GRADES AND COMPOSITION

Adipic acid sold in commerce is usually sold as ‘fiber-grade adipic acid’ suitable for the production of nylon 66. Product purity is well in excess of 99%. Below are the fiber-grade specifications for ADA sold by Invista and by Radici.

Table 3.15
INVISTA FIBER-GRADE ADIPIC ACID SPECIFICATION

Specification	Limit
Adipic Acid, wt%	99.7 min.
(Assay)	
Water, wt%	0.2 max.
Ash, ppm	2.0 max.
Iron, ppm	0.5 max.
Methanol Solution Color, APHA	6.0 max.
Total Nitrogen (TN), mpm*	15.0 max.
ppm	1.5 max.

* moles per million moles (mol/10⁶ mol)

Table 3.16
RADICI FIBER-GRADE ADIPIC ACID SPECIFICATION

Specification	Units	Value
Purity	%	99.8 min
Total nitrogen	ppm	20 max
Color (methanol solution)	HAZEN	5 max
Melt color	APHA	10 max
Iron	ppm	0.2 max
Crystallization temperature	°C	152 ± 0.5
Water	%	0.2 max

Smaller volumes of food-grade adipic acid are sold as an acidulant, while some companies also sell a ‘technical grade,’ or ‘urethane grade’ of adipic acid for the esters business.

TECHNOLOGY LICENSORS AND DEVELOPERS

Several of the process licensors for adipic acid technology are current or former producers of adipic acid. A list of the claimed licensors, and the status of their adipic acid technology offerings, are presented in the table below.

Table 3.17
ADIPIC ACID ACTIVE PROCESS LICENSORS

Licensor	Technology Offering	Status
DuPont Technology Bank/Invista	Process package for ADA via liquid-phase oxidation of cyclohexane to KA oil, then oxidation to ADA using HNO ₃ , NOx reduction technologies	Commercially used in Invista plants. DuPont retained resin IP when nylon 66 manufacturing assets sold to Invista. ADA license not currently offered by DuPont
Solvay Rhodia	Process package for ADA via liquid-phase oxidation of KA oil from cyclohexene made by hydrogenation of benzene	Used in Rhodia plants except in S Korea. Used in PetroChina Liaoyang plants. Feedstock is cyclohexene. Licensed in 1980s in first China ADA plant for PetroChina as Rhone-Poulenc technology
BASF	Process package for ADA via liquid-phase oxidation of cyclohexane to KA oil, then oxidation to ADA using HNO ₃ , NOx reduction technologies	ADA IP used in BASF plants and licensed two ADA plants in Ukraine. Also offers process license and catalyst for N ₂ O destruction, and has sold N ₂ O destruction process to PetroChina
Halcon-Scientific Design (Sabic/Sud Chemie)	Offered one-step technology for converting KA oil to ADA using air oxidation in acetic acid solution using boric acid, with purification by crystallization.	Commercial plant built for Rohm and Haas. Shutdown due to poor product quality. No longer active in business
Asahi Kasei	Process package for ADA via benzene hydrogenation to cyclohexene, hydration to cyclohexanol, and HNO ₃ oxidation to ADA	Used by Asahi in Japan ADA plant. Licensed ADA process to Rhodia in Korea, and licensed plants for Saudi Arabia. Used in one existing Chinese ADA plants (ex. China Shenma) practicing cyclohexane/cyclohexene process
Invista Performance Technologies	N ₂ O destruction	Recently available for 3rd-party ADA licensing, and discussing a specific project in China
AO Giap/Alvigo (Russia)	Improvements on previously licensed BASF ADA plant in Ukraine	Used in debottlenecking and improving yield in two Ukraine ADA plants licensed by BASF
Tianchen Corp (China)	Offers ADA licensing and EPC project capability	Built first Chinese ADA plant for PetroChina using Rhodia process technology, subsequently offered their own technology and EPC capability to build ADA plants for Shandong Haili and Xinjiang Dushanzi. Negotiating in 2012 new ADA plant with China customer
Uhde (Thyssen Krupp)—Uhde India	Offers complete turnkey services for adipic acid	Designed and built Radici ADA plant in Zeitz

BIO-BASED ADIPIC ACID PROCESS DEVELOPERS

Many bio-based technology developers are research-intensive companies with little experience in commercial chemical plant design, construction, and operation. As a result, several adipic acid technology developers have partnered with established chemical companies in order to quicken the pace of commercialization. Examples of such partnerships are listed in the table below.

**Table 3.18
ADA TECHNOLOGY DEVELOPER/OPERATING COMPANY PARTNERSHIPS**

Biochemical Developer	Operating Company
Renmatix	BASF
Purac	BASF
OPX Bio	Dow Chemical
Myriant	PTT Chemical
Novomer	DSM
Segetis	DSM
BioAmber	Mitsui
Genomatica	Mitsubishi Chemical
Gevo	Lanxess
Cobalt Technologies	Rhodia

Source: IHS Chemical CEH Report, Adipic Acid (284006)

A summary of the bio-based technologies for adipic acid is presented in the table below.

Table 3.19
BIO-BASED ADIPIC ACID TECHNOLOGY SUMMARY

Bio-Developer	HQ Location	Feedstock	Technology	2012 Commercialization Status
BioAmber	Plymouth, MN, USA	Carbohydrates	Fermentation via genetically modified enzymes. Advanced purification scheme	Dedicated lab built in Plymouth, Mn USA for ADA purification
Celexion	Cambridge, MA, USA	Carbohydrates	Modified bacteria (<i>Escherichia coli</i>) applied to C ₆ substrates	Modifying its commercial succinic acid fermentation know-how to ADA
Draths/Amyris	Lansing, MI, USA	Muconic acid	Produces commercial C ₆ -based nylon precursors (ADA, HMDA, Capro)	Acquired by Amyris, who is developing higher performance fermentation organisms
Genomatica	San Diego, CA, USA	Sugar	Genetically modified bacteria applied in direct fermentation	Bio-ADA patent files in 2010
Rennovia	Menlo Park, CA, USA	Glucose	Catalytic hydrogenation and oxidation	Continuous pilot plant operating and making KG quantities. Design of demonstration unit initiated. Targets commercial production in 2015
Verdezyne	Carlsbad, CA, USA	Sugars, fatty acids and esters	Fermentation using genetically modified bacteria	Pilot plant start-up in 2011. Commercial plant expected in 2014
DSM	Heerlen, Netherlands	Glucose	Fermentation	Patents filed. Plans to commercialize at 100 kty by 2017. Invested in Verdezyne
Novozymes	Waltham, MA, USA	Glucaric acid	Fermentation of sugars using genetically modified enzymes	Developing lab scale product in partnership with Cargill and BASF

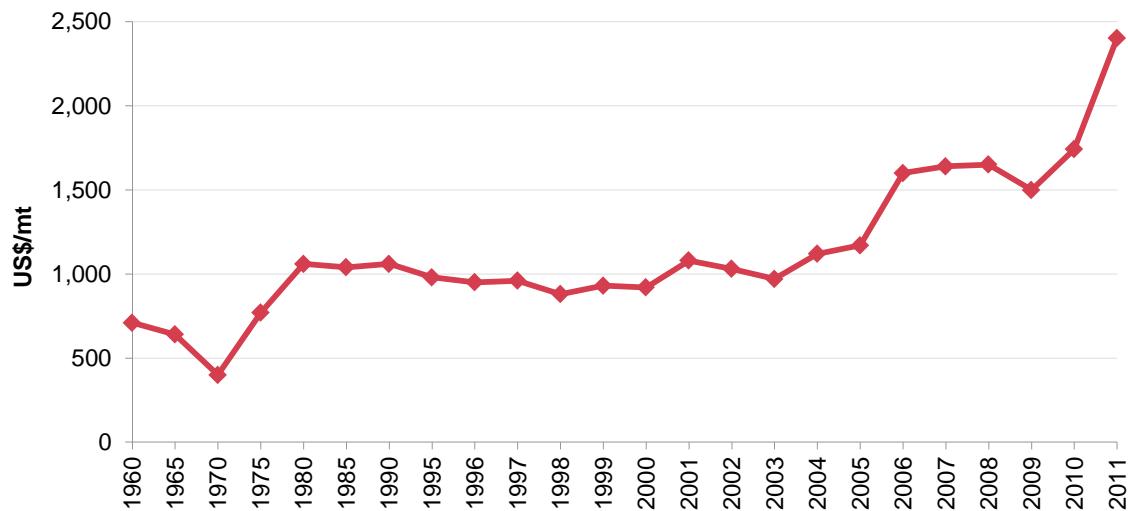
Source: IHS

ADIPIC ACID PRICE AND MARGIN HISTORY

Historical Annual Prices for Adipic Acid

Historical prices for adipic acid have been considerably lower than end-use product nylon 66, and considerably higher than feedstocks cyclohexane or phenol. Historic annualized US export prices for adipic acid are presented in the table below for the period 1960–2008. Note that US prices dropped during the recession of 1970, but nearly doubled soon thereafter when the Arab Oil Embargo resulted in crude oil price increases from a long term \$3/bbl, to \$15/bbl. Prices remained stable until 2003, when a second dramatic increase in the price of crude oil caused a corresponding increase in the price of adipic acid.

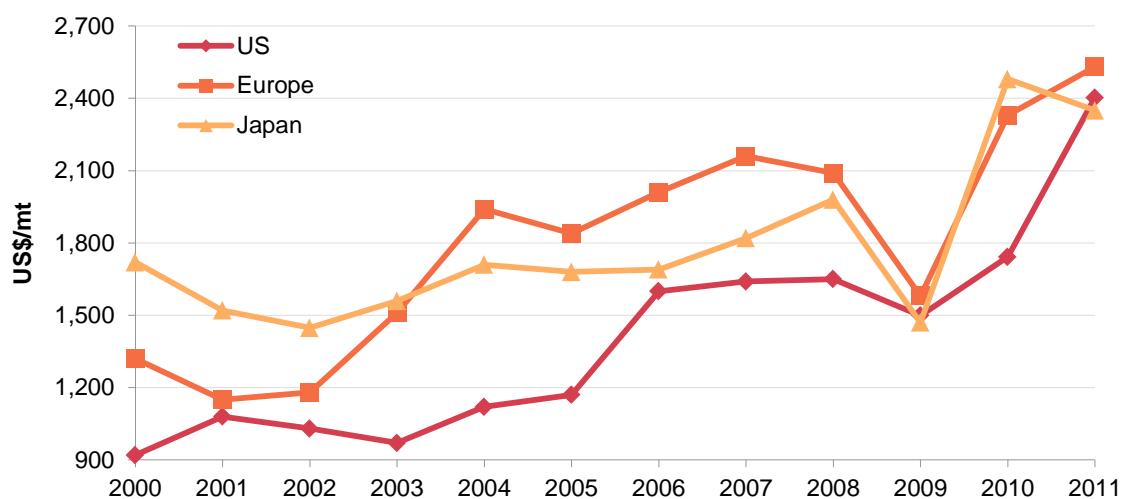
Figure 3.10
HISTORICAL US EXPORT PRICE OF ADIPIC ACID



Source: IHS Chemical CEH Report, Adipic Acid (284006)

A comparison of US, European, and Japanese prices for adipic acid between 2000 and 2008 is presented in the table below. European and Japanese adipic acid prices have generally sold at a slight premium to US prices, as shown in the table below. US prices historically have been lower than in Europe or Japan. However, the global economic recession of 2008–2009 brought parity to global adipic acid prices. Since then, prices in all regions have increased significantly.

Figure 3.11
REGIONAL ADIPIC ACID PRICES 2000–2011

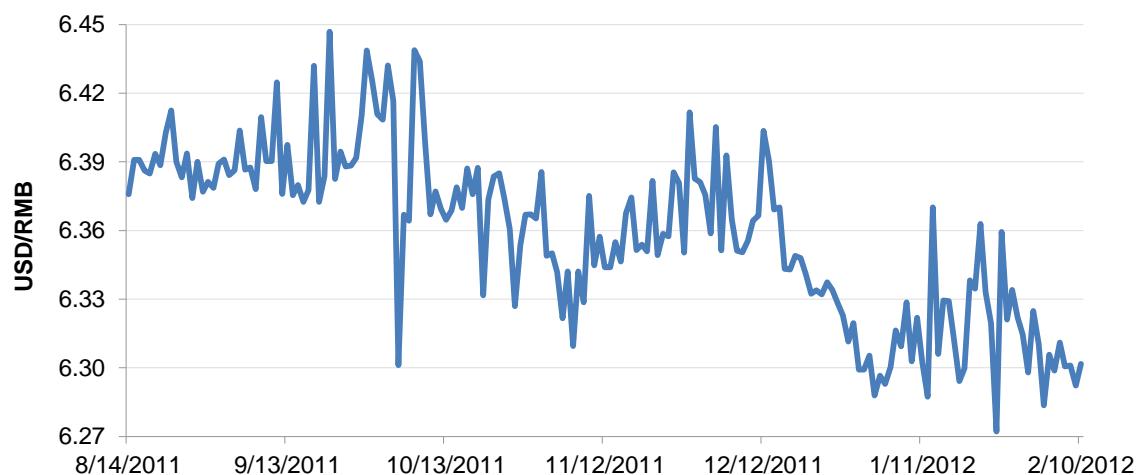


Source: IHS Chemical CEH Report, Adipic Acid (284006)

Short-Term Prices for Adipic Acid

The 27-January-2012 issue of IHS Chemical Market Advisory Service: Global Nylon Fibers & Feedstocks report presents then current adipic acid price data. The Chinese spot price during that period was 11,750 RMB/mt (\$1,865/mt at an exchange rate of 6.3 RMB/US\$). This compared to a delivered (CFR) price in north Asia of \$1,575.

**Figure 3.12
EXCHANGE RATES (US\$/RMB) EARLY 2012**



Source: Exchange-Rates.org

For the month of January 2012, Alibaba posted the following offering prices for adipic acid by producers in China.

**Table 3.20
ALIBABA OFFERING PRICES FOR CHINESE ADIPIC ACID (JANUARY 2012)**

US\$/MT

Supplier	FOB Price
Henan Premtec Enterprise	1,800–2,300
Zibo Aiheng Industry & Trade Co	2,300–2,600
Hebei NuoQiChemical Technology Co	1,650–2,200
Changshu Jinfeng Chemicals Co	2,400–2,600
Zouping Daixi Industry and Trade Co.	1,680–1,850
Dowpol Chemical Intl Corp	1,800–1,850
Jinan IFT Science and Technology	2,000–2,500
Shandong Hongye Chemical Group Corp	1,500–1,900
Wuji Xinhui Chemical Co	2,400–2,600

Nylon 66 versus Adipic Acid Margins

The 27-January-2012 issue of IHS Chemical Market Advisory Service: Global Nylon Fibers & Feedstocks report presents then current pricing data for the adipic acid required to make nylon 66, and the caprolactam required to make nylon 6. Also included is the basic feedstock for both precursors, benzene. The data for this time period in Asia are presented in the table below.

The table shows that nylon 66 and nylon 6 sell at near price parity. To make nylon 66, one needs the combination of ADA and HMDA. To make nylon 6, one only needs caprolactam. The magnitude of the raw materials margin indicates that the cost of converting naphtha to benzene is modest, while the cost of converting benzene to either adipic acid or caprolactam is significant.

Table 3.21
NYLON RAW MATERIAL MARGINS (27-JAN-2012)

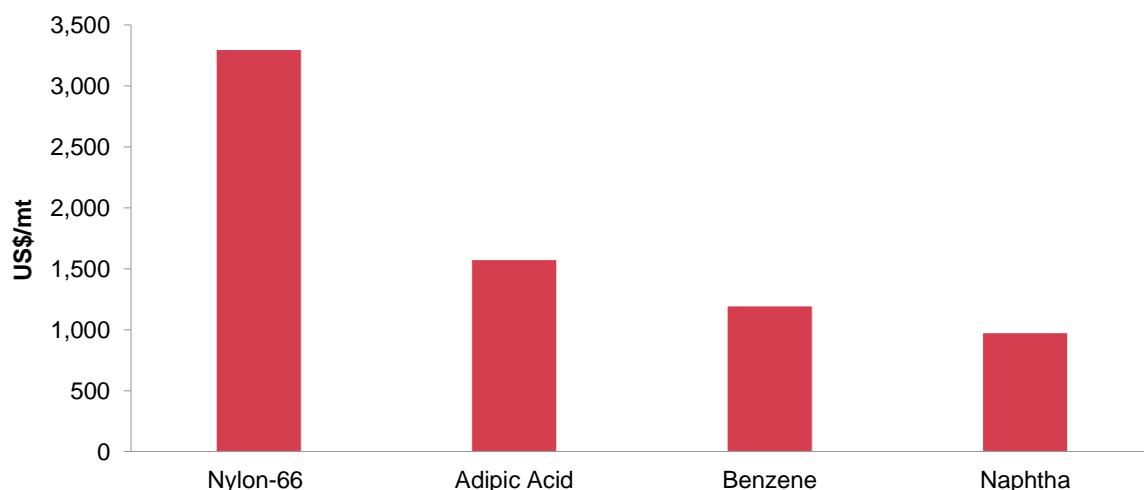
US\$/MT

Nylon 66 Chain	Price	Margin	Nylon 6 Chain	Price	Margin
Nylon 66	3,300		Nylon 6	3,075	
Adipic Acid	1,575	1,725	Caprolactam	2,800	275
Benzene	1,195	380	Benzene	1,195	1,605
Naphtha	975	220	Naphtha	975	220

Source: IHS Chemical

The build-up in cost for making nylon 66 starting with naphtha is shown graphically in the figure below. As shown above, the significant raw material elements are the conversion cost of benzene to adipic acid, and also the conversion cost of adipic acid to nylon 66.

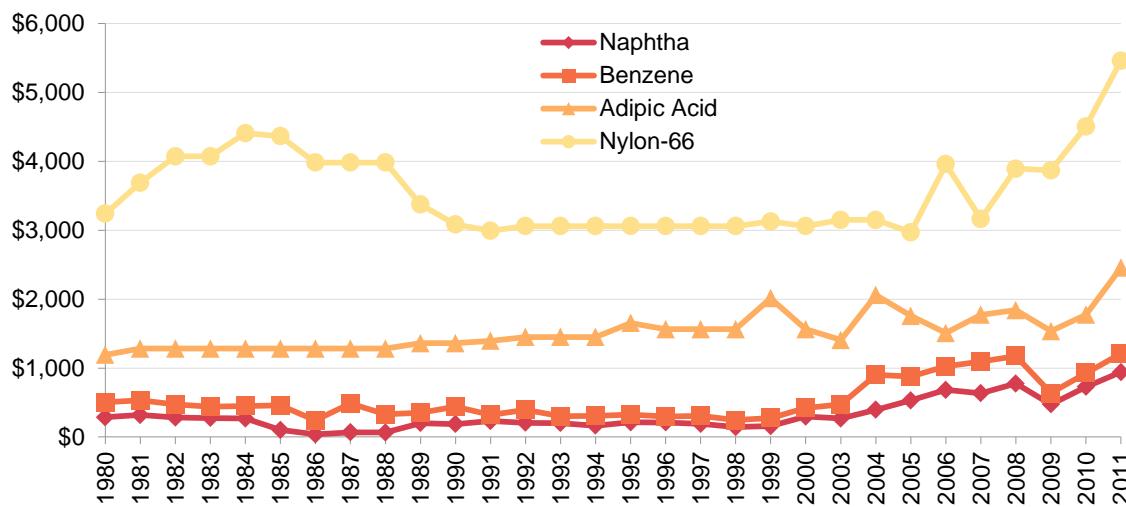
Figure 3.13
NYLON 66 RAW MATERIAL PRICES (27-JAN-2012)



Source: IHS Chemical

For the period between 1980 and 2011, the annual US price for the nylon 66 integrated product chain components are shown in the figure below. For most of the period, the raw material margin between naphtha and benzene has been narrow. As prices for crude oil increased significantly after 2000, prices for all of the nylon 66 raw material components also increased, while their margins also expanded during this period.

Figure 3.14
LONG-TERM NYLON 66 PRODUCT CHAIN PRICES



Source: IHS Chemical PEP Yearbook

4 TECHNOLOGY OF CONVENTIONAL ADIPIC ACID PRODUCTION

NOMENCLATURE

Adipic acid is a mildly corrosive substance (weak organic acid) that is a colorless and odorless crystalline powder at room temperature. Alternate naming conventions for adipic acid are listed in the table below.

**Table 4.1
ADIPIC ACID ALTERNATE NAMES**

Hexane-1,6-dioic acid
Hexandioic acid
1,6-Hexanedioic acid
Adipinic acid
Hexanedioic acid
1,4-Butane dicarboxylic acid

Internationally recognized nomenclature for adipic acid is shown in the table below.

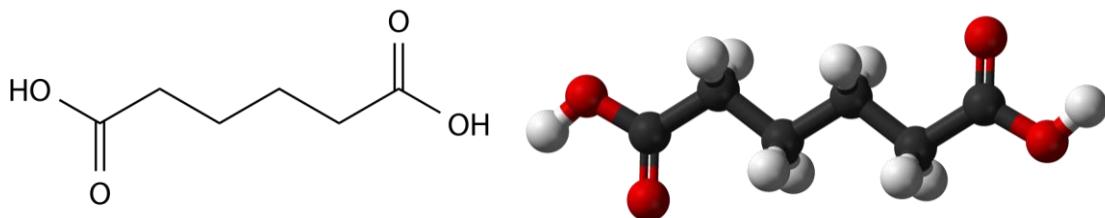
**Table 4.2
ADIPIC ACID NOMENCLATURE**

CAS Number	EC Number	ChemSpider	RTECS
124-04-8	204-673-3	191	AU8400000

MOLECULAR STRUCTURE

Adipic acid is a linear C₆ molecule with carboxylic acid groups on both of the terminal carbon atoms, while the internal carbon atoms are fully saturated with hydrogen. Adipic acid is termed a dicarboxylic acid. Its structure is shown in the figure below.

Figure 4.1
ADIPIC ACID MOLECULAR STRUCTURE



PROCESS SAFETY AND DESIGN IMPLICATIONS

A summary table of adipic acid manufacturing hazards is presented below.

Table 4.3
ADIPIC ACID SUMMARY HAZARDS TABLE

Types of Hazard/ Exposure	Acute Hazards/ Symptoms	Prevention	First Aid/Firefighting
Fire	Combustible.	NO open flames.	Powder, water spray, foam, carbon dioxide.
Explosion	Finely dispersed particles form explosive mixtures in air.	Prevent deposition of dust; closed system, dust explosion-proof electrical equipment and lighting. Prevent build-up of electrostatic charges (e.g., by grounding).	In case of fire: keep drums, etc., cool by spraying with water.
Exposure		PREVENT DISPERSION OF DUST! STRICT HYGIENE!	
Inhalation	Cough. Sore throat.	Local exhaust or breathing protection.	Fresh air, rest. Refer for medical attention.
Skin		Protective gloves. Protective clothing.	Remove contaminated clothes. Rinse skin with plenty of water or shower.
Eyes	Redness. Pain.	Safety goggles or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
Ingestion		Do not eat, drink, or smoke during work.	Rinse mouth. Rest. Refer for medical attention.

Source: International Chemical Safety Card

Chronic Health Effects

Research has not indicated (284007) that adipic acid is carcinogenic, mutagenic, or teratogenic. It may be toxic to the nervous system and gastrointestinal tract.

Combustion

Having a hydrocarbon backbone, adipic acid is susceptible to combustion when exposed to open flames or high temperatures, and should be contained in a vessel made of metal rather than cardboard or plastic (drums). Adipic acid should be stored in a cool place, and away from sources of ignition. Due to its solid nature at room temperature, adipic acid exerts very low vapor pressure, minimizing the chance of vapor induced ignition.

Dust Explosion Potential

Since adipic acid is a crystalline solid in product form, it is transported at room temperature via mechanical conveyors or pneumatic conveyors, creating the potential for dust explosions. Explosions can occur if air is present, if adipic acid dust becomes finely dispersed in air, or if poor design and/or operating practices lead to accumulations of adipic acid dust in HVAC dead spots or bends, which eventually can become dislodged and lead to explosions. Beside the process area, ventilation systems that remove adipic acid dust are also subject to explosions if not operated and maintained in a suitable fashion. To minimize the potential for explosions, inert gas (nitrogen) ventilation systems should be considered, as well as rotary valves for precisely controlling adipic acid powder flow rate. The layout of adipic acid conveying systems should be designed to minimize flat horizontal surfaces on which adipic acid dust can accumulate, and eliminate dead legs. Conveying systems should be blown frequently with an inert gas to remove accumulated adipic acid dust.

In manufacturing, the potential for dust explosions exists during the crystallization of adipic acid from the nitric acid solution in which it is produced, and from downstream purification and packaging operations. As a result, all sections of a manufacturing plant that deal with adipic acid in solid form should be well ventilated. A dust filter should be located upstream if an air blower if induced pressure is used to remove dust.

Given the case history of two adipic acid dust fires occurring at a DuPont manufacturing site in the rotary dryer area, adipic acid solid transport facilities should be designed to conform with the US NFPA 654 standard (National Fire Protection Agency) for protection from combustible dust explosions, or an equivalent safety standard. This includes providing facilities for adequate explosion venting (NFPA 68), and facilities and procedures for explosion prevention (NFPA 69).

The minimum ignition energy (MIE), a measure of dust explosivity, is 5 mJ. Tests show that unloading 1,000 Kg big bags of adipic acid can generate voltage levels necessary to constitute a spark hazard. The spark hazard is of concern, as it can potentially be an ignition source for solvent/air mixtures typical for some ester reaction applications. The explosion severity indices below (Kst and Pmax) are determined using ASTM E1226-10 methods.

Table 4.4
ADIPIC ACID HAZARD PARAMETERS

Minimum explosive concentration (MEC)	39 to 60 g m ⁻³
Minimum ignition energy (MIE)	5–50 mJ
Minimum ignition temperature (MIT)	375 to 490°C
Minimum ignition temperature (MIT)	375 to 490°C
Limiting oxygen concentration (LOC)	10.5% by volume
Explosion severity (Kst)	159 to 184 bar m s ⁻¹
Explosion severity (Pmax)	7.5 to 8.0 bar

Exposure and Personal Protective Equipment

Since adipic acid is a mildly corrosive acid in solid form, personal protective equipment should be used at all times to minimize contact with skin, including safety goggles, full length lab coat, gloves, boots, and respirator. Contact lenses should be removed prior to working in an area where direct contact is possible. Physical exposure will cause irritation of skin, eyes, and the respiratory track (284008). Inhalation can cause asthma. The Organization of Economic Cooperation and Development (OECD) has made (284009) the following summary of health impacts associated with adipic acid.

In limited studies in animals and humans it was shown that adipic acid is absorbed after oral administration, partially metabolized to various metabolites and CO₂ which are excreted via urine and breath, resp. None of the studies was conducted according to GLP. Adipic acid is of very low acute toxicity. The oral LD₅₀ in rats in a study similar to OECD TG 401 is approximately 5,560 mg/kg bw. Clinical signs at lethal doses included acute dilatation of the heart and acute congestive hyperanemia, ulceration of glandular stomach (bleeding-corrosive gastritis), intestinal atony, pale liver and reddening of intestinal mucosa. The LD₅₀ for mice was reported to be 1,900 mg/kg bw. In an inhalation test similar to OECD TG 403 in rats neither mortality nor symptoms were observed during and after four hour exposure to 7,700 mg/m³ of adipic acid. Reduced appetite and activity were the only effects reported following occlusive dermal administration of 7,940 mg/kg bw of adipic acid to two rabbits for 24 hours.

As documented in the OECD report on adipic acid, there is no evidence of genotoxic effects or carcinogenicity. ADA is readily biodegradable in the environment.

Operational Safety Issues

The chemical oxidation of KA oil by nitric acid is normally limited to opening up the cyclic ketone or alcohol ring, and adding hydroxyl groups to each terminal carbon atom. However, at elevated temperature (above 180°C), nitric acid oxidation will cause the combustion of the feedstock (284010) to CO₂, water, and the resulting nitrogen oxides. Such occurrences are violently exothermic. Without adequate heat removal capability, the reaction will cause a large adiabatic temperature rise within the reactor that will eventually lead to either a thermal induced explosion, or an elevated pressure condition that may also cause an explosion.

One of the process hazards to consider when manufacturing adipic acid is temperature control within the nitric acid reactor. The nitric acid oxidation reaction is highly exothermic, and heat exchange cooling tubes must be incorporated in the design to remove the heat of reaction.

During operation, the heat exchange surfaces tend to frost, significantly reducing the heat transfer coefficient, resulting in loss of cooling capacity. Loss of cooling leads to thermal runaways. The oxidation reaction can result in an auto-catalytic thermal runaway if the temperature exceeds 150°C (284011).

Spark Reducing Packaging

In order to minimize the potential for adipic acid dust explosions when adipic acid is used by customers, one producer (Invista) uses product bag containers that are designed for a breakdown voltage of 4kv across the bag wall, which should prevent a spark from causing ignition of the adipic acid in the bag. The bag is designed with small conductive wires that are designed to be grounded when the bag is being filled, emptied, or used in process.

ADIPIC ACID PROPERTIES

Physical Properties

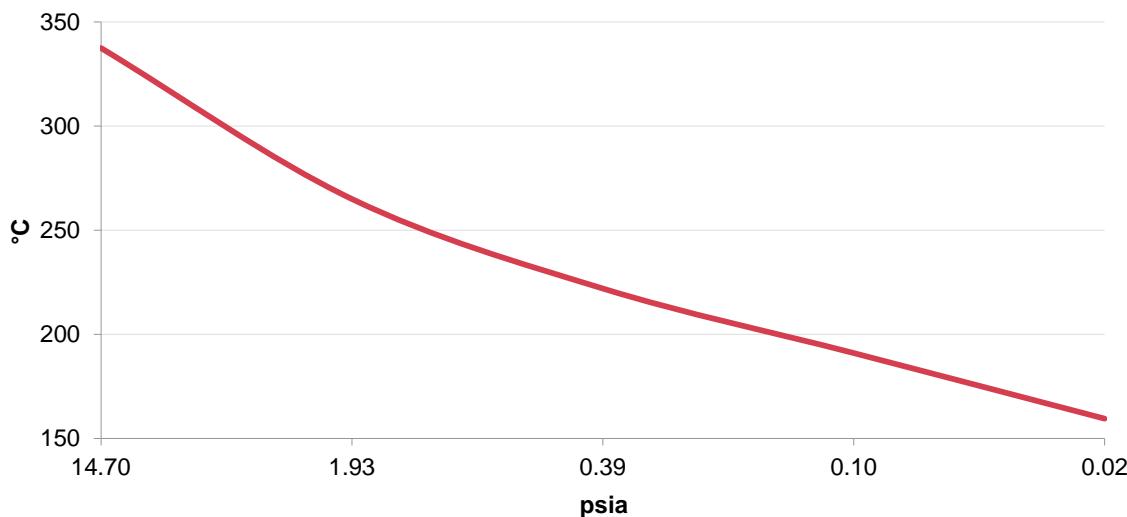
Adipic acid, with a molecular formula of C₆H₁₀O₄, and a molecular weight of 146, has a solid specific gravity of 1.36 g/cm³, but a bulk density when loaded as a powder of 0.6–0.7 g/cm³, depending on average particle size and particle distribution. Adipic acid boils at 337.5°C, and melts at 152.1°C. The table below lists principal physical properties of adipic acid.

Table 4.5
ADIPIC ACID PHYSICAL PROPERTIES

Property	Units	Value
Physical state		White, odorless, crystalline solid, monoclinic needles
Molecular Weight		146.14
Melting point	°C	152
Boiling point	°C	337.5
Solid Density at 25°C	g/cm ³	1.36
Liquid Density at 163°C (325.4°F)	g/cc	1.093
Bulk Density		
Loose	kg/m ³	640–720
Packed	kg/m ³	800–930
Vapor pressure at 18.50°C	Pa	9.7
Octanol/water partition coefficient (log Kow) at 25°C		0.093
Water solubility at 25°C	g/l	23
Flash point (closed cup)	°C	196
Auto flammability (ignition temperature)	°C	420
Ionization constants at 25°C		pKa1 = 4.34, pKa2 = 5.44
Conversion factors at 25°C (calculated)		1 ppm = 5.96 mg/m ³ 1 mg/m ³ = 0.168 ppm
Lower flammable (explosive) limit	gm/m ³	35
Dust cloud ignition temperature	°C	550
pH value at 25°C		2.7 (saturated solution) 3.2 (0.1% solution)
Vapor density in relation to air		5.04
Thermal decomposition temperature (decarboxylation)	°C	230
Hygroscopicity		Non-hygroscopic at 27°C and 85% RH
Acidity	pKa	4.43, 5.41

The boiling point curve for adipic acid is shown in the figure below as a function of absolute pressure. As the temperature of liquid adipic acid increases toward its boiling point, adipic acid begins to thermally degrade by dehydration. To avoid this during processing, adipic acid distillation is usually conducted under vacuum conditions to maintain the temperature below 250°C.

Figure 4.2
ADIPIC ACID BOILING POINT CURVE



Other representative physical properties are shown in the table below.

Table 4.6
OTHER ADIPIC ACID PHYSICAL PROPERTIES

Property	Typical Value	
Flash Point, Cleveland Open Cup	210°C	
Flash Point, Tag Closed Cup	196°C	
Vapor Pressure, Molten	Temperature 159.5°C (319.1°F) 205.5°C (401.9°F) 240.5°C (464.9°F) 265.0°C (509.0°F) 312.5°C (594.5°F) 337.5°C (639.5°F)	Vapor Pressure 0.13 kPa (1 mmHg) 1.33 kPa (10 mmHg) 5.33 kPa (40 mmHg) 13.33 kPa (100 mmHg) 53.32 kPa (400 mmHg) 101.31 kPa (760 mmHg)
Viscosity, Molten	Temperature 160°C (320°F) 193°C (379.4°F)	Viscosity 4.54 cP 2.64 cP

Thermodynamic Properties

As an organic acid, adipic acid evolves significant heat when mixed in water. As a result, mixing and dilution operations that involve concentrated solutions require jacketed pressure

vessels for heat removal, in order to prevent significant thermal excursions. Adipic acid thermodynamic properties are shown in the table below. Adipic acid also absorbs large amounts of heat when crystallized from a solution, such that the design of conventional two-stage crystallization systems requires heat input to compensate for the heat loss during crystallization. A table of adipic acid thermodynamic properties is presented below.

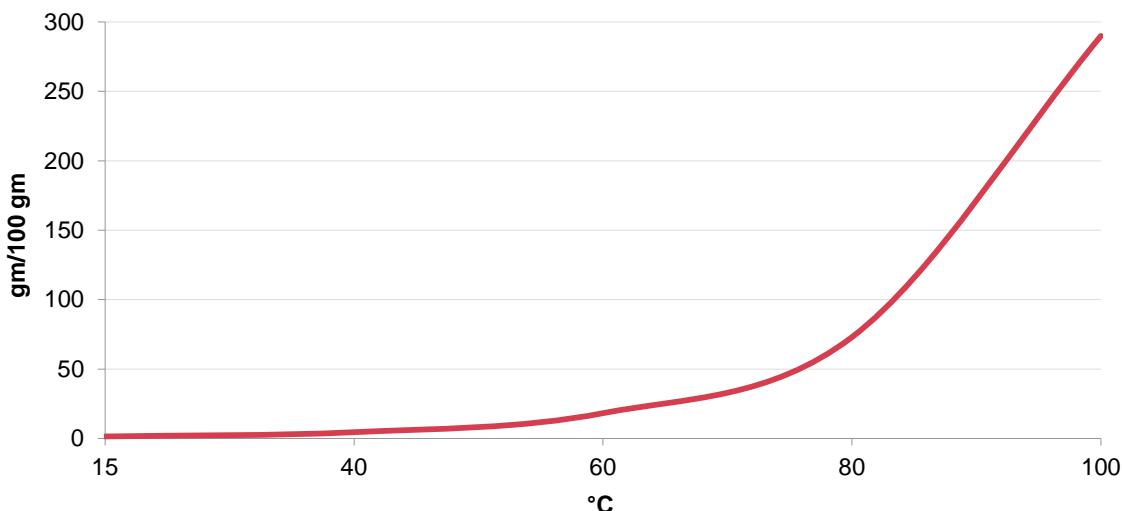
Table 4.7
ADIPIC ACID THERMODYNAMIC PROPERTIES

Property	Units	Value
Specific Heat		
Solid	kJ/kg·°K	1.59
Liquid at 200°C	kJ/kg·°K	2.26
Vapor at 300°C	kJ/kg·°K	1.68
Heat of Formation	kJ/kg	-6,503
Heat of Fusion	kJ/kg	238.5
Heat of Vaporization	kJ/kg	560.3
Heat of Sublimation at 25°C (77°F)	kJ/kg	881.8
Heat of Combustion	kJ/kg	19,149
Heat of Solution, Water		
10–20°C (50–68°F)	kJ/kg	-213.6
90–100°C (194–212°F)	kJ/kg	-240.5
Heat of Crystallization from water	kJ/kg	265.3

Solution Properties

Adipic acid is highly soluble in oxygenated hydrocarbon solvents such as alcohols and ketones, but insoluble in ethers. It is insoluble in most covalent hydrocarbon liquids, including benzene. Adipic acid is only slightly soluble in cold water, but highly soluble in hot water. The water solubility change with temperature is shown in the figure below.

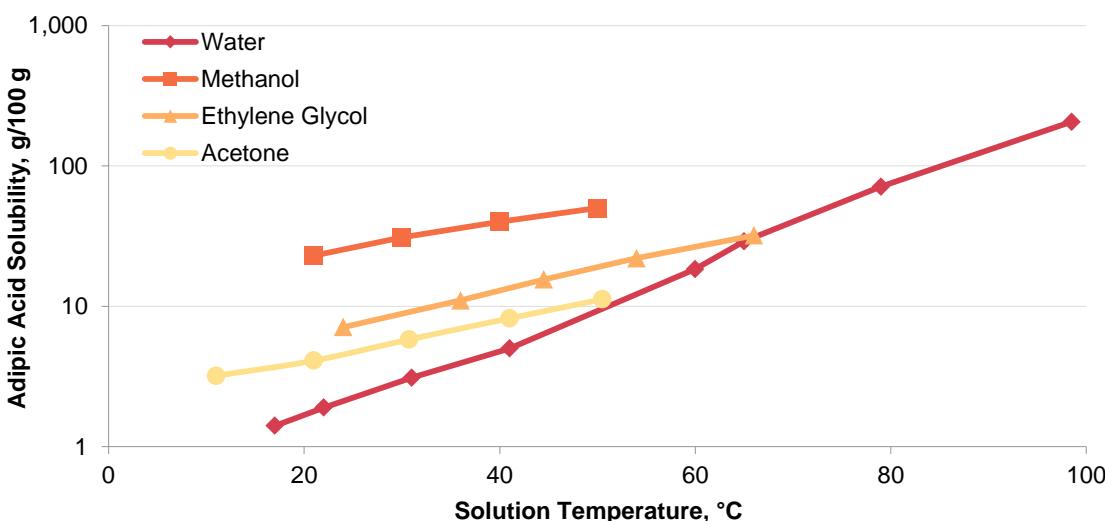
Figure 4.3
ADIPIC ACID—WATER SOLUBILITY RELATIONSHIP WITH TEMPERATURE



Source: Invista

The graph below shows how the solubility of adipic acid in water compares to its solubility in oxygenated hydrocarbons as a function of temperature. For each of the solvents shown, the solubility of adipic acid is higher in hydrocarbons than it is in water at the same temperature.

Figure 4.4
ADIPIC ACID HYDROCARBON SOLUBILITY WITH TEMPERATURE



Source: Invista

Other adipic acid solution properties are shown in the table below.

Table 4.8
ADIPIC ACID SOLUTION PROPERTIES

Property	Typical Value	
Solubility	see Figure 4.4 above	
pH of Aqueous Solutions at 25°C (77°F)	Concentration	pH
	0.10%	3.2
	0.20%	3.1
	0.40%	3.0
	0.60%	2.9
	1.20%	2.8
	2.50%	2.7
Density of Saturated Aqueous Solutions	Temperature	Density
	20°C (68°F)	1.0045 g/cc
	40°C (104°F)	1.0050 g/cc
	60°C (140°F)	1.0125 g/cc
Ionization Constant (K) in Water at 25°C	Step 1: 3.71×10^{-5} (p K ₁ = 4.43) Step 2: 3.87×10^{-6} (p K ₂ = 5.41)	

The conventional process for making adipic acid from cyclohexane produces KA oil (a mixture of cyclohexanol and cyclohexanone) as intermediate products. The table below presents basic physical properties of both intermediate products.

Table 4.9
KA OIL BASIC PHYSICAL PROPERTIES

	Cyclohexanone	Cyclohexanol
Molecular weight	98.15	100.16
Melting point °C	-47	25.15
Normal boiling point °C	156.4	161.4
Liquid density gm/l	0.9493	0.9455
Solubility in water gm/100 gm	3.6	9
Water solubility gm/100 gm	12.6	5.7
Heater of vaporization kJ/mol	45.51	44.92

COMMERCIAL ADIPIC ACID PRODUCTION BY-PRODUCTS

The conventional two-stage oxidation process for producing commercial quantities of adipic acid produces sufficient quantities of by-product dicarboxylic acid glutaric acid and succinic acid to justify recovery for commercial sale. Rather than purify these acids via distillation, they are often instead reacted with alcohols to produce the corresponding esters, which are then sold as

commercial products into the coatings industry. The general yield of these acids in commercial processes using two-step cyclohexane oxidation is as follows (284012).

**Table 4.10
ADIPIC ACID YIELDS**

Adipic acid	95%
Glutaric acid	3%
Succinic acid	2%

Alternatively, some producers sell the mixed dicarboxylic acid by-product as a single product stream, usually called AGS (adipic, glutaric, succinic) in commerce. For example, Ascend Materials (formerly Monsanto) sells a commercial AGS liquid product that is approximately 50% dicarboxylic acid dissolved in water, with up to 2% nitric acid content. A typical composition is shown in the table below.

**Table 4.11
ASCEND MATERIALS AGS PRODUCT COMPOSITION**

Compound	Typical Analysis, wt%	Formula	CAS Number
Adipic Acid	7.7	C ₆ H ₁₀ O ₄	124-04-09
Glutaric Acid	32.7	C ₅ H ₈ O ₄	110-94-1
Succinic Acid	9.6	C ₄ H ₆ O ₄	110-15-6
Nitric Acid	1.0	HNO ₃	7697-37-2

Invista sells a commercial product consisting of dibasic acids (284013). A typical composition is shown in the table below.

**Table 4.12
INVISTA DIBASIC ACID COMPOSITION**

Compound	Typical Analysis, wt%	Formula	CAS Number
Adipic Acid	15–25	C ₆ H ₁₀ O ₄	124-04-09
Glutaric Acid	51–61	C ₅ H ₈ O ₄	110-94-1
Succinic Acid	18–28	C ₄ H ₆ O ₄	110-15-6
Nitric Acid	0.2	HNO ₃	7697-37-2
N ₂ Compounds	1.0		
Copper	0.2		
Vanadium	0.01		

BASF produces and markets (284014) a similar mixed AGS stream trade-named Sokalan® DCS. Beside AGS, smaller quantities of by-products pentanoic acid and hexanoic acid are also produced. During purification, these acids separate also as a mixed stream with adipic acid, and are sold as a mixed acid product. The mixed AGS stream is a suitable feedstock for producing polyester polyols that are used in polyurethane shoe bottoms.

Physical properties of adipic, glutaric, and succinic acid are listed in the table below.

**Table 4.13
PHYSICAL PROPERTIES OF ADIPIC, GLUTARIC, AND SUCCINIC ACID**

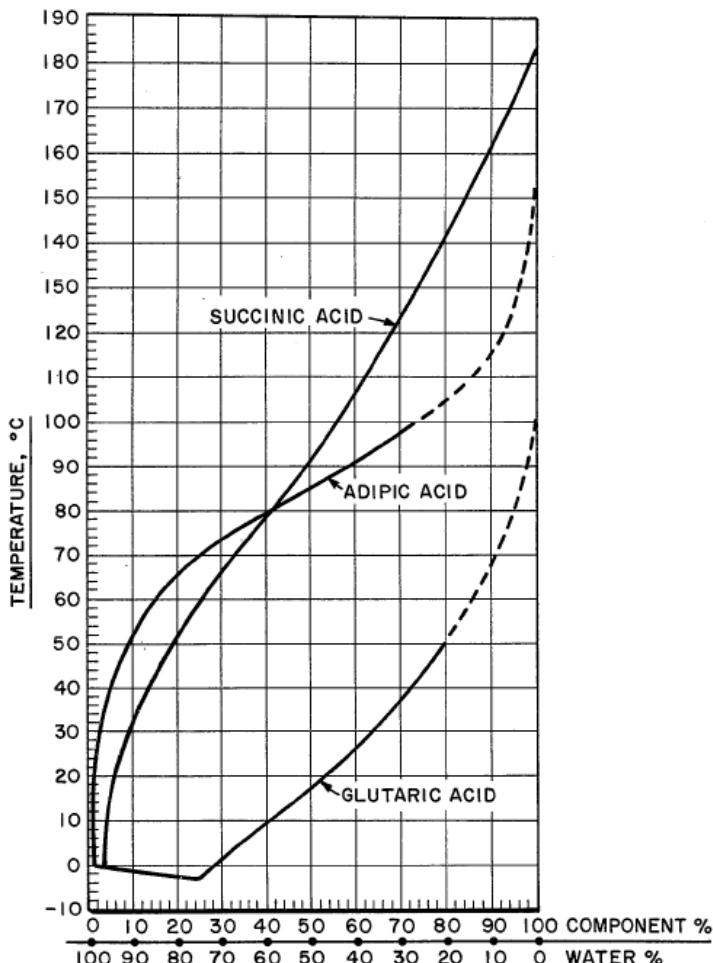
	Adipic Acid	Glutaric Acid	Succinic Acid
CAS Number	124-04-9	110-94-1	110-15-6
Chemical Name	Hexanedioic acid	Pentanedioic acid	Butanedioic acid
Form	Crystalline solid	Crystalline solid	Crystalline solid
Formula	(CH ₂) ₄ (COOH) ₂	(CH ₂) ₃ (COOH) ₂	(CH ₂) ₂ (COOH) ₂
Melting Point °C	152	98	186
Boiling Point °C	330.5	303	235
Specific Gravity at 25°C	1.36	1.429	1.564
Vapor Pressure at 25°C (mm Hg)	3.18 x 10 ⁻⁷	2.88 x 10 ⁻⁶	1.90 x 10 ⁻⁷
Water Solubility at 25°C (mg/L)	3.00 x 10 ⁴	1.60 x 10 ⁶	8.30 x 10 ⁴

An alternative separation approach was patented by DuPont in 1971 (USP 3818081), in which the AGS stream was reacted with ammonia under sub-stoichiometric conditions to produce imides, which could then be separately recovered by distillation. The DuPont patent provides guidance on reacting the mixed acid by-product stream from aqueous crystallization with sub-stoichiometric quantities of ammonia. Since succinic acid and glutaric acid are far more reactive than adipic acid to ammonia, they are preferably converted to the corresponding imide, which is then separated from adipic acid by conventional distillation. Reaction temperature is 200°C. A patented Monsanto approach (USP 4254283, 3-Mar-1981) is to dry the mixed acid stream by heating to 230°C in order to convert succinic acid to succinic anhydride, which can then be separated from the balance of the solution by distillation.

A 1993 Bayer patent (USP 5264624) presents another method for recovering adipic acid from the mixed AGS liquor from aqueous crystallization by adding to the mixture additional quantities of water and adipic acid, and then cooling the solution to preferably crystallize adipic acid while glutaric and succinic acids, having a higher solubility in water, remain as liquids in the crystallization liquor.

The difficulty in separating the AGS components by crystallization is shown in the crystallization curve (figure below) incorporated into Monsanto USP 4254283 (3-Mar-1981). As an AGS mixture that is totally dissolved as liquid is cooled below 190°C, succinic acid begins to crystallize at 186°C, but the crystallization is not completed before adipic acid begins to crystallize at 152°C. As the temperature is further reduced, glutaric begins to crystallize at 98°C. All three acids are crystallizing before adipic acid is totally removed from the dissolved solution, resulting in a solid crystalline product that contains all three acids.

Figure 4.5
CRYSTALLIZATION CURVE FOR AGS MIXTURES (MONSANTO USP 4254283, 3-MAR-1981)

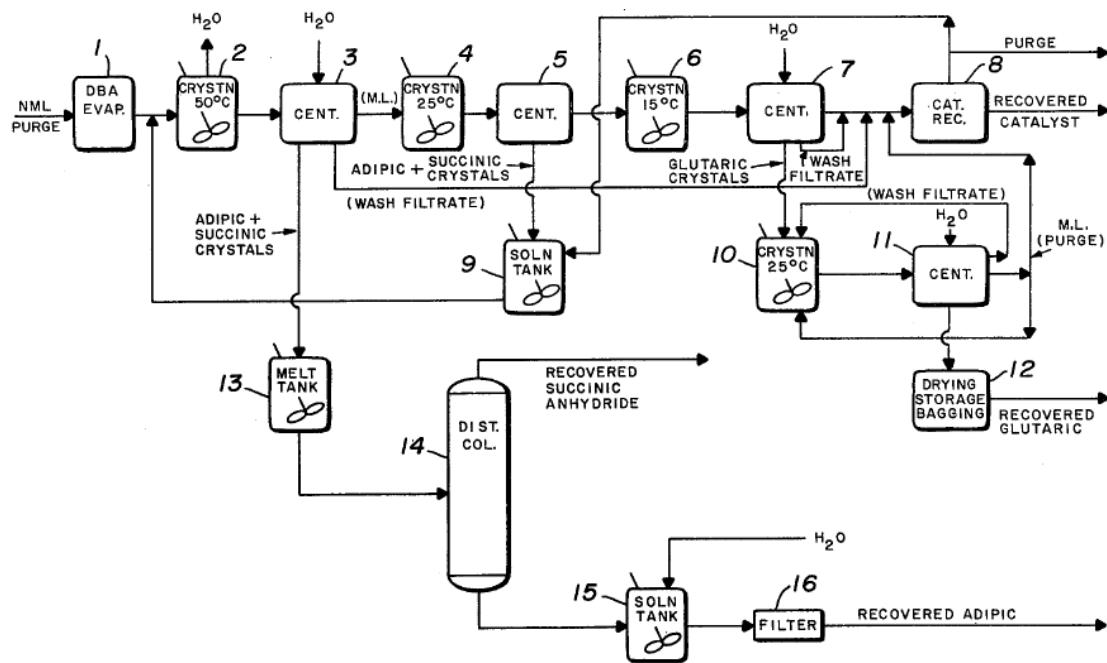


The Monsanto patent (USP 4254283) proposes an alternate process for selectively crystallizing, redissolving, and recrystallizing components of the AGS system to individually purify the three acid components as crystal products, as shown in the figure below.

In this process configuration, the nitric acid-rich mother liquor purge stream from the initial crystallization of adipic acid is directed to an evaporator for the purpose of removing nitric acid residue (boiling point = 83°C). To effectively evaporate both the nitric acid and water, typical evaporator conditions are 120°C and 1.5 psia pressure. Under these conditions, succinic acid dehydrates to succinic anhydride. The solution then undergoes two stages of suspension crystallization: the first stage at 50°C, and the second stage at 25°C, for the purpose of crystallizing out of solution both adipic acid and succinic anhydride. Formed crystals in the suspension are physically removed by centrifugation with water washing. The crystals of mixed succinic anhydride and adipic acid are remelted, and distilled to recover succinic anhydride as the overhead distillate product, and adipic acid as the bottoms product. The remaining liquor, now rich in glutaric acid, undergoes two stages of suspension crystallization for the purpose of removing the glutaric acid as crystallized solids. The first stage of glutaric acid crystallization occurs at 15°C, and the second stage at 25°C. The remaining liquor after removal of dicarboxylic

acid is processed through Amberlyst weak acid ion exchange resin (Rohm and Haas product) for the recovery of the metal content (vanadium and copper) of the catalyst.

Figure 4.6
MONSANTO HIGH-PURITY CRYSTALLIZATION PROCESS (USP 4254283, 3-MAR-1981)

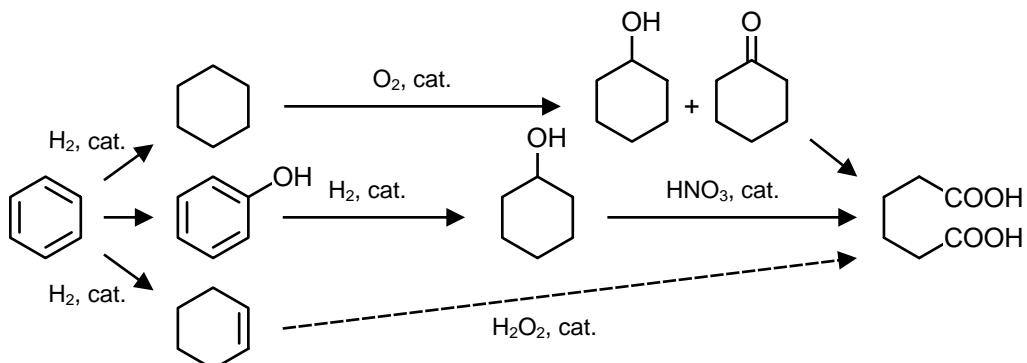


Adipic acid production also produces smaller amounts of monocarboxylic acids (n-valeric acid, n-caproic acid). Due to the potential for these acids crystallizing along with adipic acid during purification, they should be removed by fractional distillation first. Alternatively, suspension crystallization can be carefully controlled to retain monocarboxylic acids in an aqueous solution.

COMMERCIAL MANUFACTURING TECHNOLOGY OPTIONS

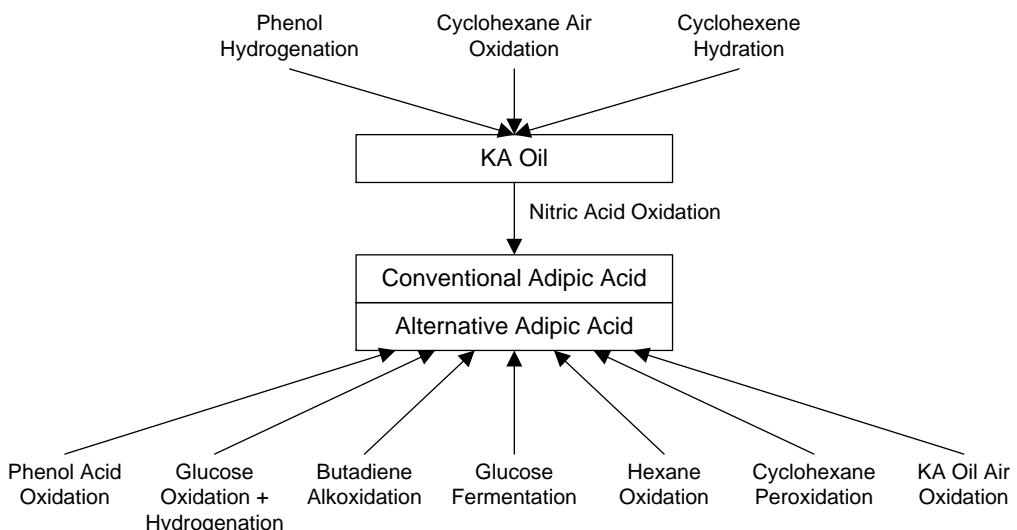
Adipic acid was developed as a commercial product after Wallace Carothers of DuPont invented nylon 66 in 1934, had the polymer patented in 1935, and introduced it as a commercial product in 1938. Major chemical producers in Europe (Rhone-Poulenc, DSM/Stamicarbon, and BASF) and in the US (DuPont, Monsanto and Allied Chemical) developed various process schemes around the two-stage oxidation of cyclohexane, first by air, and second by dilute aqueous nitric acid. The two-stage oxidation process remains the dominant adipic acid process manufacturing technology in 2012, with over 90% market share. Other commercial practiced processes use phenol hydrogenation, cyclohexene partial hydrogenation, and butadiene carboalkoxylation. Non-commercial routes that have been broadly investigated include 1-stage air oxidation, 1-stage nitric acid oxidation, 1-stage hydrogen peroxide oxidation, adipic acid dimerization, and boric acid esterification. Bio-based routes include direct chemical synthesis from glucose, and indirect synthesis via fermentation of sugars. The hydrocarbon-based routes are shown graphically in the figure below. The bio-based routes are discussed later in this section.

Figure 4.7
CONVENTIONAL PROCESS ROUTES TO ADIPIC ACID



Source: Chemical Engineering Transactions (284026)

Figure 4.8
ALTERNATIVE PROCESS ROUTES TO ADIPIC ACID



Source: "Adipic Acid—A Techno-Commercial Profile," Chemical Weekly, 7-Apr-2009 (284015)

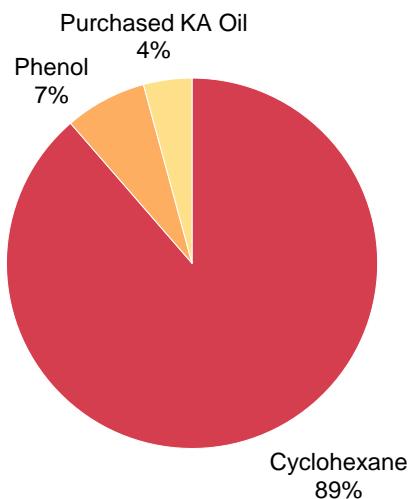
The commercial status of the various adipic acid production technologies is summarized in the table below.

Table 4.14
STATUS OF HYDROCARBON PROCESS ROUTES TO ADIPIC ACID

Process Route to ADA	Commercial Status
Oxidation of cyclohexane via KA oil using air and nitric acid	Dominant commercial process
Hydrogenation of phenol to KA oil and oxidation to ADA using nitric acid	Commercial
1-step oxidation of cyclohexane using n-hydroxyphthalimide	Piloted by Daicel Chemical Industries in Japan (not commercial)
Cyclohexane oxidation with air to cyclohexyl hydroperoxide, then decomposed to KA oil	Not commercial
Cyclohexane oxidation using boric acid to CYCLOHEXYL borate ester, then hydrolyze to cyclohexanol + boric acid, then oxidized with nitric acid to ADA	Not commercial
Hydrogenation of benzene to cyclohexene, then hydration to cyclohexanol, then oxidized with nitric acid to ADA	Commercialized by Asahi Chemical
Partial hydrogenation of butadiene to cyclohexene, then hydration to cyclohexanol, then oxidized with nitric acid to ADA	Commercialized by Asahi Chemical
Conversion of cyclohexane to cyclohexanone via bionix oxidation using metalloporphyrins	Piloted by Sinopec Baling Petrochemical
Oxidation of cyclohexene using hydrogen peroxide	Nagoya University, not commercial

The distribution of global adipic acid commercial capacity by process technology is shown in the figure below. The cyclohexane oxidation route represents over 90% of global capacity.

Figure 4.9
GLOBAL DISTRIBUTION OF ADIPIC ACID CAPACITY BY TECHNOLOGY



Source: IHS Chemical CEH Report, Adipic Acid (284006)

Several of the commercial and semi-commercial processes using conventional fossil fuel feedstock routes have been previously analyzed by IHS in its PEP report series. The unit feedstock consumptions of these processes are presented in the table below.

**Table 4.15
UNIT FEEDSTOCK CONSUMPTION FOR CONVENTIONAL ADIPIC ACID PROCESSES**

Process	Nitric Acid	Benzene	Cyclohexane	Butadiene	Phenol
ADA from benzene via cyclohexanol	0.595	0.781			
ADA from cyclohexane	0.595		0.725		
ADA from butadiene by carboalkoxylation				0.526	
ADA from cyclohexane by oxidation process	0.595		0.726		
ADA from cyclohexane via oxygen-based liquid oxidation	0.598		0.703		
ADA from benzene via cyclohexanol by partial hydrogenation, hydration and oxidation	0.595	0.781			
ADA from phenol via cyclohexanol	0.632				0.693

Source: IHS Chemical

The estimated unit energy consumption for these same processes is presented in the table below.

**Table 4.16
UNIT ENERGY CONSUMPTION FOR CONVENTIONAL ADIPIC ACID PROCESSES**

Process	Electricity (kwh/mt)	Natural Gas (MM-Btu/mt)	Steam (mt/mt)
ADA from benzene via cyclohexanol	306	0.064	14.45
ADA from cyclohexane	117		12.31
ADA from butadiene by carboalkoxylation	1,021		7.57
ADA from cyclohexane by oxidation process	139		12.31
ADA from cyclohexane via oxygen-based liquid oxidation	102		12.7
ADA from benzene via cyclohexanol by partial hydrogenation, hydration and oxidation	579	0.024	14.45
ADA from phenol via cyclohexanol	77		5.57

Source: IHS Chemical

CONVENTIONAL TWO-STAGE CYCLOHEXANE OXIDATION PROCESS

The predominant method for producing adipic acid in commercial quantities in 2012 is only slightly different from the original process developed by DuPont after the invention of nylon 66 by DuPont's Wallace Carothers in 1934. A two-step oxidation sequence is used where the first step involves oxidizing cyclohexane with oxygen in air to form a mixture of cyclohexanone and

cyclohexanol called KA oil. The second step oxidizes KA oil in an aqueous solution of nitric acid for form crude adipic acid. Purification is accomplished by multi-stage suspension crystallization. Both steps use homogeneous metal catalysts for the oxidation reactions.

First-Stage Air Oxidation of Cyclohexane to KA Oil

In the first stage of oxidation, liquid-phase fresh cyclohexane feedstock is combined with recycle cyclohexane, heated at pressure, and fed into multiple CSTR reactors in series where air is injected. The oxidation reaction occurs at modest temperature (150–175°C) and modest pressure (115–175 psia).

Prior to being fed to the first-stage oxidation reactors, cyclohexane feed is used to scrub vapor-phase reactor product gases containing mostly air, but also light hydrocarbons, in order to transfer residual cyclohexane in the vapor-phase stream to the liquid-phase feed.

In order to maximize selectivity to 85% or greater, the reaction is designed to only provide 10–15% conversion per pass. As a result, several continuously stirred tank reactors are provided in series configuration, or in a vertical column configuration separated by stages that each represents a constant composition tank reactor (CSTR). A liquid catalyst is fed to the reaction at a rate of 0.3 to 3.0 ppm, and catalyst is usually fed to more than just the first reactor.

The product from one reactor discharges to the subsequent reactor at the desired conversion. Additional cyclohexane and catalyst are added to each reactor to reduce the inlet concentration of KA oil such that the reaction can again proceed to a total conversion of approximately 10–15%.

The homogeneous liquid-phase catalyst is a mixture of manganese, chromium, copper, and/or cobalt salts (acetate or naphthenate, as liquid) that produces cyclohexyl hydroperoxide as a temporary intermediate oxidation reactor product, which continues to react to oxidize to produce a combination of C₆ cyclic alcohol (cyclohexanol) plus C₆ cyclic ketone (cyclohexanone). A small quantity of adipic acid is also formed, along with by-products glutaric and succinic acids from stepwise oxidation degradation. Glutaric acid is a C₅ dicarboxylic acid, and succinic acid is a C₄ dicarboxylic acid. The carbon atoms stripped from the C₆ molecule backbone during oxidation degradation are converted to a combination of CO and CO₂ gases.

Some process configurations feed catalyst to each reactor in series. At the low per pass conversion rates, selectivity to KA oil can exceed 90%. As per pass cyclohexane conversion rate increases, selectivity decreases.

Product from the last first-stage air oxidation reactor is passed through a conversion reactor to complete the oxidation of residual cyclohexyl hydroperoxide (CHHP) to a combination of cyclohexanone and cyclohexanol. Decomposition of CHHP to a mixture of cyclohexanone and cyclohexanol is accomplished at approximately 150°C using iron, stainless steel, copper, or cobalt oxide heterogeneous catalyst in a fixed bed reactor.

This product stream is then neutralized in a solution using dilute caustic soda. By-product acids are extracted with an aqueous alkali solution to form esters, which are hydrolyzed following de-esterification back to acid.

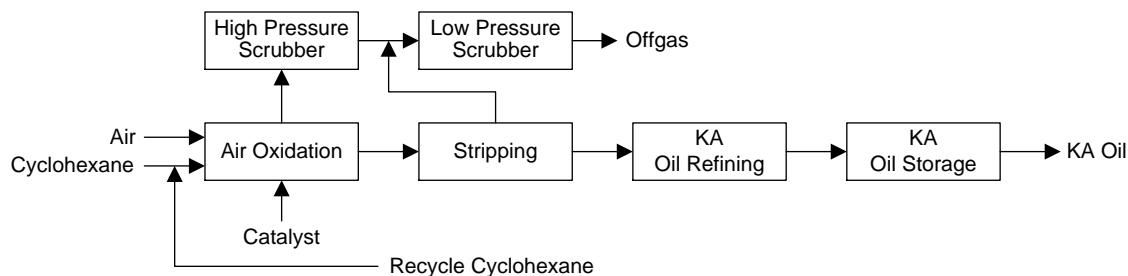
Due to the low per pass conversion of cyclohexane, unreacted cyclohexane from the reactor product stream is distilled to recover the cyclohexane as an overhead product, which is subsequently recycled to the front of the first-stage oxidation sequence. Water is then removed from the product solution via vacuum distillation. The combined product cyclic C₆ ketone and alcohol (KA oil) can be obtained at 99.5% purity by conventional fractional distillation, although most industrial companies simply direct this stream to the next process step (nitric acid oxidation) without distillation to higher purity.

The overhead vapor product from the first-stage oxidation reactors contains nitrogen and other components of air, unconverted oxygen, a small amount of hydrocarbons (principally cyclohexane), CO and CO₂. As mentioned above, this vapor stream is scrubbed with lower temperature fresh feed to absorb and recover the hydrocarbons, principally cyclohexane. Scrubbing can be accomplished in either one scrubbing column, or two columns in series at progressively lower temperature. Following scrubbing with cyclohexane feedstock, the overhead vapor stream is again scrubbed with an aqueous caustic soda solution at elevated pH to remove light, acidic organic compounds. The scrubbed gases are either vented to the atmosphere, or discharged to the plant's fuel gas system for use as boiler fuel. In the future, environmental regulations may require that the vapor stream be passed through a bed of activated carbon to remove residual hydrocarbons, after scrubbing, and before being vented to atmosphere.

A block flow diagram for the preparation of KA oil from cyclohexane is shown below (284011). The conventional cyclohexane process produces KA oil that is generally in the mass ratio of 93% cyclohexanol to 7% cyclohexanone. Different adipic acid producers practice specific catalyst compositions and reactor conditions that result in slightly different proportions of ketone to alcohol in KA oil.

There are two product streams from the air oxidation reactors. Liquid reactor product is directed to a fractional distillation train for the recovery of unconverted cyclohexane. The first column removes unreacted cyclohexane as an overhead product, which is recycled to the process, while the second column removes water via vacuum distillation. The subsequent columns in series remove light monocarboxylic acids by-products as an overhead product. The next tower removes purified KA oil as overhead product, leaving a bottoms heavy hydrocarbon-rich stream containing higher molecular weight organic acids. The heavy hydrocarbon stream usually is burned as liquid boiler fuel, or is incinerated.

**Figure 4.10
CYCLOHEXANE TO KA OIL BLOCK FLOW DIAGRAM**



The cobalt naphthenate catalyzed air oxidation process is claimed to have been improved (284016) by conducting the reaction in a boric acid catalyzed reaction at 140–180°C to obtain up to 15% conversion per pass, compared to 12–13% for one-pass conversion without the use of boric acid. The large excess of unreacted cyclohexane feedstock in the reactor liquid product stream is removed by vacuum distillation and recycled as feed to the oxidation reaction system.

There are four general approaches to maximizing yield from the conventional cyclohexane first-stage air oxidation process:

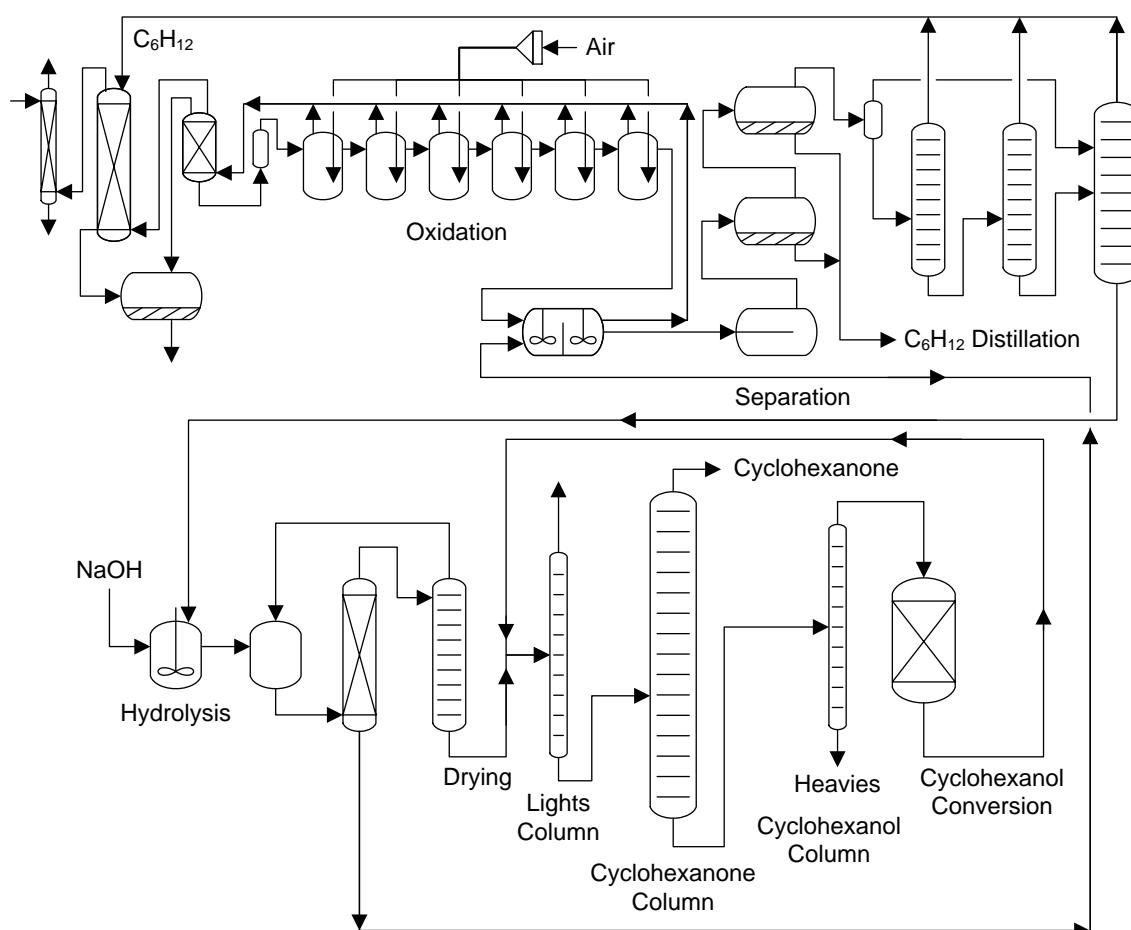
1. Operating the conventional process at low per pass cyclohexane conversion
2. Maximizing cyclohexyl hydroperoxide production (CHHP), and then dehydrating CHHP with caustic soda to maximize ketone production. This approach has been popularized by Stamicarbon

3. Add metaboric acid to cyclohexane feedstock in order to maximize cyclohexanol via production of borate ester that prevents high concentration KA oil. Later hydrolyze the ester to recover KA oil. This approach yields alcohol to ketone proportions in the molar ratio of 10:1 results. However, this process has been discontinued due to poor quality product. This approached was developed by Scientific Design, IFP, and Stamicarbon. It was commercialized by Monsanto, ICI and Bayer, and later abandoned
 4. Add metaboric acid to the existing air oxidation process to form borate ester as a means of preventing the over-oxidation of KA oil to unwanted by-products. Later, the boric ester intermediate is hydrolyzed back to KA oil and water

Process flow diagrams for the air oxidation of cyclohexane for the basic Stamicarbon KA oil process, and the Nynex Chemical (Flixborough Disaster) process are shown in the figures below.

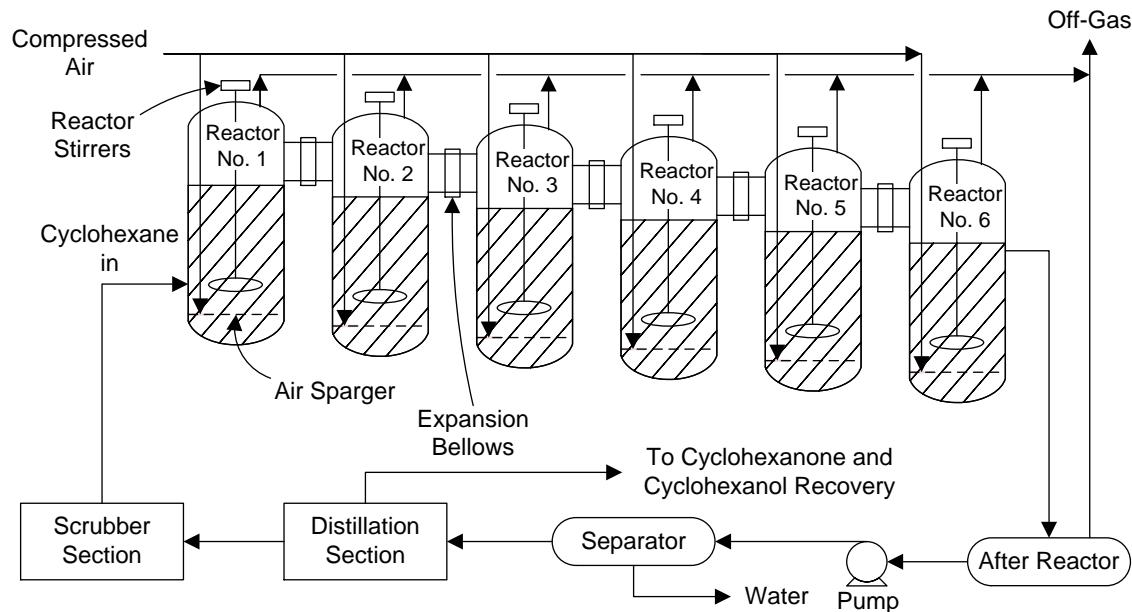
Figure 4.11

BASIC STAMICARBON KA OIL PROCESS FLOW DIAGRAM



Source: Boris Kuzmanovic 2003 dissertation—University of Twente (284017)

Figure 4.12
NYPRO CHEMICAL (FLIXBOROUGH) KA OIL PROCESS PROCESS FLOW DIAGRAM



Source: UCSB College of Engineering (284018)

KA oil is generally fed directly to the 2nd-stage oxidation part of the process, where nitric acid oxidizes the combination of ketone and alcohol to crude adipic acid. It is believed that the initial reaction in nitric acid oxidizes the C₆ cyclic alcohol component to ketone. Alternatively, KA oil can be dehydrogenated over a combination of copper and zinc oxide catalysts to convert the alcohol component of KA oil entirely to ketone.

Air Oxidation Enhanced with Boric Acid

Although attempts by Halcon/Scientific Design working with Monsanto to replace the conventional air oxidation of cyclohexane process with boric acid were not commercially successful, Halcon was commercially successful in enhancing the conventional air oxidation process by adding ortho or meta boric acid to the cyclohexane feed stream for the purpose of increasing both one-pass cyclohexane conversion and ultimate selectivity to KA oil.

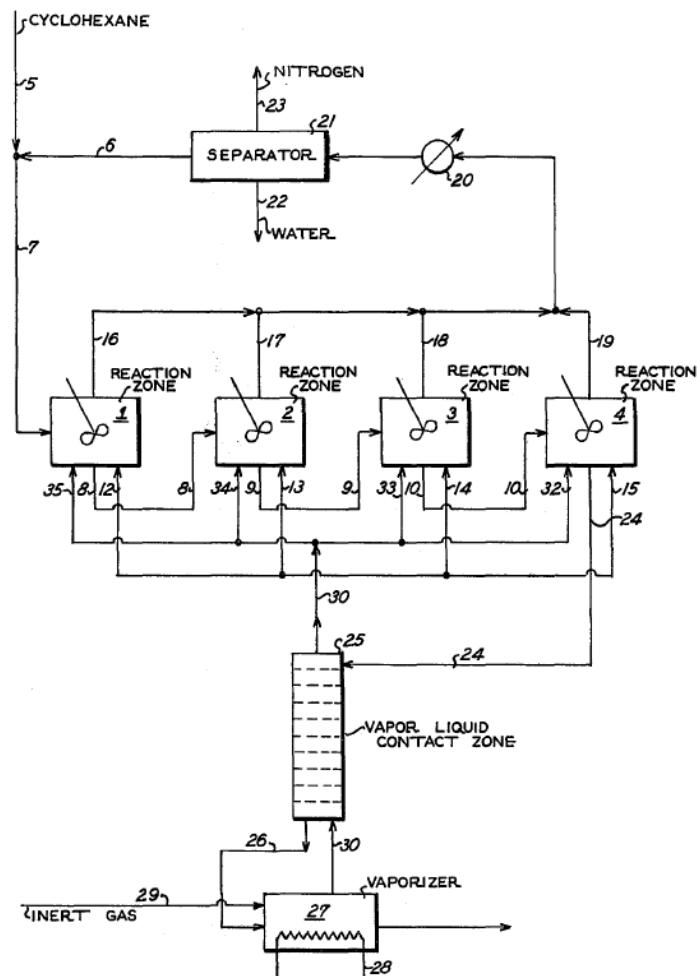
Besides Halcon, others to receive US patents for various aspects of boric acid enhanced oxidation, or recovery and recycle of the boric acid following reaction, include Esso (now ExxonMobil), Monsanto (now Ascend), ICI (now Ineos), and Bayer. A list of relevant US patents on boric acid enhancement of air oxidation of cyclohexane is presented in the table below.

Table 4.17
BORIC ACID ENHANCEMENT US PATENTS

3232704	3665028	4322558
3243449	3895067	4042630
3423471	3932513	3987100
3475500	4058565	3459805
3488740	3558687	3558687

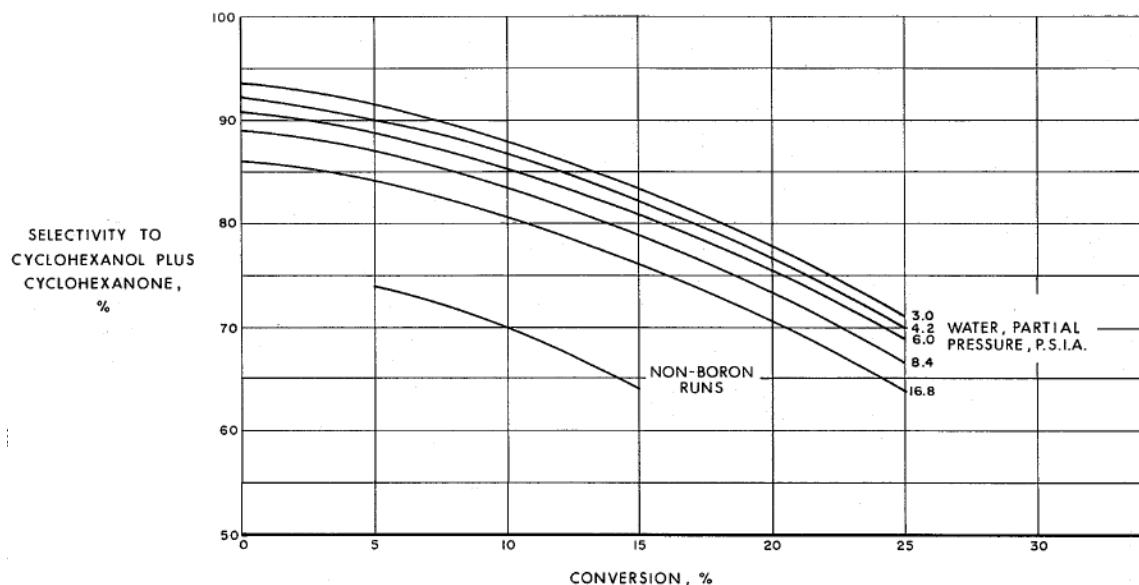
The basic process configuration for the Halcon approach to cyclohexane air oxidation is shown in the figure below from one of Halcon's US patents. Fresh liquid cyclohexane feed (containing liquid-based catalyst) is directed to the first of four air oxidation reactors configured for series processing. The overhead vapor product from the reactors is cooled and condensed to remove water, purge non-condensable air components, and recover and recycle unreacted and condensed cyclohexane. Liquid product from the last reactor in series is directed to a stripper designed to remove reactor products from the off-gases from the oxidation reactors. The bottoms product stream from the stripper is vaporized, with unreacted cyclohexane vaporizing to a gas while the heavier reactor products (KA oil, adipic acid, CHHP, other monocarboxylic and dicarboxylic acids) leaving the vaporizer as liquid product. The vapor stream is passed up through the stripper and the overhead stripper product, containing nearly pure cyclohexane, is redistributed to all of the air oxidation reactors.

Figure 4.13
HALCON AIR OXIDATION PROCESS PATENT (USP 3932513, 13-JAN-1976)



The amount of conversion improvement provided by boric acid enhancement is shown in the figure below from Halcon US patent 3243449, which plots selectivity versus conversion for non-boron and boron enhanced technology. The non-boron technology provides only 70% selectivity at 10% conversion, while the boric acid assisted process provides up to 85% selectivity at the same 10% conversion.

Figure 4.14
AIR OXIDATION IMPROVEMENT USING BORIC ACID (HALCON USP 3243449)



In the absence of boric acid, the conventional air oxidation process of cyclohexane using cobalt naphthenate catalyst suffers from the propensity of cyclohexanol formed to undergo further undesirable oxidation reactions to form degradation products (glutaric acid, succinic acid, monobasic acids) and ultimately combustion products CO, CO₂ and water. As a result, the conventional air oxidation process without boric acid enhancement is limited to overall selectivity to KA oil of 80 weight percent, requiring single pass reactor conversion of approximately 10%.

Boric acid addition to the cyclohexane air oxidation process increases KA oil selectivity to a range between 90–95 weight %, and allows one-pass oxidation reactor conversion rates of 12–15%. The oxidation of cyclohexane by air using cobalt catalysis forms both desired products cyclohexanone and cyclohexanol, and intermediate product cyclohexyl hydroperoxide. It is the cyclohexyl hydroperoxide that is most susceptible to degrading the C₆ molecule to undesirable C₅ and C₄ by-products.

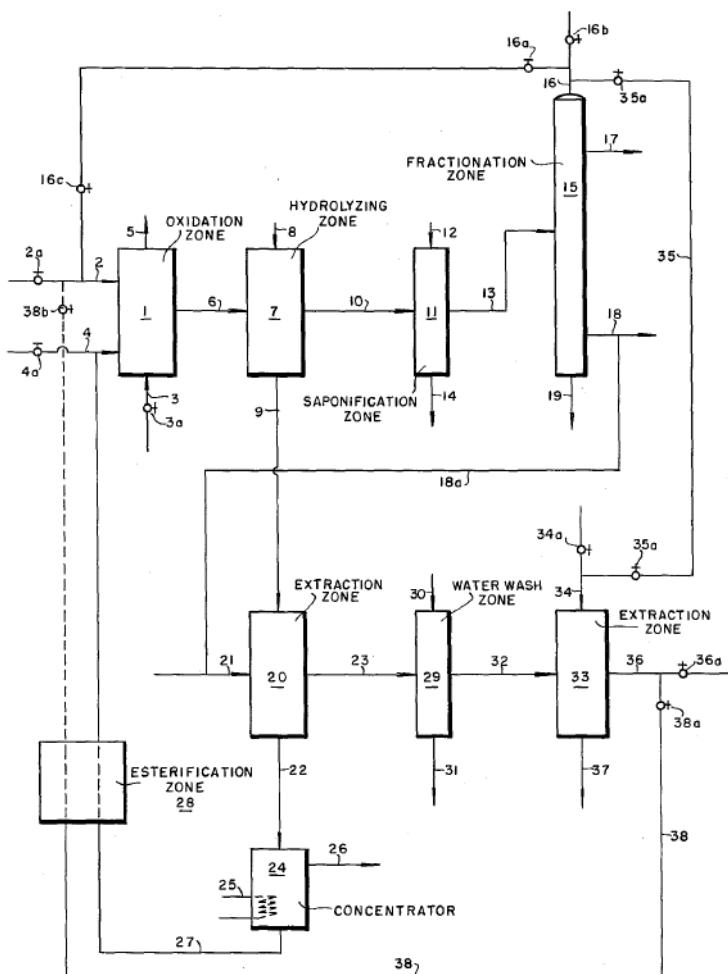
Halcon/Scientific Design patented the boric acid enhancement process (USP 3243449 and 3665028). Monsanto improved upon boric acid recovery from the process (USP 3895067), and Bayer improved the process conditions (USP 4058565).

The presence of ortho or metaboric acid in the cyclohexane liquid reactor feed causes cyclohexanol and cyclohexyl hydroperoxide to react with the boric acid to form the corresponding ester plus water. Once the ester is formed, it does not undergo further oxidation, avoiding product degradation. After removal of the liquid solution from the air oxidation reactors (and removal from the presence of reactive oxygen), the liquid solution can be heat soaked to complete the ester formation process, and then hydrolyze the CHHP with hot water to convert the ester back to cyclohexanol and boric acid. Compared to the conventional air oxidation process, the Halcon enhanced boric acid process requires a slightly higher air oxidation reactor temperature (approximately 165°C versus 160°C), and an operating pressure of about 100 psia. Since the formation of water during esterification is detrimental to the process, the higher operating temperature causes water formed in the reactor to vaporize in the reactor and leave the air oxidation reactor in the air-rich overhead vapor stream.

The use of boric acid in the air oxidation reaction scheme requires careful consideration for methods to recover economically valuable boric acid from reactor products. The high excess feed rate of cyclohexane combined with low one-pass conversion results in most commercial plants immediately distilling the oxidation reactor product liquid stream to separate unconverted cyclohexane as the overhead distillate product, which is recycled to the reactor feed. The bottoms product stream from this distillation column contains KA oil, cobalt catalyst, degradation products, heavy sludge, water, and boric acid. The stream is usually directed to a settling drum for producing a two-phase liquid (oil on top, water on bottom), in which the oil layer is primarily KA oil, and the water layer would ordinarily be dispatched to the wastewater treatment plant.

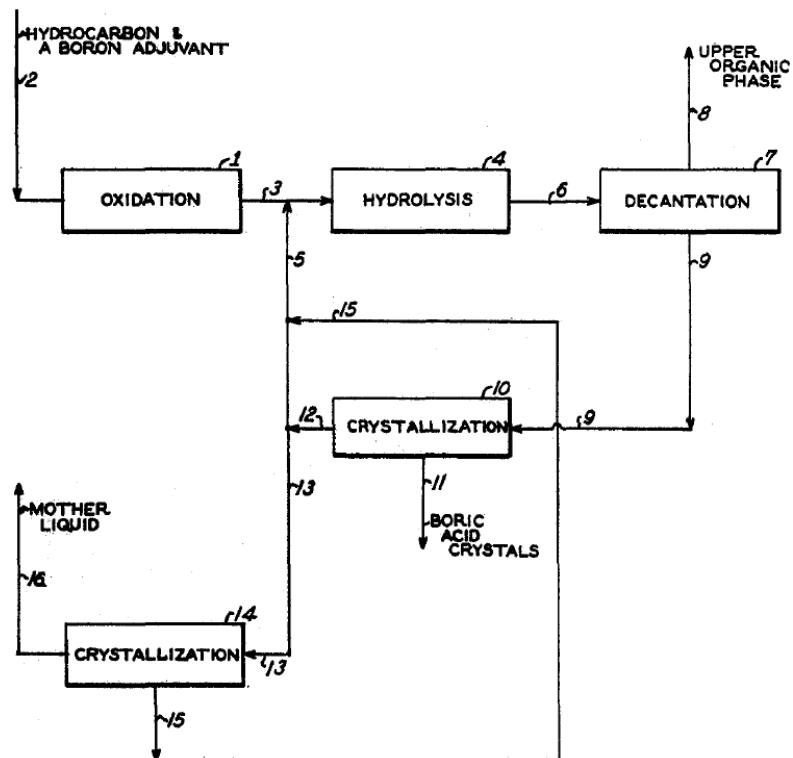
When boric acid technology is employed, the water stream will contain most of the boric acid. Rather than being directed to wastewater treatment, the water-rich stream is first processed through an extraction or crystallization process unit to separate the boric acid, remove it from the water, and recycle the boric acid to the front of the process. Such an extraction scheme is shown in the block flow diagram below for an Esso (now ExxonMobil) crystallization patent.

Figure 4.15



An alternative means of extracting boric acid from the aqueous stream from air oxidation is to use crystallization. Details are provided in Halcon US patents 3423471 and 3475500. A schematic of the Halcon crystallization approach is shown in the figure below.

**Figure 4.16
BORIC ACID RECOVERY CRYSTALLIZATION PROCESS (HALCON USP 3475500)**



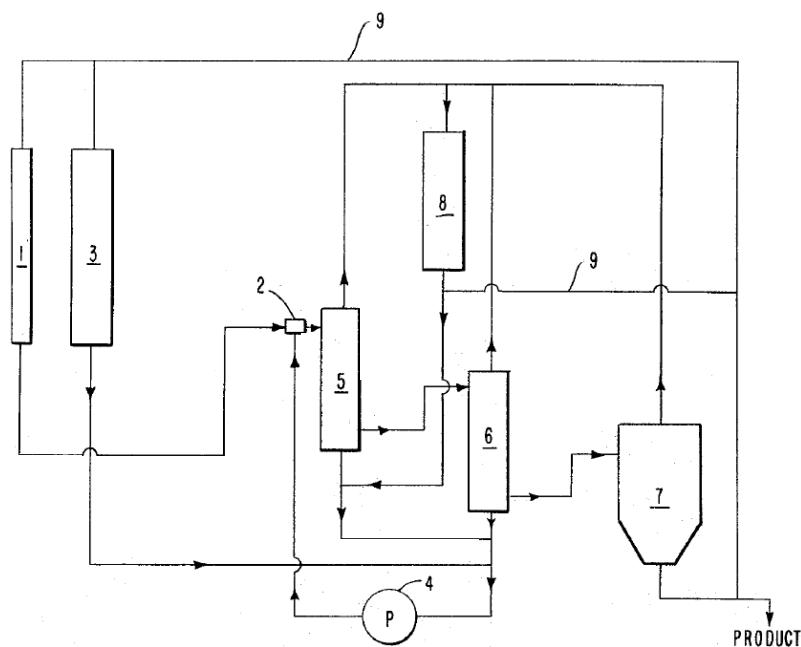
Second-Stage Nitric Acid Oxidation of KA Oil to Adipic Acid

The conversion of the intermediates cyclohexanol and cyclohexanone (KA oil) to adipic acid uses process technology similar to the original process developed by DuPont after World War II. The process effects oxidation using dilute (45–65%) nitric acid in the presence of homogeneous copper nitrate and ammonium metavanadate catalysts. This results in adipic acid product concentration slightly above 90 weight percent. The reaction is highly exothermic, requiring cooling of the primary reactor both with a jacket, and also using an external heat exchanger pump around loop, or using a shell-and-tube reactor.

Below is a block flow diagram of the basic DuPont process, as patented as USP 3359308. A reservoir of KA oil (#1) mixes with a reservoir (#3) of nitric acid solution (40–55 wt%) in a draft tube mixer (#2) and is directed to the primary nitric acid oxidation reactor (#5). Liquid discharge from the primary reactor is fed to a secondary nitric acid oxidation reactor (#6). The combination of reactors is operated in a pump around loop using a large excess of nitric acid solution, between 5 to 15 times the weight ratio of fresh KA oil feed. The primary oxidation reactor is operated at 40–90°C, while the secondary oxidation reactor is operated at 110°C. Both reactors operate at slightly above atmospheric pressure (20 psia). A pressure equalization line (#9) maintains the system of pressure vessels at equal pressure. The product liquid stream from the

secondary nitric acid oxidation reactor is discharged to a hold up tank (#7). The off-gas stream from both reactors and the hold-up tank combine and are directed to a condenser (#8) that recovers the condensate and recycles it to the pump around loop.

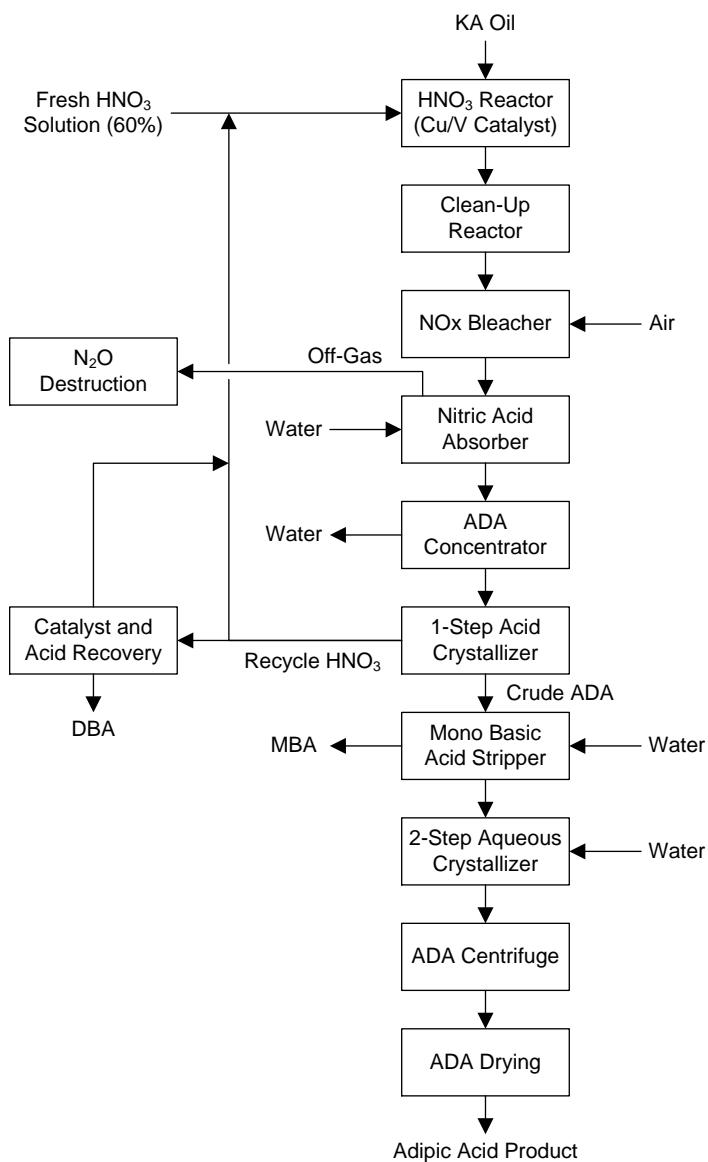
Figure 4.17
DUPONT 1967 ADIPIC ACID PROCESS (USP 3359308)



A thermal runaway reaction in the nitric acid reactors can occur if reactor temperatures exceed 150°C (302°F). Temperature control is maintained using a large excess of nitric acid, from 5 to 15 times higher than required solely by stoichiometry. Nitrogen oxides (NOx) by-products formed in the reactors are removed by bleaching the reactor product liquid stream at 90°C with compressed air. Water is removed by vacuum distillation, and the crude adipic acid is separated from the nitric acid liquor by suspension crystallization.

Multi-step crystallization is necessary to satisfy commercial specifications for polymer-grade adipic acid suitable for nylon 66 manufacture. A block flow diagram of a modern KA oil oxidation process unit for converting KA oil to adipic acid via nitric acid oxidation is shown below (284011).

Figure 4.18
ADIPIC ACID FROM KA OIL VIA NITRIC ACID OXIDATION BLOCK FLOW DIAGRAM

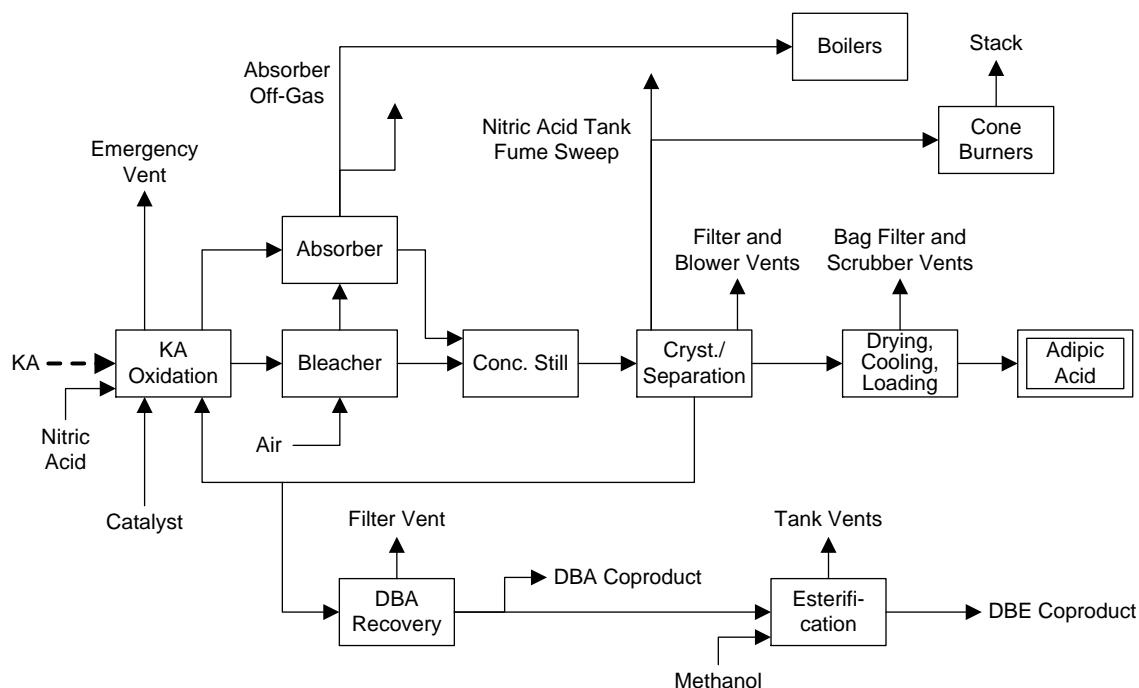


A simplified process flow diagram for nitric acid oxidation is shown in the figure below, which represents an adaptation of the basic DuPont process from the 1940s. KA oil is reacted with a solution of nitric acid in water in the presence of homogeneous catalysts consisting of copper and vanadium. Kinetics are very fast, and the reaction is highly exothermic. Two reactors are usually used, with the first reactor accomplishing 90% of the conversion. For the primary nitric acid reactor, a large excess of nitric acid is combined with KA oil via an external pump around loop (or using a shell-and-tube reactor) that contains a heat exchanger designed to remove the exothermic heat of reaction. Both the primary reactor and secondary reactor are jacketed with cooling water coils. One reason for the redundant facilities designed to remove the exothermic heat of reaction is that a potential exists for a thermal runaway if the solution temperature

approaches 150°C. Under these conditions, KA oil begins to combust rather than form acid, releasing an enormous amount of heat.

Adipic acid yield is 92–96%, with the primary by-products being other dibasic acids (C_5 glutaric acid and C_4 succinic acid). A smaller quantity of monobasic acids is also produced (valeric acid and caproic acid), which are usually discharged as a very dilute stream in water to wastewater treatment. During the reaction, the nitric acid gives up an oxygen atom to the KA oil molecule to form adipic acid, resulting in the nitric acid being reduced to a combination of nitrogen oxide gases (NO_2 , NO , N_2O and N_2). The nitric acid oxidation reactor occurs at modest temperature (60–90°C) and modest pressure (0.1 to 0.4 MPa, 14–58 psia).

Figure 4.19
ADIPIC ACID FROM KA OIL VIA NITRIC ACID OXIDATION SIMPLIFIED PROCESS FLOW DIAGRAM



Source: US EPA (284019)

In the simplified process flow diagram above, copper and vanadium salt catalyst liquid is first mixed with fresh nitric acid solution. The fresh nitric acid solution, now containing catalyst, is combined with recycle nitric acid solution, mixes with KA oil feedstock, and is fed to two nitric acid oxidation reactors in series configuration. Each nitric acid reactor discharges both a liquid product stream and a vapor product stream. The liquid product stream contains nitric acid solution with catalyst, KA oil feedstock, produced and dissolved adipic acid, by-product acids, and water produced by the primary oxidation reaction. The vapor product stream contains nitrogen oxides formed by the reduction of NO_3 to principally NO_2 .

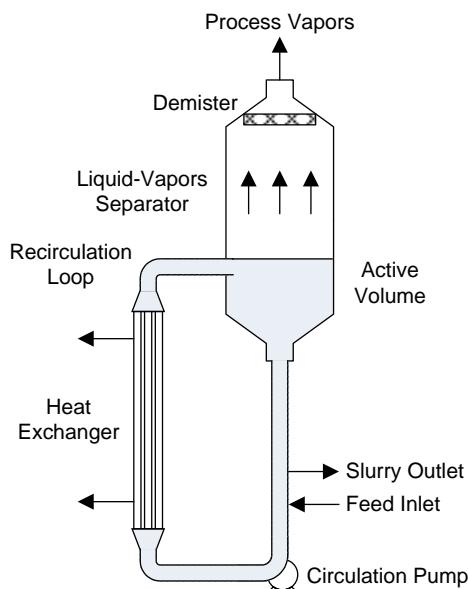
The liquid product stream from the secondary nitric acid reactor is fed to a bleacher, which operates as a stripper in which air fed to the bottom of the bleacher strips the nitrogen oxide compounds out of the liquid nitric acid solution.

The vapor product streams from both reactors and the bleacher contain NOx components that can be recovered and reconcentrated into nitric acid. These vapor product streams are directed to an acid absorber where the vapor streams enter at the bottom mix with process water injected at the top. The process water absorbs most NOx components that redissolve as dilute nitric acid. Nitrous oxide (N_2O) in the vapor streams is not absorbed in water. The overhead vapor stream from the nitric acid absorber is scrubbed or is directed to an incineration unit designed to destroy N_2O .

The liquid product stream from the bottoms of the bleacher is combined with the bottoms product stream from the absorber, and both are directed to a distillation tower concentrating still designed to remove water as an overhead product, since water is produced in the nitric acid oxidation reaction. The distillation tower operates under vacuum conditions. The bottoms product stream from the concentrator is directed to an acid crystallizer for the purpose of removing most of the adipic acid as a crude solid product. Suspension crystallization using a forced circulation method is the preferred approach for adipic acid. The nitric acid and adipic acid crystallized slurry is circulated through an external pump around loop that either heats the solution (when evaporative crystallization is employed), or chills the solution (when low temperature crystallization is employed). A schematic drawing of a forced crystallization system is shown below.

The nitric acid mother liquor, following crude acid crystallization, contains residual quantities of adipic acid plus glutaric acid and succinic acid. These three dicarboxylic acids can either be purified as a single crystal product called DBA (dibasic acid).

**Figure 4.20
FORCED CIRCULATION CRYSTALLIZATION SYSTEM**



Source: <http://www.niroinc.com>

The crude adipic acid crystal slurry is washed with water and centrifuged to produce a semi-solid cake. The non-crystallized nitric acid-rich liquor is recycled back to the process. The nitric acid-rich liquor can be sent directly back to the nitric acid oxidation reactors, or first concentrated

in the concentrator distillation tower to remove excess water before being recycled to the oxidation reactors.

The crude crystallized adipic acid solid cake from the acid centrifuge is not pure enough to be sold as commercial product. It is redissolved in water, and recrystallized in a one or two-stage aqueous crystallizer and centrifuge to increase the purity of the adipic acid crystals. Modern adipic acid plants take the redissolved adipic acid in water solution, and first pass it through a high temperature distillation tower that removes water, light impurities, and monobasic acid by-products (valeric acid, caproic acid) as an overhead product. The concentrated bottoms product from the high temperature distillation tower can then be crystallized, centrifuged, and dried to produce commercially pure adipic acid.

Recycle nitric acid solution contains dibasic acids (glutaric acid and succinic acid) that would concentrate in the system if a method is not provided for their removal. A portion of the recycle nitric acid is passed through an evaporator to remove nitric acid and water, and directed to a separate crystallizer designed to remove and recover a mixture of glutaric and succinic acid along with residual adipic acid. These acids can either be sold as a mixed dibasic acid product, or individually crystallized and sold as individual acid products. Since the liquid stream remaining from this portion of the process still contains valuable catalyst (copper and vanadium), the stream is passed through a strong acid cation exchange resin bed to remove and recover the metal catalyst from the solution. The catalyst metals are subsequently recovered when the ion exchange bed is regenerated with concentrated nitric acid.

Two nitric acid reactors are usually operated in series. The first reactor contributes approximately 90% of feedstock conversion, and generates significant exothermic heat requiring either that the reactor be designed either as a shell-and-tube reactor using the shell side for coolant flow, or that the reactor be designed as a CSTR reactor using an external pump around loop through an external cooling heat exchanger. In either case, a large excess of nitric acid is fed to the reaction system to absorb some of the exothermic heat of reaction, and to assure complete oxidation of KA oil to acid. Typical operating conditions for both nitric acid oxidation reactors are shown in the table below.

Table 4.18
TYPICAL OPERATING CONDITIONS FOR NITRIC ACID OXIDATION REACTORS

	Operating Temperature (°C)	Operating Pressure (psia)
Primary Reactor	70	50
Secondary Reactor	105	50

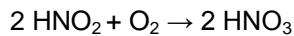
Approximately 80–90% of KA oil conversion occurs in the primary reactor at a residence time of approximately 5 minutes, while the clean-up reactor operating at higher temperature completes the KA oil conversion to virtually 100% also in a 5 minute residence time.

NOx Bleaching with Hot Air

The chemical reaction producing adipic acid from an aqueous nitric acid solution also produces nitrous acid and water. Water needs to be removed from the system in order to recycle the nitric acid. The desire is to convert nitrous acid back to nitric acid via direct oxidation in air. Since nitrous acid is unstable, it can decompose to a combination of nitric acid, nitrous oxide, and water as shown by the reaction below.



The stoichiometry of the reaction shown above reveals that decomposition results in 3 mols of nitrous oxide being converted to only one mol of nitric acid, resulting in a significant consumption of nitric acid for the overall process. If direct oxidation in air occurs, instead, all 3 mols of nitrous oxide can be converted to 3 mols of nitric acid for recycle and reuse in the process.



To accomplish the air oxidation of nitrous acid, the liquid product stream from the clean-up reactor is directed to a stripping column, called a bleacher, in which low pressure air mixes with the liquid stream in counter current configuration. The bleacher converts nitrous acid to nitric acid, while also removing from the liquid stream vapor-phase components such as NO, NO₂, and N₂O. The bleaching action changes the color of the liquid stream from very dark black to light brown.

Nitric Acid Absorber

The vapor stream product gases from the bleacher, primary oxidation reactor, and clean up reactor are combined and directed to the bottom of a scrubber called a nitric acid absorber where the gases are contacted with water in a counter current configuration. Some of the NO and NO₂ vapors are reabsorbed by the water to form dilute nitric acid that can be concentrated and recycled. N₂O (nitrous oxide) in the vapor stream is not effectively absorbed in water. Historically, this stream was vented to the atmosphere, or passed through an 'extended absorber' that provided greater residence time and lower water temperature to increase the amount of NOx components absorbed by the water stream. Given the high greenhouse gas potential of N₂O, the N₂O stream in most industrialized countries is now sent to a two-stage incinerator where it is converted at very high temperature under reducing conditions to a combination of nitrogen (N₂) and oxygen (O₂). N₂O destruction units can either be designed as catalytic or thermal units, as discussed later in this section.

Some adipic acid plants also direct vent gas streams from nitric acid tankage to the absorber, for the purpose of condensing nitric acid fumes while converting NOx components in the vapor stream back to nitric acid.

Adipic Acid Concentrator

The bottoms liquid product streams from the NOx bleacher and the nitric acid absorber are separately directed to a distillation tower for the purpose of reconcentrating the nitric acid by removing the water content of both streams via vacuum distillation. The tower is known as the 'adipic acid concentrator' by some, the 'concentrating still' or the 'nitric acid concentrator' by others. The concentrator is operated under vacuum conditions, in order to drive water into the overhead product stream at a temperature lower than water's normal boiling point (100°C). The operating conditions for the adipic acid concentrator are presented in the table below.

Table 4.19
OPERATING CONDITIONS FOR ADIPIC ACID CONCENTRATOR

	Value
Operating Pressure (psia)	3.0
Overhead Temperature (°C)	60
Bottoms Temperature (°C)	90
Water Concentration in Overhead Product (wt%)	99

The overhead product stream from the adipic acid concentrator can be used as feed water to the NO_x absorber, or can be sent to the plant wastewater treatment plant.

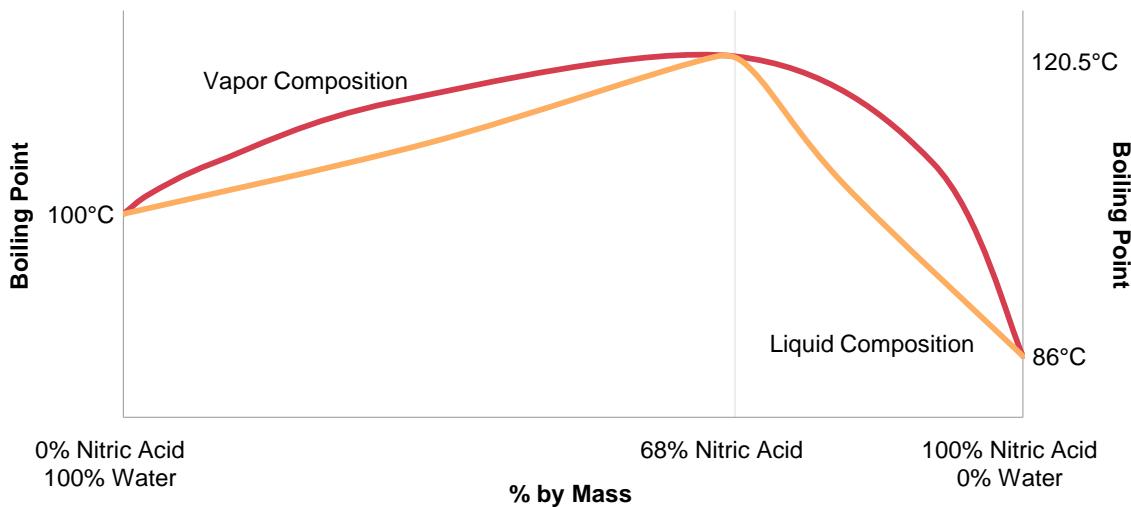
The major components of the stream being fractionated in the adipic acid concentrator, and their boiling points, are shown in the table below.

Table 4.20
BOILING POINT OF ACID CONCENTRATOR COMPONENTS

Component	Boiling Point (°C)	Water Solubility (g/l)
Cyclohexane	81	Immiscible
Nitric acid	83	Completely
Water	100	Not applicable
Cyclohexanone	156	9
Cyclohexanol	161	4
n-Valeric acid	186	50
n-Caproic acid	205	11
Succinic acid	235	58
Glutaric acid	303	430
Adipic acid	337	23

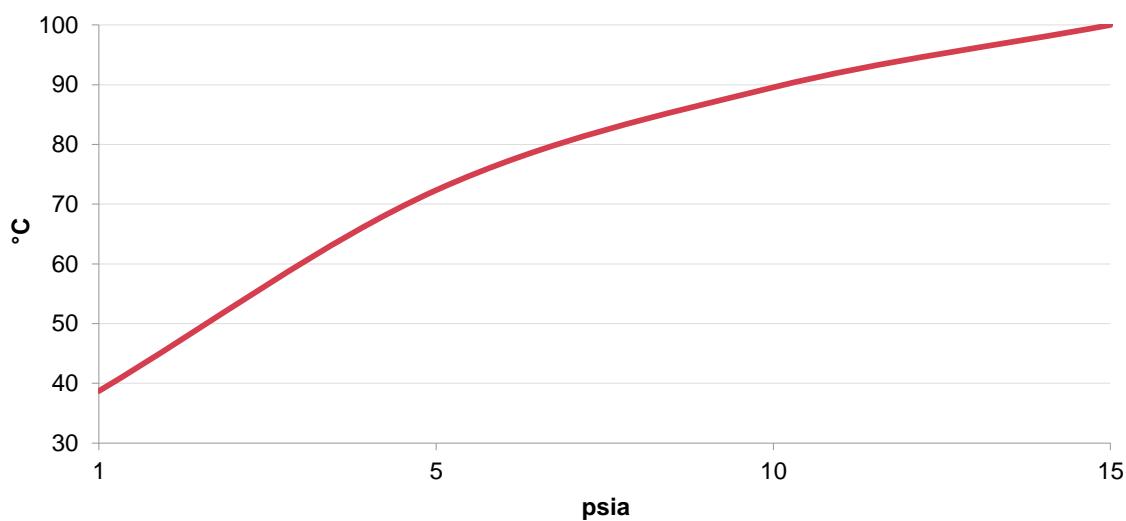
Although boiling point considerations alone would suggest that the nitric acid would exit the acid concentrator column in the overhead product stream, it actually exits the column in the bottoms product stream. This is due to the strong ionic forces and dissociation ions formed by a solution of nitric acid in water, and its strong non-ideal solution behavior. Solutions of nitric acid and water form azeotropes (see solution boiling curve below), limiting the purity of separation that can be attained by fractional distillation alone.

Figure 4.21
NITRIC ACID SOLUTION BOILING POINT CURVE



The boiling temperature of water is plotted below under vacuum conditions against absolute pressure, indicating the vacuum range under which distillation will remove substantially all of the water from the reactor product solution containing crude adipic acid. While water boils at 100°C at 15 psia pressure, it boils at 60°C at 3 psia pressure.

Figure 4.22
WATER BOILING TEMPERATURE UNDER VACUUM CONDITIONS

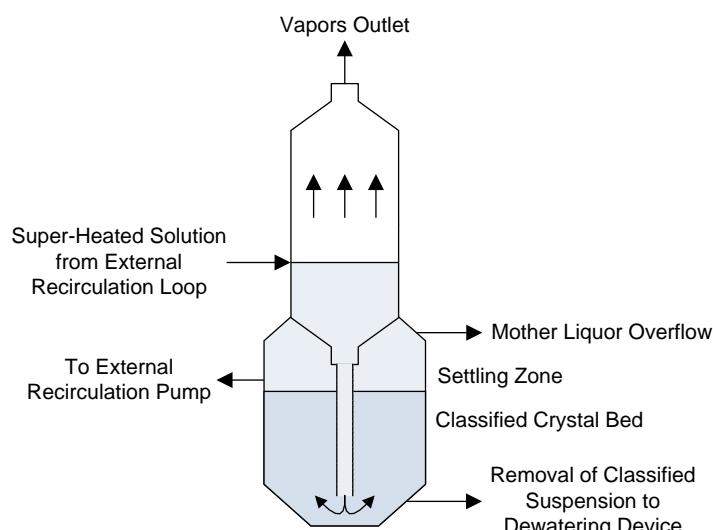


Adipic Acid Crystallization from Nitric Acid Mother Liquor

The reactor product liquid solution, now stripped of dissolved gases, and concentrated by removing water, proceeds to suspension crystallization for the purpose of recovering adipic acid as crystallized solid product. The intent of adipic acid crystallization is to produce large particle diameter crystals with a narrow range of diameters and having a large bulk density. Crystallization can be effected by either heating the solution to drive off solvent until the remaining solution becomes supersaturated, or cooling the solution below the temperature of crystal formation to cause precipitation from the solution. Adipic acid crystallization industrial practice relies on cooling the solution.

Early adipic acid purification systems relied on Oslo growth crystallizers (see figure below). In this configuration, the feed solution is pumped around a forced circulation loop that contains either an external heating element (known as evaporative heating), or an external cooling element (as used in adipic acid plants and known as adiabatic cooling) to form the crystals. Near the saturation temperature, seed crystals are introduced into the solution to accelerate crystal formation. As crystals are formed, there is a significant distribution of average crystal diameter. Small diameter crystals (called fines) recirculate around the pump around loop. Large diameter crystals fall by gravity, instead, into a bottoms growth zone in the device that is quiescent and promotes crystal size enlargement of the crystals without turbulence that could otherwise shear crystal particles into smaller particles. A tapered head at the bottom of the crystallizer vessel promotes the high concentration of crystals in slurry form that is pumped to a liquid-solid separation unit process. This liquid-solid separation unit process can be a filtration device, multiple liquid cyclones, or a centrifuge. For adipic acid solids-liquid separation, the preferred device for industrial production is a centrifuge. The discharged bottoms slurry contains 25–50% crystal solids by weight.

Figure 4.23
SCHEMATIC OF OSLO CRYSTALLIZER

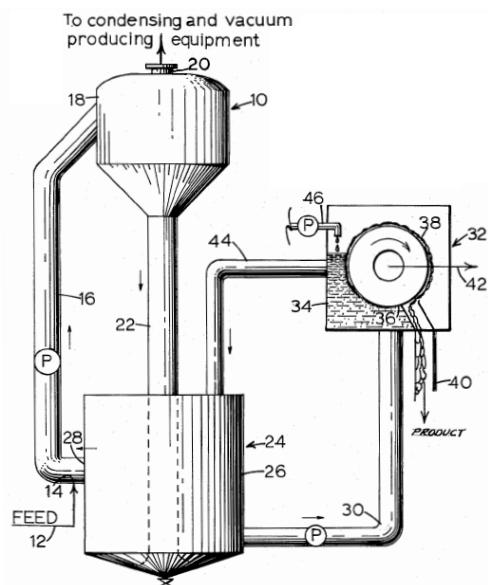


Source: <http://www.niroinc.com>

An early Monsanto patent (USP 3102908, 3-Sep-1963) describes this form of adipic acid crystallizer (see figure below) designed to operate under vacuum conditions. The Monsanto patent recommends the addition of a small amount of organo-siloxane chemical (silicone) to

minimize the build-up of adipic acid crystals on the device internals and on the internal walls of the process piping.

Figure 4.24
EARLY MONSANTO ADIPIC ACID CRYSTALLIZER (USP 3102908, 3-SEP-1963)



Modern adipic plants utilize two separate forms of crystallization to produce adequate purity product for nylon 66 polymerization. The first crystallization train feeds a slurry of adipic acid in primarily nitric acid solution to a combination of a crystallizer and centrifuge. Crystals formed in this step are centrifuged or filtered, with the mother liquor (nitric acid rich with catalyst) recirculated to the front of the nitric acid oxidation reactors. The second crystallization train washes the adipic acid crystals in high-purity water (distilled water or water treated by reverse osmosis membranes to a dissolved solids content below 50 ppmw), and then recrystallizes the adipic acid from the aqueous solution at chilled temperatures and under vacuum conditions. Both crystallization trains usually employ two-step aqueous crystallization to maximize crystal solid recovery and to maximize adipic acid crystal purity.

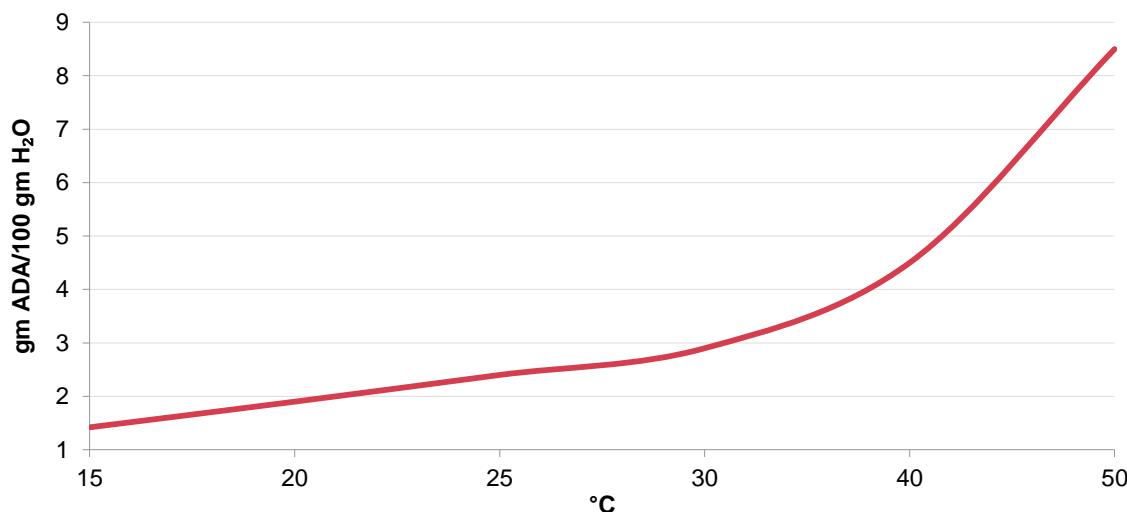
Adipic Acid Crystallization from Aqueous Solution

The second crystallization train dissolves adipic acid crystals in water, washes the solution, and recrystallizes the adipic acid in higher purity from the water. Prior to crystallization, the aqueous solution of adipic acid is processed through a stripping tower for the purpose of removing the small amount of monobasic acid (n-valeric acid, n-caproic acid) by-products formed in the nitric acid reactors. Total monobasic acid production is approximately 0.5% of total organic acid production. Water and monobasic acids are removed as the overhead product in the monobasic acid (MBA) tower overhead product. Water is added to the tower to enhance the separation of the monobasic acid (which is highly soluble in water) from the balance of the solution (adipic acid is less soluble in water). The bottoms product from the stripping tower is primarily adipic acid, with smaller amounts of glutaric acid and succinic acid, which is then diluted with water for the subsequent aqueous crystallization train.

Adipic acid crystals are separated from the suspension solution using pusher centrifuges, dried, and packaged as final adipic acid product. Dissolving adipic acid in the dilute water solution maintains the liquor at a low viscosity, which enhances the purity of the formed adipic acid crystals within the crystallizer. Since adipic acid has low solubility in water (see graph below), water addition enhances crystal purity by removing (via solubility in water) those residual monobasic acid and dibasic acid components present in the aqueous solution of adipic acid.

Since the adipic acid solubility curve shows increasing solubility with increasing temperature, adiabatic cooling is much preferred over evaporative heating as the method for driving the aqueous solution to the super-saturation state required for adipic acid crystallization.

Figure 4.25
ADIPIC ACID SOLUBILITY CURVE IN WATER



Residual Aqueous Liquor Recovery

The water-rich solution after adipic acid crystallization contains residual dibasic acids, a low concentration of nitric acid, monobasic acids, and a low concentration of uncocrystallized adipic acid. The solution is treated to recover the combined dibasic acids (DBA) as a salable product, to recover the homogeneous metals (copper and vanadium) in the homogeneous catalyst using an ion exchange resin, and to discharge the remaining aqueous waste stream to a wastewater treatment system. A representative composition of the water-rich solution stream liquor following aqueous crystallization is presented in the table below.

Table 4.21
REPRESENTATIVE WATER-RICH CRYSTALLIZATION LIQUOR COMPOSITION
(MONSANTO USP 4254283)

Component	Weight %
Water	78.0
HNO ₃	1.9
Monobasic acids	1.0
Adipic acid	2.7
Succinic acid	4.2
Glutaric acid	12.2

A Monsanto patent (USP 4254283, 3-Mar-1981) presents a process for evaporating the solution to eliminate water and nitric acid, crystallizing out a mixture of adipic acid and succinic acid, which is then melted and dehydrated to convert the succinic acid to succinic anhydride. These two components (adipic acid + succinic anhydride) can be easily separated and purified by fractional distillation. The remaining liquor from the crystallization process (now rich in glutaric acid) undergoes 3-stage crystallization/washing to produce solid and high-purity glutaric acid. The aqueous solution remaining is primarily composed of catalyst that can be recycled to the front of the process, or can be further treated for catalyst recovery.

Recycle Processing of Nitric Acid Mother Liquor

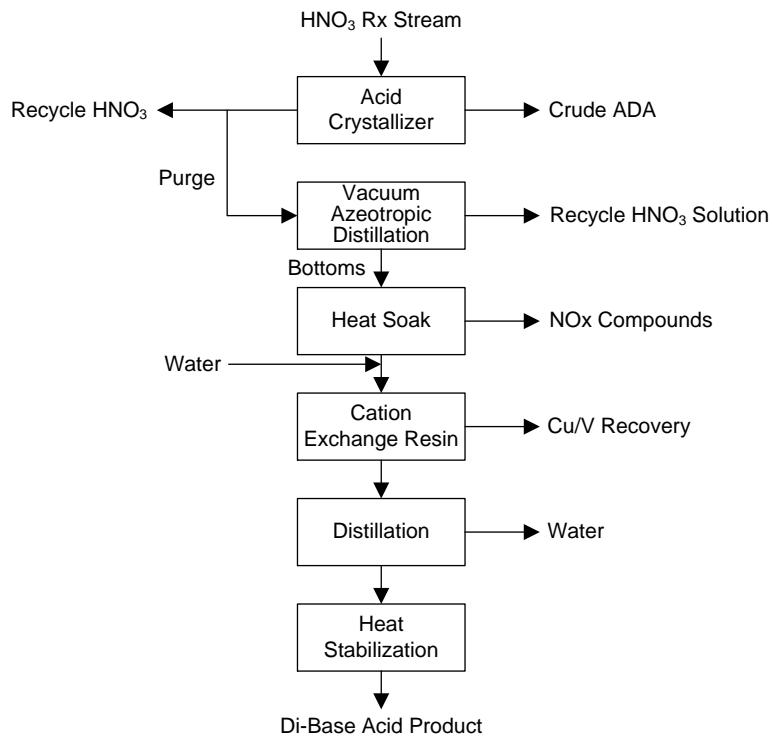
The nitric acid-rich solution from the nitric acid reactors is cooled and crystallized to yield product crude crystallized adipic acid, while the remaining liquor is recycled to the front of the process. However, over time, the nitric acid liquor would build-up an unacceptable concentration of impurities (primarily glutaric acid and succinic acid) that need to be purged from the system. BASF patent 5210297 (11-May-1993) describes an effective way to remove these contaminants from the nitric acid-rich liquor, while simultaneously recovering the vanadium and copper content of the homogeneous catalysts. Typical 'mother liquor' concentration as revealed in the BASF patent is presented in the table below.

Table 4.22
TYPICAL NITRIC ACID MOTHER LIQUOR COMPOSITION
(BASF USP 5210297, 11-MAY-1993)

Component	Weight % Range
Nitric acid	30–36%
Water	15–21%
Succinic acid	10–13%
Glutaric acid	23–30%
Adipic acid	9–11%
Copper (catalyst)	0.7–0.8%
Vanadium (catalyst)	0.08–0.09
Iron + other	0.002–0.004

The BASF patent proposes a methodology in which nitric acid and water (lowest boiling point components) are first distilled off under vacuum conditions, followed by a heat soak of the remaining solution at elevated temperature for the purpose of destroying the remaining nitrogen components plus oxalic acid. The solid mass remaining from the heat soak is redissolved in water and passed through a cationic ion exchange bed for the purpose of removing the copper and vanadium ions from the catalyst. The ion exchange resin is periodically regenerated with concentrated nitric acid to recover the copper and vanadium, which can be reprocessed to form new catalyst in liquid form for homogeneous applications. The solution is then redistilled to remove both water and residual monobasic acids. The bottoms product from the distillation column is again heat soaked to stabilize the product, which is a high-purity mixture of dibasic acids that is particularly suited for use as feedstock in producing polyester polyols. A simplified block flow diagram for the BASF process is presented below.

Figure 4.26
NITRIC ACID PURGE LIQUID PROCESSING (BASF USP 5210297, 11-MAY-1993)



The principal cationic ion exchange resin used for copper and vanadium catalyst recovery in commercial adipic acid plants is Rohm and Haas (now Dow Chemical) Amberlyst™ (284020). The resin consists of macroporous polystyrenic strongly acidic resin beads characterized by high capacity, resistant to oxidation, and having excellent chemical stability. Amberlyst™ resin specifications are presented below.

Table 4.23
AMBERLYST 40WET ION EXCHANGE RESIN SPECIFICATIONS

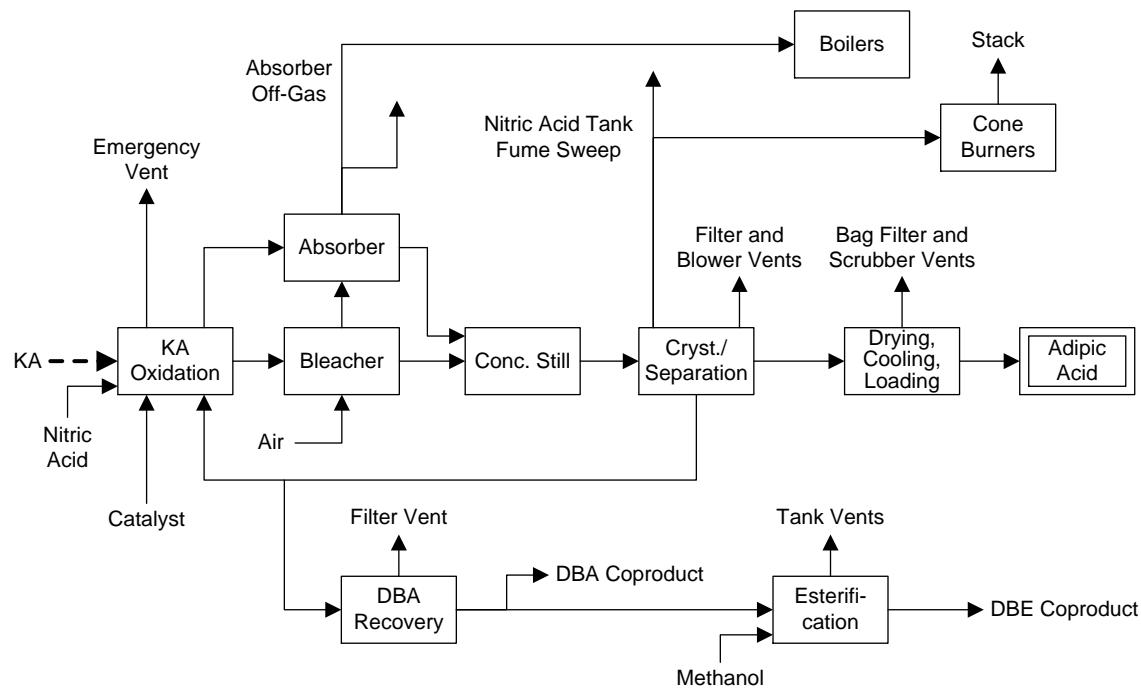
Physical form	Black, spherical beads
Ionic form as shipped	Hydrogen
Concentration of acid sites	$\geq 2.2 \text{ eq/L}$
Moisture holding capacity	44 to 53% (H^+ form)
Shipping weight	830 g/L (51.8 lbs/ft ³)
Harmonic mean size	0.58 to 0.80 mm
Uniformity coefficient	≤ 1.5
Fines content	<0.425 mm : 5.0% max
Coarse beads	>1.180 mm : 5.0% max
Maximum operating temperature	140°C (285 °F)

Source: Rohm and Haas (284021)

Amberlyst 40Wet (284022) is a sulfonated, copolymer of divinylbenzene and styrene. It is supplied wetted, in order to avoid physical expansion when dry resin is exposed to hydrocarbons.

A simplified block flow diagram for the entire two-stage cyclohexane oxidation process for making adipic acid is shown in the figure below.

Figure 4.27
TWO-STAGE OXIDATION OF CYCLOHEXANE TO ADIPIC ACID BLOCK FLOW DIAGRAM



The conventional cyclohexane oxidation process using two-stage oxidation with air and nitric acid has been previously evaluated by IHS Chemical in its PEP program, and a summary of the process description is provided below.

The continuous process described below is PEP's design based on patents reviewed in PEP report 3B. Modification from the earlier version includes increase of KA selectivity to 85%, recovery of dicarboxylic acids from the caustic wash stream, and treatment of unabsorbed off-gas. Cyclohexane is oxidized in four cascaded, agitated, jacket cooled autoclave at 10 atm and 160°C in the presence of Cobalt naphthenate catalyst. Reactor effluent passes to a peroxide converter, where cyclohexyl hydroperoxide is converted to KA oil. The resulting mixture is neutralized and washed with caustic solution. The aqueous caustic solution is treated with sulfuric acid to recover dicarboxylic acids as by-products. The washed organic stream is distilled in two columns in series to recover cyclohexane, which is recycled to oxidation operation. The bottom stream from the second column contains some esters, which are removed by hydrolyzing with aqueous caustic soda and extracting with water. The extracted KA oil is purified by evaporation. The evaporation residue is incinerated. The purified KA oil is oxidized with nitric acid at one atm and 70°C. The reactor effluent is air stripped to remove gas products, which are absorbed with water to recover nitric oxide as a nitric acid solution and recycled to the nitric oxidation operation. The unabsorbed nitrous oxide is catalytically converted to a mixture of nitrogen and oxygen, which is cooled and vented to atmosphere. The stripped crude adipic acid is purified through two steps of crystallization, centrifuging, and washing before the purified adipic acid is dried in a rotary dryer. Overall yield of adipic acid is 80.2%.

ONE-STEP AIR OXIDATION OF CYCLOHEXANE TO ADIPIC ACID

A number of process developers have tried to overcome the complexity of the two-stage combined air and nitric acid oxidation of cyclohexane by proposing one-step direct air oxidation of cyclohexane to adipic acid. In a 1993 US patent (USP 5221800, 22-Jun-1993), Amoco presented a one-step oxidation process to adipic acid by dissolving cyclohexane in an organic acid (C_2-C_4 aliphatic acids are preferred), and conducting direct air oxidation over a cobalt/manganese homogeneous catalyst with direct water injection during the reaction period. Preferred reaction conditions are a 10% weight solution of cyclohexane in acetic acid solution, reaction temperature of 80°C and approximately 1,000 psia pressure, and a residence time of approximately three hours. Overall, 88% adipic acid yield was achieved. Residence time can be reduced using a reaction initiator such as cyclohexanol. The reaction product was purified by drying the solution to a solid product, using acetone to redissolve adipic acid and separate it from other residue components such as catalyst, and then performing conventional crystallization to produce final purity adipic acid product.

SCIENTIFIC DESIGN AIR OXIDATION PROCESS

An alternative process (284023) for the second-stage oxidation was developed by Scientific Design in the 1970s, and relied upon air oxidation rather than nitric acid oxidation. The reaction was conducted in the liquid phase using acetic acid as solvent. The catalyst was a homogenous combination of copper and manganese acetate, which dissolves readily in the solvent. Reaction conditions were 80–85°C, and 6 bar (90 psia). As the reactor product liquid was cooled, adipic acid would crystallize out of solution.

KA OIL MANUFACTURING FROM PHENOL

A small proportion of global adipic acid production (<5%) is made via phenol hydrogenation. The phenol hydrogenation process is simpler than the conventional cyclohexane two-stage air

and nitric acid oxidation process, resulting in lower capital cost. However, phenol has historically been priced much higher than cyclohexane, negating some of the capital and operating cost benefits of the simpler hydrogenation process.

The predominant industrial process for producing phenol is to alkylate benzene with propylene to produce cumene over a Friedel-Crafts catalyst such as aluminum tri-chloride or solid phosphoric acid (silica support). Cumene is then easily oxidized to cumene hydroperoxide in the absence of a catalyst. The cumene hydroperoxide is cleaved by sulfuric acid to form an alcohol (phenol) plus a ketone (acetone).

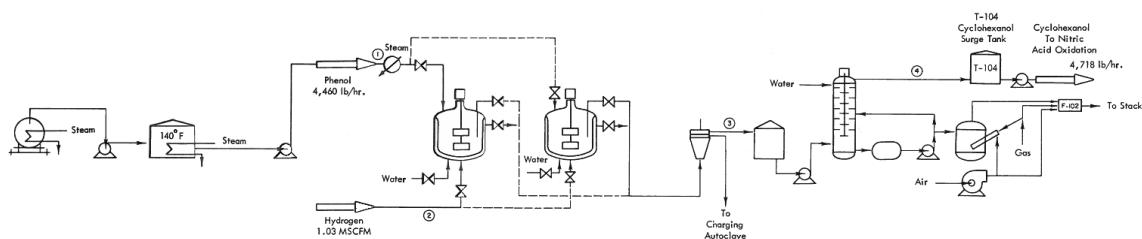
Phenol is hydrogenated in the liquid phase to a mixture of cyclohexanol and cyclohexanone (KA oil) over a palladium catalyst. Commercial hydrogenation processes have been developed both in the liquid phase and in the vapor phase, with selectivities in both cases above 95% (284024). The vapor-phase reaction occurs at 3 bar pressure (45 psia) and 300–500°C using a moving catalyst bed design. The original catalyst used for phenol hydrogenation was nickel, but this process consumed very large quantities of hydrogen, and combusted some of the phenol to CO₂ plus water.

The vapor-phase hydrogenation of phenol to KA results in over 99% KA yield. The catalyst is palladium on an aluminum oxide (Al₂O₃) substrate. A Monsanto process uses a reaction temperature of 130–160°C, and a reaction pressure of 165 kPa (15 psia). The molar ratio of H₂:phenol is 4:1. A 3-step distillation separates KA oil from light ends, high boiling temperature components (heavies), and unreacted phenol. Steam that is generated in the tubular isothermal reactor from the exothermic reaction provides heat that can be used in reboilers for distillation.

The liquid-phase hydrogenation of phenol to KA oil also has very high yield (97–99%). Purification is accomplished via ion exchange resins to remove unreacted phenol. Reactor conditions are 140°C and 400 kPa pressure (58 psia) using heterogeneous nickel catalyst on a silica support, or palladium.

A process flow diagram for the process of making cyclohexanol from phenol is presented below, as originally published in PEP Report 3. A two-stage hydrogenation reactor scheme is used in series, with reactor product being purified by extraction with water.

Figure 4.28
PHENOL HYDROGENATION TO CYCLOHEXANOL PROCESS FLOW DIAGRAM



IHS Chemical prepared a process design for a phenol-based adipic acid plant in PEP Report 3B. A comparable brief process description of the phenol-based process is provided below.

The continuous process is PEP's concept and is based on patents assigned to Allied Chemical and ICI. Molten phenol and a small stream of Ni on silica catalyst feed the first of 8 jacketed agitated hydrogenation reactors in series. Hydrogen is sparged into all of the reactors. Hydrogenation takes place at 4.1 atm and 138°C. Phenol is almost completely hydrogenated to cyclohexanol. Gas streams from the reactors, mainly unreacted H₂ and inert, are combined, compressed, and recycled after a small purge is

taken. Reaction product is centrifuged to remove catalyst slurry which is reactivated with nickel alkylbenzene sulfonate before returning to the first reactor. The clarified stream, mainly cyclohexanol, is filtered and passed through one of two parallel vessels filled with ion exchange resin, resulting in purified cyclohexanol. The cyclohexanol is oxidized with HNO_3 at 1.0 atm and 70°C in a cone bottom vertical vessel. Reactor product is air stripped to remove gases and then distilled to remove water and monobasic acid impurities. 90% of the bottoms stream is recycled to the oxidation vessel. The remaining 10% is processed for adipic acid recovery by crystallization, centrifuging, washing with dilute HNO_3 , and dissolution in an aqueous solution. The solution undergoes carbon filtration, heating, crystallization of adipic acid, centrifuging, water washing, drying in a rotary dryer, cooling in a rotary cooler, and conveying to storage bins. Product yield on phenol is 93.0%. Adipic acid from cyclohexane is the dominant process throughout the world.

CYCLOHEXANOL FROM CYCLOHEXENE

The partial hydrogenation of benzene to cyclohexene was originally developed in the Netherlands at the University of Delft (284024). The reaction is practiced commercially by Asahi in the liquid phase using benzene feedstock, in which a platinum or ruthenium powdered catalyst is coated with a layer of an aqueous solution of zinc sulfate. Since benzene is more soluble in water than cyclohexene, the reaction occurs largely in the aqueous phase, with the produced cyclohexene migrating to the more soluble benzene phase. This migration to the oil phase reduces the concentration of product cyclohexene in the aqueous phase, and minimizes the tendency of cyclohexene becoming progressively hydrogenated from cyclohexene to cyclohexane. The purified cyclohexene is then hydrated to cyclohexanol using a zeolite ZSM-5 catalyst.

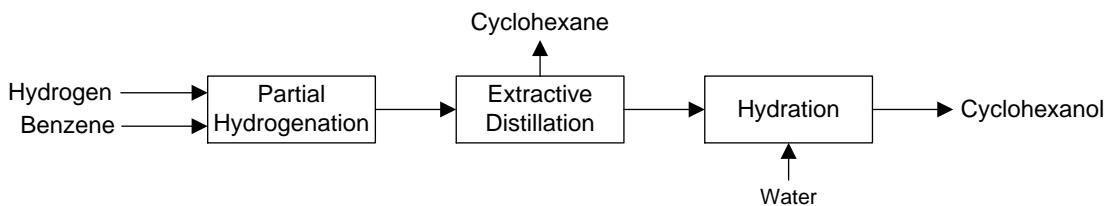
Asahi holds one European patent (EP 645363, 29-Mar-1995) and four relevant US patents for processing of cyclohexene from benzene, and subsequent conversion to KA oil and adipic acid, as listed in the table below.

Table 4.24
ASAHI KASEI US PATENTS FOR ITS CYCLOHEXENE PROCESS

US Patent	Title
6849765	Process for Producing Cyclohexanone Oxime
6552235	Process for the Preparation of Cyclohexanol
5900513	Production Method of 2-Cyclohexene-1-Ol
5455375	Process for Preparing Adipic Acid

The Asahi catalyst system contain metal oxide dispersants Al_2O_3 and zinc compound promoters, as revealed in Japanese patent 62-205037 (1987). Reactor conditions are 120–180°C and pressure between 30–100 atmospheres. The process provides a benzene conversion of 50–60% and cyclohexene selectivity of 80%. Cyclohexane is the primary by-product. A simplified block flow diagram for the Asahi process is shown in the figure below.

Figure 4.29
ASAHI KASEI CYCLOHEXENE PROCESS



Source: Kirk-Othmer 'Adipic Acid'

The reactor product from partial hydrogenation of benzene is a mixture of cyclohexene and cyclohexane, which is separated by extractive distillation using adiponitrile as the extracting agent. The purified cyclohexene is hydrated to cyclohexanol using a zeolite catalyst.

The Asahi process configuration has three major sections, with per pass conversions of 12–15% (284025):

1. Partial hydrogenation of benzene to cyclohexene, with cyclohexane by-product
2. Liquid-liquid extraction of cyclohexene from the reactor product mix using adiponitrile solvent
3. Hydration of cyclohexene to cyclohexanol using high silica zeolites suspended in water

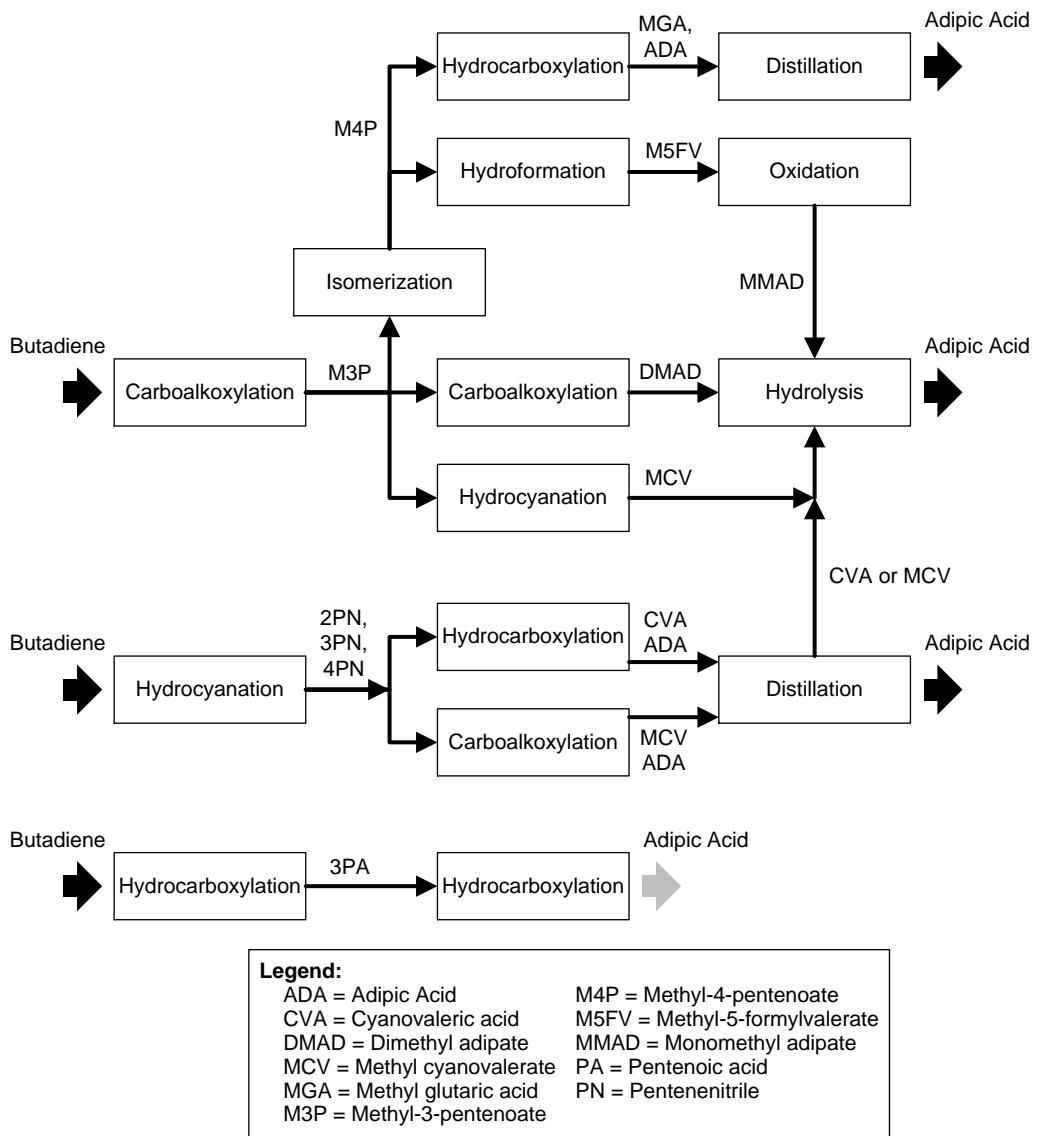
Asahi Kasei's USP 6552235 (22-Apr-2003) provides guidance on the last step in the process for the hydration of cyclohexene to cyclohexanol. The primary patent claim is the use of solvents to improve the yield when using a solid, strong acid catalyst on an ion exchange resin. The solvent used by Asahi Kasei is isophorone or ethylene glycol monophenyl ether, and the solid acid catalyst applied is ZSM-5 zeolite. Using isophorone avoids the formation of azeotropes, and its boiling point is sufficiently higher than product cyclohexanol to accomplish high-purity separation in a distillation column that does not require an excessive number of trays, nor is required to operate at high reflux ratio. An additional benefit using isophorone is that it has low solubility in water, and tends not to be removed when regenerating the catalyst with mineral acid solutions.

Asahi Kasei claims that the carbon yield of cyclohexanol plus cyclohexane together approaches 100%, with lower hydrogen consumption than the conventional phenol hydrogenation process, and significantly lower wastewater generation that requires treatment.

ADIPIC ACID FROM BUTADIENE

There are three basic chemistries that can be used to convert butadiene to adipic acid. They are: 1) hydro-carboxylation using a two-stage reaction where both stages use a rhodium catalyst with iodide as promoter and acetonitrile as accelerator, 2) hydro-cyanation using nickel catalyst and a Lewis acid promoter and 3) carboalkoxylation using palladium catalyst and pyridine solvent in the presence of methanol. The three routes are summarized in the figure below.

Figure 4.30
BUTADIENE ROUTES TO ADIPIC ACID



Source: IHS Chemical PEP Report 3B, Figure 4.1

Several companies (284023), most notably Monsanto and later BASF, developed commercially viable adipic acid processes using butadiene (rather than cyclohexane or phenol) as the primary feedstock. The Monsanto technology used the carbonylation of 1,4-dimethyl-2-butane (derived from butadiene) as the feedstock, in which carbonylation was conducted over a palladium chloride catalyst.

The BASF process was based on hydro-carbonylation of butadiene with carbon monoxide in a solution of methanol, in which the methanol formed a methyl ester intermediate in order to avoid the selectivity problems (over oxidation) requiring low per pass conversion of the conventional process. As the adipic acid was produced, it would react with methanol to form the corresponding

ester. The ester would later be hydrolyzed to produce adipic acid, and release methanol by-product for recycle.

The first stage of reaction was forming methyl 3-pentenoate ester over a cobalt catalyst in pyridine solvent at high pressure (to maximize butadiene solubility). This is accomplished by reacting butadiene with carbon monoxide and methanol to form a C₆ molecule. The ester was purified by distillation, reacted with more CO and methanol to produce dimethyl adipate (a C₈ molecule), also using cobalt catalyst in pyridine solvent. Hydrolysis of one dimethyl adipate molecule with water produces one adipic acid molecule, with by-product two methanol molecules for recycle. The resulting product molecule is adipic acid.

The BASF technology is disclosed in US patents 4169956, 4171451, and 4360695, published in 1979. The overall reaction chemistry combines butadiene with carbon monoxide to form aldehydes and ketones that are subsequently converted to adipic acid.

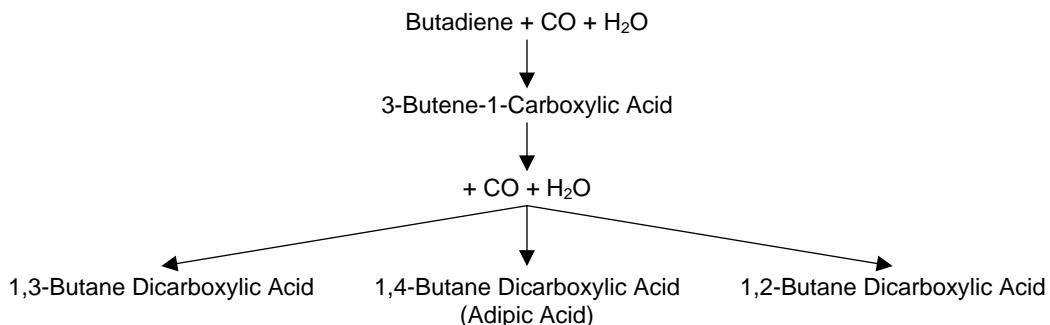
The carboalkoxylation chemistry is a two-step process operating at high pressure (>31 MPa, 4,600 psia) and modest temperature (100–150°C). The first step involves the reaction of butadiene, CO, and methanol to produce methyl pentenoates. The second step at lower pressure and higher temperature using rhodium catalyst produces dimethyl adipate, which is hydrolyzed with water to produce adipic acid and methanol. The methanol is recovered and recycled.

The hydroxyl carbonylation chemistry reacts butadiene with carbon monoxide and water (rather than methanol) to form 3-pentenoic acid. A combination palladium and crotyl chloride catalyst system has demonstrated selectivity of 92 mol % to pentenoic acid. The subsequent step reacts pentenoic acid with carbon monoxide and methanol using palladium catalyst to produce dimethyl adipate. This chemistry has demonstrated 85% mol selectivity. The dimethyl adipate is then hydrolyzed to produce adipic acid plus methanol, with the methanol being recycled.

DuPont also developed a dihydroxy carboxylation butadiene route to adipic acid using only one-step processing (284010) using noble catalyst (palladium, rhodium, iridium). The first step produces 3-pentenoic acid by reacting butadiene with CO and water to form one carboxylic acid group on one of the terminal carbons atoms, while further hydroxyl carboxylation with CO and water adds a carboxylic acid group on the other terminal carbon atom. The process is not very selective, and produces by-products 2-methyl glutaric acid and 2-ethyl succinic acid. The structure of the by-products is such that they hold the possibility of being isomerized to adipic acid by moving the second carboxylic acid group from an internal carbon atom to a terminal carbon atom position. Reaction kinetics are improved by conducting the conversion in a pentanoic acid solution, and using a halide promoter such as hydroiodic acid. Other companies that have received patents for butadiene routes to adipic acid include DSM and Rhone-Poulenc (now Solvay Rhodia).

The alternative butadiene routes to adipic acid are shown in the figure below.

Figure 4.31
BUTADIENE ENZYME PATHWAYS TO ADIPIC ACID



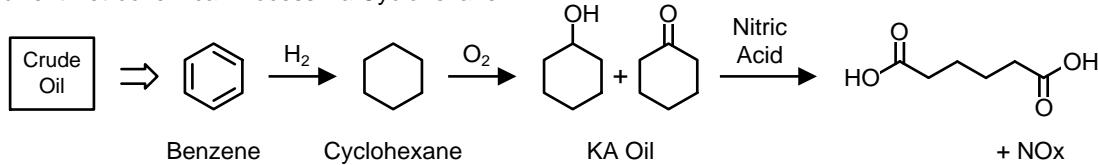
CHEMISTRY OF COMMERCIAL ADIPIC ACID PRODUCTION

Integrated Chemistry Product Chain

The dominant commercial process for producing adipic acid relies on the two-stage oxidation of cyclohexane. The overall integrated product chain chemistry is shown in the figure below. Crude oil is processed in an oil refinery with the atmospheric pipestill naphtha fraction converted to higher octane gasoline in a catalytic reformer that makes BTX aromatics (benzene, toluene, xylene). Benzene can be extracted from the reformat product, purified, and used to produce adipic acid via hydrogenation to cyclohexane. Alternatively, naphtha or lighter hydrocarbons (ethane, propane, butane, pentane) can be steam cracked in a non-catalytic process to make light olefins (primarily ethylene, propylene, butadiene), where a small fraction of the feed is converted to aromatics (pyrolysis gasoline) that can also be processed to separate and purify benzene for subsequent conversion to adipic acid.

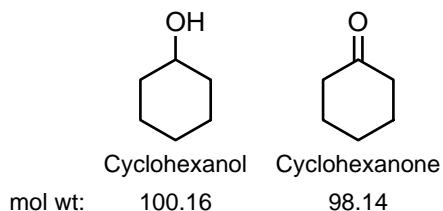
Figure 4.32
INTEGRATED CHEMISTRY FOR PRODUCING ADIPIC ACID

Current Petrochemical Process via Cyclohexane



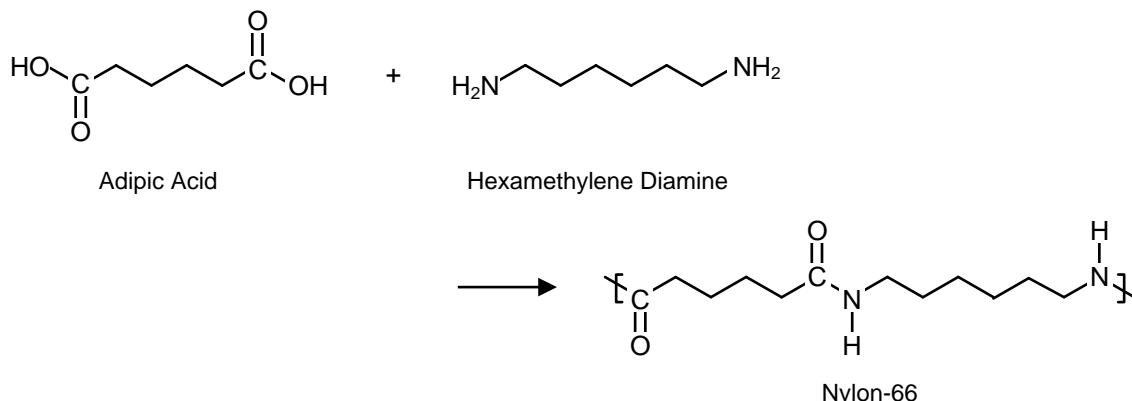
KA oil is a mixture of cyclohexanone and cyclohexanol produced primarily by the air oxidation of cyclohexane, but also by the hydrogenation of phenol using palladium catalysts. The molecular structure and molecular weights of cyclohexanol and cyclohexanone are shown in the figure below.

Figure 4.33
MOLECULAR STRUCTURE OF CYCLOHEXANOL AND CYCLOHEXANONE



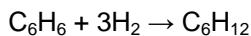
Once adipic acid is produced, it can be readily copolymerized with hexamethylenediamine (HMDA) to produce nylon 66, as shown in the figure below.

Figure 4.34
NYLON 66 FROM ADA + HMDA



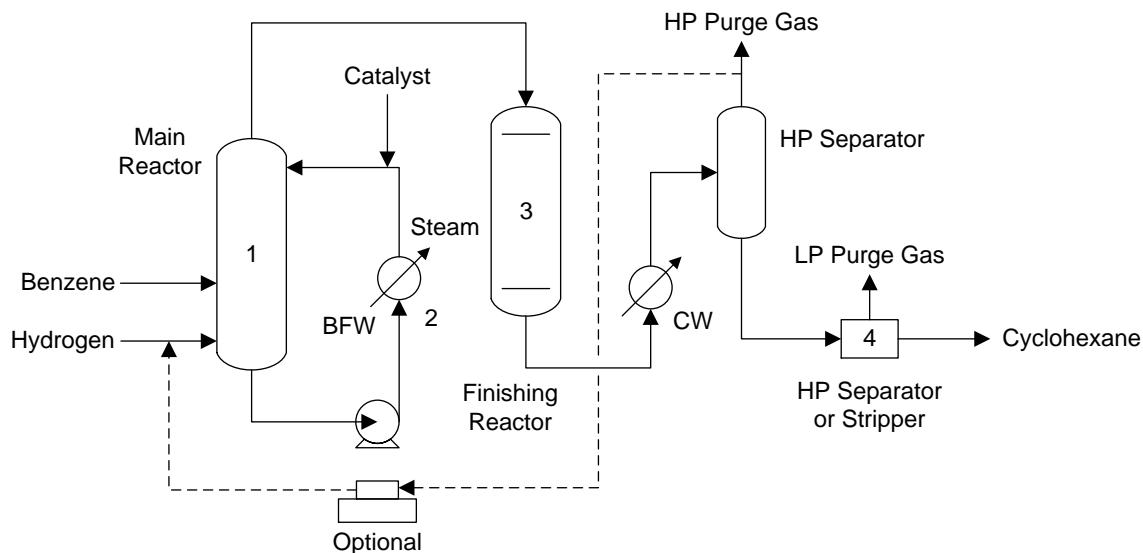
Chemistry for Producing Cyclohexane from Benzene

Cyclohexane is produced by the selective hydrogenation of benzene. The reaction chemistry is shown below.



One of the major commercial licensors of cyclohexane technology is Axens, with 38 commercial units licensed as of 2011. The Axens process (284027) relies on liquid-phase hydrogenation of benzene in an isothermal reactor. A simplified block flow diagram of the Axens process appears below.

Figure 4.35
AXENS CYCLOHEXANE BLOCK FLOW DIAGRAM



Source: Hydrocarbon Processing

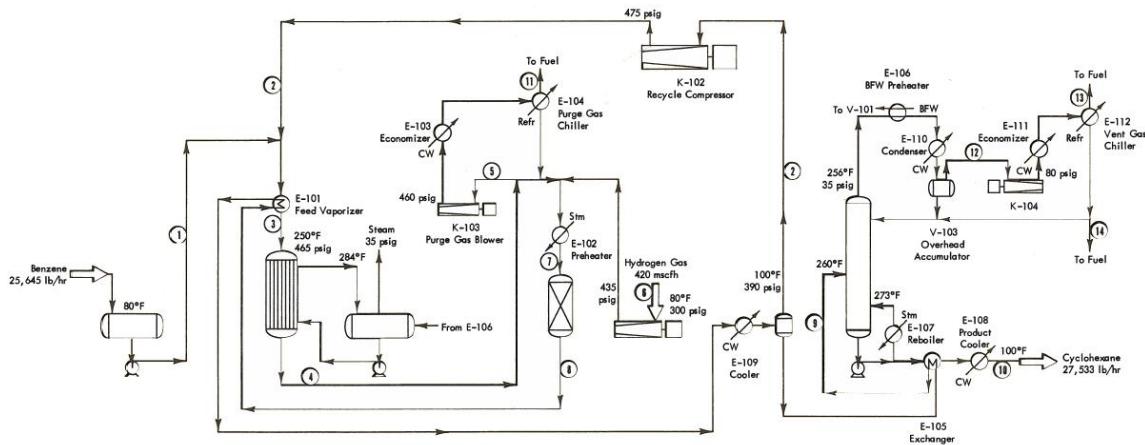
In the Axens process, benzene is mixed with a high activity homogeneous nickel catalyst and hydrogen, and fed to a 2-reactor system: primary (#1) and secondary (#3) isothermal reactors. Due to the high activity of the soluble nickel catalyst, and the high solubility of hydrogen in the liquid solution, the process can be operated at modest pressure. Axens claims high selectivity to cyclohexane, with few by-products formed by isomerization or hydrocracking. The heat of reaction is removed from the system using an external pump around loop with a heat exchanger (#2) that produces steam. The product steam is utilized within the process unit to reboil a downstream distillation tower (#4). Reactor product from the primary reactor is fed to the secondary reactor to nearly complete benzene conversion to cyclohexane. Product from the secondary reactor is cooled and depressured in a high pressure drum designed to remove principally unreacted hydrogen. The unreacted hydrogen can either be purged to the plant's burner line, or compressed and recycled within the unit. The primary by-product from the system is LPG produced via hydro-cracking. LPG is removed in the purification of cyclohexane via fractional distillation (#4). The residual benzene content of the product cyclohexane is less than 5 weight ppm.

IHS/PEP has developed a process flow diagram and resulting economics for a benzene hydrogenation unit based upon Toray patents. The Toray technology is described below.

The vapor phase process presented here uses a nickel catalyst in two reaction stages. In the first stage, four mols of recycled hydrogen to one mol of nitration grade benzene are passed through tubes of catalyst at a maximum temperature of 220°C (428°F) and about 450 psig (32 atm). The effluent from the first-stage reactor is mixed with makeup hydrogen (90%) to give a mixture of 70 mols of hydrogen to 1 mol of benzene. This mixture passes through the adiabatic second-stage reactor, where the reaction is completed. After cooling, gas separated from the liquid is recycled. The liquid stream is fractionated to remove light ends. Yield is 99.7% of theoretical.

Below is a process flow diagram from IHS Chemical PEP Report 7B showing the principal processing steps for Toray's technology to hydrogenate benzene to cyclohexane.

Figure 4.36 TORAY CYCLOHEXANE PROCESS FLOW DIAGRAM

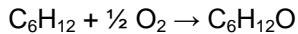


Cyclohexane is also a natural component of crude oil at very low concentration (<1 weight %), and can be recovered from the refinery atmospheric pipestill in the virgin naphtha distillation cut. Due to the presence of other hydrocarbons (mostly methyl pentanes) having nearly the same boiling point as cyclohexane, the methyl pentanes can be isomerized using aluminum chloride catalyst to cyclohexane. Refinery-based cyclohexane cannot be purified to the same level as cyclohexane produced from benzene selective hydrogenation.

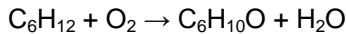
Chemistry for Producing KA Oil from Cyclohexane

The starting point for manufacturing adipic acid by the dominant technology is to feed liquid-phase cyclohexane through an air-oxidized reactor with a homogeneous catalyst (usually cobalt naphthenate) to produce a mixture of cyclic C₆ alcohol (cyclohexanol) and C₆ cyclic ketone (cyclohexanone). The combined product stream is generally known as KA oil for ketone:alcohol. The reaction chemistry is shown below.

Oxidation of cyclohexane to cyclohexanol:

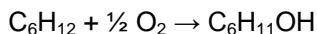


Oxidation of cyclohexane to cyclohexanone:

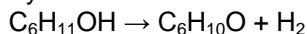


It is believed that the chemical mechanism for producing KA oil starts with the oxidation of cyclohexane to produce cyclohexanol via a hydroperoxide intermediate, with a small proportion of the cyclohexanol subsequently being dehydrogenated to cyclohexanone plus hydrogen. The by-product hydrogen produced is easily oxidized by the oxygen in air to form water.

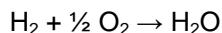
Oxidation of cyclohexane to cyclohexanol:



Dehydrogenation of cyclohexanol to cyclohexanone:



Water formation:



The dehydrogenation of cyclohexanol to cyclohexanone is shown structurally below.

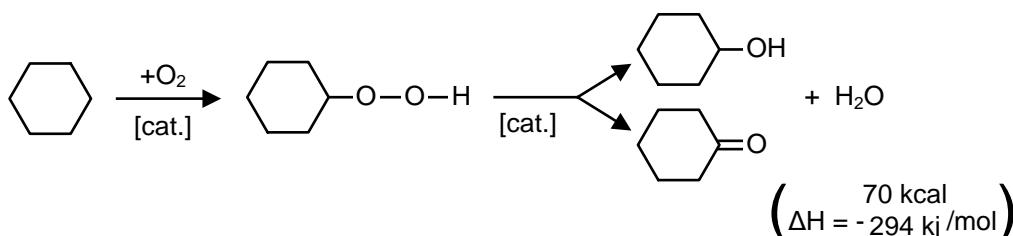
Figure 4.37
DEHYDROGENATION OF CYCLOHEXANOL TO CYCLOHEXANONE



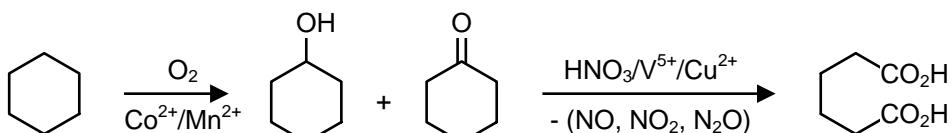
Primary by-products of the air oxidation reaction include dicarboxylic succinic acid and glutaric acid, which are separated from the reactor stream prior to downstream processing. Minor amounts of monocarboxylic valeric acid and caproic acid are also produced.

The reaction pathway for air oxidation of cyclohexane to KA oil is believed to occur through the formation of peroxy intermediates. The peroxy intermediates initially bond to the cyclohexane molecule, and then cause the terminal oxygen atom to detach from one molecule (forming the ketone), and reattach to another cyclohexane molecule forming the alcohol. The chemical pathway is shown in the figure below.

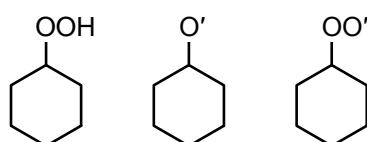
Figure 4.38
PEROXY INTERMEDIATES FOR OXIDIZING CYCLOHEXANE TO KA OIL



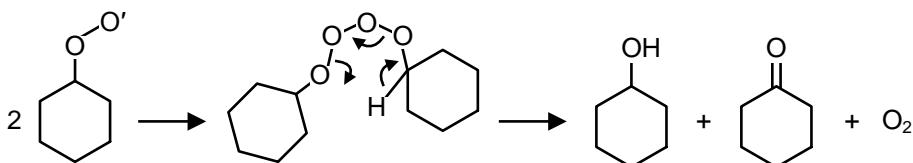
Oxidation of Cyclohexane-Reaction Intermediates



Generation of Peroxy Radical



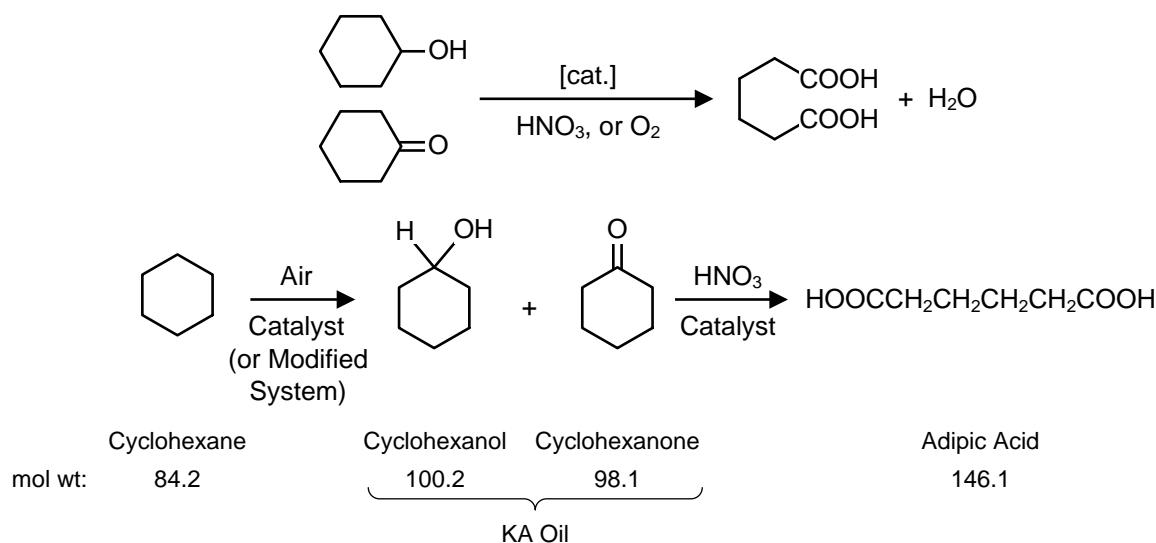
Conversion of Peroxy Radical



Chemistry for Oxidizing KA Oil to Adipic Acid Using Aqueous Nitric Acid

KA oil is reacted with aqueous nitric acid (a very strong acid) to cause an oxidation reaction to occur by first opening up the ringed structure, and then oxidizing the terminal carbon atoms. The reaction pathway is shown in the figure below.

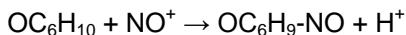
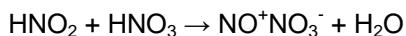
Figure 4.39
NITRIC ACID OXIDATION OF KA OIL TO ADIPIC ACID



The first step appears to be the reaction between nitric acid and the C₆ cyclic alcohol in KA oil (cyclohexanol) to form the C₆ cyclic ketone (cyclohexanone). The reaction chemistry is shown below.

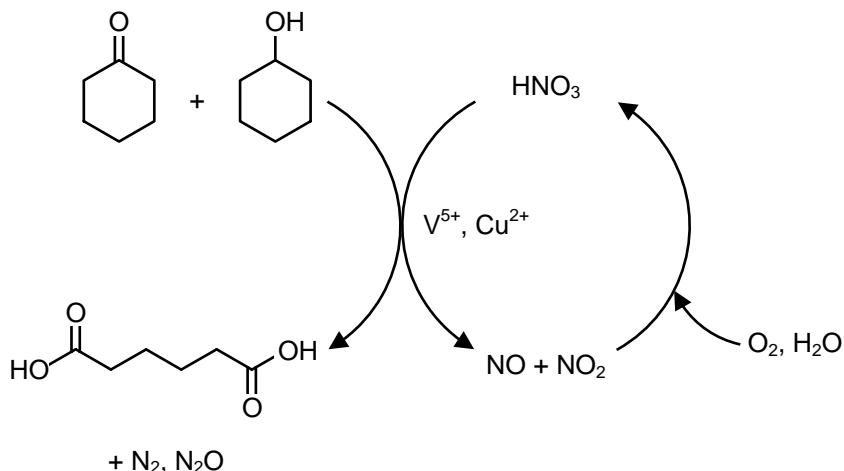


The subsequent reaction with nitric acid first opens up the ring (cyclohexanone) at the carbon atom that contains the ketone group, and then oxidizes both terminal carbon atoms to incorporate acidic (OOH) radicals at both terminal carbon atoms, thus forming the linear di-acid. The relevant chemical reactions are shown below.



The current understanding of the multitude of chemistry pathways for converting KA oil to adipic acid using nitric acid is shown by the pathways in the diagram below.

Figure 4.40
CHEMICAL PATHWAYS TO ADIPIC ACID FORM KA OIL



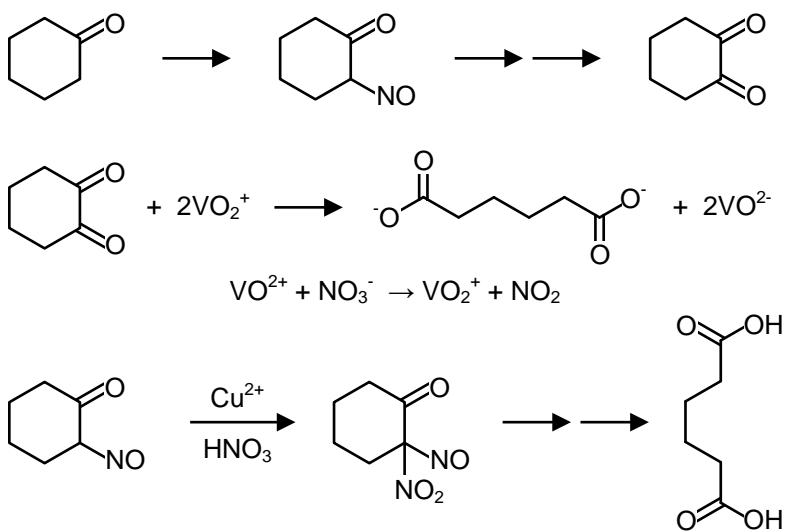
Source: Dr. K.R. Krishnamurthy, "Homogeneous Catalysis HMC-5-2010"

It is believed that two stable intermediates are formed when cyclohexanol reacts with nitric acid to form adipic acid: 6-hydroxyimino-6-nitro hexanoic acid, and hemi-hydrate of 1,2-cyclohexanedione.

Role of Vanadium Catalyst

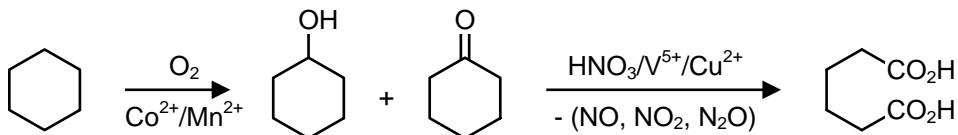
Vanadium catalyst rapidly converts the hemi-hydrate to adipic acid. Without this catalyst, the hemi-hydrate is more likely to degrade into hydrocarbon fragments with smaller carbon numbers than C₆: C₅ glutaric acid and C₄ succinic acid are the significant by-products. Copper catalyst impedes the deterioration of other less stable intermediates to smaller hydrocarbon fragments. The chemical roles of these catalysts are shown in the figure below.

Figure 4.41
ROLE OF VANADIUM AND COPPER CATALYSTS IN NITRIC ACID OXIDATION



The role of nitric acid in promoting the oxidation reaction is more apparent. HNO_3 gives up an oxygen atom to the KA oil to accomplish selective oxidation rather than combusting the molecule to $\text{CO}_2 + \text{H}_2\text{O}$. The resulting reduction of HNO_3 to HNO_2 is temporary, as the addition of air and water reoxidizes HNO_2 back to HNO_3 , as shown in the figure below.

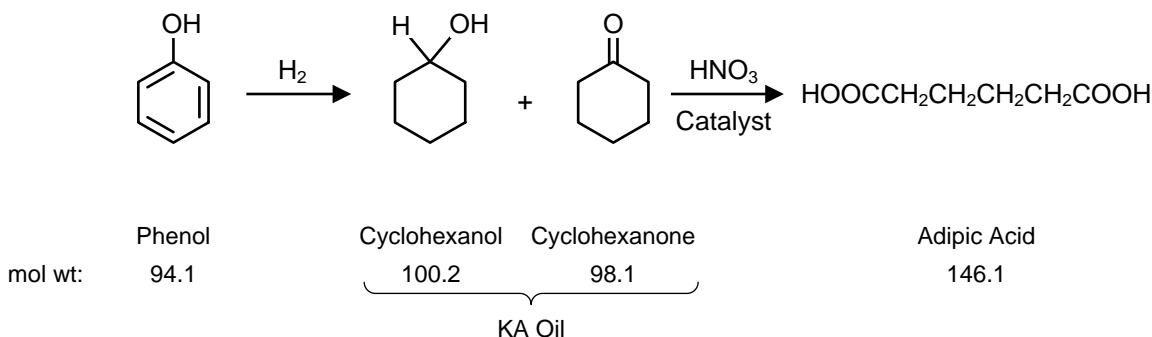
Figure 4.42
SEQUENTIAL REDUCTION AND REOXIDATION OF HNO_3



Chemistry for Producing KA Oil from Phenol

A small proportion of global adipic acid production (<5%) occurs via phenol hydrogenation. Commercial plants conduct the reaction in the liquid phase using palladium catalysts at about 150°C and 150 psia. The overall chemistry is shown below.

Figure 4.43
CHEMISTRY FOR CONVERTING PHENOL TO KA OIL



The stoichiometry for hydrogenating phenol to cyclohexanone and to cyclohexanol is shown below.



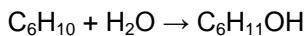
Early commercial adipic acid plants used nickel catalyst to dehydrogenate phenol directly to only cyclohexanol. From a molecular structure, this approach saturates the bonds inside the ring, but results in a product that was entirely alcohol (cyclohexanol). In order to also produce ketone (cyclohexanone), a separate dehydrogenation step was required using copper-zinc oxide catalyst that would not affect the cyclic ring, but only convert the alcohol ligand (-OH) to ketone ligand (=O). Unfortunately, the dehydrogenation step was not adequately selective, and resulted in a significant production of unwanted degradation products (C_5 and C_4 oxygenated compounds). The discovery of palladium catalysts (on carbon substrates) that would selectively hydrogenate phenol directly to cyclohexanone at very high selectivity (>95%) represented a significant contribution to the art, and resulted in superior production economics by maximizing yield. Commercial processes were developed using palladium catalysis for both liquid-phase and vapor-phase hydrogenation of phenol to cyclohexanone.

Asahi Chemistry for Producing Cyclohexanol from Cyclohexene

Asahi Kasei operates a commercial adipic acid plant in Japan, and has licensed an adipic acid plant in China to Shenma Chemical using cyclohexene process technology (284028) in which the feedstock is benzene. Kailuan Energy Chemical in China also practices cyclohexene process technology. The process introduces a two-phase liquid (oil phase and water phase) into the reactor such that the benzene feedstock reacts while in the more soluble water phase, but the reaction producing cyclohexene migrates to its more soluble oil phase, reducing the chance of subsequent over-hydrogenation. Selectivity is about 60% to cyclohexene, with the balance of the benzene being converted to cyclohexane. The relevant reactions are shown below.

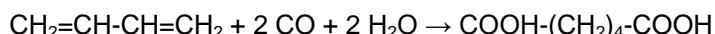


The reaction occurs using a dispersed heterogeneous ruthenium complex catalyst containing zinc, with the cyclohexene hydrated to cyclohexanol using a strong acid ion exchange resin on a zeolite catalyst. The relevant hydration reaction is shown below.



Chemistry of Butadiene-Based Adipic Acid

The hydro-carboxylation of butadiene to adipic acid using carbon monoxide and water is shown by the chemical reaction below.



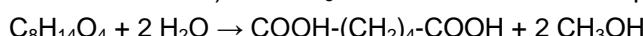
Alternative chemistry using methanol rather than water is shown by the reaction sequence below. The methanol approach has been studied by Monsanto, DuPont, and BASF. The first reaction between butadiene and one molecule each of CO and methanol forms a C₆ monoester with the ester group on the beta carbon atom.



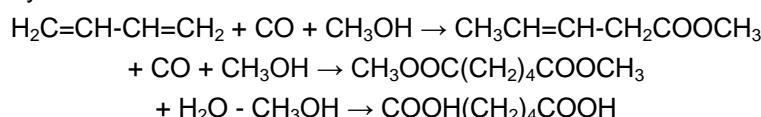
The C₆ monoester continues to react with an additional molecule each of CO and methanol to form a C₈ diester, with the ester groups on both beta carbon atoms.



Hydration of the C₈ diester releases one methanol molecule from each terminal carbon atom (2 methanol molecules released in total) of the C₈ diester molecule to form product adipic acid.



This chemistry is summarized below.

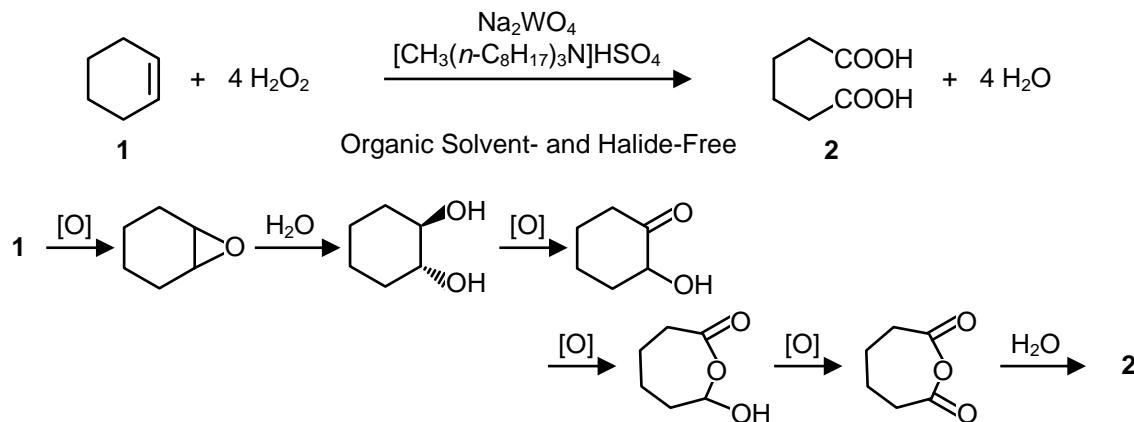


Hydrogen Peroxide Chemistry for Producing Adipic Acid

The patent and trade literature (284029) contains a variety of references for oxidizing cyclohexane and/or cyclohexene to adipic acid using hydrogen peroxide (H₂O₂), rather than the conventional air or nitric acid as oxidizing agents. In all reported cases, for safety reasons the H₂O₂ is supplied and used as an aqueous solution of between 15–60 weight % concentration. The economic benefits for using a fast oxidizing agent such as H₂O₂ versus air or nitric acid are somewhat compensated by the much higher cost of consuming H₂O₂ as a feedstock than either air or nitric acid.

Researchers at Nagoya University (284030) successfully oxidized cyclohexene to adipic acid using H₂O₂ in a 60% aqueous solution as the oxidant and sodium tungstate as the catalyst. The chemical pathway is shown in the figure below. Reaction of cyclohexene with H₂O₂ initially forms an epoxide ring. Upon hydration, the ring opens with unstable alcohol groups formed at each terminal carbon atom. The unstable molecule re-forms a saturated ring upon H₂O₂ reaction with a ketone group and an alcohol group on adjacent carbon atoms. Subsequent peroxidation results in an oxygen atom being incorporated into the backbone of the ring. Additional peroxidation causes the alcohol group to revert to a ketone group via dehydrogenation, while still containing an oxygen atom as part of the ring. Additional hydration of the ring causes the ring to open at the oxygen atom, forming carboxylic acid groups on both terminal carbon atoms, and resulting in the production of adipic acid.

Figure 4.44
CHEMICAL PATHWAY TO ADA FROM CYCLOHEXENE USING H₂O₂

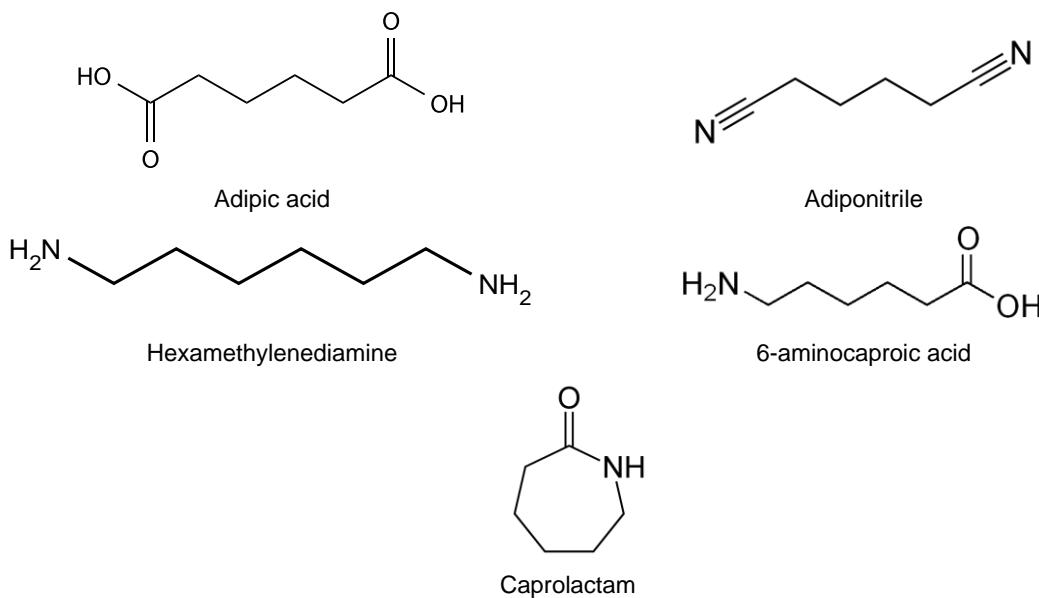


An alternative approach for the use of H₂O₂ is to use it as an oxidizing agent after the air oxidation of cyclohexane to produce KA oil. Researchers at the Fushun Petroleum Institute in China (284031) used sodium tungstate catalyst to convert cyclohexanone directly to adipic acid using a solution of 30% hydrogen peroxide in water. Yield was 82%.

5 TECHNOLOGY FOR NON-COMMERCIAL BIO-BASED ROUTES TO ADIPIC ACID

Bio-based routes to adipic acid include two categories of relevant chemistry: 1) bio-processing technologies such as fermentation using either naturally occurring or synthetically generated enzymes and bacteria, and 2) conventional industrial processing of bio-based feedstocks generically characterized as 'biomass,' but more specifically sugars such as glucose and fructose. Bio-based routes can not only produce adipic acid, but can produce a wider family of similar chemicals that are industrially produced at commercial scale today using crude oil derived feedstock. Some of the similar industrial chemicals are shown in the figure below.

Figure 5.1
BIO-BASED SIX CARBON MOLECULES

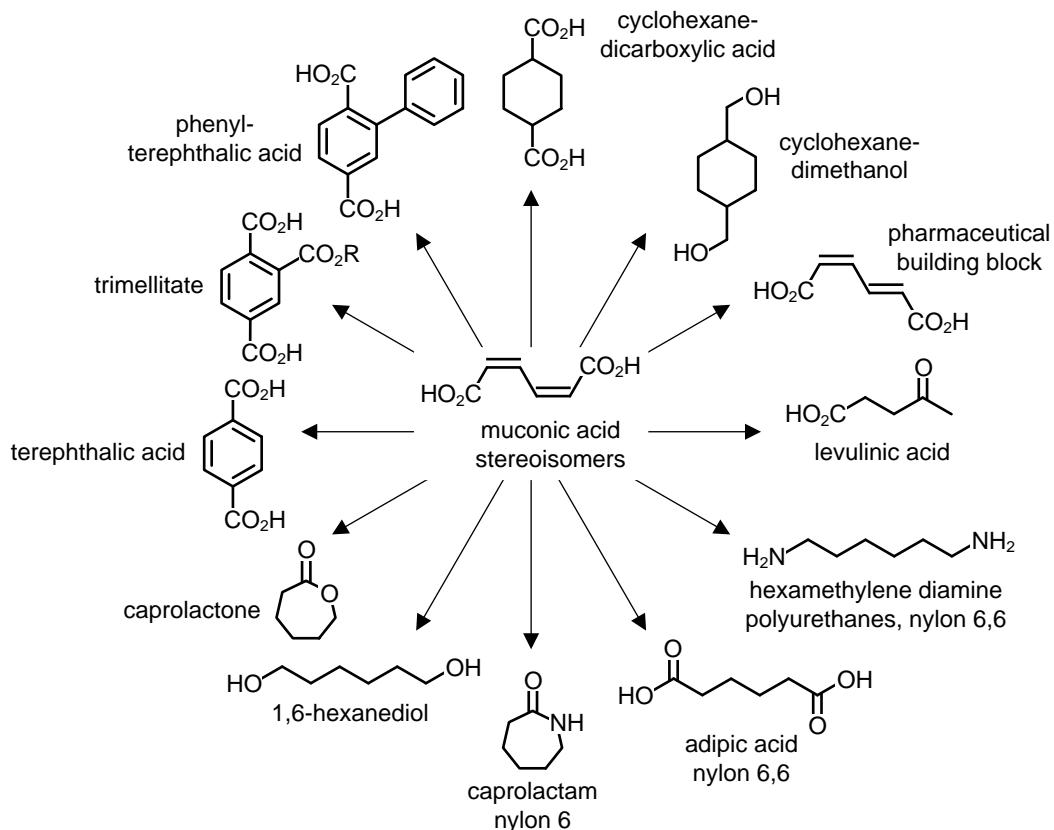


DRATHS' FERMENTATION PROCESS USING MUCONIC ACID

Professor Karen Draths and associates (284032) have been involved in fermentation processing of muconic acid (hexa-2,4-dienedioic acid) to adipic acid since the 1990s. In 2011, Draths' business was acquired by Amyris. Gene modified e-coli bacteria (*E. coli* AB2834) are used to convert D-glucose to cis,cis-muconic acid. Muconic acid concentration in the fermentation broth was reported at 36.8 gm/l after 48 hours of batch fermentation, with a 22% mol/mol yield on glucose. After completion of the fermentation, the cells were removed, and the remaining solution paper filtered and then passed through a charcoal filter to yield high-purity muconic acid. The muconic acid was hydrogenated over conventional 10% base metal on carbon catalyst at 3,400

kPa (494 psia) of hydrogen pressure for 2.5 hours. A variety of commercial chemicals can be produced from muconic acid, as shown in the figure below.

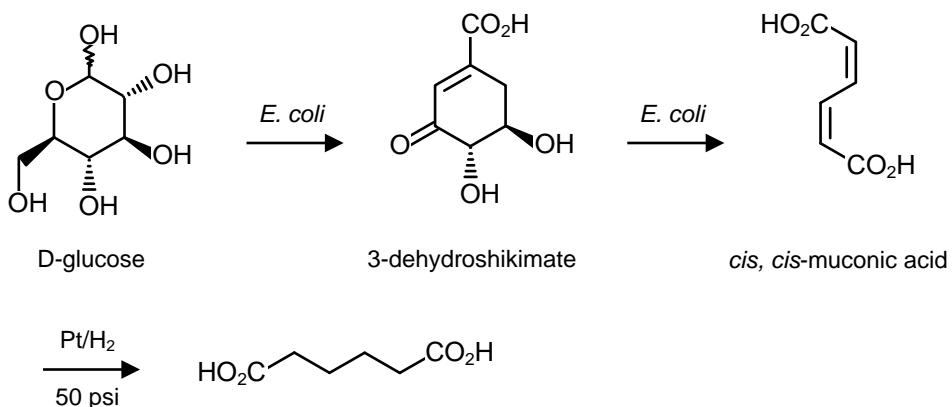
Figure 5.2
MUCONIC ACID PLATFORM



Source: Amyris

Draths has also been able to conduct the hydrogenation at a much lower pressure (50 psia) using platinum catalyst. This resulted in 97% molar conversion of muconic acid to adipic acid. The pathway for reaction is shown in the figure below. Draths' 1997 US patent 5616496 claims to convert 56 mM of glucose to 17 mM cis, cis-muconic acid within 48 hours. Fermentation production rate was 0.35 millimols per liter per hour.

Figure 5.3
DRATHS MUCONIC ACID FERMENTATION PATHWAY TO ADIPIC ACID (USP 5798236)



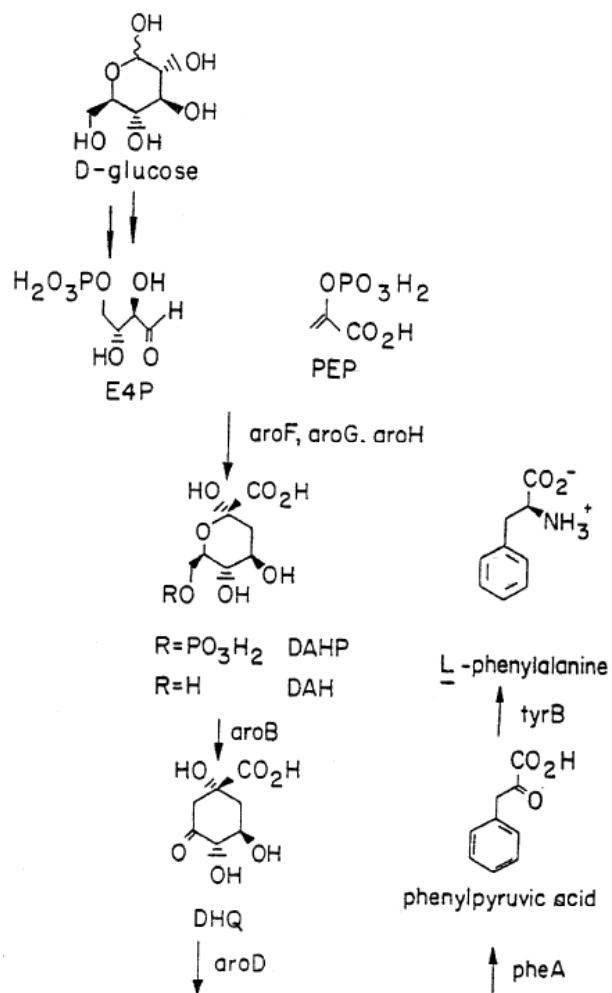
Relevant US patents for the technology practiced in the Draths process are listed in the table below.

Table 5.1
RELEVANT US PATENTS ON DRATHS PROCESS

US Patent	Title
5798236	Synthesis of Quinic Acid from Glucose
5629181	Synthesis of Catechol from Biomass-Derived Carbon Sources
5616496	Bacterial Cell Transformants for Production of Cis,Cis-Muconic Acid and Catechol
5487987	Synthesis of Adipic Acid from Biomass-Derived Carbon Sources
5272073	Biocatalytic Synthesis of Catechol from Glucose

The detailed pathway provided by Draths US patent 5616496 (figure below) shows the initial conversion of D-glucose to a combination of E4P (erythrose 4-phosphate) and PEP (phosphoenolpyruvate).

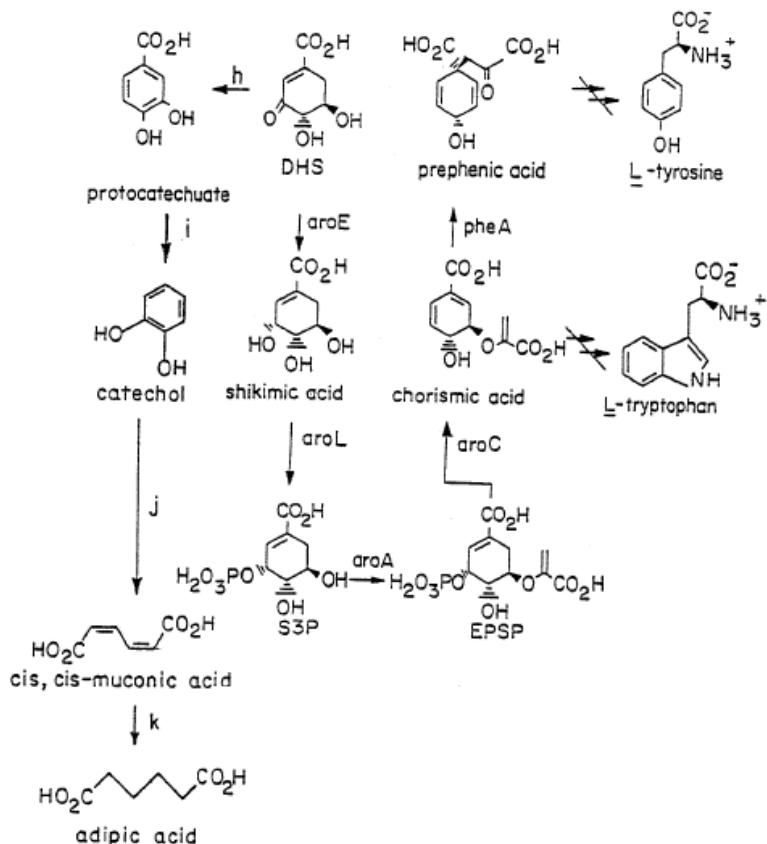
Figure 5.4
DETAILED PATHWAY FOR DRATHS FERMENTATION SYNTHESIS OF ADA—INITIAL STEPS (USP 5616496)



In the Draths process, D-glucose derived from sugars and starches, or perhaps cellulose like wood chips, after intense chemical processing, is converted using bacteria in a fermentation broth to a combination of erythrose 4-phosphate (E4P) and to phosphoenolpyruvate (PEP). The E4P and PEP are subsequently converted using genetically modified bacteria to aromatic amino acids precursor 3-deoxy-D-arabino-heptulosonic acid 7-phosphate (DAHP) and then 3-dehydroquinate (DHQ).

As shown in the figure below, the DHQ is subsequently converted via 3-dehydroshikimate (DHS) to protocatechuate, which is subsequently converted to catechol, shikimic acid, charismic acid and L-tryptophan. The catechol finally is converted in the fermentation pathway to cis, cis-muconic acid, which is subsequently separated from the fermentation broth, and converted by industrial hydrogenation to adipic acid.

Figure 5.5
DETAILED PATHWAY FOR DRATHS FERMENTATION SYNTHESIS OF ADA—FINAL STEPS
(USP 5616496)



BIOAMBER/CELEXION PROCESS

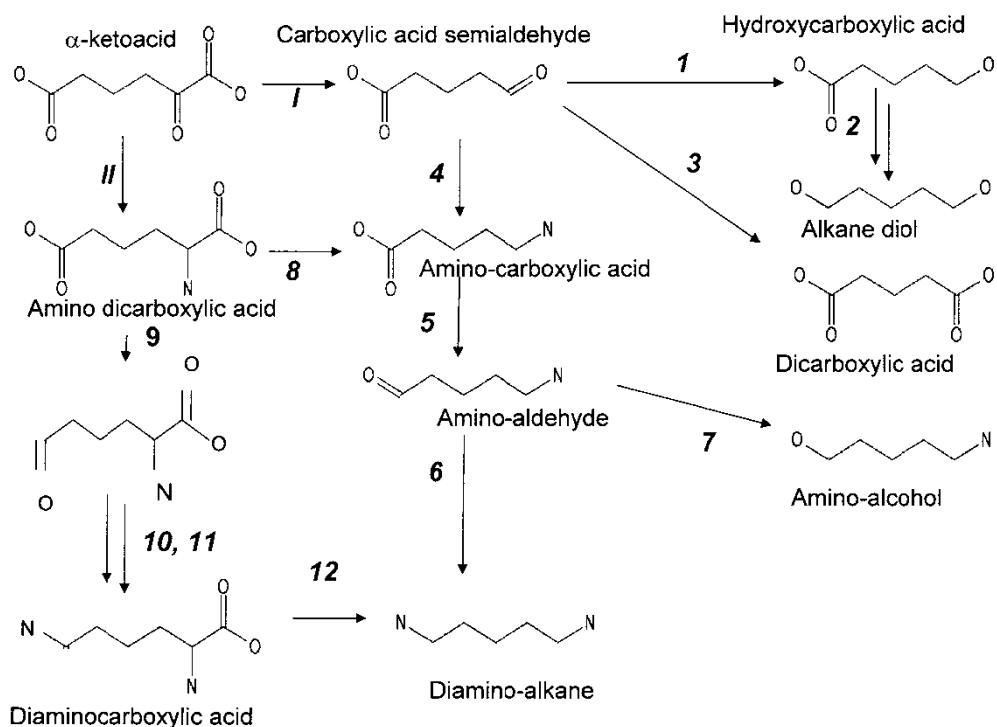
BioAmber (Plymouth, Minnesota, USA) has successfully commercialized bio-based technology for producing succinic acid (C₄ dicarboxylic acid), and is using a similar approach for producing adipic acid (C₆ dicarboxylic acid). There are three major 'know how' issues to successfully developing fermentation-based bio-chemicals: 1) producing genetically modified bacteria/enzymes to catalyze the fermentation process, 2) developing economically efficient fermentation for producing the desired product at high production rates and at high concentrations, and 3) developing economically efficient and commercially viable purification procedures so that the product specifications for bio-based industrial chemicals are equivalent to the product specifications for producing the chemicals via conventional synthetic chemistry. When these objectives are accomplished, bio-based product can then be used as a 'drop-in' replacement for conventional product.

BioAmber has partnered with Cellexion (Cambridge, Massachusetts, USA) in the adipic acid development process; since Cellexion has developed genetically modified bacteria targeted specifically to producing C₆ carbon products (adipic acid, caprolactam, hexamethylenediamine).

Cellexion patent WO 2010/068944 A2 and USP 8133704 describe the invention of modified organisms that selectively convert carbohydrates to di-functional alkanes via 2-ketopimelic acid,

as shown in the figure below. The primary pathway produces a dicarboxylic acid with a ketone group ($C=O$) on an internal carbon atom. Bacteria remove both the oxygen atom from the ketone group and an oxygen atom from the adjacent carboxylic group producing a molecule with the remaining carboxylic group at one end, and an adipate semi-aldehyde group at the opposite end of the molecule. One pathway converts the semi-aldehyde group to a hydroxyl group, and a different pathway converts the semi-aldehyde directly to a dicarboxylic acid via oxidation.

Figure 5.6
**CELEXION FERMENTATION PATHWAYS TO ADIPIC ACID (WO 2010/068944 A2,
USP 8133704)**



BioAmber has obtained two US patents for the hydrogenation of the dissolved diammonium salt of succinic anhydride in a fermentation broth to dicarboxylic acids, and the use of these products in aircraft de-icing fluid and as a heat transfer fluid. BioAmber has also supplied an additional 14 applications to the US patent office on relevant technology inventions.

Table 5.2
BIOAMBER US PATENTS

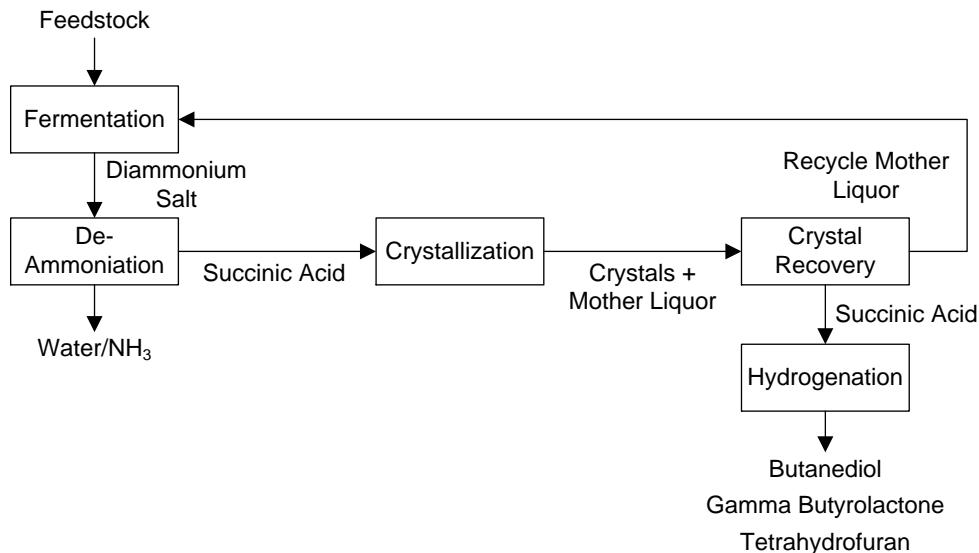
US Patent	Title
8084626	Processes for the Production of Hydrogenated Products
7938981	Deicing and Heat Transfer Fluid Compositions

Table 5.3
BIOAMBER US PATENT APPLICATIONS

US Patent	Title
20120021473	Processes for Producing Carboxylic Acids from Fermentation Broths Containing Their Ammonium Salts
20110306777	Processes for the Production of Hydrogenated Products
20110301364	Processes for the Production of Hydrogenated Products
20110297529	Processes for Producing Monoammonium Succinate from Fermentation Broths Containing Diammonium Succinate, Monoammonium Succinate and/or Succinic Acid, and Conversion of Monoammonium Succinate to Succinic Acid
20110297527	Processes for Producing Succinic Acid from Fermentation Broths Containing Diammonium Succinate
20110272269	Processes for Producing Succinic Acid from Fermentation Broths Containing Diammonium Succinate
20110269993	Processes for Producing Adipic Acid from Fermentation Broths Containing Diammonium Adipate
20110266133	Processes for Producing Monoammonium Adipate from Fermentation Broths Containing Diammonium Adipate, Monoammonium Adipate and/or Adipic Acid, and Conversion of Monoammonium Adipate to Adipic Acid
20110245515	Processes for the Production of Hydrogenated Products
20110245514	Processes for the Production of Hydrogenated Products
20110237831	Processes for Producing Monoammonium Succinate from Fermentation Broths Containing Diammonium Succinate, Monoammonium Succinate and/or Succinic Acid, and Conversion of Monoammonium Succinate to Succinic Acid
20110089364	Processes for Removing Color during Production of Runway Deicer
20110073796	Deicing and Heat Transfer Fluid Compositions
20100234320	Emulsifying Compositions Based on Alkyl Polyglycosides and Esters

BioAmber's approach to processing its fermentation product to a salable commercial product involves reacting the acid with ammonium to form an ammonium salt that does not acidify the fermentation broth, separating the ammonium salt with an extracting solvent, and splitting the salt to obtain the acid form again, crystallizing the acid from its aqueous solution, and finally hydrogenating the acid to desired derivative products. For the example shown below for producing succinic acid, the derivative products are butanediol, gamma butyrolactone, and tetrahydrofuran.

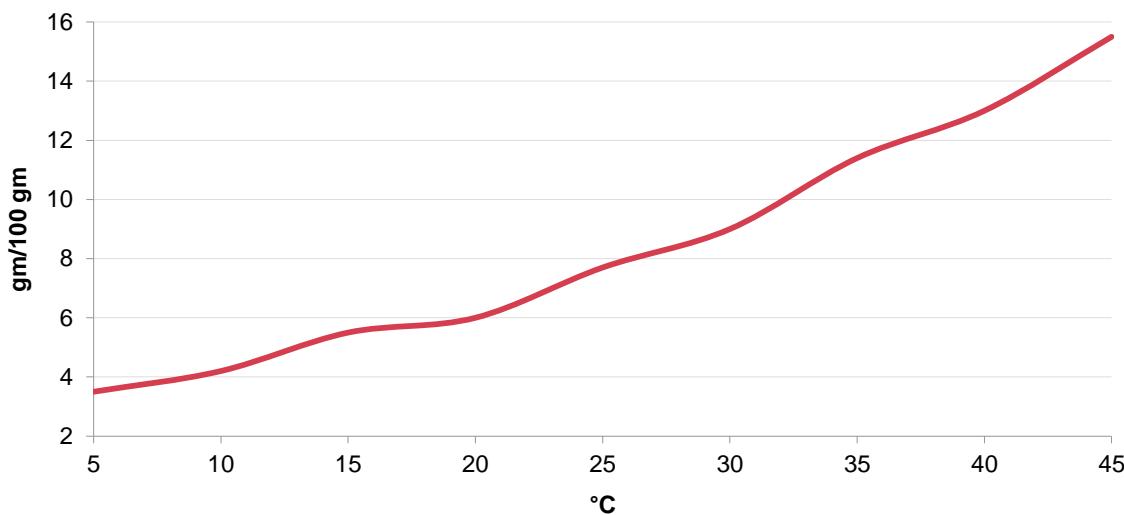
Figure 5.7
BIOAMBER PATENT FOR SUCCINIC ACID PROCESSING (USP 8084626)



The process involves fractionating the broth at high enough temperature to drive water and ammonia from the top of the distillation column, leaving the balance of the feedstock in the bottoms product. The bottoms product stream is subsequently cooled to cause the precipitation of substantially pure succinic acid, which is then hydrogenated at high pressure using conventional Group VIII catalysis (ex., palladium, ruthenium, rhenium, rhodium, iridium, platinum, nickel, cobalt, copper, iron) and technology.

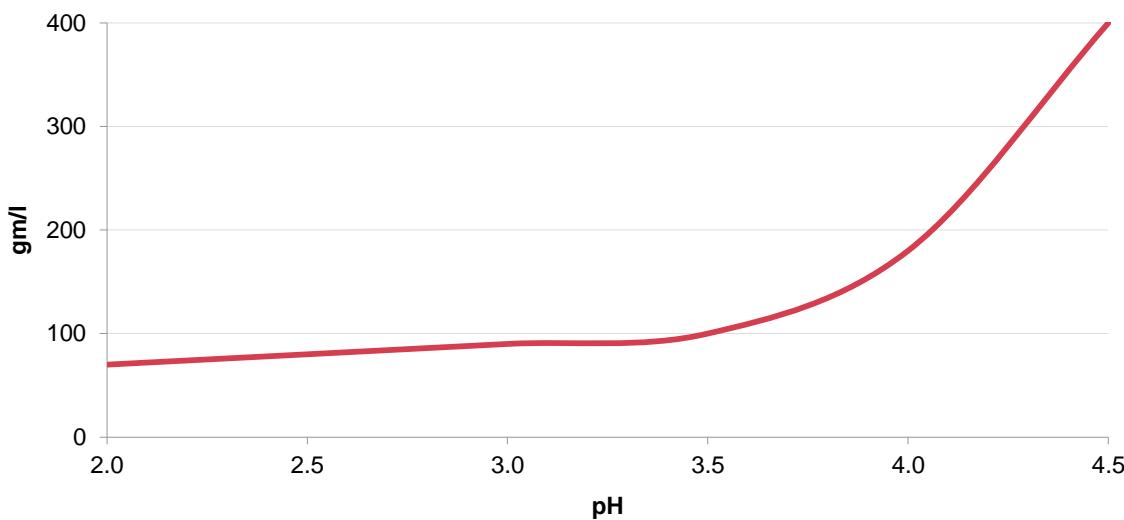
The use of solution cooling to precipitate substantially pure succinic acid from the fermentation broth is possible due to the reduction in succinic acid solubility as broth temperature is reduced. The figure below plots succinic acid solubility in water with temperature.

Figure 5.8
SUCCINIC ACID SOLUBILITY (BIOAMBER USP 8084626)



The solubility of succinic acid in water can be influenced by other components in the solution that are acidic, as shown in the plot below of solubility at 25°C as a function of pH.

Figure 5.9
SUCCINIC ACID SOLUBILITY AS FUNCTION OF PH



GENOMATICA FERMENTATION PROCESS FOR ADIPIC ACID

Genomatica has developed genetically modified bacteria that can produce adipic acid directly in a fermentation broth from sugar feedstock. Genomatica's primary US patents and US patent applications in this technology are listed in the tables below.

Table 5.4
GENOMATICA US PATENTS INVOLVING ADIPIC ACID

US Patent	Title
8088607	Microorganisms for the Production of Adipic Acid and Other Compounds
8062871	Microorganisms for the Production of Adipic Acid and Other Compounds
8048661	Microbial Organisms Comprising Exogenous Nucleic Acids Encoding Reductive TCA Pathway Enzymes
7856317	Systems and Methods for Constructing Genomic-Based Phenotypic Models
7799545	Microorganisms for the Production of Adipic Acid and Other Compounds

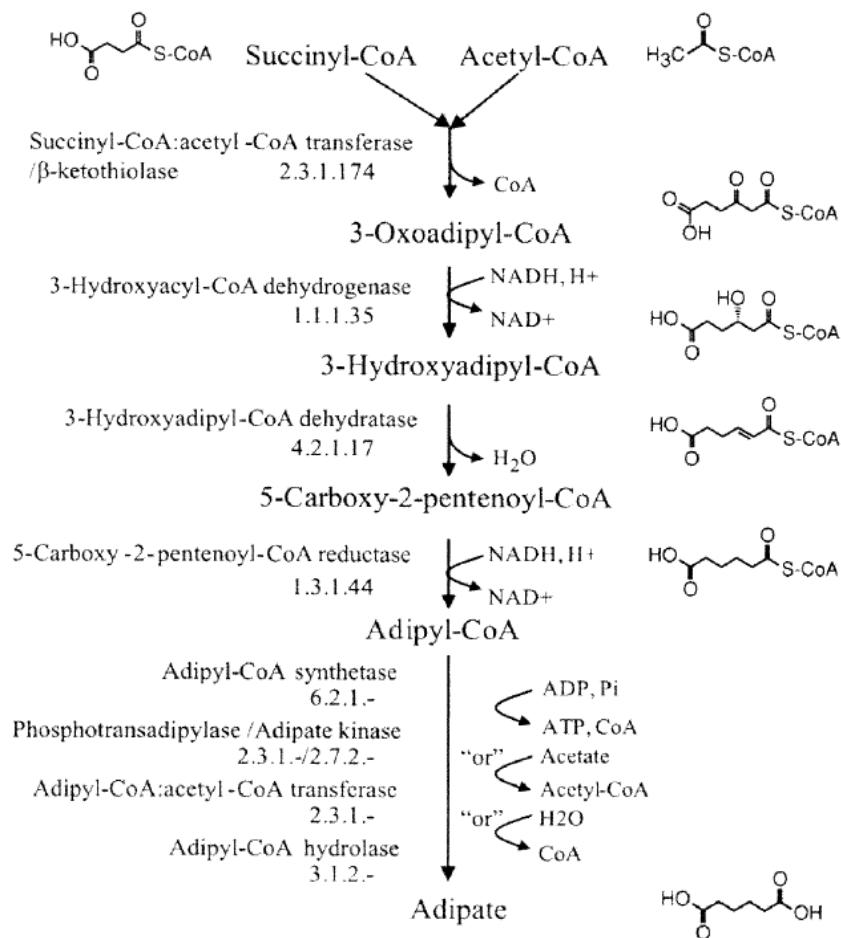
Table 5.5
GENOMATICA US PATENT APPLICATIONS INVOLVING ADIPIC ACID

US Patent	Title
20110231166	Systems and Methods for Constructing Genomic-Based Phenotypic Models
20110195466	Microorganisms for the Production of Adipic Acid and Other Compounds
20110003355	Process of Separating Components of a Fermentation Broth
20100330626	Microorganisms for the Production of Adipic Acid and Other Compounds
20090305364	Microorganisms for the Production of Adipic Acid and Other Compounds
20060147899	Multicellular Metabolic Models and Methods

Genomatica US 8088607 presents a method for producing adipic acid and similar structured compounds by genetically modifying an enzyme catalyst by encoding it with a nucleic acid component that demonstrates an ability to convert glucose to some combination of caprolactam, 6-aminocaproic acid, and/or adipic acid.

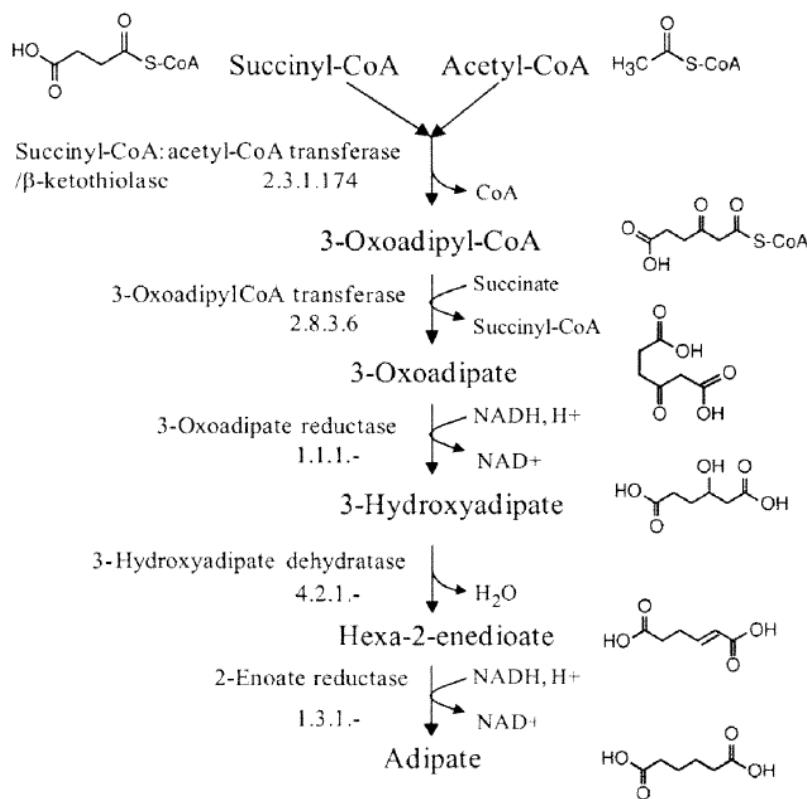
One fermentation pathway begins by combining fermentation intermediates derived from succinic acid (Succinyl-CoA) and acetic acid (Acetyl-CoA), in which the genetically engineered enzyme catalyst first combines the C₄ and C₂ components to produce a C₆ molecule. The enzyme selectively substitutes hydroxyl (-OH) groups for oxy (=O) groups, and then removes the hydroxyl groups from the internal carbon atoms while hydrating the transfer agents located on the terminal carbon atoms, forming carboxylic acid groups resulting in the production of adipic acid. This pathway sequence is shown in the figure below.

Figure 5.10
GENOMATICA HYDROXY PATHWAY FROM C₄ + C₂ FRAGMENTS TO ADIPIC ACID
(USP 8088607)



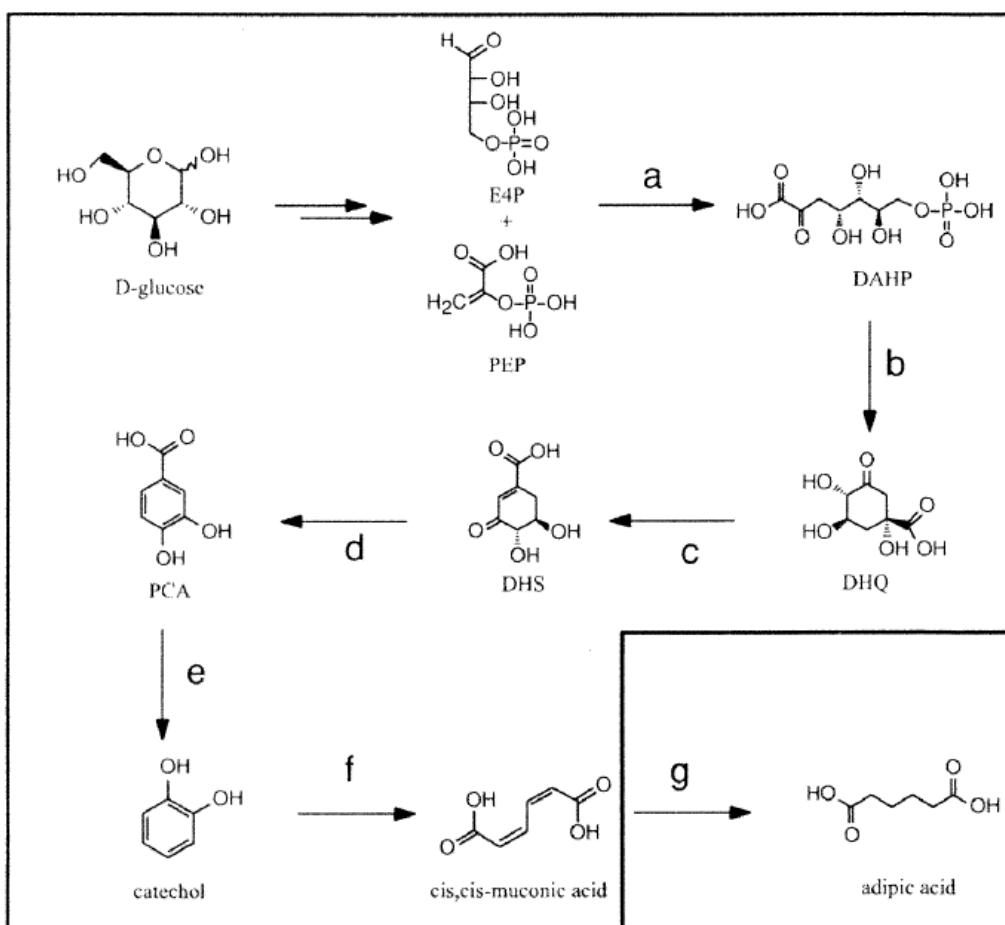
A slightly different fermentation pathway starts with the same C₄ and C₂ fragments, but rather than adding a hydroxyl group to form the intermediate product, the enzyme catalyst instead adds an oxo group to form an oxo dicarboxylic C₆ molecule. The next step removes the oxo group, producing the final adipic acid product. This pathway is shown in the figure below.

Figure 5.11
GENOMATICA OXO PATHWAY FROM C₄ + C₂ FRAGMENTS TO ADIPIC ACID
(USP 8088607)



An alternate bio-fermentation synthesis starting with glucose is shown in the figure below, and is similar to the Draths process. D-glucose feedstock is subjected to genetically modified enzymes that initially produce a combination of D-erythrose 4-phosphate (E4P) and phosphoenolpyruvic acid (PEP). These molecules combine to form 3-deoxy-D-arabino-heptulosonic acid 7-phosphate (DAHP), which is a linear C₇ molecule having a carboxylic acid group on one terminal carbon atom, and a phosphate group on the opposite terminal carbon atom. In between the terminal carbon atoms are internal carbon atoms containing hydroxyl groups. Further activity by the enzyme breaks off the phosphate group and its carbon atom, producing a C₆ ringed molecule (3-dehydroquinic acid—DHQ), which modifies to form 3-dehydroshikimic acid (DHS). Further enzyme activity removes an oxo group to form protocatechuc acid (PCA), with further elimination of the carboxylic acid group to form catechol, being a ringed compound with two hydroxyl groups on adjacent carbon atoms. Catechol further converts from its ringed structure to an open structure in which each of the hydroxyl groups converts to a carboxylic acid group to form cis, cis-muconic acid. The muconic acid is then selectively hydrogenated using industrial catalysis to form adipic acid. This pathway is shown in the figure below.

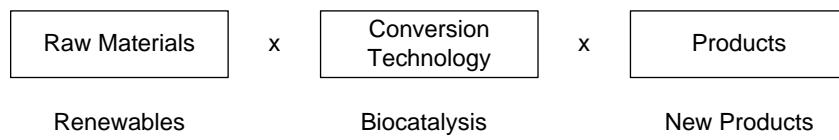
Figure 5.12
GENOMATICA MUCONIC ACID PATHWAY FROM D-GLUCOSE TO ADIPIC ACID
(USP 8088607)



RENNOVIA INDUSTRIAL CHEMISTRY PROCESS FOR ADIPIC ACID PRODUCTION

Rennovia (Menlo Park, California, USA) applies industrial chemistry (284034) to glucose feedstock (rather than using bio-processes) to produce adipic acid. Rennovia's approach (see figure below) is to develop industrial chemicals using bio-based feedstocks, but not necessarily bio-based fermentation technologies (284035).

Figure 5.13
RENNOVIA APPROACH TO BIOCHEMICALS PRODUCTION

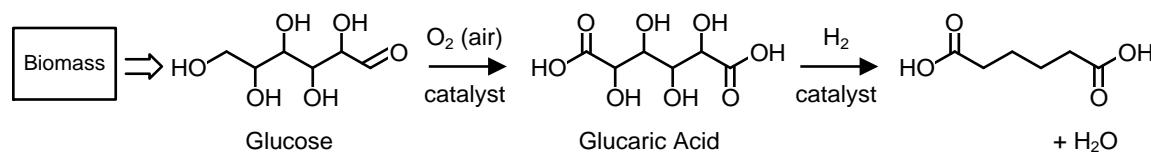


Source: Rennovia (284035)

Rennovia Glucaric Acid Route

One Rennovia bio-based process technology converts glucose to glucaric acid, which is then hydrogenated to produce water plus adipic acid. Glucose is an abundant by-product of corn processing via corn wet milling. The industrial catalytic pathway proposed by Rennovia from glucose to glucaric acid is shown below. Air oxidation of glucose converts the terminal carbon atoms to carboxylic acid groups, without affecting the internal carbon atoms that each contain hydroxyl groups. The glucaric acid formed this way is then hydrogenated to drive oxygen atoms off the hydroxyl groups, fully saturating the internal carbon atoms without affecting the terminal carbon atoms. The product thus formed is adipic acid.

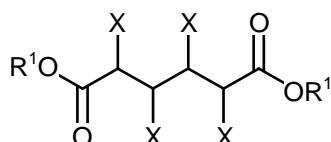
Figure 5.14
RENNOVIA PATHWAY FROM GLUCOSE TO GLUCARIC ACID



Source: Rennovia (284035)

By-products from the air oxidation step include monolactones (D-glucaro-1,4-lactone, D-glucaro-6,3-lactone) and dilactones (D-glucaro-1,4:6,3-dilactone), most of which will also be converted to adipic acid when subjected to hydrodeoxygenation. The general structure of the intermediate product is shown in the figure below, where the terminal carbon atoms have carboxylic acid groups, while the internal carbon atoms contain oxygenated radicals.

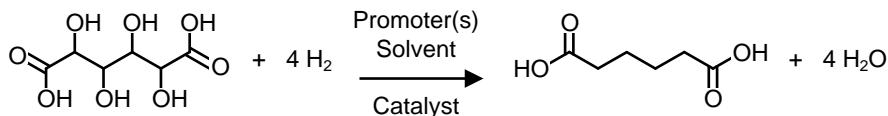
Figure 5.15
STRUCTURE OF HYDROXY DICARBOXYLIC ACID



Although the desired intermediate contains four hydroxyl (-OH) groups on the internal carbon atoms, some by-product will be made containing aliphatic internal ketone groups (2-ketoglucaric acid, 3-ketoglucaric acid) and ringed aliphatic lactone groups (C=O) rather than hydroxyl groups (D-glucaro-1,4-lactone, D-glucaro-6,3-lactone, D-glucaro-1,4:6,3-dilactone).

Once glucaric acid is produced at a yield of about 80 molar %, a second process of hydrodeoxygenation strips the four hydroxyl groups off the internal carbon atoms to yield adipic acid, as shown in the figure below. The reaction may be enhanced by the presence of a halogen (HI, HBr) promoter. The molar feed ratio of halogen to intermediate is 0.5. Rennovia believes that the halogen substitutes for the oxygen atoms on the internal carbon atoms as an intermediate step, and is then replaced by a hydrogen atom to saturate the internal carbon atoms. As shown in the figure below, the stoichiometry produces a significant amount of water.

Figure 5.16
RENNOVIA PATHWAY FROM GLUCARIC ACID TO ADIPIC ACID



Source: Rennovia (284035)

Typical hydrodeoxygenation reaction conditions are listed in the table below.

Table 5.6
TYPICAL RENNOVIA HYDRODEOXYGENATION REACTOR CONDITIONS

Temperature (°C)	160
H ₂ partial pressure (psia)	1,000
Solvent	Acetic acid
Active #1 metal catalyst	Platinum (5%)
Active #2 metal catalyst	Rhodium (3%)
#1:#2 Ratio	2:3
Catalyst support	silica
ADA molar yield	90%

An alternative path to glucaric acid via glucose bio-fermentation has been submitted by MIT to the US Patent Office as an application (USPA 201101240065 A1, 26-May-2011).

Rennovia's other technology converts glucose to hydroxymethylfurfural (HMF), which is sequentially reacted via a combination of selective oxidation, hydrogenation, and hydrodeoxygenation, to adipic acid.

The table below lists Rennovia's US patent applications.

Table 5.7
RENNOVIA US PATENT APPLICATIONS FOR ADIPIC ACID

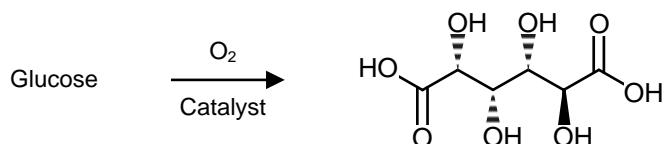
US Patent	Title
20110306790	Oxidation Catalysts
20110218318	Composition of Matter
20100317825	Production of Glutaric Acid and Derivatives from Carbohydrate-Containing Materials
20100317823	Production of Adipic Acid and Derivatives from Carbohydrate-Containing Materials
20100317822	Production of Adipic Acid and Derivatives from Carbohydrate-Containing Materials

Rennovia's air oxidation step uses water as a solvent, and results in glucose conversion of approximately 80 molar %. Unlike other patents using alternative chemistry (USP 6498269),

Rennovia's oxidation chemistry does not require the presence of an alkaline material. As is common in many liquid-vapor phase reactions, operating at elevated pressure increases the solubility of the vapor-phase reactant within the liquid solution, increasing kinetics and one-pass feedstock conversion.

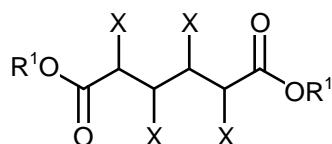
As more glucaric acid is made and its concentration in the solution increases, the pH of the solution will correspondingly decrease. Typical oxidation reactor conditions are 100°C and up to 500 psia. Effective primary catalysts include palladium and platinum, as the absence of feedstock sulfur eliminates concern about catalyst deactivation. Combining the primary catalyst with a secondary catalyst (Al, Ga, Ti, In, Sn, Pb, or Bi) improves conversion and selectivity. The total proportion of active metal catalyst on the final heterogeneous catalyst plus support is approximately 5 weight %. Additional active metals as catalyst components are documented in Rennovia's US patent applications. The major reaction by-products are glucurolactone, which will subsequently also be converted to adipic acid via hydrodeoxygenation.

Figure 5.17
RENNOVIA OXIDATION OF GLUCOSE TO GLUCARIC ACID (USPA 20100317823)



Rennovia's hydrodeoxygenation step uses a conventional heterogeneous transition metal catalyst and halogen (HI, HBr) promoter to strip hydroxyl groups off the internal carbon atoms (as shown by the 'X' in the figure below), without affecting the carboxylic acid groups that are on the terminal carbon atoms, as shown in the figure below.

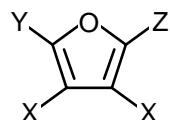
Figure 5.18
RENNOVIA HYDRODEOXYGENATION OF GLUCARIC ACID TO ADIPIC ACID (USPA 20100317823)



Rennovia Furan Route to Adipic Acid

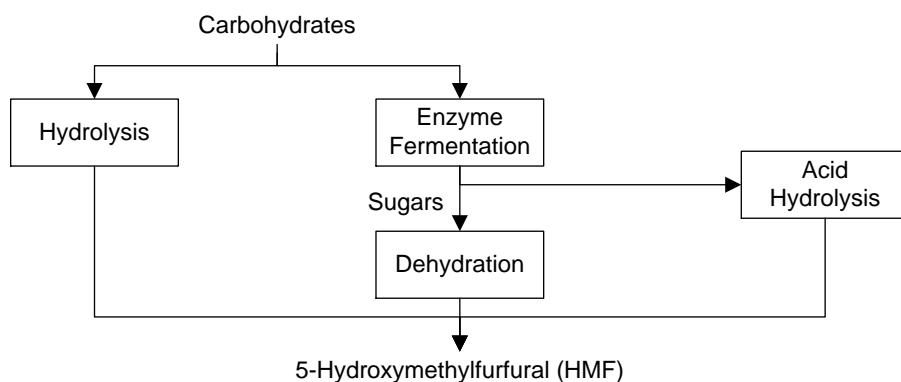
Rennovia also provides fundamentally different process technology for converting carbohydrates to adipic acid via furan chemistry. Rennovia's fundamental technology proposition is that biomass can be converted using conventional pretreatment methods to furan derivatives, which can then undergo a three-step process (selective oxidation, hydrogenation, hydrodeoxygenation) to make adipic acid from a furan derived from carbohydrates. The generalized furan molecular structure is shown in the figure below. In the figure, the 'X' radicals are carboxylic acid groups, the 'Y' radical is a hydroxyl acid group, and 'Z' is an oxo group.

Figure 5.19
RENNOVIA FURAN INTERMEDIATE PRODUCT FROM CARBOHYDRATE



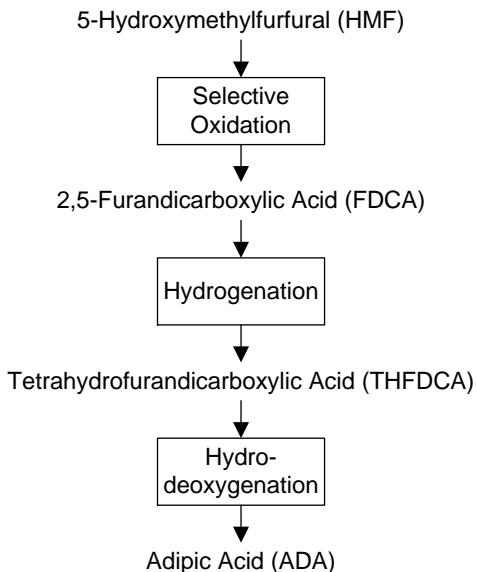
Rennovia's building block chemical intermediate is 5-hydroxymethylfurfural (HMF). HMF is well published as being able to be produced easily from carbohydrates using conventional biomass processing. The pretreatment steps are shown in the figure below.

Figure 5.20
RENNOVIA HMF PRODUCTION FROM CARBOHYDRATES



Once HMF is produced via the pretreatment of biomass-based carbohydrates, conventional industrial chemical processes are employed to convert HMF to adipic acid, as shown in the figure below.

Figure 5.21
RENNOVIA ADIPIC ACID PRODUCTION FROM HMF



VERDEZYNE FERMENTATION FOR PRODUCING ADIPIC ACID

Verdezyne (Carlsbad, California, USA) is developing yeast fermentation technology (284036) to produce adipic acid from nonfood biomass. It has developed (284037) both a C₆ (hexose sugar) pathway to adipic acid, and a C₅ (xylose) isomerase pathway to adipic acid. Verdezyne has also developed enzymes for producing adipic acid from higher cost natural surfactant oils (coconut oil, palm oil, palm kernel oil). Verdezyne has partnering relationships (284038) with BP and with DSM for developing and eventually commercializing its technology. World patent WO 2011/003034 A2 (6-Jan-2011) summarizes Verdezyne intellectual property discoveries. Verdezyne US patents and patents applications are listed below

Table 5.8
VERDEZYNE PATENTS AND APPLICATIONS

Verdezyne Relevant Patents and Applications		
US	8227236	Engineered Microorganisms with Enhanced Fermentation Activity
US	8114974	Engineered Microorganisms with Enhanced Fermentation Activity
US	8093037	Engineered Microorganisms with Enhanced Fermentation Activity
US	20120077252	Combinatorial Methods for Optimizing Engineered Microorganism Function
US	20120184465	Combinatorial Methods for Optimizing Engineered Microorganism Function
US	20120184020	Engineered Microorganisms with Enhanced Fermentation Activity
US	20120156761	Biological Methods for Preparing Adipic Acid
US	20120077252	Biological Methods for Preparing Adipic Acid
US	20120077237	Biological Methods for Preparing Adipic Acid
US	20120021474	Biological Methods for Preparing Adipic Acid
US	20110229959	Biological Methods for Preparing Adipic Acid
US	20110224416	Engineered Microorganisms with Enhanced Fermentation Activity
US	20110165661	Engineered Microorganisms with Enhanced Fermentation Activity
US	20110165660	Engineered Microorganisms with Enhanced Fermentation Activity
EP	2451960	Engineered Microorganisms with Enhanced Fermentation Activity
EP	2449091	Biological Methods for Preparing Adipic Acid
WO	2011/006136	Engineered Microorganisms with Enhanced Fermentation Activity
WO	2011/011292	Combinatorial Methods for Optimizing Engineered Microorganism Function
WO	2011/006126	Engineered Microorganisms with Enhanced Fermentation Activity
WO	2011/003034	Biological Methods for Preparing Adipic Acid

BioAmber Relevant Patent Applications

US	20110266133	Processes for Producing Monoammonium Adipate from Fermentation Broths Containing Diammonium Adipate, Monoammonium Adipate and/or Adipic Acid, and Conversion of Monoammonium Adipate to Adipic Acid
US	20110269993	Processes for Producing Adipic Acid from Fermentation Broths Containing Diammonium Adipate

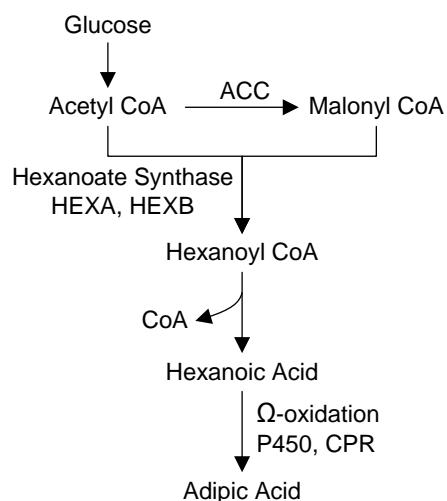
Verdezyne's genetically modified enzymes (Verdezyne prefers using a modified *Candida* yeast for making adipic acid) can convert several types of bio-based feedstock to adipic acid in relatively high yield and at relatively fast production rates. Performance claims for each of Verdezyne's US patent applications for adipic acid are summarized in the table below.

Table 5.9
VERDEZYNE ADIPIC ACID PERFORMANCE CLAIMS

USPA			
	20120077237 A1	20120021474 A1	20120077252 A1
Enzyme	Candida yeast	Candida yeast	Candida yeast
Feedstock	Vegetable oil	Vegetable oil	Glucose
Productivity	2 gm/l culture medium	0.4 gm/l culture medium	0.3 gm ADA/gm glucose up to 5 gm/l-hr

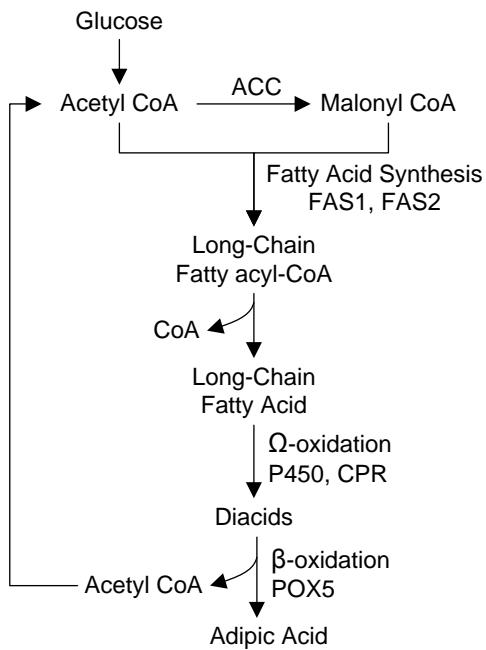
As shown in the figure below, Verdezyne's preferred starting material is glucose. Its enzymes divide glucose into two molecules: an acetyl component and a malonyl (C_3) component, which are recombined to form a C_6 ester that is subsequently converted to a C_6 monocarboxylic acid (hexanoic acid). Subsequent oxidation converts the monocarboxylic acid to dicarboxylic acid, and removes the hydroxyl radicals on internal carbon atoms to produce adipic acid.

Figure 5.22
VERDEZYNE PATHWAY TO ADIPIC ACID FROM GLUCOSE (USPA 2012 0156761)



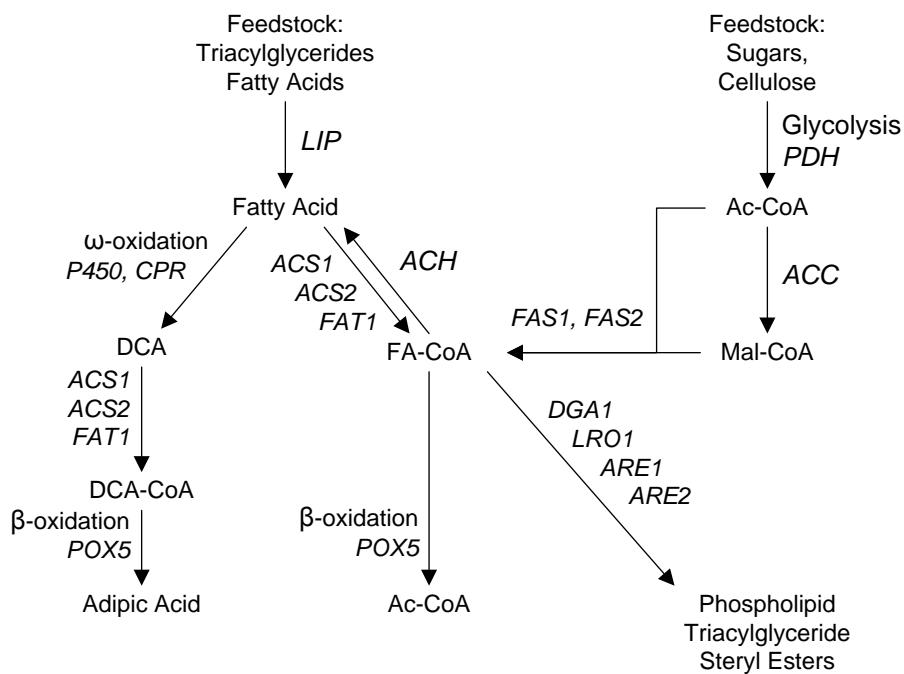
Verdezyne has also developed different enzyme yeasts that result with an alternative pathway to adipic acid by first combining C_6 fragments to form a larger carbon number molecule (fatty acid precursors) that are converted to a monocarboxylic acid with the carboxylic acid group on a terminal carbon atom. Subsequent oxidation removes the acetyl group from the substrate so that the substrate is again a C_6 molecule, which is oxidized to adipic acid.

Figure 5.23
VERDEZYNE ALTERNATIVE PATHWAY TO ADIPIC ACID VIA FATTY ACID
(USPA 2012 0156761)



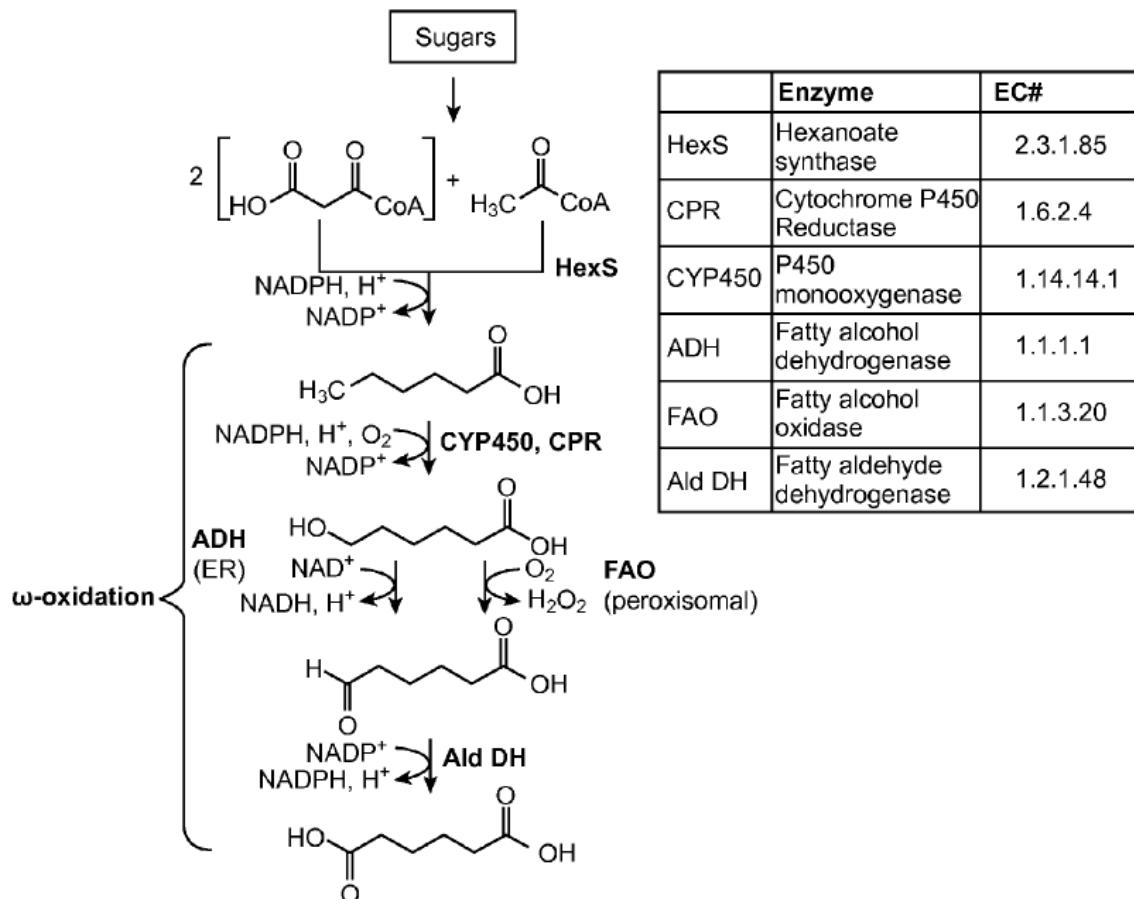
Alternatively, the intermediate fatty acid can be produced directly from triglyceride starting material by methanol trans-esterification followed by hydrogenation. Once the fatty acid is formed, the enzyme systematically converts the hydroxyl group on the other terminal carbon atom to a carboxylic acid group via oxidation, forming a hydroxy dicarboxylic acid. The enzyme then strips off hydroxyl groups from the internal carbon atoms to produce adipic acid product, as shown in the figure below.

Figure 5.24
VERDEZYNE PATHWAY TO ADIPIC ACID FROM SUGARS AND TRIGLYCERIDES
(USPA 2012 0156761)



The various intermediate products made along the pathway from sugar to adipic acid are shown in the figure below. The first step adds carbon backbone to the initial feedstock via a C₄ + C₂ synthesis to produce a C₆ monocarboxylic acid. Subsequent oxidation strips off the internal carbon atom hydroxyl groups while also oxidizing a terminal carbon atom radical to carboxylic acid, forming adipic acid.

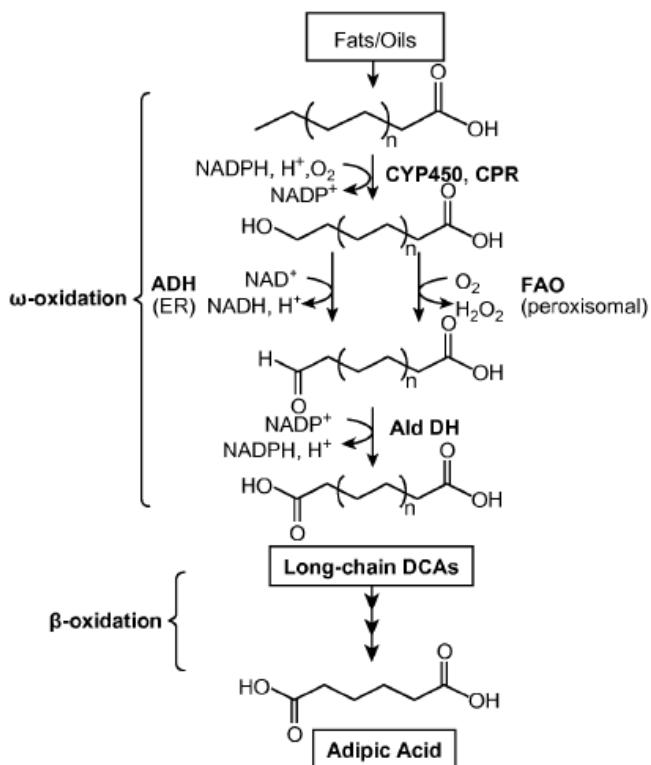
Figure 5.25
VERDEZYNE INTERMEDIATES PRODUCTS TO ADIPIC ACID FROM SUGAR



Source: USPA 2012/0156761

Verdezyne's patent estate includes enzymes capable of making adipic acid from natural fats and oils that are long chain monocarboxylic acids, in addition to producing adipic acid from sugars (principally glucose). The enzymes oxidize the hydroxyl group on a terminal carbon atom to a carboxylic acid group, and remove hydroxyl groups from the internal carbon atoms to form long chain dicarboxylic acids. Subsequent oxidation removes internal carbon atoms from the backbone of the molecule until the backbone is only a C₆ material (adipic acid). This pathway is shown in the figure below.

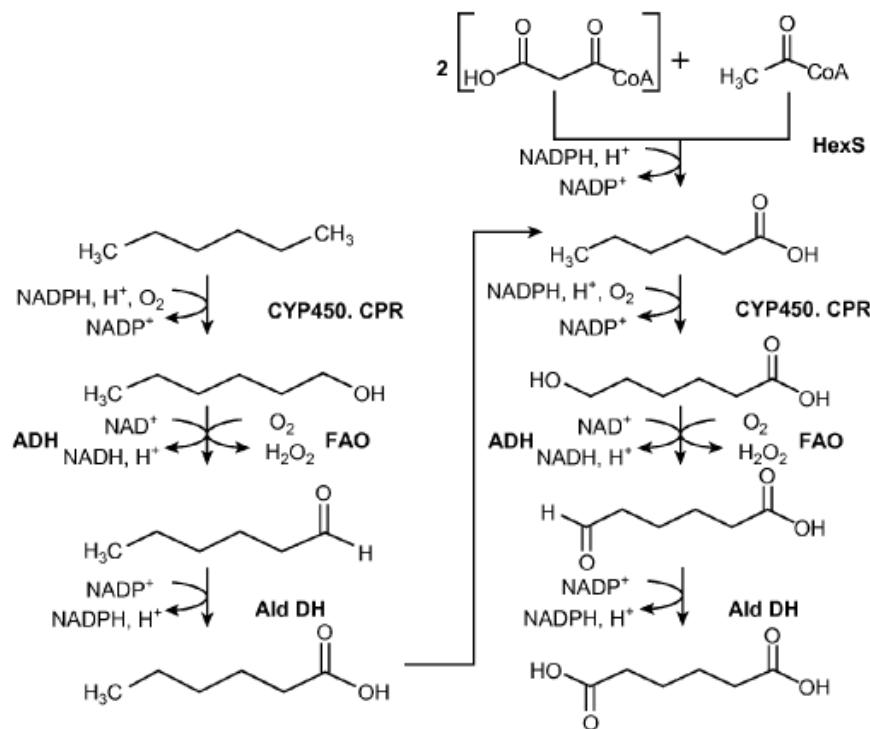
Figure 5.26
VERDEZYNE ADIPIC ACID FROM FATS AND OILS



Source: USPA 2012/0156761

Verdezyne's fermentation pathway when using paraffins as the starting material for adipic acid production is shown in the figure below. The enzyme initially acts on a terminal carbon atom, replacing a hydrogen atom with a hydroxyl group. The terminal carbon atom, now with the hydroxyl group, is acted on by adding an oxo radical (=O) and removing another hydrogen atom, producing a monocarboxylic acid. Once formed, the enzyme works the same procedure on the opposite terminal carbon atom until it also contains a carboxylic group, thereby forming adipic acid. This sequence is shown in the figure below.

Figure 5.27
VERDEZYNE ADIPIC ACID FROM PARAFFINS

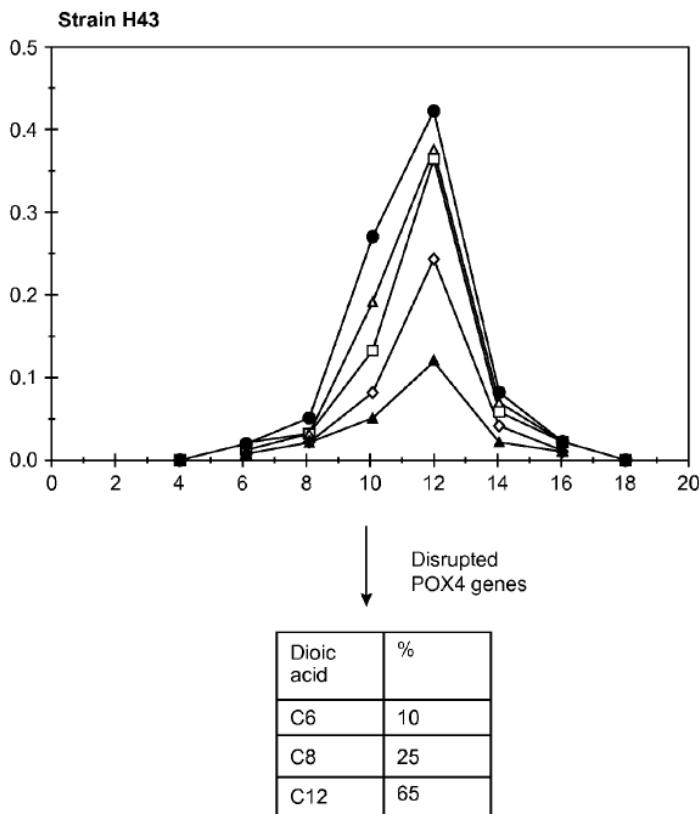


Source: USPA 2012/0156761

From Verdezyne US patents and applications, claimed adipic acid product yields of at least 0.15 grams product per gram glucose are made, and up to almost 100% of theoretical yield on other feedstock. Some results on yield were up to 1,000 grams adipic acid per liter of culture medium. Adipic acid production rates ranged from 0.5 to 5.0 gm/liter per hour of fermentation time. Use of a synthetic enzyme developed by Verdezyne is claimed to increase production rate up to 500 fold greater than when using natural (wild) enzymes.

The distribution of fermentation product yields is a function both of the enzyme strain developed, and of the processing conditions. The product distribution by carbon number for Verdezyne Strain H43 is shown in the figure below, where the enzyme catalyst is tailored to maximize the C₁₂ dicarboxylic acid yield. Produced are molecules with a carbon number range between C₄ and C₁₈.

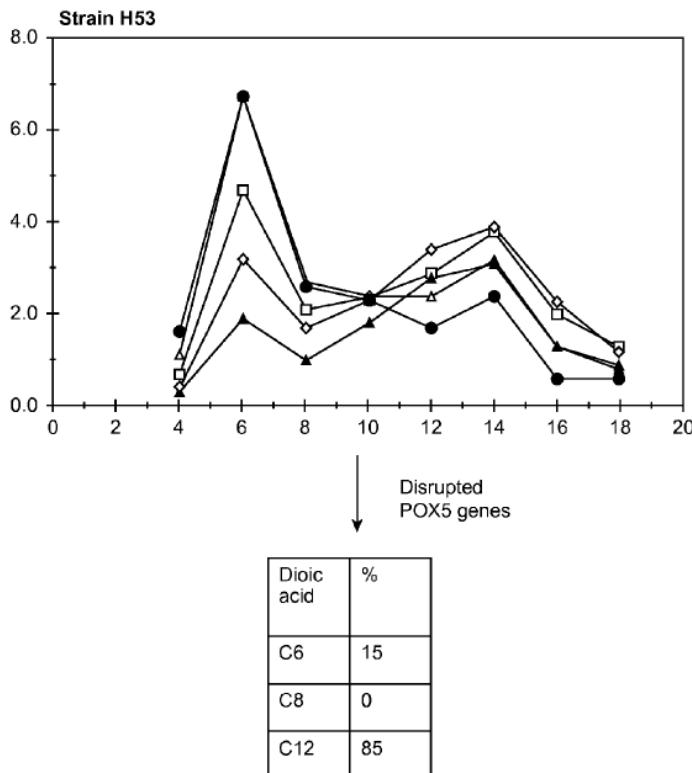
Figure 5.28
VERDEZYNE CARBON NUMBER SELECTIVITY FOR STRAIN H43



Source: USPA 2012/0156761

Verdezyne enzyme strain H53 provides a bimodal distribution of products by carbon number, with one peak for C₆ product, and the other peak for C₁₂–C₁₄ product. Produced are molecules with a carbon number range between C₄ and C₁₈.

Figure 5.29
VERDEZYNE CARBON NUMBER SELECTIVITY FOR STRAIN H53



Source: USPA 2012/0156761

Verdezyne's activities have not been limited to research. In November 2011, Verdezyne opened (284039) its first pilot plant in Carlsbad, California (USA), designed to produce kilogram quantities of product for customer testing and analysis. The pilot plant will also develop engineering design parameters for industrial scale-up.

6 DESIGN BASIS FOR ADIPIC ACID PRODUCTION

BUSINESS OBJECTIVES

The principal business purpose of this assessment is to provide technical and economic insights into the potential installation of industrial scale adipic acid plants utilizing bio-based feedstocks and/or bio-processing technologies such as fermentation. It is also a purpose to compare the economics (capex, opex) of such proposed processes to the conventional industrial process using two-stage oxidation of cyclohexane, with the first stage being air oxidation, and the second stage being nitric acid oxidation.

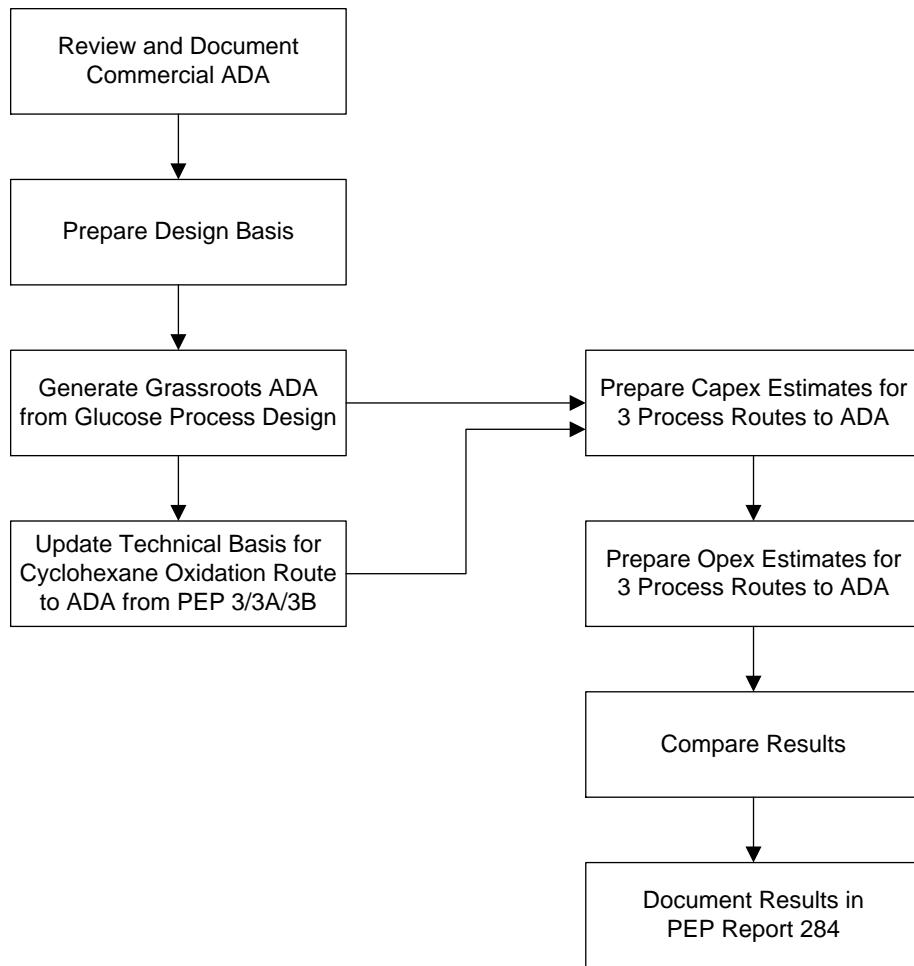
We have chosen to use our understanding of the DuPont/Invista process for making adipic acid from cyclohexane as the benchmark representing 'best in class' current conventional practice. We have chosen to compare the DuPont/Invista process with two bio-based processes being currently developed: Verdezyne's fermentation of glucose using genetically modified candida yeast, and Rennovia's industrial catalytic conversion of glucose first to glucaric acid through selective oxidation, followed by hydrodeoxygenation of glucaric acid to adipic acid. All of the processes examined were designed to purify crude adipic acid to fiber-grade adipic acid using two-stage aqueous crystallization employing Oslo suspension crystallizers and pusher centrifuges, followed by rotary drying to achieve commercial specifications.

Since petrochemical plant production economics are dominated by two factors: feedstock cost and capital cost, we have focused our efforts on developing suitable process configurations based upon the recent patent and trade literature from DuPont, Invista, Verdezyne and Rennovia that currently (as of 2012) dominate the conventional and bio-based business. Both Verdezyne and Rennovia have signed joint venture agreements with conventional adipic acid producers, suggesting that conventional producers perceive sufficient potential in the proposed technologies to provide equity and expertise to the commercial development process.

The methodology used to conduct this effort is summarized in the figure below, which shows how the project scope of work was developed, step by step. We first prepared a technical design basis for all of the three process routes after reviewing the commercial adipic acid business, as we understand it. Since PEP has never evaluated a bio-based route to adipic acid, we developed a grassroots Class-3 process design packages around patents and applications assigned to Verdezyne and Rennovia. For purification of the Verdezyne fermentation broth, we used technical and trade literature provided by BioAmber. For the conventional two-stage cyclohexane oxidation route, we updated the technical basis previously documented in PEP Reports 3, 3A, and 3B, and reworked the design information.

When the process engineering information was completed, we developed current (for 2012) pricing information for feedstocks and products, as well as utilities. We then prepared a capital cost estimate for each process, and a production cost estimate for each process, and compared results to draw conclusions about the viability of both noncommercial processes from glucose as compared to the conventional cyclohexane oxidation route.

Figure 6.1
PROJECT SCOPE OF WORK



SCOPE OF PROJECT

The scope of the project effort is to provide process design and corresponding economics (capital cost, manufacturing unit cost) for manufacturing commercial volumes (160 kty) of adipic acid in a single process train.

Project deliverables include this design basis, process descriptions accompanied by process flow diagrams, stream-by-stream heat and material balances, equipment lists that include duty specifications, itemized capital costs segmented to the equipment list items on both an FOB purchase basis, and on an installed basis, a build-up of plant total fixed capital cost, and finally unit manufacturing cost estimates for adipic acid segmented to include variable cost elements (generally feedstock and energy cost components), plant operating and maintenance expenditures, allocated plant overhead costs, and corporate overhead costs. Unit manufacturing cost estimates are provided in terms of both cash cost and fully loaded totally production cost (including depreciation).

Discussions with industry participants and publicly available literature suggest that construction schedules for grassroots ADA plants usually take about two years from site clearing to commissioning and commercial start-up.

Units of measure used for process design work are metric units. Economic evaluations are done using US dollars as the currency.

DESIGN PHILOSOPHY

The design philosophy for this adipic acid manufacturing facility is state-of-the-art performance applying commercially proven technologies and practices in a facility utilizing the highest international standards for safety and environmental performance. The plant is expected to operate for at least 25 years of economic life, and be flexible for periodic capacity and technology upgrading purposes. Given that expected industry demand growth is expected to average 2%+/y, the plant should be designed for ease of capacity debottlenecking.

This project, if commercialized, is expected to be built via a two-step process in which a process license is first acquired from a firm like Invista, Rennovia, or Verdezyne, and then the construction of the plant via normal lump sum turnkey manufacturing based on the basic engineering package provided by the licensor. Significantly more capital cost is expected to be incorporated into this project if a bio-based technology is selected, than would be likely in a conventional technology plant, since this plant is 'first of a kind.' The extra capital cost would be justified in providing at least 15% DCF return on the incremental economic benefits it would provide over the kind of design that is likely to be offered on an LSTK basis. The nature of these benefits is likely to be:

- Better overall yield (conversion x selectivity) of feedstock to cells
- Higher energy conversion efficiency
- Lower lifetime cost to operate
- Short cycle times for manufacturing cells and installing them in panels
- Longer run time between scheduled turnarounds
- Minimum unit use of feedstock and energy
- Ability to optimize economics over a variety of future economic scenarios

The extra capital costs likely to be expended for this kind of project involve the use of customized process equipment, extremely high durability materials, more instrumentation that would be needed at a conventional plant, and higher design throughput in order to assure that capacity guarantees can be satisfied.

DESIGN PRIORITIES

The priorities for process design on this project, in order of importance from highest to lowest, are:

- Process safety
- Operating reliability
- Ease of producing on-spec product consistently
- Environmental conformance to emissions requirements
- Flexibility for economic optimization
- Ease of operations and maintenance
- Maximum return on investment (ROI) consistent with the other priorities
- Adequate security and vulnerability analysis

Process Safety

Adipic acid production using the conventional cyclohexane oxidation process involves using flammable liquids (cyclohexane) at elevated temperatures and pressures. Most of the safety problems documented by this industry have been in the form of explosions and fires caused by leaks of flammable materials. Beside project-specific safety mitigations, the project incorporates conventional fire protection facilities (fire monitors, inert gas deluge system, portable extinguishers). Two independent process flare systems interconnected by flare blowdown piping manifolds are provided in the design.

A safety issue particular to adipic acid is the potential for dust explosions. There are two documented instances of fires occurring at a DuPont (now Invista) adipic acid plant in Texas that got started in the rotary dryer section, where crystallized adipic acid is dried for final packaging. Given the amount of adipic acid solids being stored, conveyed, or dried in our process, we have provided inert nitrogen gas blankets for adipic acid storage tanks and silos, and closed conveying systems that are also nitrogen blanketed.

Operating Reliability

In today's highly competitive environment, the major difference between economically competitive and economically non-competitive chemical production facilities is plant reliability. Low reliability facilities produce more off-specification product that is reprocessed, or sold at a significant price discount to desired premium product grades.

This facility is designed to operate for two years between scheduled turnarounds, and incur non-scheduled outages no more frequently than once year. Catastrophic failures should never happen.

This project is designed to be able to operate through a temporary system-wide power quality incident, which is expected to be either in the form of a voltage sag or phase synchronization problem. The entire process control system, from sensor to centralized computer and distributed facilities (Foundation Fieldbus), will be automatically isolated from the bulk power requirements of the plant, and be able to operate for up to 24 hours on an uninterruptible power system (UPS) that includes back-up batteries plus an emergency diesel generator. The back-up system will be on-line, and be able to maintain sufficient power quality continuously to avoid having sensitive instruments trip on temporary power quality incidents. Emergency back-up power, in the form of the proposed uninterruptible power supply (UPS), also minimizes the chance of work in progress going off-spec. The plant is not designed to operate without a normal power supply. Emergency facilities (fire water pumps, process flare system, wastewater treatment system) will have their critical rotating machinery provided with dual drivers (one electric motor, one diesel engine) to operate through a power interruption.

Consistency in Producing On-Spec Adipic Acid

Due to the relatively low selectivity of both oxidation reactions to produce adipic acid from cyclohexane, many other acids are formed by the reaction chemistry that are difficult to separate from adipic acid using conventional separation techniques. If allowed to stay in the product, these contaminants actively react with HMDA during the copolymerization to produce nylon 66, resulting in an inferior product with inferior performance characteristics. As a result, significant process complexity is required to remove these contaminants from adipic acid via two stages of aqueous suspension crystallization under high vacuum conditions and subambient temperatures. To achieve these results, we have provided what we believe is a robust process design to assure the consistent production of 99.8%+ purity adipic acid.

Environmental Emission Conformance

The proposed facilities are designed to meet the environmental emissions requirements of regulatory agencies in the United States, EU, and Japan for best available and commercially demonstrated technology. Explicit environmental design criteria are provided elsewhere in this section of the report. In general, the major environmental features of this design include:

- Near-zero liquid discharges
- Wet scrubbers (caustic soda fed when appropriate) followed by activated carbon filters for vent gases
- Fugitive emission source monitoring
- Noise reduction facilities for rotating machinery and high power electrical equipment
- Perimeter sensors and alarms
- On-purpose destruction of nitrous oxide (N_2O) in a dedicated incineration facility
- Tertiary wastewater treatment plant

This facility is designed to meet current and anticipated environmental regulatory requirements for hydrocarbon production and upgrading facilities in the United States, EU, and Japan. It is not designed for the more rigorous requirements that may exist under special site-specific conditions such as prevention of significant deterioration, non-attainment areas, and/or proximity to wilderness or sensitive cultural facilities. We assume that the plant site has been zoned as a general industrial production area. The design does not address site-specific environmental sensitivities such as the presence of endangered species, critical habitat, or the presence of preexisting cultural resources. This design does not incorporate facilities to address environmental justice concerns.

The key recurring environmental emission from adipic acid manufacturing facilities is discharge gases from the high temperature reactors, hydrocarbon leaks from seals, vapor discharges from pressure safety valves. Provided in the design is a flare gas header and process flare discharge system with blowdown drum, water seal, and steam assisted flare tip for mixing and dispersion. The system is not provided with a flare gas recovery and recycle system.

The principle sources of noise in the complex are the large rotating equipment (compressors and pumps). Rotating equipment will be designed with sound deadening material to reduce ambient noise levels to 80 DBA or less.

Miscellaneous wastes that are not addressed above but are treated site wide include:

- Sanitary wastes from human activities will be comminuted and pumped to the municipal wastewater treatment facility.
- Site-wide storm water runoff from the first 30 minutes of a precipitation event will be collected, retained, and pumped to the wastewater treatment facility.

The utility steam generation boilers will fire natural gas and be equipped with low NOx burners. The expected pollutant emissions of combustion gas from the boilers when burning natural gas are:

Carbon monoxide (CO)	<100 mg/m ³
Nitrous oxides (NOx)	<100 mg/m ³
Sulfur oxides (SOx)	<40 mg/m ³
Particulates	<5 mg/m ³

Fugitive emissions from pump seals, valve stems, and flanged fittings will be tested periodically to assure that hydrocarbons levels remain below 500 ppmv.

Boiler blow down rates will be established via automatic conductivity meters on the steam drums. Boiler blow down will be flashed to the next lower pressure level. Low pressure (4 bar) boiler blow down will be cooled and recycled to the boiler feed water make-up system. Cooling tower blow down will be treated in a reverse osmosis recovery unit, and recycled to avoid a build-up of dissolved solids in the cooling water circuit. Concentrate discharge from the RO system will be concentrated in a brine concentrator or crystallizer, and deep well injected.

We have provided in our design for the Verdezyne fermentation process a requirement to cover all fermentation tanks, and vent them to a combined caustic scrubber and activated carbon filtration bed. Liquid emissions from the wastewater treatment plant will be disinfected (chlorine, ozone, or UV) prior to discharge.

Hazardous Waste Incineration

An on-purpose thermal incinerator operated in continuous mode, and meeting local environmental requirements, will be incorporated in the project to incinerate hazardous materials, which are expected to be primarily sludge from the wastewater treatment plant, and heavy hydrocarbons from the process area. It is expected that the facility will use high temperature air blown incineration in a rotary kiln having at least 30 seconds residence time, plus combustion gas scrubbing. For the design of the Verdezyne fermentation plant, we intend to use the incinerator as the disposition for spent enzyme catalyst.

Flexibility for Economic Optimization

Since the process design for the Verdezyne fermentation plant, or Rennovia catalytic adipic acid plant would be a ‘first of a kind plant,’ they have been designed very conservatively in order to deal with the unanticipated conditions that always exist in ‘first of a kind’ plants. Based upon actual operating conditions, there should be considerable opportunities to optimize operations to achieve the following results:

- Greater production rate
- Higher product quality/purity
- Lower feedstock and utility unit consumption
- Lower consumption of catalysts and chemicals
- Lower operations and maintenance costs than anticipated

For these purposes, a conservative design is warranted that provides generous reactor volume and catalyst loading, ample instrumentation and controls to modify set-points based on the reality of operations, additional heat exchanger surface area, piping design at using low pressure drop criteria, and the use of low corrosion potential materials of construction.

Ease of Operations and Maintenance

A typical, world scale ADA production and upgrading facility will incur annual operations and maintenance costs (excluding turnaround costs) that represent approximately 2–4% of the replacement cost of the facility, excluding fuel. Our production economics assumes 3% of the battery limits capital investment will be spent on plant maintenance each year, segmented equally between maintenance materials and maintenance labor.

To perform cost efficient maintenance, the plant layout will be generous with plenty of room between process equipment to bring in construction equipment (heavy lift cranes, cherry pickers) or scaffold key process equipment, as warranted by the operation at hand. The plant will be laid out in a grid pattern with mobile equipment pathways every 10 meters.

Process equipment will be laid out in a logical manner to facilitate ease of operation and maintenance. The offsites portion of the capital investment will include a suitable maintenance warehouse facility, with mechanical capability for the following operations:

- Calibrate and repair instrumentation
- Repair control valves and their operators
- Trouble shoot and rewind electric motors
- Laser align rotating equipment with piping
- Turn low capacity pump and vacuum compressor wheels
- Full welding capability (TIG/MIG)
- Clean and repair process furnace internals
- Scaffold vessels
- Paint and insulation shop
- Repair motor controllers
- Rebuild pumps and compressors
- Perform full code vessel repairs
- Re-line vessel internal layers with insulation
- Repair and replace induction and resistance heating coils

Scheduled Plant Turnarounds

An adipic acid plant designed to these standards should be capable of operating continuously for a period of two years, followed by a scheduled turnaround of four weeks. Consideration has been made in the design to use corrosion resistant materials (primarily stainless steel) for wetted parts, and in select areas highly corrosion resistant materials (titanium) for high temperature environments in the presence of nitric acid and acetic acid. Heat exchangers susceptible to fouling (primarily distillation column reboilers) have been provided with 2 parallel, 50% capacity units such that one heat exchanger can be taken out of service and cleaned while the plant remains operating at reduced production rate. Sufficient volume has been provided in reactors containing fixed bed catalyst to allow operation for the two year intended period. Key reactors have also been designed as two parallel, 50% each capacity units.

Reciprocating Machinery Drivers

Rotating machinery under 1,000 bhp is designed to be driven by 480 volt, 3-phase induction motors. Driver requirements above 1,000 bhp are provided by back pressure steam turbines. For this project, there are two large vacuum compressors on the aqueous crystallization units. Both compressors are driven with steam turbines. Emergency facilities (firewater pumps, safety shower water, and back-up generators are driven by diesel engines.

Maximum return on investment

To be appropriated by management, any discretionary capital investment such as a grassroots chemical plant requires an adequate return on investment (ROI). Beyond the necessary facilities to provide a safe and efficient operating plant, we have incorporated obvious heat integration opportunities when presented by the design conditions. However, we have intentionally not incorporated in our design (and its cost) discretionary energy conservation opportunities that may or not be economically justified by site-specific conditions.

An inherent characteristic of the purification train is the redundant dilution and then reconcentration of adipic acid in water to drive off impurities such as other dicarboxylic acids

(succinic acid, glutaric acid) and monocarboxylic acids (valeric acid and caproic acid). A site and project-specific PINCH analysis would identify opportunities for heat integration, while a detailed analysis of the composition of dilute waste water streams would identify opportunities for recovery and recycle. Such analysis is beyond the scope of this project.

Buildings

Process equipment will be located outdoors, rather than in buildings. There will be localized enclosures for motor control centers and instrument sheds. The project will be provided with a centralized process control building containing four process operator work stations, two non-operator engineering work stations, and offices for plant and control engineers. The project will be provided with an administration building, a maintenance shop, cafeteria, and a security building. Large process compressors will be housed in roof covered but open sided building structures.

It is not intended for this plant to have its own fire house, or fire engines.

Security and Vulnerability Analysis

A number of governments require large chemical manufacturing facilities to comply with regulations involving security vulnerability analysis. These involve both design considerations and operating considerations. In the United States, events surrounding September 11 have resulted in the Chemical Security Act of 2003. Subsequent terrorist activities blowing up hydrocarbon facilities and pipelines in Saudi Arabia, Iran and Iraq have demonstrated the need to consider the design, layout (e.g., buffer zones), chemicals storage, operation, fencing, employee background checks, and in-plant access to facilities such as hydrocarbon processing facilities that are vulnerable to attack either by terrorists or by disgruntled employees and ex-employees.

The design of facilities in this report conforms to the security and vulnerability analysis guidelines prepared and documented by the following agencies:

- American Chemistry Council (Site Security Guidelines for the US Chemical Industry), in concert with SOCMA and the Chlorine Institute
- API and NPRA (Security Vulnerability Assessment Methodology for the Petroleum and Petrochemical Industries)

IHS Chemical PEP Review 2002-1 (December 2003), "Security Vulnerability Assessments for the Chemical Industry: Proposed Legislation in the United States and Methods for Addressing Relevant Security Concerns" provides the guidelines used in preparing this design.

Specific security measures incorporated into this design include:

- Plant layout that shields the chemical process facilities from easy access by locating non-hazardous site facilities (parking lots, administration building, wastewater treatment plant, cooling tower facilities, etc.) at the perimeter, with the chemical process facilities near the center.
- Limited access to the chemical process facilities (one process access gate).
- Secondary containment of large flammable gas storage tanks.
- Centralized warehousing of chemicals and catalysts/adsorbents.
- Secure perimeter fencing with remote camera supervision (electronic surveillance) and intrusion detection (motion) sensors.
- Reducing public visibility of the plant.
- Keeping large inventories of flammable chemicals outside the battery limits (ISBL) process area.
- Providing a firewall between the process area and main storage tanks in the field.

- Providing a trench around the process area.

Production Design Criteria

The plant designs provided by this effort are intended to operate instantaneously at full, 100% nameplate capacity. Annual production assumes a 90% overall capacity utilization factor. Production turn-down ratio capability for the ADA manufacturing plant is 50%. Spare parts and equipment are assumed to represent 10% of the FOB purchase cost of equipment, and represent vendor recommendations for spare parts (not spare systems).

The operating philosophy for the ADA plants is to maximize production consistent with running a safe and environmentally responsible plant that meets government requirements and industry ‘best practices’ for process safety and maximum pollution abatement that is economically sustainable. Given the technical key performance indices (KPIs) that dominate production economics, the intent is to minimize feedstock and energy unit consumption while meeting product specifications.

From a process design perspective, the objective is to also minimize capital costs for plant construction, which has the secondary benefits of reducing regular operations and maintenance costs required to keep the plant running at design conditions.

It is expected that scheduled plant turnarounds will occur every two years, while the provision of multiple reactors and redundant heat exchangers in dirty service provides the opportunities to keep the plant running at reduced capacity while individual reactors are taken out of service for catalyst change-out, and individual heat exchangers are taken out of service for surface area cleaning.

PLANT LOCATION FACTOR

The adipic acid manufacturing plants are assumed to be sited at grassroots facilities, rather than brownfield industrial sites that have been previously used. Our capital cost estimates incorporate factored estimates for offsite battery limits facilities required for operable plants, but do not include remote infrastructure investments such as highway extensions, port improvements, utility high voltage transmission lines, hazardous waste incineration facilities, or social amenities (construction worker housing, religious facilities, environmental set-asides).

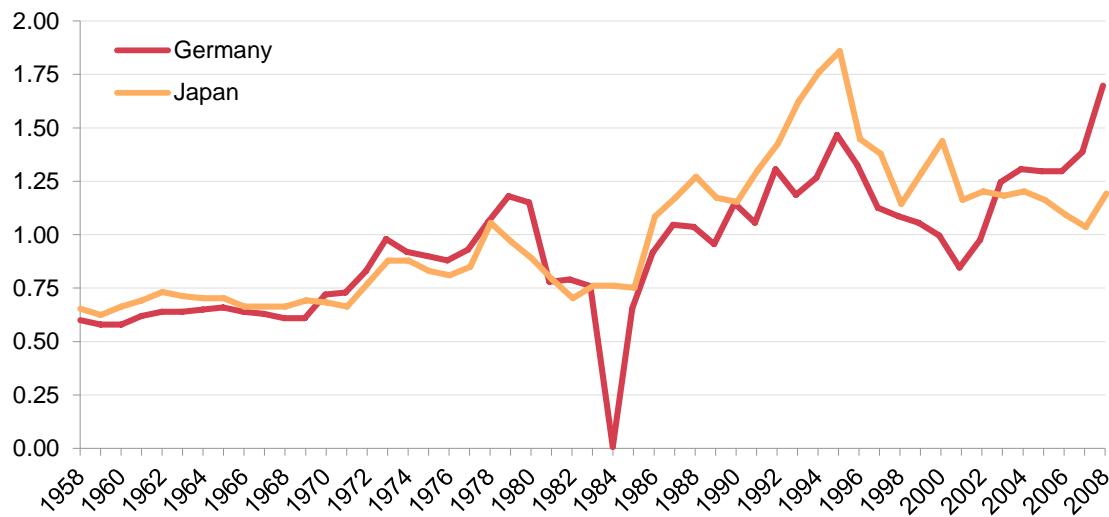
IHS Chemical capital cost estimates are based on mid-2012 US prices on the US Gulf Coast. IHS Chemical utilizes a ‘location factor’ that can be used to estimate the construction cost of a process plant in a regional location indexed to the US location used in this study. Mid-2012 location factors are presented below. The economic factor that dominates the difference in location factor between geographical regions is currency translation rates.

Table 6.1
CONSTRUCTION COST LOCATION FACTORS

Location	Location Factor
USGC	1.00
Alberta	1.15
Germany	1.50
Japan	1.45
Saudi Arabia	1.08
Mexico	1.06
Thailand	0.92
Colombia (coastal)	1.03
India	0.85

The following graph shows how the location factors for Germany and Japan have changed over an extended period of time. The high values post-2000 are mostly driven by currency exchange values between the euro, yen, and US dollar.

Figure 6.2
HISTORICAL LOCATION FACTORS FOR GERMANY AND JAPAN

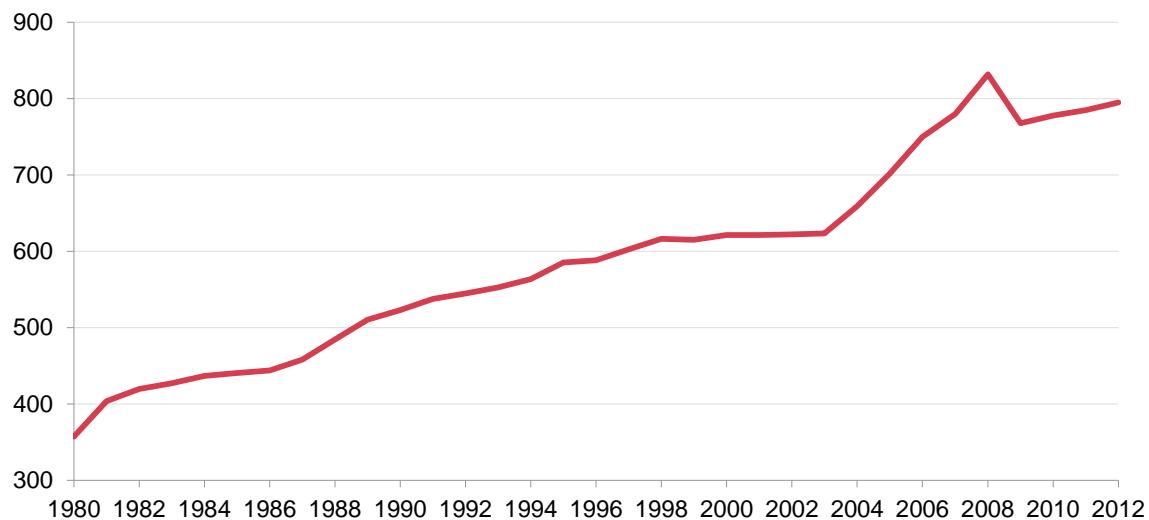


PEPCOST FACTOR

The capital costs estimated for this project are based on a standardized, US Gulf Coast location. We have previously described in this section comparable construction cost location factors for other major regions of the world. IHS's PEP publishes an annual construction cost index for chemical and petrochemical facilities that represents our judgment of current business

conditions in the engineering and construction industry. The PEP Cost Index used in this study is 795. Historic values for the index for the United States are presented in the graph below.

Figure 6.3
HISTORICAL VALUES OF US PEP COST INDEX



REGULATORY ENVIRONMENT AND EHS STANDARDS

The design and operation of the manufacturing plants will conform to ISO 9000 standards for quality, ISO 14,000 for environmental protection, and ISO/OHSAS 18000 for occupational health and safety.

It is assumed that the environmental, health and safety standards for building the proposed assets, and then operating them at commercial scale, will represent current practice in EU countries or the United States. Wastewater will either be treated onsite using tertiary treatment technology to achieve 95% removal of BOD/COD, the elimination of suspended solids to 20 ppmw, and 100% removal of hazardous materials. Non-hazardous solid waste will be removed and disposed of by an approved landfill operator. Hazardous materials will either be incinerated onsite, or removed by a licensed hazardous waste treatment firm. Atmospheric emissions of process gases will be, at a minimum, caustic scrubbed, passed through a bed of activated carbon, and only then vented. Process gases with high concentrations of combustible gases will be separately collected, directed to a catalytic oxidizing facility, and then discharged. Process flares will only be used for emergency releases, and not routine operating emissions. Safety standards will include industry-accepted process safety management analysis, incorporation of HAZOP analysis, and conform to the OHSAS 18001 standard for process safety and worker protection.

It is expected that plans for facilities will have undergone environmental impact reviews, have been approved by government regulatory agencies, and are built and operated in conformance with government permits.

CONSTRUCTION METHODOLOGY

The basis used for design and construction cost estimating in this project is conventional field fabrication (stick built plants), rather than shop fabricated modules that are subsequently

shipped to the site for installation. Module size is limited by highway restrictions on vehicles that transport the process modules. These limitations are on the order of 40 feet long and 12 feet high.

The prevailing industry practice is to modularize relatively small process components that are piping and instrumentation intensive (small furnaces and fired heaters, rotating equipment such as compressors, process drivers, control houses, motor control centers). The project philosophy stresses field fabricating physically large or high pressure (and heavy wall) process equipment (process furnaces, fired heaters, chemical tankage).

OFFSITE FACILITIES

IHS's capital and manufacturing cost estimates are based upon the use of AACE (Association for the Advancement of Cost Engineering International) Class-3 process design information for inside-battery-limits (ISBL) process facilities, and factored estimates for offsite and infrastructure facilities. The kind of offsite and infrastructure facilities normally factored into IHS offsite costs are listed below, along with the specific offsite facilities that are incorporated in the capital and operating cost estimate for this project.

Table 6.2
IHS OFFSITE CAPITAL COST COMPONENTS

ADA	ADA
Cooling Water Supply	√
Process Water Supply	√
Boiler Feed Water Preparation	√
Steam Generation	√
Inert Gas Generation	√
Instrument Air Plant	√
Feedstock and Product Storage	√
Fencing and Plant Security	√
Laboratory	√
Administrative Building	√
Storehouse	√
Maintenance Warehouse and Shop	√
Fire Fighting Facilities	
Rail and Truck Loading	√
Extra Catalyst Charges	√
Maintenance Vehicles	√
Car/Truck Fleet	√
Polymer Warehouse and Loading Dock	
Wastewater Treatment Plant	√
Process Waste Incinerator	√
Safety Flare and Flare Header	√
Fuel Gas Header	√
Religious/Cultural Facilities	
Safety/Health Care Facility	√
Cafeteria	√
Training Facility	√
Electricity Generation	
Power Distribution & Letdown Transformers	√
Sanitary Facilities	√
Air Separation Plant	
Desalinated Water Facility	
Crude Oil Storage	
Pier/Jetty for Crude Receipts	
Refined Products Pier	
Liquids Loading Dock	√

Black Start Capability

Many industrial manufacturing plants are designed with 'black start' capability. This means that the project scope of work includes facilities to provide all of the necessary utilities, especially power and process steam without external resources. The ADA plants are not designed to operate with black start capability.

PROCESS CONTROL PHILOSOPHY

The overall approach to process control for the ADA manufacturing plants is to maximize automation for the twin purposes of minimizing labor and maximizing conformance with specifications. A comprehensive process control system such as Honeywell Experion or Invensys/Foxboro Aventis systems is assumed to be included in the project, and is included in the capital cost for the project.

Critical interlocks will be provided for safety and environmental protection. If parameters get out of the safe and recoverable working range, the process control system will over-ride the operator and automatically shut the process down according to pre-established and preprogrammed sequences.

The control system is expected to be entirely digital (no analog), and use electrical solenoid rather than pneumatic control valve actuators. Distributed control systems will be utilized. Foundation Fieldbus architecture will be utilized to minimize the amount of bus wire and cable, and Hart protocols will be utilized for machine condition monitoring. Wireless facilities will be used where economically justified to provide information, but not for process control.

Project to Provide Machine Condition Monitoring Instrumentation

Most chemical process plants have spare in-line pumps; almost none have spare in-line compressors. A wealth of inexpensive, on-line machinery monitoring equipment can keep the unit up, reveal conditions that can be fixed without a shut-down, and prepare for an eventual machine tear-down by having the needed spare parts in hand when the casing is split. Most of the downtime associated with equipment failure is spent waiting for needed parts to arrive, rather than for tear-down, diagnosis, repair, or reinstallation. Machine conditioning instrumentation systems are provided in this project for:

- Vibration signature analysis
- Alignment sensors
- IR thermography for hot spots
- Electric motor load sensor (wattmeter)
- Power consumption sensors
- Lube oil analysis for contamination and acoustic wave viscometry
- Over speed protection
- Ultrasound sensors for equipment integrity
- Pressure ratio on compressors and turbines
- Differential thrust bearing temperature
- Specific fuel or electricity consumption

MATERIALS OF CONSTRUCTION

Due to the corrosion potential of adipic acid, the most suitable materials (284040) of construction and storage are austenitic stainless steels (>18% Cr + Ni + Mo). According to the American Iron and Steel Institute, the composition of 304SS is 18% chromium and 8% nickel.

Austenitic stainless steel contains (284041) between 16–30% chromium, and 3–22% nickel. At elevated temperatures ($>100^{\circ}\text{C}$), stainless steels and tantalum are no longer suitable for service (284042). In this environment, the recommended material is titanium. For the particular case of aqueous nitric acid, 310L stainless steel has been found to be particularly corrosion resistant, and cost competitive with 304L SS.

For elastomers used in seals and gaskets, Viton and Teflon have been found to provide acceptable service and long-term reliability.

ENGINEERING AND DESIGN STANDARDS

The most comprehensive set of engineering and design standards for the US-based organic chemical manufacturing industry have been established by the American Petroleum Institute (API). Other industry organizations that have established design and engineering standards relevant to ADA manufacturing are:

**Table 6.3
RELEVANT PROJECT STANDARDS SETTING ORGANIZATIONS**

API	American Petroleum Institute
ANSI	American National Standards Institute
ISO	International Standards Organization
ASTM	American Society for Testing Materials
ASME	American Society of Mechanical Engineers
NACE	National Association of Corrosion Engineers
IEEE	Institute of Electronic and Electrical Engineers
UL	Underwriters Laboratories
NEMA	National Electrical Manufacturers Association
NFPA	National Fire Protection Association
FM	Factory Mutual

Our design conforms to API standards for equipment in flammable service, and ASME pressure code standards for vessels and process piping. Electric power and process control systems conform to IEEE standards.

SITE-SPECIFIC DESIGN CONDITIONS

Design and cost calculations are based on an assumed plant location in the US Gulf Coast, and constructed in the year 2012. For utility calculations specific temperature assumptions are:

Table 6.4
TEMPERATURE DESIGN CONSIDERATIONS

Dry bulb air temperature	100°F (38°C)
Wet bulb air temperature	80°F (27°C)
Groundwater temperature	80°F (27°C)
Minimum winter temperature	20°F (-7°C)
Cooling water inlet temperature	90°F (32°C)
Cooling water temperature rise	20°F (11°C)

CAPITAL AND OPERATING COST BASES

Below, we outline the criteria for calculating capital investment and production costs, and the effect of the operating level on production costs.

Capital Investment

Equipment costs are estimated primarily from correlations developed by PEP and supplemented by vendors' estimates. If an equipment item is specialized or contributes substantially to the cost of the facility, a vendors' quote has been obtained if possible. When necessary, the costs are corrected to a PEP Cost Index of 795.

Direct installation costs are estimated by a modular method developed by PEP; the details are described in detail in PEP Report 145, Battery Limits Cost Estimating (April 1982). The indirect costs in capital investment are estimated by adding allowances for engineering, field expenses, overhead, purchasing, and contractor's profit. The bases for the estimation of these allowances are detailed in Section 7 of PEP Report 162, Computer Program for Estimating Plant Investment (March 1985). These indirect cost estimates are then added to the direct investment (FOB costs plus direct installation costs) to get the overall installed costs.

Investment in utilities is computed for the entire plant and allocated to each major operation according to use. Indirect costs for utilities and off-site tankage (generally raw material and product storage) are assumed to be 20% of the direct utilities investment.

General service facilities not directly associated with process operations are assumed to be 20% of the battery limits installed cost and utilities-plus-storage investment. An allowance for waste treatment facilities is also made. These allowances are determined prior to the addition of contingencies to the installed costs.

The total fixed capital for the facility includes total investment in battery limits, utilities and tankage, general service facilities, and a contingency. Usually the contingency is taken as 25% each of the battery limits investment and the off-site investment. All of the above investment estimates have been calculated with the aid of IHS Chemical's computer estimation program PEPCOST ver. 3.0.

In comparing IHS's estimates with actual plant costs or contractors' estimates, the following should be borne in mind:

- The processes may be the same generally but differ enough in detail to affect costs significantly.
- The estimates may not be strictly comparable because of omission of process sections (for example, by-product recovery) in one or another of the designs.

- Actual plants are frequently overdesigned for reasons unique to the particular situations.
- During periods of rapid escalation of equipment costs, and when long delivery times are anticipated, cost indexes probably are not an accurate reflection of actual costs.
- During periods of depression in chemical plant construction, equipment vendors and engineering contractors will provide goods and services at little or no profit.

IHS subdivides capital cost estimates into two segments: battery limits investment and offsites (utility) investments. The combination of these represents our estimate of "total fixed capital" cost. "Battery limits" in this evaluation means the process equipment, including that for feed treatment, product separation and purification, recycle handling, computer process control building, incineration of process wastes, and product packaging. "Offsites" means utilities (energy), bulk storage, and general service facilities such as administration buildings, bulk warehouses, maintenance buildings, security, environmental abatement, process flares, product and feedstock logistics (piers, loading racks, rail spurs), and fire protection.

Our analysis assumes international procurement of process equipment, without regard to import duties on such equipment. We assume that 30% of the investment cost of a typical plant is set by the international market. This portion corresponds to equipment and machinery, whereas construction labor and bulk materials are procured on a domestic basis.

Included in our capital cost estimates is a factored amount for basic engineering and detailed mechanical design, EPC construction contract, and non-tagged equipment such as bulk piping, foundations, instrumentation, and infrastructure such as roads, plant lighting, and pipe racks.

Our capital cost estimates do not include several key items that are often incorporated in the total capital project estimates of our client companies. We do not include capital cost provisions for:

- Owner's costs during construction
- Land purchases or site preparation
- Demolition of existing structures
- Process engineering or feasibility studies
- Cost of permitting or engineering required for permits (environmental impact statements, dispersion modeling, etc.)
- Process technology license costs
- Testing or laboratory analysis during construction (concrete break tests, equipment certifications, run-in tests, etc.)
- Interest on capital loans during construction
- Commissioning and training costs
- Plant guarantee tests (capacity, turndown, product specifications, etc.)

Project Construction Timing

Our capital cost estimate, and the pricing we employ for feedstock, chemicals and catalysts, energy costs, and utilities are based upon mid-year 2012. In estimating plant capital costs, we assume "overnight construction."

Available Utilities

Our design assumes that the ADA plant does not share common utilities with adjoining chemical plant complexes. The utilities included in this report that will be self-provided are:

- Cooling water
- Process water

- Process steam
- Boiler feed water
- Inert gas (N_2)
- Instrument air
- Fuel gas header (w/o compression)

The utilities that will be purchased are:

- Electricity
- treatment of sanitary wastewater

Production Cost Factors

The operating labor wages are based on estimated prevailing rates in Houston, Texas, multiplied by 1.10 to represent skilled oil worker direct wage rates in the United States. The base rate is derived from US national average rates in industrial chemical plants, corrected to the Houston area on a relative basis for production workers. With an allowance for fringe benefits and a 10% shift overlap assumed,, the effective total rate is \$42.54 per hour. The operating labor requirements have been estimated subjectively based on the number of major equipment items in the process. The number of men per shift includes the working supervisors. The cost of staff supervision—such as the assistant operating department manager, etc.—is assumed to be included in our allowance for plant overhead.

The total maintenance costs are estimated to be 3% of the battery limits investment, split evenly between maintenance labor and maintenance materials.

Plant overhead has arbitrarily been assumed at 60% of total labor. It includes all staff personnel located at the plant site, and services directly associated with plant operations and maintenance.

G&A, sales, and research costs are assumed for each product by making allowances for the stage of process development in estimating research expense, and for the character of marketing channels and technical service requirements in estimating selling expense. These estimates are customarily assigned a percentage of the sales value of the product, generally in the range of 2–5%. When actual prices are unknown, we base the G&A, sales, and research expense on the calculated product value (total production cost plus 25%/yr pretax return on fixed capital).For this project, we have assumed a corporate overhead rate of 3% of sales price, which we believe is consistent for process units like adipic acid that are primarily captive producers within an integrated nylon 66 facility.

The cost of taxes and insurance is calculated at 2% of total fixed capital. Depreciation is based on a book life of 10 years for fixed capital.

Feedstock, Product, and Energy Pricing

Our techno-economic analysis is based upon feedstock and product pricing as of mid-2012. In this environment, desired US crude oil prices have been targeted as between a range of \$70–100/bbl, with a desired average of \$90/bbl. As recently as mid-2003, actual crude oil prices were approximately \$30/bbl, and spiked up later in the decade to as high as \$149/bbl in mid-2008. The crude oil price range is based upon the average transaction price of a “marker crude” representing a basket of Middle East crude oils.

The natural gas price used for the economic analysis in this report is \$3.05/MM-Btu based upon the higher heating value (24,000 Btu/lb) of commercial specification pipeline natural gas in the United States at the Henry Hub terminal. A summary of utility unit cost factors is listed in the table below.

Table 6.5
PROJECT UTILITY UNIT COSTS

Process Water	\$0.2803/m ³
Cooling Water	\$0.0187/m ³
Electricity	\$60/mwh
Process Steam	\$8.28/mt
Fuel Gas	\$3.05/MM-Btu
Glycol Refrigeration	\$0.18/ton

Unit feedstock costs for project economics are listed below, and are based on mid-2012 US bulk costs on a contract FOB basis.

Table 6.6
PROJECT FEEDSTOCK UNIT COSTS

Raw Materials	US\$/mt	Raw Materials	US\$/mt
Adipic Acid	1,600	Glucose	300
Cyclohexane	1,250	Methanol	360
Nitric Acid	250	Verdezyne Enzymes	4,000
Caustic Soda (100%)	300	Ammonia	750
Boric Acid	1,050	Vitamins	3,500
Methanol	360	Other nutrients	600
Cobalt Naphthenate	4,200	Mixed Methyl Ester By-Product	500
Ammonium Vanadate	12,700	Hydrogen	565
Copper Nitrate	2,500	Acetic Acid	675
AGS By-Product	750	Caustic Soda	300
Mixed Methyl Ester By-Product	500	Hydrogen Bromide	2,000
		Ethyl Acetate	1,400

Effect of Operating Level on Production Costs

Variations in production costs with plant capacity and with operating rate are based on the following assumptions:

- The annual costs of process plant operating labor, control laboratory labor, and operating materials are invariant with plant capacity. Also, the entire process plant labor force remains on the payroll when the plant is operating at reduced capacity or is shut down.
- Investment-related items, including maintenance labor, maintenance materials, taxes, and depreciation, are directly proportional to investment, and their annual cost remains constant with reduced operating rate.

- Corporate overhead charges are constant to various plant capacities, and the annual allocation is also constant, regardless of plant operating rate.
- Production costs generally do not include any allowance for packaging or shipping; i.e., they represent bulk costs, fob plant.
- Working capital is not included in the fixed capital cost, nor are start-up costs. Interest on working capital is not included in the production cost or in the product value.
- Royalties are not included in any of the estimates. Royalties for any given licensed process may vary considerably, depending on terms of the agreement, geographic location, etc. Initial payments or paid-up royalties may be substantial, and they should be considered in specific estimates.
- Annual costs for raw materials and utilities are directly proportional to the annual plant production.

In accordance with the last assumption, unit costs for raw materials and utility consumption do not change with either plant capacity or operating rate.

Project Design Capacity

Design capacity for each of the three adipic acid technologies presented is 160 thousand metric tons per year, assuming a 90% service factor. We believe that this value represents the upper end of the largest commercially available, single process train plants.

FEEDSTOCK AND PRODUCT SPECIFICATIONS

Adipic Acid Product

Adipic acid is sold into the marketplace in three basic grades: high-purity resin grade (>99.6% purity) for copolymerization with HMDA to make nylon 66, food grade, and mixed grade for ester production. Resin-grade adipic acid requires conformance with 5 major specification requirements: 1) purity, 2) color, 3) water content, 4) ash content, and 5) iron concentration. Color specifications are used to indicate the presence of contaminants at very small concentrations that can reactivate the nylon catalyst. Water is present in the nitric acid oxidation reactant, and must be removed to avoid deactivation of the nylon catalyst. Iron contamination in adipic acid product is normally associated with corrosion caused by nitric acid, and can result in both nylon catalyst deactivation, and also putting product nylon 66 off-specification.

Adipic acid is commercially produced on large scale with a purity of 99.7%+ because of the extreme sensitivity of polyamide synthesis to impurities. Typical impurities include other acids (monobasic acids and lower dibasic acids) (60 ppm), nitrogenous materials, trace metals such as iron (2 ppm) and other heavy metals (10 ppm), arsenic (3 ppm) and hydrocarbon oil (10 ppm) impurities. Our design is capable of producing fiber-grade adipic acid consistent with Invista's product specification for adipic acid, as shown in the table below.

Table 6.7
ADIPIC ACID FIBER-GRADE PRODUCT SPECIFICATION

Specification	Limit
Adipic Acid, wt%	99.7 min.
(Assay)	
Water, wt%	0.2 max.
Ash, ppm	2.0 max.
Iron, ppm	0.5 max.
Methanol Solution Color, APHA	6.0 max.
Total Nitrogen (TN), mpm*	15.0 max.
ppm	1.5 max.

* moles per million moles (mol/106 mol).

Cyclohexane Feedstock

Cyclohexane purchased and used as the primary feedstock for the two-stage air and nitric acid oxidation technology to produce adipic acid is required to satisfy the following specification.

Table 6.8
CYCLOHEXANE FEEDSTOCK SPECIFICATION

Property	Sunoco Specification	ASTM Test Method
Composition		D3054
Cyclohexane, Wt%	99.9 Min	
Benzene, Wt. ppm	20 Max	
Total Aromatics, Wt. ppm	150 Max	
Methylcyclopentane, Wt. ppm	200 Max	
Methylcyclohexane, Wt. ppm	200 Max	
Color, Pt-Co Scale	10 Max	D1209 or Equiv.
Total Sulfur, Wt. ppm	1 Max	D4045
Free Water	None	Visual

Glucose Feedstock

Glucose purchased and used as the primary feedstock for both the Verdezyne fermentation process for producing adipic acid, and the Rennovia catalytic process for producing adipic acid, is required to satisfy the following specification.

Table 6.9
GLUCOSE FEEDSTOCK SPECIFICATION

Appearance	Clear Liquid
Taste	Sweet, Bland
Odor	Characteristic
% Dry basis	
Dextrose	99.0
Fructose	0.1
Maltose	0.6
Maltotriose	0.2
Higher saccharides	0.1
Fermentables %	99.5
Refractive index at 20°C	1.4629–1.4653
Refractive index at 45°C	1.4581–1.4604
Total solids (%)	70.5–71.5
Moisture %	28.5–29.5
Sulfated ash %	0.05 max

ADIPIC ACID PRODUCT PACKAGING AND SHIPPING SPECIFICATIONS

Adipic acid is sold and transported in 20–25 kg bags, usually on 1-metric ton pallets, and also in bulk containers such as 1-ton collapsible containers, 20-ton and 40-ton bulk containers. Due to corrosion potential, adipic acid is shipped in aluminum or stainless steel containers. The modular packaging unit provided in this design is capable of packaging ADA in each of these modes.

7 ADIPIC ACID FROM CYCLOHEXANE VIA CONVENTIONAL TWO-STAGE OXIDATION PROCESS

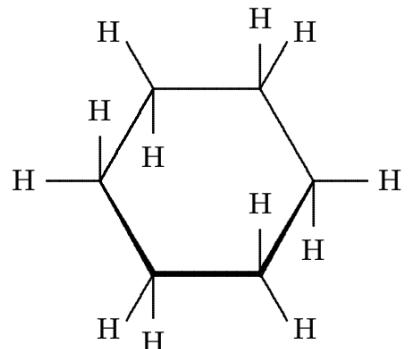
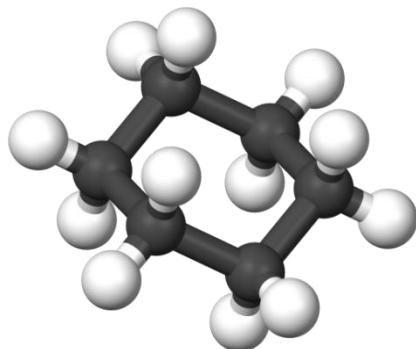
This section presents our design of a 160 kty adipic acid plant from cyclohexane utilizing conventional two-stage air and nitric acid oxidation technology, and enhanced with boric acid. We have chosen the basic DuPont/Invista process, with upgrades in technology to improve conversion and selectivity, additional recovery of by-products to commercially salable products, and destruction of nitrous oxide (N_2O) via two-stage incineration to N_2 plus O_2 . Our process recovers both AGS as a salable by-product, and mixed methyl ester by-product.

Based upon the design, we have also estimated the capital cost to build a plant, and the expected production costs to operate the plant. The bulk of the process configuration is based upon DuPont process technology as revealed in the patent, technical and trade literature, and supplemented with boric acid enhancement technology as patented by Halcon/Scientific Design and enhanced by several other adipic acid operating companies. We have also contacted other adipic producers to identify other elements of current manufacturing technology that represent the current (as of 2012) state of the art.

CYCLOHEXANE PROPERTIES AND DESIGN ISSUES

Our design is based upon using cyclohexane (CAS 110-82-7) as the fundamental feedstock for producing adipic acid using conventional two-stage oxidation technology. The physical structure of the cyclohexane molecule is shown in the figures below.

**Figure 7.1
PHYSICAL STRUCTURE OF CYCLOHEXANE MOLECULE**



Cyclohexane Sourcing and Specifications

Cyclohexane is widely available in the global market. The 10 largest producers of cyclohexane in the world are listed below, in descending order of nameplate production capacity. A more comprehensive listing of cyclohexane producers can be found at the end of this section of the report.

Table 7.1
MAJOR CYCLOHEXANE PRODUCERS

Producer	Location	qty
Chevron-Phillips	Port Arthur, TX, USA	481
Sabic	Wilton, UK	300
ExxonMobil	Rotterdam, Netherlands	280
Conoco-Phillips	Sweeny, TX, USA	272
BP	Lingen, Germany	270
Flint Hills Resources	Port Arthur, TX, USA	265
Idemitsu Kosan	Chiba and Shunan City, Japan	240
ExxonMobil	Singapore	227
Japan Energy	Aichi, Japan	220
PTT Aromatics and Refining	Rayong, Thailand	200

Cyclohexane is commercially sold as a single grade, often called polymerization grade, at an industry accepted purity of 99.9 weight percent. The American Society of Testing Materials (ASTM) has established an industry standard (ASTM D5309) for cyclohexane purity called 'cyclohexane 999.' Provided are composition limits on benzene, n-hexane, methylcyclohexane, methylcyclopentane, sulfur, appearance, color and distillation range. A representative product specification for cyclohexane is shown below, as sold by Chevron-Phillips Chemical Company.

Table 7.2
CHEVRON-PHILLIPS CYCLOHEXANE SALES SPECIFICATION

Property	Units	Value	Method
Purity, minimum	Weight %	99.9	ASTM D3054
Methylcyclopentane, maximum	mg/kg	150	ASTM D3054
Methylcyclohexane, maximum	mg/kg	200	ASTM D3054
Sulfur, maximum	mg/kg	1	ASTM D4045
Color, maximum	Pt-Co Scale	10	ASTM D1209
Distillation range including the temperature 80.7°C at 101.3 kPa (760 mm Hg) pressure	°C	1–1.1	ASTM D1078
Benzene, maximum	mg/kg	50	ASTM D3054

Physical Properties of Cyclohexane and Design Implications

Relevant physical properties for cyclohexane are listed in the table below. Three properties are particularly important with respect to process design: 1) cyclohexane is immiscible in water, 2) cyclohexane has a relatively high freezing point (6.5°C), and 3) cyclohexane is highly flammable. The first property allows mixtures of water and cyclohexane to be effectively separated in a

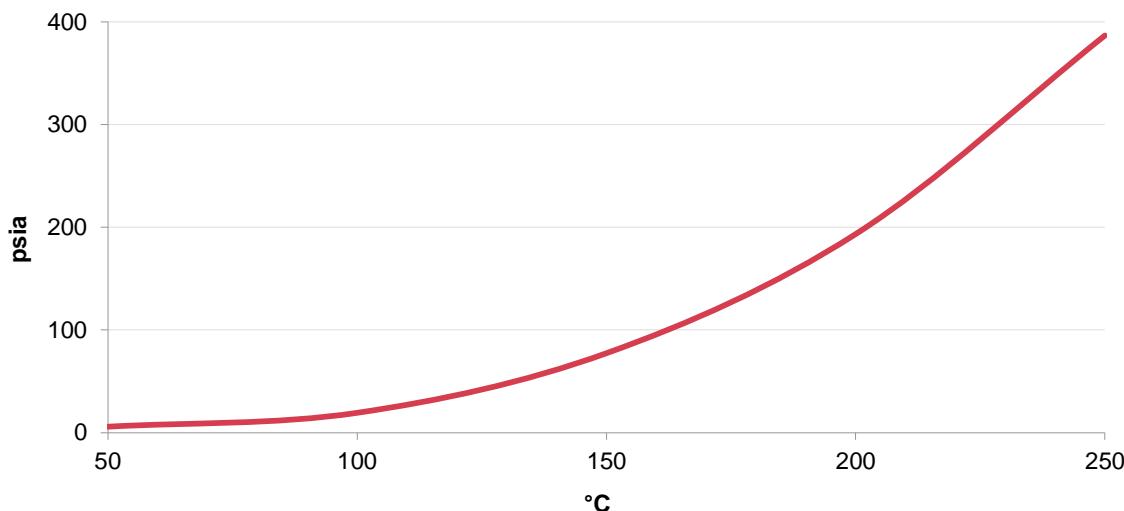
quiescent separating drum, rather than requiring fractional distillation. The high freezing point requires that in most geographies the potential for freezing at 6.5°C will require heated and insulated tankage with insulated and traced process piping. At room temperature, cyclohexane has a viscosity comparable to water (1.02 cP), and is thus easily pumpable. The high flammability of cyclohexane requires that equipment design conform to API design standards, in order to minimize the potential for atmospheric leaks, spillage, and/or ignitable vapor clouds. Cyclohexane should only be contacted in well ventilated spaces that are protected from sparks or open flames. Cyclohexane is not believed to be a significant toxicological, carcinogenic, or reproductive risk when properly handled.

Table 7.3
PHYSICAL PROPERTIES OF CYCLOHEXANE

Parameter	Units	Value
Physical state		Clear Liquid
Formula		C ₆ H ₁₂
Molecular weight	g/mol	84.16
Density (Liq)	g/ml	0.779
Boiling point	°C	80.7
Freezing point	°C	6.5
Triple Point	°C	6.55
Critical Point	°C	281
Viscosity (@ 17°C)	cP	1.02
Dynamic viscosity	Pa-s	8.94 x 10 ⁻⁴
Vapor pressure	mmHg	168.8
Flash point	°C	-18.33
Autoignition temperature	°C	245
Surface tension	N/m	0.02499
Solubility in water	gm/l	Immiscible
Refractive index		1.426
UV cutoff wavelength	nm	210
Lower explosive limit	% conc	1.2
Upper explosive limit	% conc	8.3
Critical pressure	Psia	598
Vapor density (air=1)		2.9
Di-electric constant	@20°C	2.024

The boiling point curve for cyclohexane appears in the figure below. At atmospheric pressure (760 mmHg), cyclohexane boils at 80.7°C, which is below the boiling point for water. Cyclohexane's boiling point increases gradually with increasing pressure.

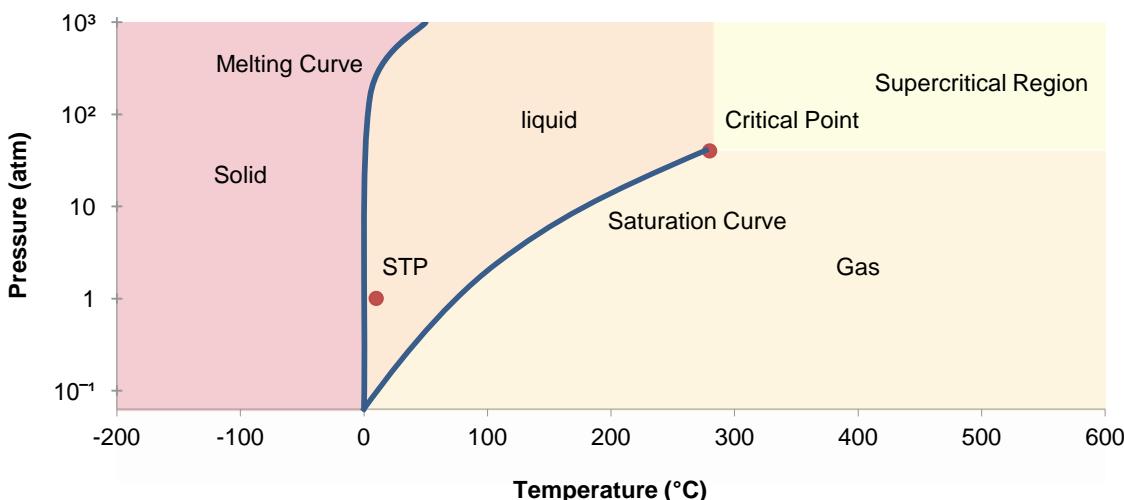
Figure 7.2
CYCLOHEXANE BOILING POINT CURVE



Source: CRC Handbook of Chemistry and Physics, 44th ed.

The phase diagram for cyclohexane is shown in the figure below. The relatively high freezing point of cyclohexane (6.5°C) is relatively insensitive to pressure. Since the optimal temperature for the air oxidation of cyclohexane to KA oil is between $125\text{--}165^{\circ}\text{C}$ (depending on catalyst selection, and whether boric acid is used as a yield enhancer, the oxidation reactors must be operated at elevated pressure (50–100 psia) to avoid vaporization and maintain the reactor mixture in the liquid state.

Figure 7.3
CYCLOHEXANE PHASE DIAGRAM



Source: WolframAlpha

Thermodynamic Properties of Cyclohexane and Design Implications

Thermodynamic properties of cyclohexane are presented in the table below. While the heat of reaction to form KA oil is relatively modest (-294 kJ/mol), over oxidation that could lead to combustion is more than 10x higher (-3,920 kJ/mol), requiring significant safety and design provisions to minimize the chance of over oxidation, that would certainly cause a reactor thermal runaway. Also note that there is a small but measurable heat of crystallization, requiring that energy be added to the crystallization process, or the temperature of the crystallizing solution will decrease.

**Table 7.4
THERMODYNAMIC PROPERTIES OF CYCLOHEXANE**

Heat of combustion	-3,920 kJ/mol
Heat of vaporization	32 kJ/mol
Heat of crystallization	2.68 kJ/mol
Heat of reaction to KA oil	-294 kJ/mol
Heat of formation	-156 kJ/mol
Specific heat capacity (vapor)	105.3 J/mol-K
Specific heat capacity (liquid)	156 J/mol-K
KA oil heat of reaction	-294 kJ/mol

Cyclohexane Bulk Storage Considerations

Due to its high freezing point, cyclohexane needs to be stored in a heated and insulated tank with agitation. Although cyclohexane only exerts modest vapor pressure, most environmental authorities will require that it be stored in floating roof tanks, with a nitrogen blanket on the vapor space between the floating roof and the fixed roof, in order to minimize fugitive volatile organic hydrocarbon (VOC) emissions across the floating roof seals.

With a boiling point of 80.7°C, bulk storage of cyclohexane should be done using API welded steel tanks (API 650) designed for hydrocarbon service, with floating roofs based upon the relatively low boiling point (and relatively high vapor pressure) of cyclohexane. In cold climates, the freezing point of cyclohexane at 6.5°C requires a means of maintaining tankage and process piping above this temperature. In cold climates, cyclohexane tanks should be equipped with an internal heater and recirculation mixer to avoid solidification.

Cyclohexane standards for safe transport, distribution, storage and use are well documented in the Chevron-Phillips publication, "Tank Truck Product Integrity Protection Guidelines for Styrene, Cyclohexane, Polyalphaolefins, and Normal Alpha Olefins" prepared by Chevron-Phillips Chemical Company LP (284043). Acceptable and unacceptable prior cargo materials are listed in the table below.

Table 7.5
CYCLOHEXANE PRIOR CARGO RESTRICTIONS

Unacceptable Prior Cargo	Acceptable Prior Cargo
Adhesives	Aviation fuel
Animal Oil	Caustic soda
Crude Oil	Diesel fuel
Dark colored products	Fuel oil
High sulfur organic chemicals	Gasoline
Latex	Inorganic acids
Lube oil	Organic acids
Naphtha, natural resin	Oxygenates
Paint	Water soluble synthetic resins
Strong odor	
Water insoluble synthetic resins	
Vegetable oil	
Waxes	

Source: Chevron-Phillips Chemical Company

Cyclohexane can be safely stored in bulk tankage made of stainless steel or aluminum (284044). Cyclohexane is provided in bulk quantities by commercial companies at very high purity, limiting the concerns associated with managing contaminants in the processing of cyclohexane to KA oil. Primary contaminants of concern are water, sulfur, and benzene.

Cyclohexane Feedstock Specification

Our design is based upon a cyclohexane as presented in the table below from Sunoco. This specification represents an industry standard, and is also consistent with product specifications from Chevron-Phillips, BASF, ExxonMobil, and CITGO.

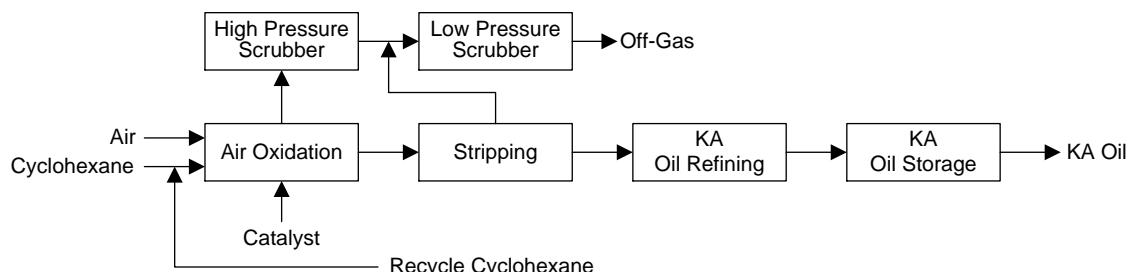
Table 7.6
PROJECT CYCLOHEXANE FEEDSTOCK SPECIFICATION

Property	Sunoco Specification	ASTM Test Method
Composition		D3054
Cyclohexane, Wt%	99.9 Min	
Benzene, Wt. ppm	20 Max	
Total Aromatics, Wt. ppm	150 Max	
Methylcyclopentane, Wt. ppm	200 Max	
Methylcyclohexane, Wt. ppm	200 Max	
Color, Pt-Co Scale	10 Max	D1209 or Equiv.
Total Sulfur, Wt. ppm	1 Max	D4045
Free Water	None	Visual

PROCESS DESCRIPTION

Our process design for adipic acid uses the boric acid enhanced air oxidation of cyclohexane in the liquid phase to KA oil, followed by nitric acid oxidation of KA oil to adipic acid. Purification of adipic acid is effected primarily by two-step suspension crystallization (first in nitric acid, second in water) followed by concentration in a pusher centrifuge, then drying and packaging of the crystalline product using rotary dryers. An overall block flow diagram for the air oxidation of cyclohexane to KA oil is shown in the figure below.

Figure 7.4
AIR OXIDATION OF CYCLOHEXANE TO KA OIL BLOCK FLOW DIAGRAM



Overall design basis assumptions are provided in the table below.

Table 7.7
CYCLOHEXANE TO ADIPIC ACID—OVERALL DESIGN BASIS

	Air Oxidation	Nitric Acid Oxidation	Crystallization	Overall
Feedstock	Cyclohexane	KA oil + 60% HNO ₃	Adipic acid	
Molar Selectivity	90%	95%	96%	82%
Mass Selectivity Stoichiometric (mt/mt)	0.84	0.68	1.00	0.57
Mass Selectivity Design (mt/mt)	0.93	0.72	0.96	0.70
One-Pass conversion	14%	99%	96%	na
Significant By-Products	Glutaric + succinic acid (5%) CO/CO ₂ degradation products (5%) Monocarboxylic acids (2%)	Glutaric + succinic acid (2%) Nitrous oxide (N ₂ O) Monocarboxylic acids (1%)		AGS (8%) Monocarboxylic acids (3%) CO/CO ₂ degradation products (5%)
Reactor Temperature	165°C	70/110°C		
Reactor Pressure	150 psia	50 psia		
Catalyst	Cobalt naphthenate	Ammonium vanadate + copper nitrate		
Process Enhancer	Boric acid		Dodecane dioic acid	
Reactor Design	4 CSTR in series	1 S&T + 1 CSTR in series	1-stage acid crystallization + 2 stages of aqueous crystallization	
Material of Construction	304L SS	304L SS/Ti	304L SS	304L SS/Ti

We have segmented the ADA plant into the following process sections:

- Section 100—Air oxidation of cyclohexane to crude KA oil
- Section 200—Purification of crude KA oil
- Section 300—Nitric acid oxidation of KA oil to crude adipic acid
- Section 400—Adipic acid crystallization
- Section 500—Adipic acid drying and packaging
- Section 600—By-product recovery to methyl esters
- Section 700—AGS by-product production
- Section 800—Nitrous oxide destruction

The primary design basis assumptions used for the front end design of the plant, where cyclohexane is oxidized by air to KA oil, are listed in the table below.

Table 7.8
DESIGN BASIS-AIR OXIDATION OF CYCLOHEXANE TO KA OIL

Design Parameter	Value
Reactor type	CSTR
Number of reactors in series	4
Type reaction	Isothermal
Coolant	CTW
Method of heat recovery	50 psia sat steam
Rx Design temperature (°C)	165
Rx Design pressure (psia)	150
Residence time (per reactor, min)	15
1-Pass overall CyHex conversion (%)	14
Catalyst	Co naphthenate
Air feed rate	Stoichiometric
Enhancer (1:6 molar ratio)	Boric acid

Section 100—Air Oxidation of Cyclohexane to Crude KA Oil

Cyclohexane Scrubbing

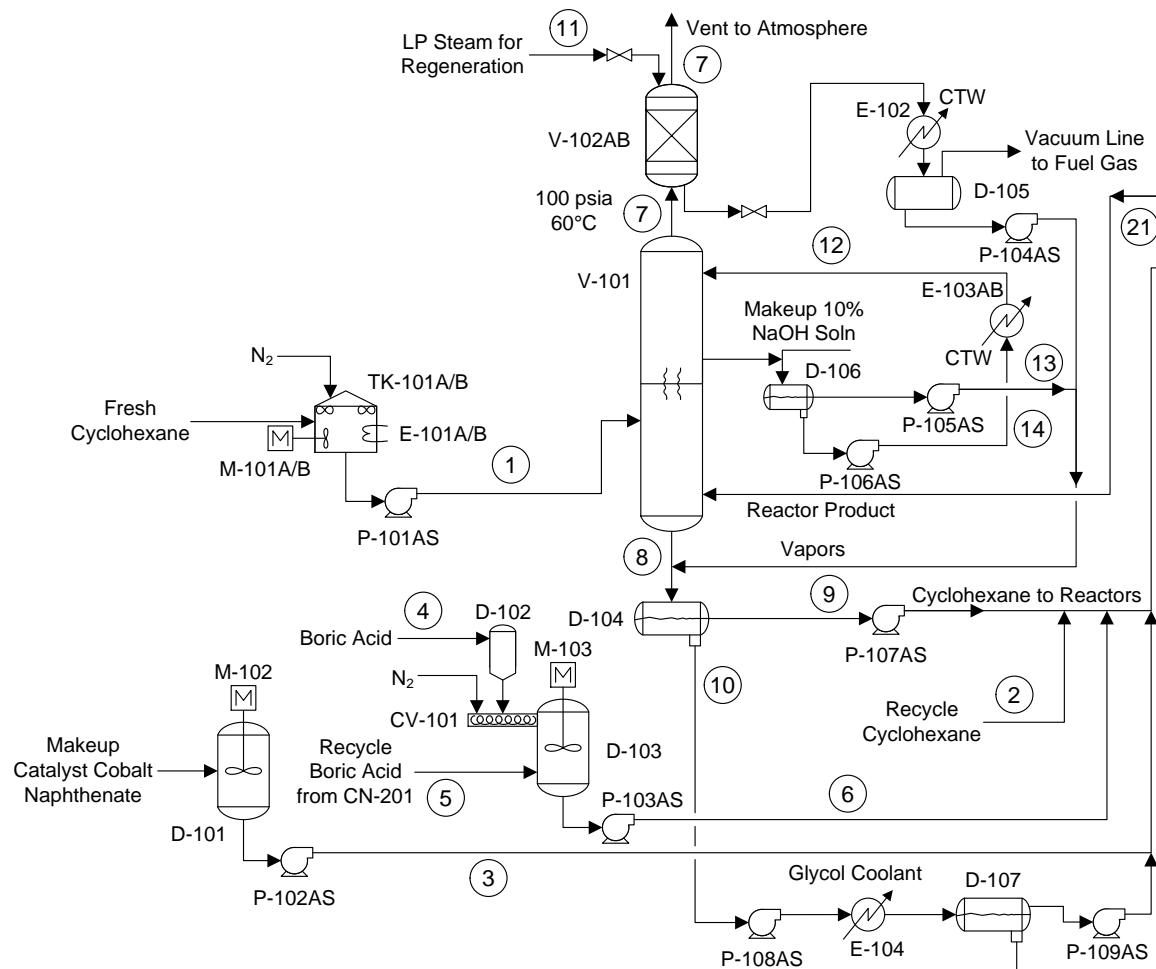
Fresh cyclohexane and recycle cyclohexane are stored in a 304L stainless steel day tank having 24 hour capacity. The tank is equipped with a floating roof and inert N₂ blanket in the space between the top of the floating roof and the bottom of the fixed cone roof. The tank has an internal bayonet steam heater, side entering mixer, and is insulated to minimize the potential for cyclohexane freezing during cold weather.

The mixed cyclohexane feed is preheated in a two-stage scrubber designed for counter-current flow of cyclohexane liquid feed (first stage) and dilute caustic solution (2nd stage) down the scrubber, and air oxidation reactor vapor product flowing up the scrubber. The cyclohexane preheating occurs in the first-stage bottom section of the scrubber. The purpose of the scrubber first stage is to use relatively cool cyclohexane liquid feed to condense residual hydrocarbon vapor (primarily cyclohexane) contained in the air oxidation reactor vapor product stream. The contents of the reactor vapor product stream are primarily unconverted cyclohexane, water formed by the oxidation of cyclohexane to KA oil, nitrogen from the air feed to the reactor, CO and CO₂ degradation products from the formation of glutaric acid and succinic acid, and small quantities of by-product monocarboxylic acids (valeric acid and caproic acid).

The second (upper) stage of the scrubber uses a dilute 10% caustic solution in process water to further cool the remaining vapor product gases from the first stage of scrubbing down to ambient temperature. By scrubbing the vapor stream at a lower temperature while also providing additional residence time, more residual hydrocarbons in the vapor phase from the air oxidation reactor product overhead stream will condense. The dilute caustic scrubbing solution is pumped

to the top of the 2nd stage of the scrubber through a heat exchanger first to remove heat in a pump around loop configuration. The caustic solution scrubbing liquid discharged from the bottom of the second stage of the scrubber is directed to a horizontal settling tank where an oil phase is expected to form above the caustic aqueous solution lower phase. The oil phase is expected to contain residual cyclohexane and possibly other hydrocarbons. The lower aqueous phase is expected to contain the caustic solution and a small quantity of soluble organic acids that have been neutralized by the aqueous solution to their corresponding sodium salts.

Figure 7.5



Activated Carbon Polishing Beds

The vapor stream discharged from the top of the 2nd stage of scrubbing still contains a minor quantity of volatile organic carbon (VOC) components that condense below the temperature of the scrubbing solutions. Most legal jurisdictions in industrial countries will not allow this stream to vent directly to atmosphere. To remove nearly all of the residual VOCs in the vapor stream, the stream is first passed through a bed of activated carbon for VOC removal. Two 100%

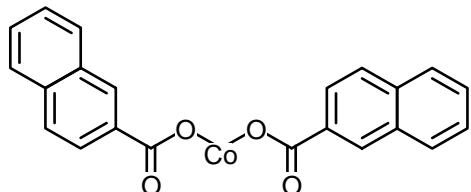
activated carbon containing columns are operated, such that one column can be online while the other is being regenerated via steam stripping. The stripping stream removes hydrocarbons from the activated carbon beds, and the stripping steam containing residual hydrocarbons is then passed through a heat exchanger to condense both the steam and condensable hydrocarbons, which are pumped from the receiving drum to the feed drum of the air oxidation reactors. Non-condensable hydrocarbon vapors in the stripping stream are discharged to the plant's vacuum line for use as fuel gas in the plant's utility steam boilers.

Cobalt Naphthenate Catalyst Addition

The catalyst used for air oxidation is conventional cobalt(II) naphthenate in homogeneous (liquid) form. It is formed as a metal salt of the corresponding naphthenic acid. The molecular structure for cobalt naphthenate is shown in the figure below. In pure form, cobalt(II) naphthenate is a solid. However, it is available commercially as a 6% cobalt concentration of 55% cobalt naphthenate and 45% mineral spirits in viscous liquid form for ease of handling. Cobalt(II) naphthenate is available commercially in many standard grades when applicable, including Mil Spec (military grade); ACS, Reagent and Technical Grade; Food, Agricultural and Pharmaceutical Grade; and Optical Grade. The ASTM standard for cobalt(II) naphthenate is D-600, Class B, 35EF-49.

Cobalt(II) naphthenate can be custom manufactured using cyclohexane as the diluent for use in adipic acid plants, in order to avoid the contamination that mineral spirits would present during processing. Our design is based upon cobalt naphthenate purchased as a solution in cyclohexane.

Figure 7.6
MOLECULAR STRUCTURE OF COBALT(II) NAPHTHENATE



Some operating companies provide the active cobalt in the form of cobalt acetate rather than naphthenate. Other catalyst formulations include the use of other active metal catalysts including chromium, manganese, and/or copper. The design catalyst addition rate is 1–3 ppm weight on total cyclohexane feedstock. The properties of cobalt(II) naphthenate are presented in the table below.

Table 7.9
COBALT(II) NAPHTHENATE PROPERTIES

Pure Form	Amorphous solid
Commercial Form	55% in mineral spirits as viscous liquid
CAS Number	61789-51-3
Formula	Co(C ₁₁ H ₇ O ₂) ₂
Molecular Weight	401.3
Boiling Point, °C	310–390
Melting Point, °C	140
Density, gm/cc	0.96
Flash Point, °C	48.9
Solubility in Water	Immiscible

Due to its high boiling point and immiscibility in water, cobalt(II) naphthenate catalyst will exit the cyclohexane air oxidation section of the process in the recycle tower in the bottoms product upper oil phase, which can be filtered and then recycled to the process. For our design, cobalt naphthenate will be supplied as a 55% solution of cobalt naphthenate in cyclohexane.

Boric Acid Addition

Boric acid (in crystalline or powdered solid form) is added to the cyclohexane feed to the air oxidation reaction section to enhance selectivity and increase conversion by forming an ester with produced cyclohexanol, in order to minimize the oxidative degradation of produced cyclohexanol to lower carbon number by-products. The patent literature suggests adding boric acid at a ratio of 1 mol of boric acid per 6 mols of KA oil being produced in the air oxidation section of the process. Properties of boric acid are listed in the table below. Boric acid is a weak acid with very low solubility in water and polar hydrocarbons (alcohols, aldehydes, and ketones). Boric acid is insoluble in covalent solvents like cyclohexane, and higher molecular weight oxygenates such as KA oil. Boric acid can be made slightly soluble in water by heating water to its boiling point. Pure boric acid is commercially available in high purity as a mined mineral in solid form. A typical commercial sales specification is provided below.

Table 7.10
TYPICAL BORIC ACID COMMERCIAL SPECIFICATION

Appearance	White crystals
Minimum Purity	99% wt
Phosphate Content	<0.001%
Sulfate Content	<0.005%
Insolubles	<0.005% in methanol
Ca Content	<50 ppm
Cl Content	<10 ppm
As Content	<1 ppm
Heavy Metals as Pb	<10 ppm

Physical properties of boric acid are provided in the table below. As a high boiling inorganic chemical, it must be slurried into cyclohexane feedstock used in producing KA oil. Due to its high boiling point, it will exit the KA oil purification train in the water layer, where it has a slight solubility. Boric acid can be recovered from the water layer by crystallization at ambient temperature.

Table 7.11
PROPERTIES OF BORIC ACID

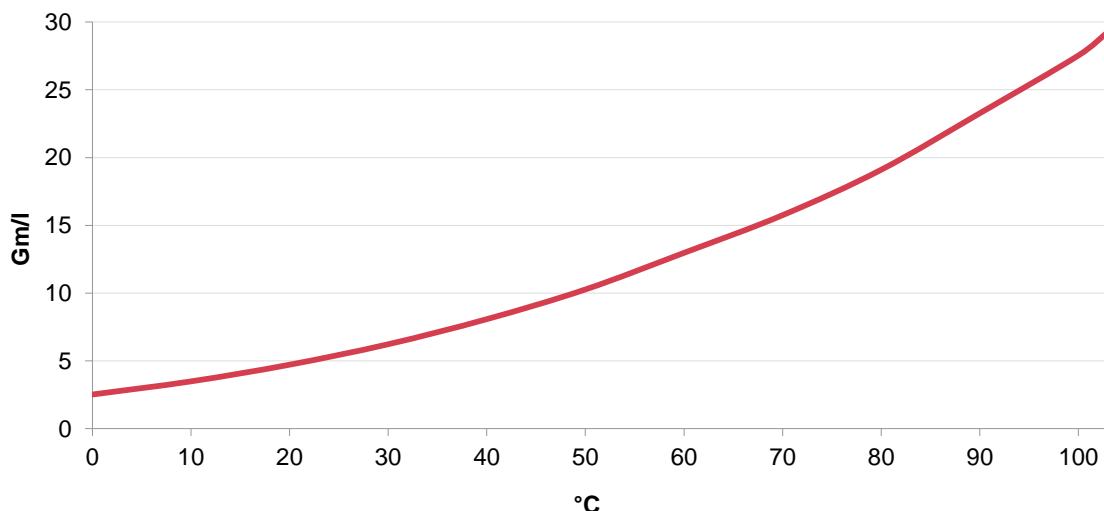
Form	White, crystalline solid
CAS Number	10043-35-3
Formula	H ₃ BO ₃ or B(OH) ₃
Molecular Weight	61.8
Density, gm/cm ³	1.435
Boiling Point, °C	300
Melting Point, °C	170
Commercial Purity	99.9%+ (hydrates)
Solubility in Water, gm/l	49.2

When heated, boric acid will first dehydrate, as it is often supplied as a hydrate. Further heating will cause the molecule itself to release water forming metaboric acid (HBO₂), as shown in the reaction below.



The solubility curve for boric acid in water is shown in the figure below.

Figure 7.7
BORIC ACID SOLUBILITY CURVE IN WATER



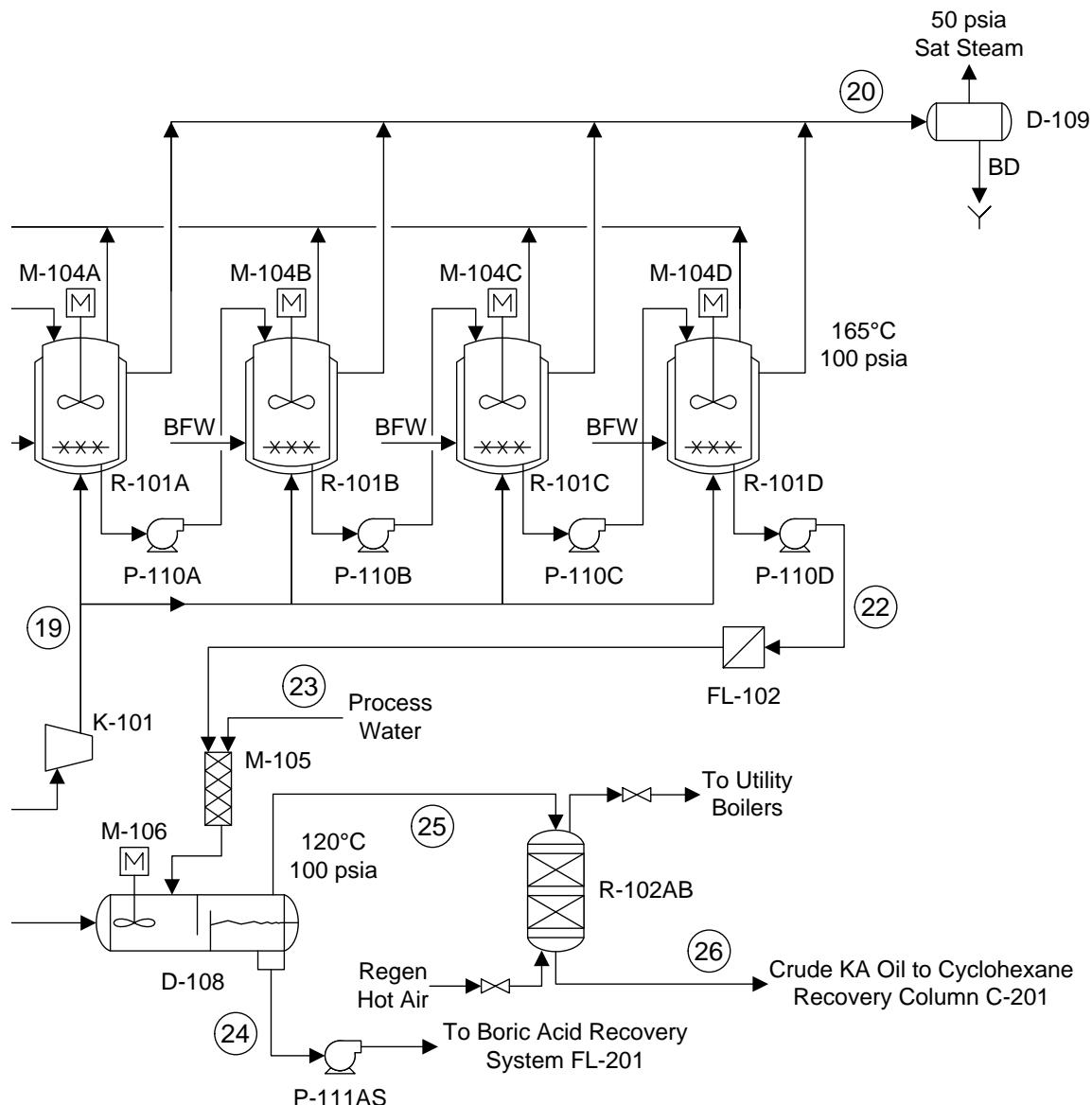
For this process, boric acid powder is slurried at low concentration in a tank of cyclohexane, and fed to the process at a rate of 10 weight % of cyclohexane feed. Following air oxidation, the liquid product stream containing an oil phase and a water phase is directed to a settling tank for phase separation. The water phase is cooled to room temperature in a heat exchanger, and boric acid is recovered from the aqueous stream via suspension crystallization followed by centrifugation. The recovered crystals are recycled to the process.

The primary ester formed by combining boric acid with principally cyclohexanol is tricycle hexyl borate. Its chemical formula is $C_{18}H_{33}O_3B$, and its calculated molecular weight is 307. Its boiling point at atmospheric pressure is 305°C. It is a solid at room temperature, and its melting point is 56.4°C.

Cyclohexane Air Oxidation Reaction to KA Oil

The preheated cyclohexane feed (containing both fresh feed and recycle cyclohexane) is combined with make-up liquid process catalyst (cobalt naphthenate) and make liquid boric acid (process enhancer), directed through a trim heater designed to heat the cyclohexane liquid stream to reaction temperature (165°C). The heated liquid stream is directed primarily to the first of four constantly stirred tank reactors arranged in series configuration. Smaller quantities of cyclohexane feed are also directly fed to the last three reactors. The reaction is designed to occur at 165°C and 150 psia. The total residence time is 60 minutes, nearly evenly distributed among the four reactors in series. Early versions of the process arranged the four CSTR reactors at different elevations so that flow between reactors occurred via gravity, eliminating the need for pumps. The Nupro air oxidation section had 6 reactors in series. Given the size of the CSTR reactors, and the degree of tight process control required to assure high selectivity, inter-reactor low head centrifugal pumps are used in our process configuration. The portion of the process flow diagram representing air oxidation is shown below.

Figure 7.8
AIR OXIDATION REACTION DIAGRAM



Fresh air is directed through a pulsed baghouse dust collecting filter, and fed to a single axial compressor designed to increase the air to a discharge pressure of 200 psia. The compressed air is discharged to a manifold that splits the air flow evenly to the four CSTR reactors. Compressed air enters the reactors from the bottom, and is fed to an air distribution grid at the bottom of each reactor that is designed to evenly distribute air upward.

The overhead vapor product stream from the reactors consists primarily of nitrogen from the feed air, CO/CO₂ degradation products from oxidation, unconverted oxygen from the air feed, unreacted cyclohexane feedstock, low molecular weight hydrocarbons from cyclohexane degradation, water vapor product from the reaction, and light oxygenated hydrocarbons. This

stream is scrubbed with cyclohexane feedstock (first stage) and dilute caustic aqueous solution (second stage).

Cyclohexyl Hydroperoxide (CHHP) Converter

Air oxidation reactor liquid product remains rich in intermediate product cyclohexyl hydroperoxide (CHHP), which can be further oxidized to a combination of cyclohexanone and cyclohexanol. CHHP can be quickly and efficiently oxidized almost entirely to preferentially cyclohexanone by using chromium oxide catalyst at elevated temperature and pressure. Rhone-Poulenc (USP 3927105), Stamicarbon (USP 4024630), and BASF (USP 4543427) have foundation patents for CHHP oxidation. The Rhone-Poulenc process uses a homogeneous chromium octanoate catalyst, while the Stamicarbon patent uses chromium oxide heterogeneous catalyst. A comparison of the approaches is shown in the table below.

Table 7.12
FOUNDATION PATENTS FOR CHHP OXIDATION

	Assignee		
	Rhone-Poulenc	Stamicarbon	BASF
USP	3927105	4024630	4543427
Catalyst form	Homogeneous	Heterogeneous	
Catalyst	Chromium octanoate	Chromium oxide	Cobalt oxide on zeolite substrate
Temperature (°C)	100–130	60–100	80–120
Pressure (atm)	1–25	1–20	Atm
Stages	2 to 6	1	1

The Rhodia and Stamicarbon patents recognize the need to remove free water of reaction that would otherwise deactivate the chromium catalyst. The BASF patent indicates that cobalt oxide catalyst is not adversely affected by the presence of free water. The Rhone-Poulenc patent presents a multi-bed reactor with inter-stage coolers and separating drums resulting in an oil layer and a water layer that can be separated. The separation removes free water from the feedstock. The Stamicarbon patent proposes the use of nitrogen sweep gas to remove water of reaction as a vapor as the water vapor is formed. Each of the assignees shown above, plus other companies in the adipic acid business, have subsequently patented additional discoveries that incrementally improve the basic technology for converting CHHP primarily to cyclohexanone. The US patents for cyclohexyl hydroperoxide conversion are listed below.

Table 7.13
SUBSEQUENT US PATENTS FOR CHHP OXIDATION

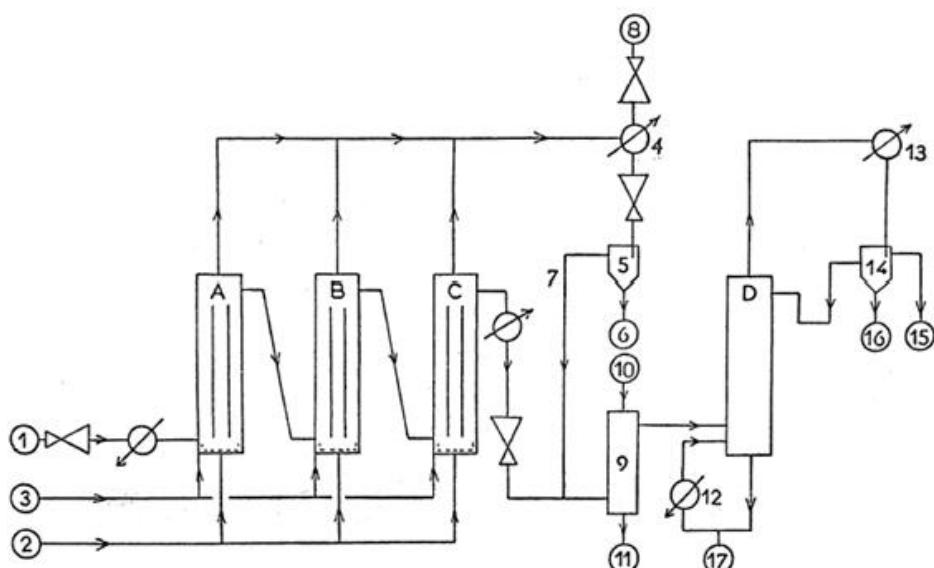
US Patent	Title
8026398	Catalysts Comprising a Combination of Oxidized Metals and a Method for Cleaving Phenylalkyl Hydroperoxides Using the Catalysts
7396961	Process for Catalytically Decomposing Organic Hydroperoxides
7081552	Catalysts for Cycloalkanes Oxidation and Decomposition of Cycloalkyl Hydroperoxide
6806390	Hydroperoxide Decomposition Catalyst
6677490	Method for Producing Alcohol/Ketone Mixtures
6284927	Hydroperoxide Decomposition Process
6160183	Direct Oxidation of Cycloalkanes
5905173	Process for Decomposing Cycloalkyl Hydroperoxide
5859301	Process for Preparing Alkanones and Alkanols
5672778	Process for Increased Yields of Oxygenated Products in Two-Step Oxidation of Hydrocarbons
5206441	High Rate Process for Preparation of Cyclohexanol and Cyclohexanone
5126505	KA Oil Recovery
5043481	Cyclohexane Oxidation
4551553	Decomposition of Hydroperoxides in the Presence of Homogeneous Binary Catalysts
4551553	Decomposition of Hydroperoxides in the Presence of Homogeneous Binary Catalysts
4543427	Preparation of Cyclohexanol and Cyclohexanone
4508923	Oxidation of Hydrocarbons
4503257	Cyclohexyl Hydroperoxide Decomposition Process
4499305	Process for Preparation of Cyclohexyl Hydroperoxide Decomposition Catalysts
4482746	Staged Catalyst Process for Cyclohexyl Hydroperoxide Decomposition
4465861	Process for Producing a Mixture Containing Cyclohexanol and Cyclohexanone
4326084	Process for Producing a Mixture Containing Cyclohexanol and Cyclohexanone from Cyclohexane
4322558	Oxidation Process
4250118	Process for the Preparation of Cyclohexanone
3927105	Process for the Preparation of Mixtures of Cycloalkanols and Cycloalkanones

Rhone-Poulenc (now Rhodia) recommends a CHHP conversion reactor temperature range between 100–130°C. Below this temperature, the rate of oxidation is slow. Above this range, CHHP has a propensity to oxidize to degradation products (C₅ and below hydrocarbons), reducing selectivity to desired KA oil. The Rhone-Poulenc processing scheme is shown in the figure below. In its patent, RP claims that heterogeneous CHHP conversion catalysts have a tendency to coat with polycondensates that deactivate active catalyst surfaces, and are therefore not suitable for commercial production plants. Catalyst addition is at a rate of one gram catalyst per kg of CHHP in the feedstock. The conversion process is moderately exothermic.

In the figure below, stream #1 is the cyclohexane-rich feedstock stream containing CHHP. Stream #1 is processed sequentially through three cylindrical reactors (A, B, and C). Homogeneous chromium octanoate liquid catalyst (stream #3) is fed to each of the three reactors in parallel. Nitrogen sweep gas (stream #2) is fed to the bottom of each reactor for the purpose of removing water of reaction as a vapor overhead product stream from each reactor. The reactor product gas is processed through a condenser (item #4) to reduce its temperature to 40°C. At this temperature, both cyclohexane and water will both form liquids that can be separated in a decanter (item #5) since the liquids are virtually immiscible. Water forms as a bottoms layer (stream #6) which is discharged to wastewater treatment, while cyclohexane forms a lighter oily liquid phase (stream #7) above the water phase in the decanter. Non-condensable gases (mostly N₂) are stream #8 and are vented from the process.

The condensed cyclohexane stream (#7) and the liquid product stream from the reactor are combined and directed to the bottom of an ammonia (stream #10) scrubber (item #9). The scrubbing action results in the production of a bottoms discharge aqueous stream (stream #11) that is discharged to the wastewater treatment plant. The hydrocarbon-rich product stream from the scrubber is directed to a distillation column (item #D) that drives a combined vapor stream of cyclohexane and water into the overhead product stream that is condensed (item #13) and decanted (item #14) to produce separate streams of hydrocarbon (stream #15) and an aqueous phase (stream #16)

**Figure 7.9
RHONE-POULENC PROCESS FOR CHHP CONVERSION (USP 3927105)**



Stamicarbon's foundation US patents for CHHP conversion (3987101, 4024630) recommend conducting the reaction below the thermal decomposition temperature (150°C) of CHHP. If allowed to occur, thermal decomposition of CHHP results in the production of degradation products (not KA oil or precursors) that seriously compromise selectivity and yield. Stamicarbon's heterogeneous catalyst is chromium oxide, and activity is increased by using Cr(+6) rather than Cr(+3). Loading of the chromium on the substrate is less than 15% by weight, and 10% loading is recommended. Since prior Japanese patents disclosed the use of a catalyst composition containing both chromium and copper, the Stamicarbon patents claim that their catalyst and

process is copper free. The range of adequate reaction temperature is 60–110°C. CHHP conversion to primarily cyclohexanone ranges between 95–100%. Reaction pressure is not critical to performance, but should be high enough to assure that at the reaction temperature the feedstock remains in the liquid phase. Stamicarbon recommends 4–50 atmospheres. To minimize catalyst deactivation, Stamicarbon also recommends a water wash step prior to reaction to remove contaminants from the air oxidation reaction. Stamicarbon's insight to catalyst deactivation was that it was caused primarily by the presence of free water from the air oxidation reaction, resulting in slow kinetics and worsening selectivity over time. To prolong catalyst activity, Stamicarbon's approach is to use stripping gas to remove water of reaction as an overhead vapor product stream from the CHHP conversion reactor. This will keep the water concentration below the saturation level. The patents suggest that air or CO₂ are both suitable stripping gases. Suggested reaction residence time is 30 minutes.

BASF has patented the standard approach (USP 4543427, 24-Sep-1985), using cobalt oxide catalyst on zeolite substrate technology rather than chromium oxide. For this catalyst, reactivation can be accomplished using air oxidation at 150–500°C. The primary benefit of this approach, versus either the Rhone-Poulenc or the Stamicarbon approach, is the claim that this formulation is not deactivated by the presence of acids or water. As a result, sweep gas or decanters are not needed to remove water as it is formed by the deperoxidation reaction. BASF does recommend washing the feedstock prior to the catalytic reactor in order to remove contaminants that might physically foul the catalyst.

The subsequent US patents listed above on CHHP decomposition (oxidation) were reviewed for relevancy to this design. We have listed below the key contributions from what we thought were the more relevant patents for this work.

Table 7.14
RELEVANT CHHP FOLLOW-UP US PATENTS

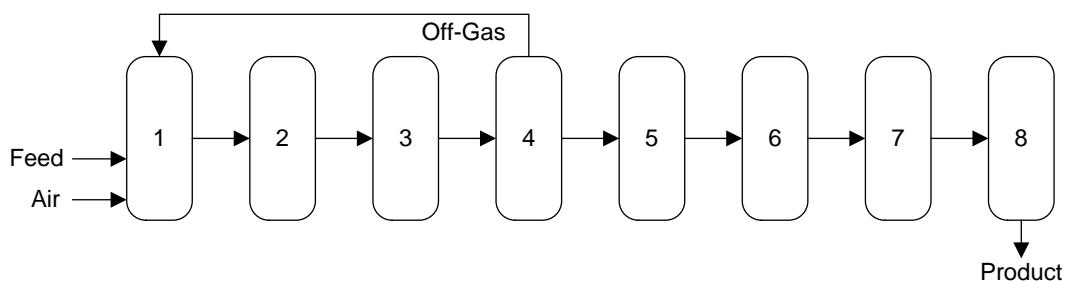
US Patent	Assignee	Active Catalyst	Catalyst Support	Processing Conditions
8026398	Inventors	Sn + Zr		50–90°C, 15–7,000 kPa, LHSV=0.1–100 Hr ⁻¹
7396961	Rhodia	Heterogeneous ruthenium on carbon, doped with Ti,k Zr, V, Ni or Ta	Inorganic oxide	80–130°C, CHHP varies from 0.5–20%, residence time 30 minutes, 0.01–10% active metal on catalyst
7081552	Solutia	Heterogeneous gold	Silicate	150–180°C, 552–1,380 kPa, residence time <120 mins
6806390	Invista	Heterogeneous gold, but also palladium and platinum	Silica or alumina	Organo silicon reagent
6677490	Rhodia	Heterogeneous organometallic, Cr + Cu	Inorganic oxide (silica preferred)	70–150°C
6284927	DuPont	Heterogeneous noble metal (Au, Ag, Pd, Pt)	Inorganic oxide	80–170°C, 29–2,760 kPa
6160183	DuPont	Gold in sol-gel containing Cr, Co, or Ti + 2nd group containing Zr, Ta, Sb, or Si		160–200°C, 69–2,760 kPa, propionaldehyde initiator
5905173	DSM			Mix in aqueous basic solution containing sodium or potassium hydroxide to form salt, separate to decompose CHHP, 60– 180°C, 1–6 bar
5859301	DSM	Mn, Fe, Co, Ni or Cu group		Mix in basic solution and decant to remove water, acids, and salt. React with active catalyst

A slightly different approach to cyclohexane air oxidation and CHHP conversion is disclosed in DuPont US patent 6703529 (9-Mar-2004). The oxidation reaction liquid product stream is immediately washed with water, and allowed to phase separate in a drum producing an upper oil layer and a lower water layer. The upper oil layer contains primarily unconverted cyclohexane, cyclohexanol and cyclohexanone, as well as cobalt naphthenate catalyst. The lower water layer contains polar oxygenated products, which are primarily monocarboxylic and dicarboxylic acids, plus minor amounts of metal containing corrosion products originating either as catalyst or as wetted materials of construction (iron, chromium, nickel, etc.).

The oxidation reactor liquid stream is processed through the sequence of unit processes shown in the figure below. Unit #1 is the oxidation reactor. Unit #2 is the liquid-phase separator producing an upper oil layer and a lower water layer. The upper oil layer is directed to a CHHP converter that uses homogeneous chromium octanoate catalyst to convert CHHP to a combination of cyclohexanol and cyclohexanone. Unit #4 is a cyclohexane recovery distillation column that recycles unconverted cyclohexane as the overhead product, and reaction products as the lower bottoms product. The bottoms product is then directed to Unit #5, which is a KA oil purification distillation column that takes KA oil as the overhead product, and heavy materials as

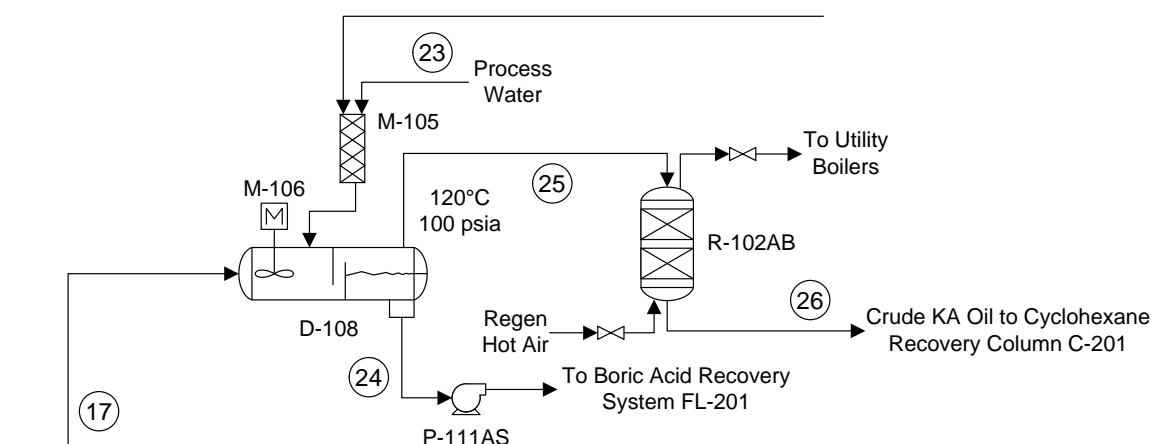
the bottoms product, defined by DuPont as non-volatile residue (NVR). Since the NVR stream contains chromium corrosion products from both stainless steel materials of construction, and chromium catalyst, DuPont proposes a method to substantially reduce the content of chromium in the NVR stream so that the NVR stream can be burned in a boiler as fuel without requiring costly chromium pollution abatement facilities. The DuPont discovery is to process the NVR stream through an acid solvent to dissolve the acidic components of NVR to form a non-aqueous layer substantially free of chromium, and a chromium-rich aqueous stream. Unit #6 is the acid treatment reactor, while Unit #7 is an electrolyte mixing reactor that further concentrates the chromium in the aqueous phase. Unit #8 is a settling drum in which the chromium free organic phase (<2 ppm chromium) separates from the chromium-rich aqueous phase.

Figure 7.10
DUPONT CYCLOHEXANE OXIDATION AND CHHP CONVERSION APPROACH
(USP 6703529, 9-MAR-2004)



For our design, we've chosen to pretreat the air oxidation reactor liquid product stream by first water washing the filtered stream at elevated temperature to hydrolyze the boric acid esters and convert them back to alcohol/ketone and $B(OH)_3$. Our process then decants the resulting two-phase liquid into an upper oil phase containing a combination of KA oil, unconverted cyclohexane, and cobalt naphthenate catalyst, and a lower aqueous phase containing water, boric acid, and organic acids formed during the oxidation reaction. A simplified PFD of this portion of the process is shown below.

Figure 7.11
CHHP DECOMPOSITION REACTOR SECTION



The upper oil phase is passed through 2–100% CHHP decomposition reactors containing beds of heterogeneous cobalt oxide catalyst. With water and acids removed during the pretreatment step, the catalyst is less likely to either dissolve or to deactivate. Provision is provided in the design to periodically reactivate the catalyst offline by passing hot air through the catalyst bed. This approach eliminates the need for sweep gas to remove free water, and eliminates the need for the recovery of homogeneous catalysts that are used in other competing technologies.

The design basis for the CHHP converter is provided in the table below.

**Table 7.15
CHHP CONVERTER DESIGN BASIS**

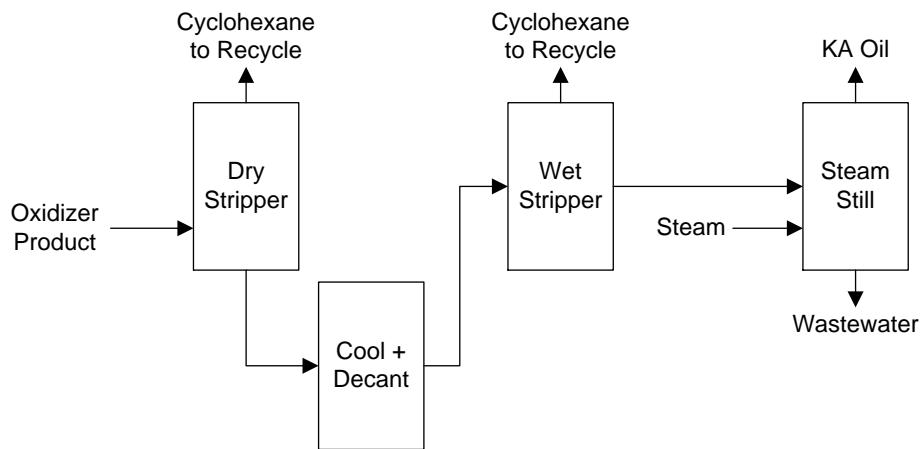
Catalyst	Substrate	Operating Temperature	Operating Pressure	Residence Time
Cobalt oxide	Zeolite	120°C	125 psia	30 min

Section 200—Purification of Crude KA Oil

Cyclohexane Recovery Column

The oil-phase stream discharged from the CHHP conversion reactors contains primarily unconverted cyclohexane feedstock, KA oil product, cobalt naphthenate catalyst, and residual quantities of dissolved water, boric acid, and organic acids. Cyclohexane represents over two-thirds of this stream. The current commercial purification scheme for KA oil is not significantly different from the process configuration patented by DuPont in USP 3365490 in 1968, as shown in the figure below.

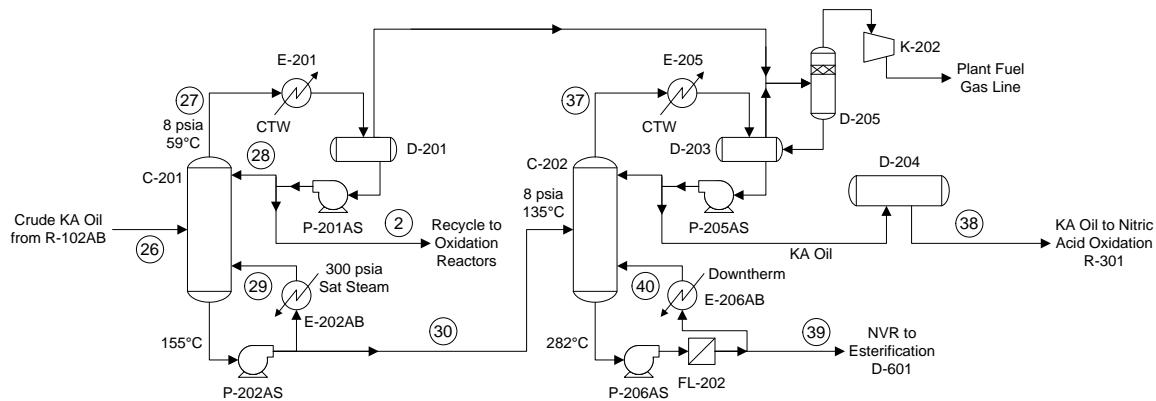
**Figure 7.12
KA OIL CONVENTIONAL PURIFICATION SCHEME (DUPONT USP 3365490)**



For our design, we've chosen to design a two distillation column train in which the first column purifies cyclohexane as an overhead product for recycle to air oxidation, with the bottoms feeding the second tower that purifies KA oil as an overhead product stream, leaving a 'non-

'volatile residue' bottoms product that is directed to a methanol esterification unit. Both columns are designed to operate at moderate vacuum, in order to reduce operating temperatures and therefore reduce the amount of product that would otherwise thermally degrade at higher operating temperatures. The simplified process flow diagram for this portion of the plant is shown in the figure below.

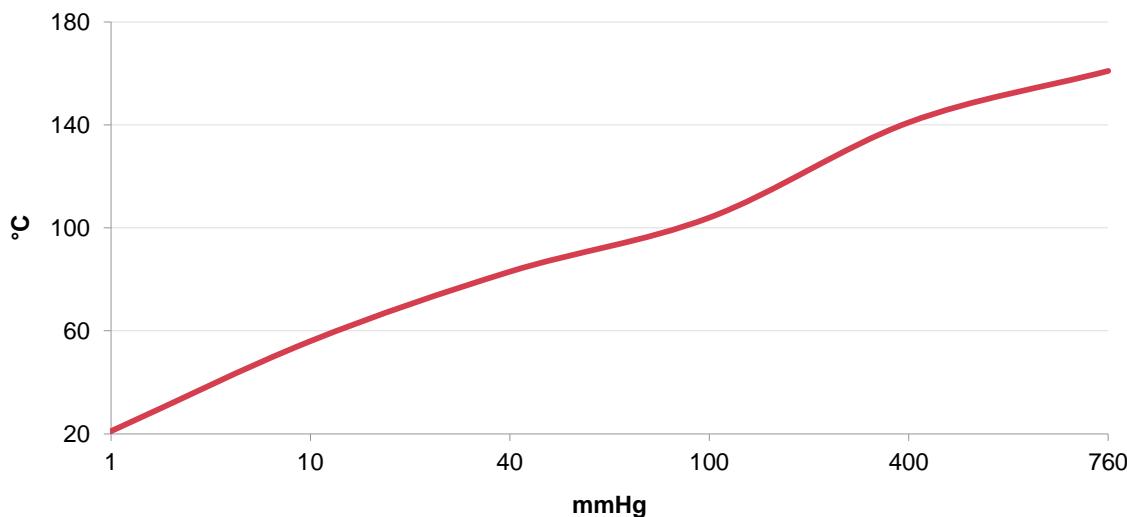
Figure 7.13
KA OIL PURIFICATION SCHEME



The reactor product stream from air oxidation first passes through two separate distillation columns designed to take unconverted cyclohexane as the overhead product stream from the first column, and recycle it to the front of the air oxidation process. Since the crude KA product reactor product stream contains water, the figure below from the early DuPont US patent uses two distillation columns for cyclohexane removal: one column processing water containing oxidation product, and the other column processing a stream in which the water has been removed via cooling and decantation (cyclohexane and KA oil have very low solubility in water). Modern adipic acid plants accomplish cyclohexane recovery in a single distillation column operating under modest vacuum pressure, and therefore at a lower operating temperature than if operated at elevated pressure. The rationale for vacuum operation is to maintain temperatures throughout the column below 160°C, at which temperature thermal degradation of desired products can begin to occur.

The upper oil layer from a water washed and decanted crude KA oil reaction product is directed to the cyclohexane recovery column that operates under modest vacuum conditions (400 mmHg, 8 psia), allowing for an overhead temperature of 59°C, and a bottoms temperature of 155°C. For comparison purposes, the boiling curve for cyclohexanol is shown below, which is the major component of crude KA oil. The purpose of sub-atmospheric pressure distillation is to operate the column at relatively low temperature, which minimizes the thermal degradation of product and product precursors to undesirable by-products. A column using structured packing and 36 actual stages provides adequate purification of cyclohexane (95 weight%) using a reflux ratio of 4. The balance of the overhead stream is water and light hydrocarbons. Vacuum is created by pulling a vapor stream off the distillate receiver, and directing it to a vacuum pump equipped with a condenser and knock-out drum. Non-condensable gases from the vacuum pump are directed to the plant's fuel gas recovery line.

Figure 7.14
CYCLOHEXANOL BOILING CURVE



KA Oil Purification Column

The bottoms product stream from the cyclohexane recovery distillation column is processed through a second distillation column to take KA oil as a high-purity overhead product (>95% purity), and a heavy residue stream (NVR) as a bottoms product. The heavy residue stream has historically been incinerated, but more recent technology has been used to recover some of the components in that stream that can have economic value when purified to high concentration. These components include mono- and dicarboxylic acids as well as non-cyclic oxygenated hydrocarbons (alcohols, ketones, ethers, esters). Other components of the non-volatile residue stream are heavy tars and polymer, dimers, and catalyst degradation products.

The KA purification column is operated under modest vacuum conditions for the purpose of minimizing the thermal degradation of stream components that have commercial economic value. We have chosen to operate the KA oil purification column at a 400 mmHg vacuum level (0.53 atm, 7.7 psia), using a vacuum pump with condenser and knock-out drum. Since both the cyclohexane recycle column, and KA oil purification column operate at identical vacuum conditions, a single vacuum circuit is provided to serve both columns. 24 stages of structured packing are used in the KA oil purification column.

Design conditions for the KA oil purification column are an overhead temperature of 135°C, and a bottoms product temperature of 282°C. Non-condensable gases from the vacuum pump are discharged to the plant's fuel gas line. Purified KA oil (overhead distillate product) is discharged directly to the nitric acid oxidation section of the process, with an intermediate pressurized surge drum available to store 24 hours of production. The bottoms product from the KA oil purification column, called in the industry non-volatile residue (NVR), is directed to a purification unit designed to remove contaminants while converting acids into mixed methyl esters for sale into the polyurethanes business.

Boric Acid Recovery and Recycle

Boric acid used to improve cyclohexane oxidation conversion and selectivity forms an ester (CHHP) with cyclohexanol produced in the air oxidation reactors, reducing the propensity of

cyclohexanol to degrade into lower carbon number undesirable by-products (glutaric acid, succinic acid, hydroxycaproic acid, and caproic acid). Following hydrolysis of the air oxidation reactor liquid product stream to convert the ester back to boric acid plus cyclohexanol, the boric acid preferentially dissolves in the aqueous phase, leaving the oil phase (cyclohexane, KA oil, higher molecular weight acids) nearly boron free. A fundamental patent for boric acid recovery is Monsanto US patent 3895067 (15-Jul-1975).

One approach to boric acid recovery would be to simply recycle the aqueous phase containing boric acid back to the front of the air oxidation section. Since the solubility of boric acid drops significantly with temperature, it would seem reasonable to simply chill the aqueous product stream down until the boric acid crystallized out of solution at lower temperature. The solid boric acid could then be recovered by filtration or centrifugation, and recycled to the front end of the air oxidation process.

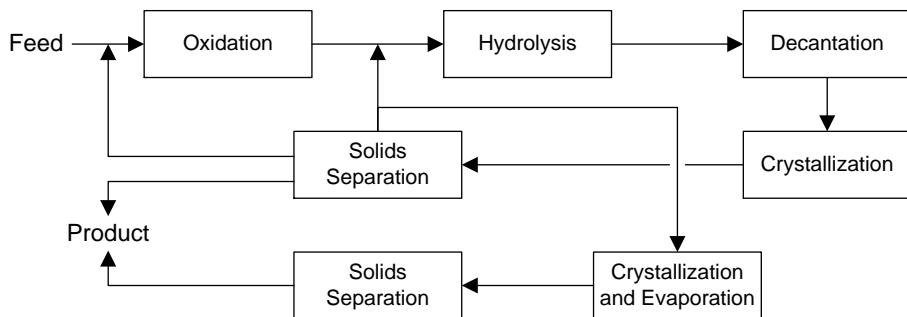
However, some amount of by-product acids (adipic acid, glutaric acid, succinic acid) from the air oxidation reactors also dissolves in the water layer, and also tends to precipitate out of the aqueous solution along with the boric acid. Recycling these acid components with the boric acid will suppress cyclohexane air oxidation, reducing both conversion and selectivity.

To recover boric acid while removing the undesirable by-products, the Monsanto process (see figure below) directs the air oxidation (item #2) liquid product stream (stream #9) through CHHP hydrolysis (item #3), directing the two-phase liquid (stream #11) to a decanter (item #4). The upper oil layer containing crude KA oil (stream #12) is sent to distillation for cyclohexane recycle and KA oil purification.

The aqueous lower layer (stream #13) from the hydrolysis separation drum (item #4) is directed through a boric acid evaporator and crystallizer (item #5) to recover greater than 55% of the boric acid in the first stage, and recover 74% of the remaining boric acid (>88% total recovery of boric acid) through a 2nd-stage evaporator and crystallizer (item #6). The aqueous feed stream (stream #13) to the first-stage evaporator is approximately 9% boric acid plus 15% hydrocarbons (mostly mono- and dicarboxylic acids). This stream is evaporated under vacuum conditions to remove 65% of the water, leaving a water concentration of 53%. This stream is cooled to 20°C, which causes most of the boric acid to crystallize out of solution. The cooled liquid (stream #16) is centrifuged (item #8) to produce a 55% water slurry (stream #21) containing boric acid that is recycled (stream #20) to the feed of the air oxidation reactors. The boric acid crystal free aqueous liquid (stream #10) from the centrifuge is recycled to the hydrolysis feed drum as hydrolysis water.

Recycling the crystal free stream (stream #10) will cause the minor concentrations of mono- and dicarboxylic acids to accumulate in the hydrolysis loop. This stream has a water concentration above 62%, a boric acid concentration of 5–10%, with the balance being mono- and dicarboxylic acids. To prevent the acid accumulation, a slip stream of recycle hydrolysis water (stream #17) is directed to the 2nd stage of evaporation and crystallization (item #6). The evaporator reduces the water concentration of the 2nd-stage feed from 76% to 27%, causing most of the balance of the boric acid in this stream to crystallize when cooled to 20°C. The boric acid cooled slurry is passed through a vacuum filter (item #7), producing a boric acid slurry (stream #22) that is recycled to the air oxidation reactors, and a hydrocarbon-rich stream (stream #18) for wastewater treatment.

Figure 7.15
BORIC ACID RECOVERY AND RECYCLE APPROACH (MONSANTO USP 3895067)



Other approaches to recovery of boric acid are well patented in the literature. A partial list of approaches to boric acid recovery is presented in the following table.

Table 7.16
APPROACHES TO BORIC ACID RECOVERY

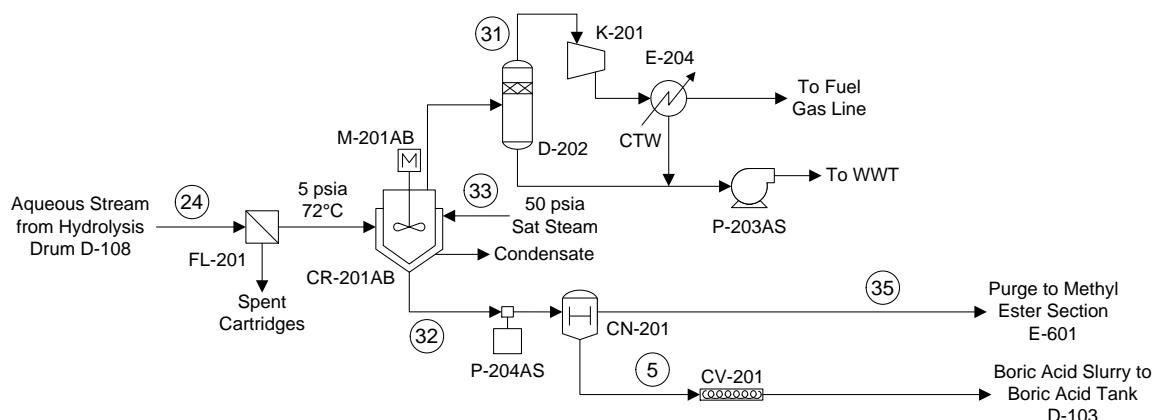
US Patent	Assignee	Technology
5235117	IFP	React with methanol to form methyl borate, and separate from methanol via distillation
4183904	Monsanto	Incineration of organics, followed by dehydration of boric acid to boron oxide
4058565	Bayer	Oxidizing aqueous stream then concentrated by crystallization
3983220	US Government	Ion exchange resins
3895067	Monsanto	Two-stage evaporation and crystallization
3679751	Halcon	Liquid-liquid extraction with alcohol

For this design, we've chosen the two-stage evaporation/crystallization for boric acid recovery from the aqueous product stream leaving the hydrolysis separating drum. The aqueous stream is pumped through a 0.5 micron dual cartridge filter to remove solids, tars, polymer, and dispersed oil. The stream is directed to a suspension crystallizer in which the vessel jacket is steam heated with 50 psia saturated steam. An overhead nozzle on the crystallizer is directed through a knock-out drum to a single-stage sliding van vacuum pump that creates an absolute pressure within the crystallizer of 1.0 psia (0.07 atm, 52 mmHg) that will result in the liquid within the crystallizer boiling off its water content at 39°C. The vacuum system contains a knock-out drum before the vacuum pump, and a condenser after the vacuum pump. Condensed liquid from both the knock-out drum and condenser are returned to the crystallizer. Non-condensable gases from the vacuum pump are directed to the plant's fuel gas line.

Liquid product is removed from the bottom of the 1st-stage crystallizer and pumped using a diaphragm pump to a 1st-stage centrifuge for the purpose of separating the crystallized boric acid from clear liquid. A 55% boric acid slurry from the centrifuge is recycled to the boric acid feed tank.

75% of the clear liquid from the 1st-stage centrifuge is recycled to the hydrolysis drum. A slip stream containing the remaining 25% of clear liquid from the 1st-stage centrifuge is directed to a 2nd-stage crystallizer. The 2nd-stage crystallizer overhead nozzle is tied into the 1st-stage vacuum system. The 2nd-stage crystallizer also uses 50 psia steam to evaporate water from its feed stream, and also operates at a temperature of 39°C and 1.0 psia pressure. The bottoms product stream from the 2nd-stage crystallizer is pumped using a diaphragm pump to the 2nd-stage centrifuge, where concentrated boric acid slurry is recycled to the boric acid feed tank. The clear liquid from the 2nd-stage centrifuge is directed to the methyl ester reaction section for recovery of mono- and dicarboxylic acids to commercial product as mixed methyl esters. The configuration of the boric acid recovery section is shown in the figure below.

**Figure 7.16
PROPOSED BORIC ACID RECOVERY SYSTEM**

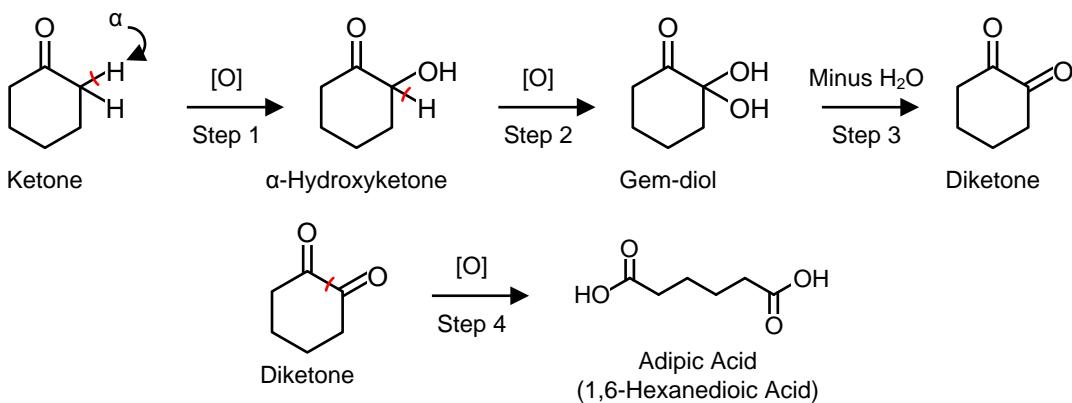


Section 300—Nitric Acid Oxidation of KA Oil to Crude Adipic Acid

Overall Processing Scheme

Our approach to the nitric acid oxidation of KA oil to crude adipic acid follows the principles of the early DuPont patents, with minor updates to reflect current commercial practice. Nitric acid oxidation of KA oil first dehydrogenates cyclohexanol to cyclohexanone as shown in the figure below, and then progressively converts the ketone to a hydroxyl-ketone, dihydroxy-ketone, diketone, and finally dicarboxylic acid upon opening of the ring.

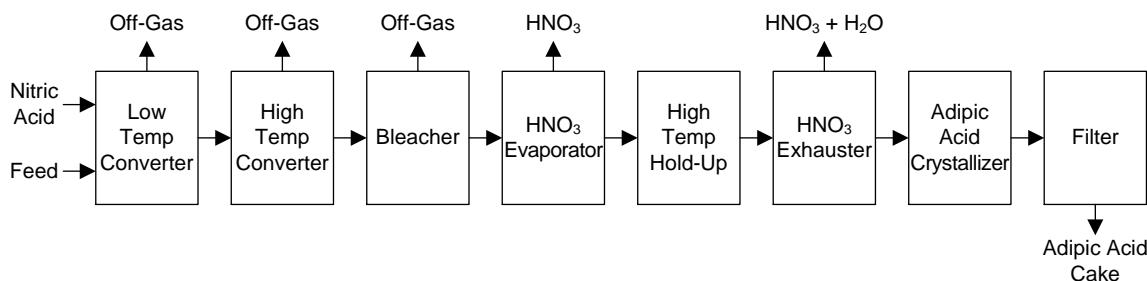
Figure 7.17
OXIDIZING CYCLOHEXANONE TO ADIPIC ACID VIA NITRIC ACID



Source: DuPont

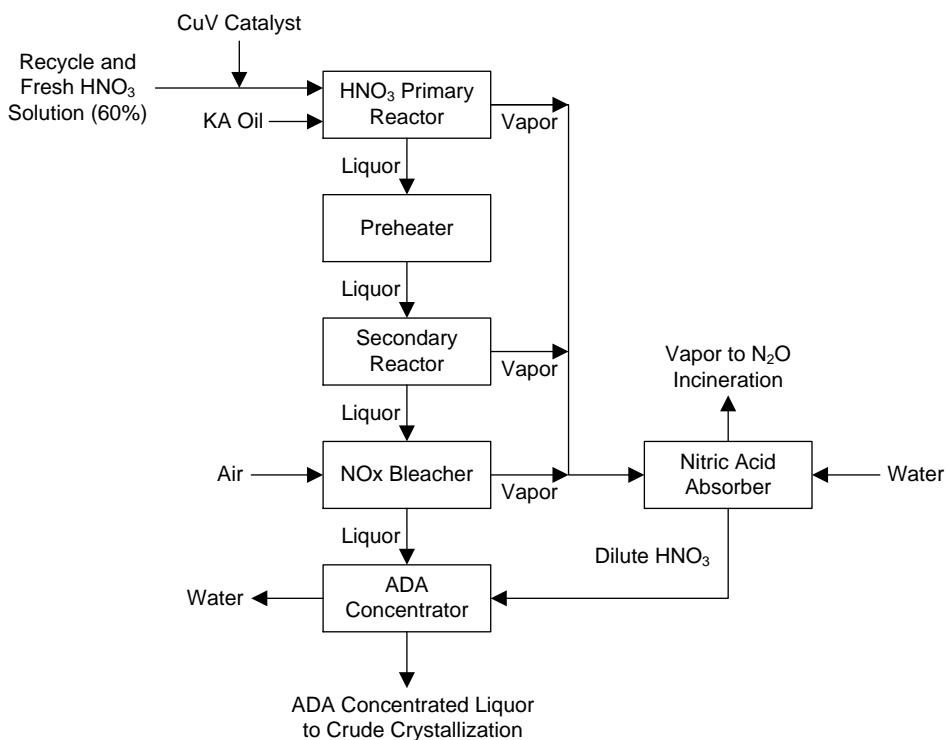
The basic configuration of the KA oil nitric acid oxidation section is very similar to a 1968 patent by DuPont (USP 3365490), as shown in the figure below.

Figure 7.18
KA OIL NITRIC ACID OXIDATION BLOCK FLOW DIAGRAM
(DUPONT USP 3365490, 23-JAN-1968)



The DuPont technology relies upon two nitric acid oxidation reactors operating in series to oxidize KA oil to crude adipic acid. Since the oxidation process is extremely exothermic (6,000 Btu/kg), a number of measures are used to remove exothermic heat of reaction as it is formed. The first approach is to use a large excess of circulating nitric acid for the purpose of absorbing some of the exothermic heat in the reactor, to be removed outside the reactor. The early technology relied on an external pump around loop through a heat exchange cooler to remove the exothermic heat of reaction. The current technology uses for the first (primary reactor) a vertical shell and tube reactor operating at 70°C with nitric acid solution containing catalyst and KA oil on the tube side, and cooling water on the shell side. The reaction operates at slightly elevated pressure (50 psia). Due to the corrosion potential of nitric acid at elevated temperatures, the tubes are made of titanium. The block flow diagram below describes current practice.

Figure 7.19
NITRIC ACID OXIDATION CURRENT PROCESSING SCHEME



There have been reported thermal runaway incidents with primary nitric acid reactors, caused by a combination of short-term pressure surges, and the tendency of heat exchanger cooling surfaces to freeze up, substantially reducing the heat transfer coefficient. To address these issues, our design for the primary nitric acid oxidation reactor incorporates both a shell-and-tube reactor configuration, and an external pump around cooling loop through an external heat exchanger. The resulting high rate of heat removal allows our design to use a modest ratio of feed nitric acid to feed KA oil (7.5:1), since a large excess of nitric acid is not required for exothermic heat of reaction heat removal.

The primary nitric acid oxidation reactor accomplishes 90% of the total conversion in a residence time of 5 minutes (284045). Product from the primary reactor is processed through a jacketed CSTR secondary reactor operating at slightly higher temperature (110°C) with a much larger volume to complete the conversion of KA oil to crude adipic acid at a residence time of approximately 30 minutes. Both reactors are operated at slightly above atmospheric pressure (50 psia). The modern approach uses a weight ratio of 7.5 parts nitric acid (on a 100% acid basis) to 1 part KA oil. The nitric acid is provided and used as a 60% weight solution in water. Since four mols of nitric acid are required to convert 1 mol of KA oil to adipic acid, the minimum stoichiometric weight ratio of nitric acid to KA oil is 2.5:1.

The oxidation of KA oil causes a corresponding reduction of nitric acid to a combination of nitrogen oxides (NO₂, NO₃, N₂O, NO) which are present as dissolved gases in the nitric acid oxidation reactor product. These nitrogen containing gases are removed from the liquid reactor liquor solution by blowing air through the solution in a stripping vessel called a 'bleacher' at approximately 90°C. The nitrogen containing gases leaving the bleacher are combined with the overhead vapors from the primary and secondary reactors and are directed to a nitric acid

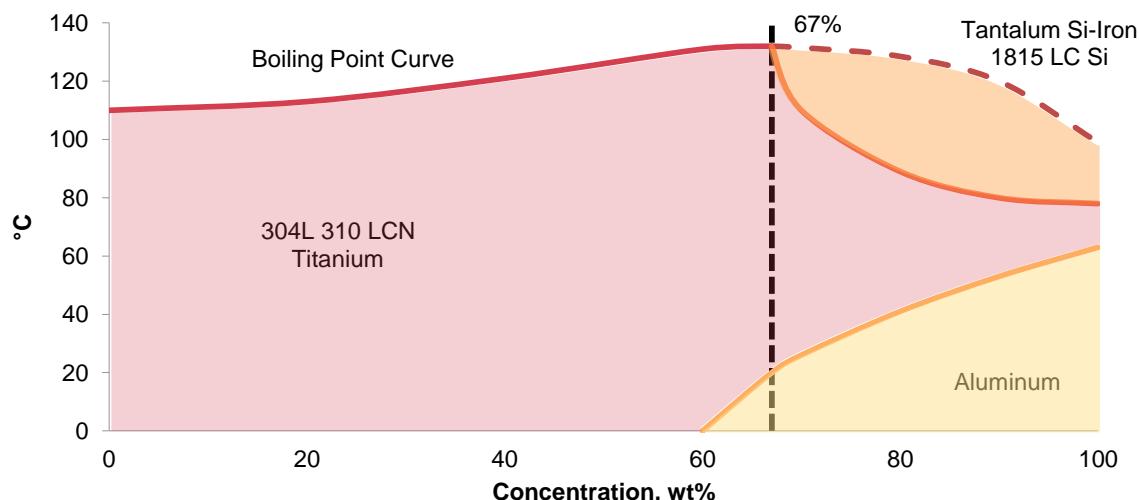
absorber in which process water mixes with the gases in a counter current fashion for the purpose of absorbing the gases into the liquid, and converting NO_x back to dilute nitric acid. Nitrous oxide (N₂O) is not absorbed in the water, and remains in the vapor phase. Due to its high greenhouse gas potential, the nitrous oxide vapor stream is directed in most plants in western countries to an incineration process unit where two-stage incineration using natural gas in a deficit of air reduces nitrous oxide to a combination of nitrogen and oxygen. In our process, the N₂O is directed to a process unit that converts it back to a combination of NO and NO₂, which are subsequently reabsorbed in water to produce dilute nitric acid.

The KA oil oxidation reaction to adipic acid produces water as a by-product, which also dilutes the 60% nitric acid reactor feed solution. Crude nitric acid oxidation reactor product liquor is directed to an adipic acid concentrator which is a distillation column designed to remove primarily water as the overhead product, and adipic acid along with concentrated nitric acid liquor as the bottoms product. Dilute nitric acid formed in the nitric acid absorber is also directed to the concentrator. The concentrated liquor product from the ADA concentrator is directed to a multi-stage crystallization unit for recovery of product adipic acid as a dry solid powder.

Wetted Materials Considerations for Nitric Acid

Below its boiling point in water, suitable materials of construction are stainless steel grades 304L and 310LCN. At higher temperatures and in vapor-phase environments, titanium is used for heat transfer surfaces. At both elevated temperatures and concentrations above 60%, tantalum or silicon-iron is recommended, with silicon iron used generally for pressure vessel materials, and tantalum used for tubing. Recommended materials of construction in nitric acid service are presented in the figure below as a function of acid concentration and temperature.

**Figure 7.20
RECOMMENDED MATERIALS IN NITRIC ACID SERVICE**



Source: Otto Drescher (284046)

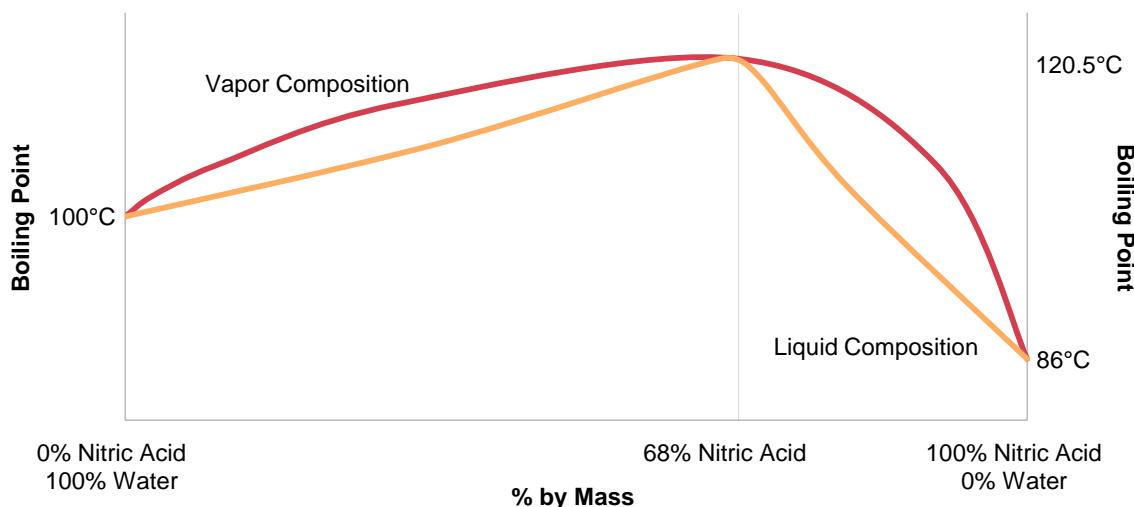
Nitric Acid Storage Day Tanks

Two storage day tanks are provided for 60% nitric acid in water solution. Each contains sufficient volume for 12 hours of operation, and is constructed of 304L stainless steel conforming to API standard 650. Fresh nitric acid is supplied to the plant as a 60 weight % solution. Recycle

nitric acid from the crystallization process unit is maintained in a separate tank prior to being recycled to the nitric acid oxidation reactors. Although concentrated nitric acid will fume (284047) at ambient temperatures and require a condenser, at the proposed 60% concentration its vapor pressure is high enough to avoid a condenser. However, a nitrogen blanket will be provided over the tank liquid surface.

When used in the oxidation of KA oil to adipic acid, mixtures of nitric acid and water form an azeotrope at 68% nitric acid concentration, at a boiling temperature of 120.5°C. Pure nitric acid boils at 86°C, while pure water boils at 100°C. The boiling curve for mixtures of nitric acid in water is presented below. 68% nitric acid in water concentration is the normal sales specification for technical-grade nitric acid purchased in bulk quantities.

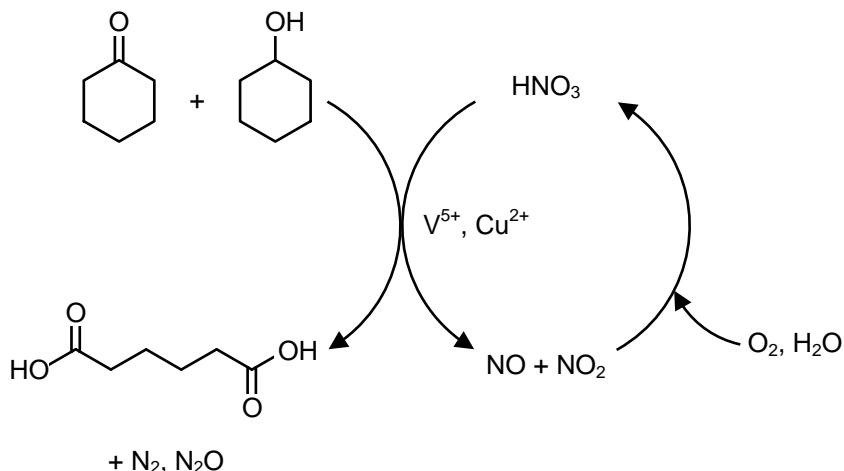
Figure 7.21
NITRIC ACID IN WATER BOILING CURVE



Copper Vanadate Catalyst Composition and Use

A premixed liquid catalyst formulation containing copper vanadate is injected into the 60% nitric acid aqueous solution and directed to the nitric acid oxidation reactors. The feed concentration of liquid catalyst is approximately 500 ppm to nitric acid (on a 100% basis). As shown in the figure below vanadium (+5) is the primary catalyst for oxidizing cyclohexanone to the intermediate diketo species and opening up the ring to form dicarboxylic acid. Copper is used primarily to prevent over-oxidation of formed adipic acid to degradation products glutaric acid and succinic acid.

Figure 7.22
ROLE OF VANADIUM AND COPPER CATALYST



Source: Dr. K.R. Krishnamurthy, "Homogeneous Catalysis HMC-5-2010"

The liquid form of catalyst used is ammonium (NH_4)-metavanadate (MW=117.0, NH_4VO_3) and copper nitrate, using the $V(+5)$ and $\text{Cu}(+2)$ valence states of the metals. In pure form, ammonium metavanadate (CAS: 7803-55-6) is a crystalline solid powder (density = 2.3 gm/cm³) with a yellow color. Ammonium metavanadate is slightly soluble in water and polar organics such as alcohol and ketone. For use in this process, ammonium metavanadate is dissolved in nitric acid solution offsite to provide a liquid form for dosing. Commercial suppliers of ammonium metavanadate include Evraz Stratcor (Russia), Alcan (Canada), and Energy & Chemicals/Itochu (Japan). A commercial specification for ammonium metavanadate from Evraz Stratcor is provided in the table below.

Table 7.17
AMMONIUM METAVANADATE COMMERCIAL SPECIFICATION

Specification	Limit
Vanadium (as V_2O_5)	77.0% min.
Ammonium Metavanadate	99.0% min.
Carbonate (CO_3)	0.3% max.
Chloride	0.2% max.
Iron	0.013% max.
Molybdenum	0.01% max.
Sodium	0.004% max.
Silicon	0.008% max.

Copper nitrate ($\text{Cu}(\text{NO}_3)_2$) catalyst is made available either in anhydrous solid form (MW=187.6: CAS 3251-23-8) as blue crystals, or in hydrated form usually as the tri-hydrate

(MW=241.6: CAS 13778-31-9). If purchased in sold form, available commercial purities range from 99% to 99.999%. Specific gravity in sold form is 2.05 gm/cm³. Since copper nitrate is highly soluble in water, it is made available in bulk quantities as a 41–53% liquid solution. Commercial suppliers include Yara (Norway) and American Elements (USA). The table below is a typical commercial specification for copper nitrate in dry form. For this project, copper nitrate will be dissolved in nitric acid offsite, combined with ammonium metavanadate solution (also in nitric acid), and pumped from bulk offsite tankage to a day tank within the process area.

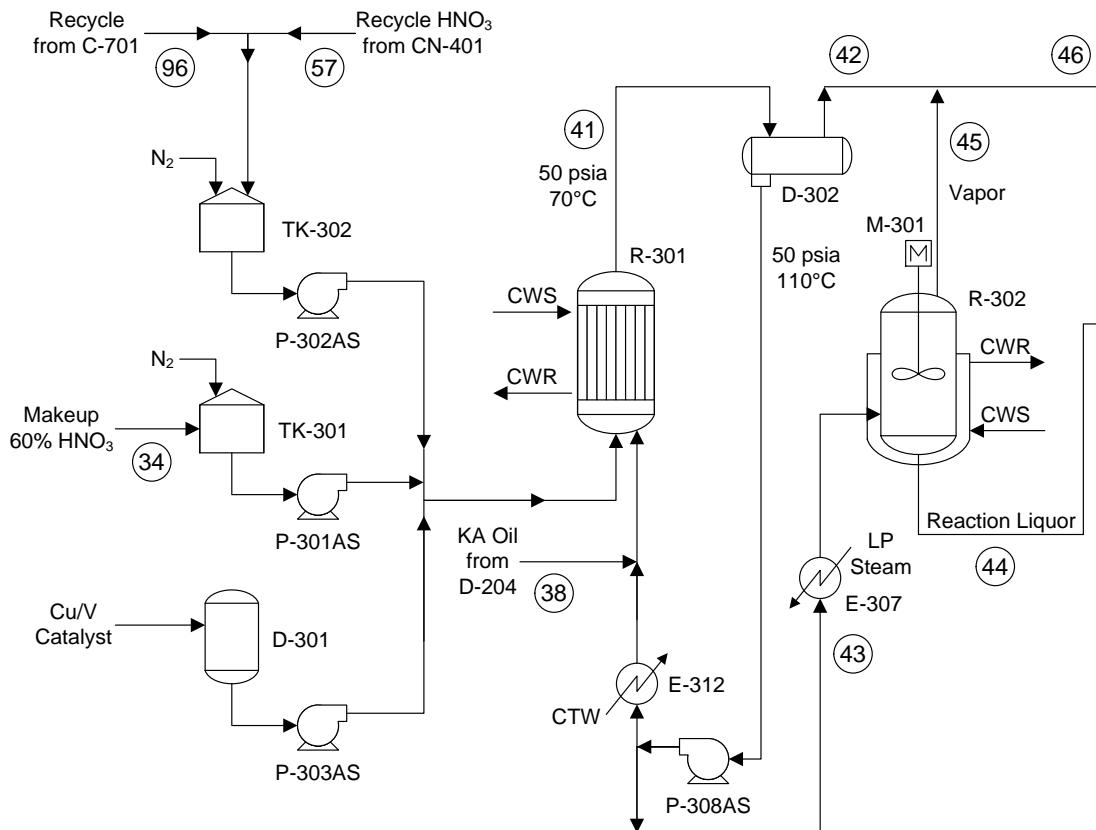
Table 7.18
COPPER NITRATE GENERIC COMMERCIAL SPECIFICATION

Component	Symbol	Specification
Copper	Cu	27.0% +/- 1.0%
Iron	Fe	0.01% Max
Nickel	Ni	0.01% Max
Zinc	Zn	0.01% Max
Chloride	Cl	0.01% Max
Sulfate	SO ₄	0.01% Max
Insolubles		0.01% Max

Nitric Acid Oxidation Reactors Design

A premixed liquid catalyst formulation containing copper vanadate is injected into the 60% nitric acid solution prior to the solution being fed to the primary nitric acid oxidation reactor. KA oil is separately fed to the primary reactor. The primary nitric acid oxidation reactor is configured as a vertical shell and tube reactor in which process fluid enters the tube section at the bottom, and flows upward. The tubes are made of titanium, while the balance of the reactor is made of 310L stainless steel. Cooling water supply is fed to the shell side of the primary reactor near its top, and exits as cooling water return near the bottom of the pressure vessel on the shell side. The portion of the process flow diagram associated with the nitric acid oxidation reactors is shown below.

Figure 7.23



Nitric Acid Bleacher Design

Liquid product from the 2nd nitric acid oxidation reactor contains a significant quantity of dissolved gases containing primarily nitrogen oxides (NO, NO₂, NO₃, N₂O), which must be removed prior to adipic acid crystallization. The liquid product is passed through a stripper (called a bleacher) using hot air to remove the nitrogen oxide gases as an overhead vapor product from the bleacher. The design temperature of the bleacher is approximately 110°C, and the design pressure is approximately atmospheric pressure. Since the nitrogen oxide gases give the liquid reactor product a dark brown color, their removal changes the color of the liquid to a light brown. The vapor product stream is combined with the nitrogen oxide vapor product streams from both nitrogen oxide reactors, and is directed to a nitric acid absorber. The bleached liquid product stream exits the bleacher at its bottom, and is directed to a distillation column (ADA concentrator) that is designed to remove most of the water from the stream.

Adipic Acid Concentrator Design

Liquid product from the nitric acid bleacher contains nitric acid, water, adipic acid, catalyst, a small amount of unconverted KA oil (principally cyclohexanone), and a small amount of monocarboxylic and dicarboxylic degradation products, plus heavier polymer, tar and dimer. Since the initial 60% nitric acid solution has been diluted by water formed by the oxidation of KA oil to adipic acid, this stream is filtered to remove suspended solids, and reconcentrated in a

distillation column that is designed to remove primarily water as the overhead distillate product, leaving the remaining components suitable for recovery of adipic acid in downstream crystallization process units. In order to minimize the further thermal degradation of adipic acid, the column is operated under vacuum conditions using a vacuum pump and downstream condenser that are connected to the top side of the distillate receiver.

The ADA concentration column is designed to operate at subambient pressure (260 mmHg, 5 psia), with an overhead temperature of 72°C, and a bottoms temperature of 101°C. Such a separation can be accomplished using a column with 60 actual sieve trays (made of titanium) within a 304L SS pressure vessel, at a design reflux ratio of 6.

Nitric Acid Absorber

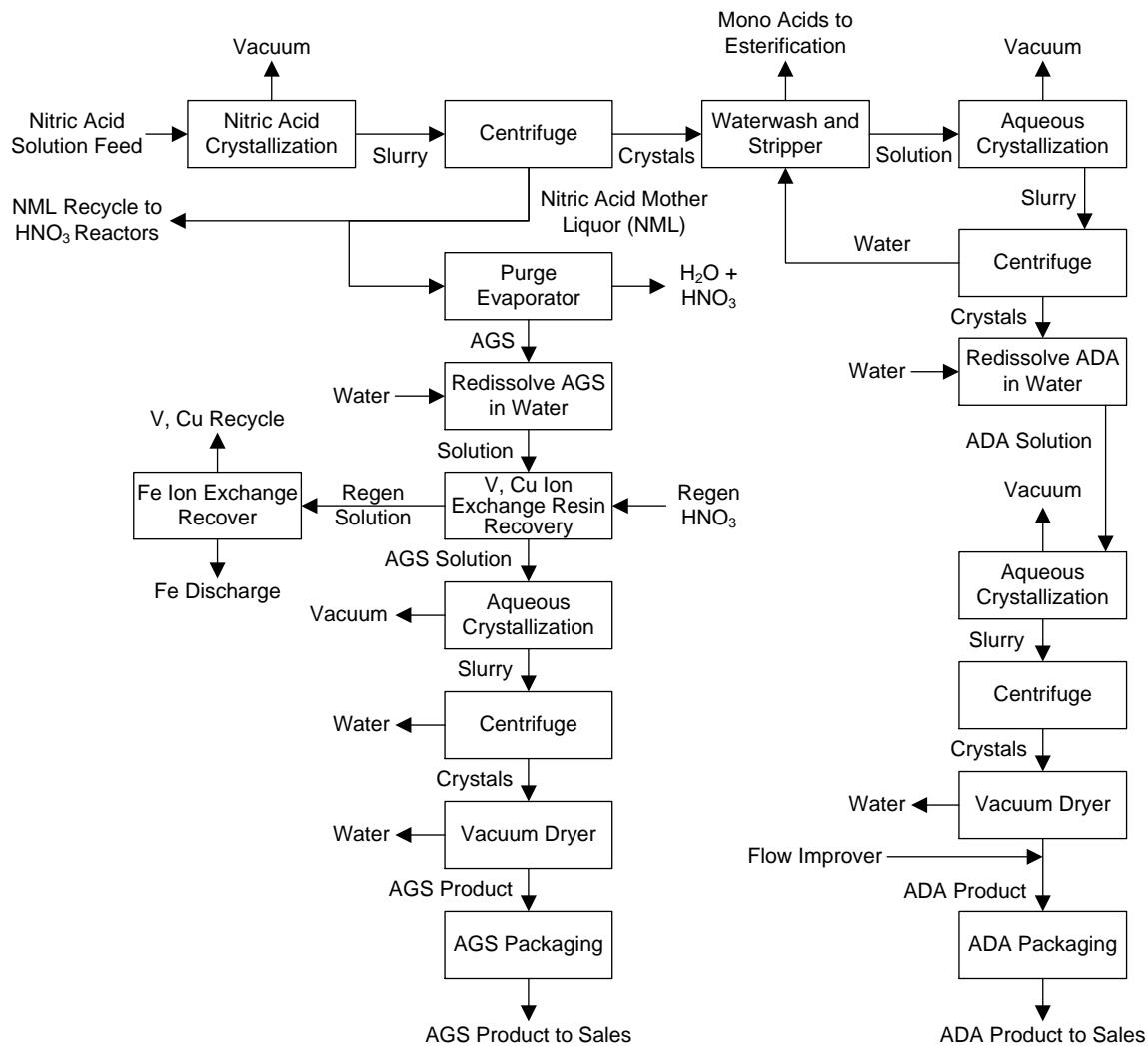
Nitrogen oxide containing vapors from the bleacher, and both nitric acid oxidation reactors, are combined and directed to a nitric acid absorber for the purpose of using process water to redissolve and oxidize the nitrogen oxides back to dilute nitric acid. Since the absorption of nitrogen oxides and subsequent oxidation to nitric acid is highly exothermic, the absorber operates with a pump around loop through an external heat exchange cooler that maintains the feed water temperature to the absorber at just above ambient temperature. NO readily oxidizes to NO₂ while NO₂ and NO₃ readily dissolve in water. N₂O does not dissolve in water. Vapor absorption increases as operating temperature decreases. The absorber operates at slightly elevated pressure, such that the overhead product vapors can be directed to the N₂O incinerator without the use of a booster compressor.

Section 400—Adipic Acid Crystallization

Commercial practice is to crystallize adipic acid first from the nitric acid solution produced in the nitric acid oxidation reactors, and then to further purify the crude adipic acid product from acid crystallization by two-stage aqueous crystallization. This three-step basic process was patented by Stamicarbon in 1963 (USP 3096369). All of the crystallization steps are conducted under vacuum conditions at approximately 50°C, which recovers over 95% of the adipic acid produced in the nitric acid oxidation reactors. The balance of the adipic acid leaves the system in a mixed dibasic acid commercial by-product that is combined with glutaric acid and succinic acid (AGS product).

As crystallization proceeds by chilling the solution in which the adipic acid is formed, the first dibasic acid that precipitates in the crystallizer is adipic acid. Below 50°C, succinic acid begins to co-crystallize with adipic acid, preventing recovery of this adipic acid at acceptable commercial specifications. A variety of complicated process sequences have been patented for eliminating dibasic acid coproduct, and recovering virtually all of the produced adipic acid and other dicarboxylic acids (glutaric acid, succinic acid) in high purity via a combination of advanced crystallization, dehydrating succinic acid to convert it to corresponding anhydride (which can be separated from the other components via distillation), and vacuum distillation. Several of these approaches are documented in section four of this report. Our proposed adipic acid purification sequence is shown in the block flow diagram below.

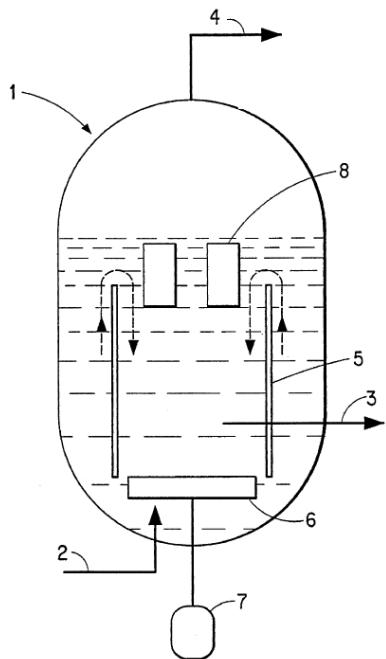
Figure 7.24



Crude Acid Suspension Crystallization Using Oslo Crystallizer

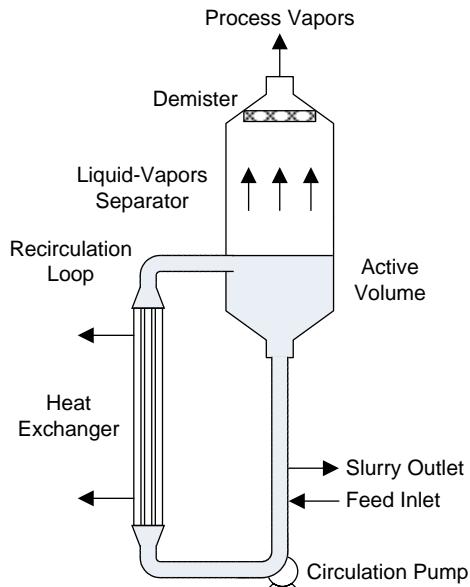
Feedstock for adipic acid purification by suspension crystallization is the bottoms product stream from the adipic acid concentrator. It is directed to a suspension crystallization unit (Oslo crystallizer) operating at high vacuum (1–2 psia, 50 mmHg). Materials of construction for the nitric acid crystallizer have historically been 304L stainless steel, but a recent US patent application by Rhodia (20110274591) recommends the use of 310L stainless steel. The fundamental characteristic of a forced circulation crystallizer is the use of a cylindrical vessel (#1) containing the solution, a feed inlet nozzle (#2), product outlet nozzle (#3), nozzle to a vacuum pump (#4), vessel baffles (#5), mechanical impeller (#6), and motor driver for the impeller (#7). The basic crystallization mechanism is shown in the figure below, based upon DuPont patent USP 5471001.

Figure 7.25
EVAPORATIVE CRYSTALLIZATION MECHANISM (DUPONT USP 5471001, 28-NOV-1995)



The feedstock is circulated between the crystallization vessel and an external heat exchanger designed to use refrigerant (glycol solution) to chill the solution down to 50°C. This form of crystallizer is known as a forced circulation crystallizer, or 'Oslo Crystallizer,' as shown in the figure below. Crystals of small dimensions are circulated in the solution through the pump around cooler loop until the crystals grow large enough to sink (by gravity) to the bottom of the crystallizer as concentrated slurry for removal.

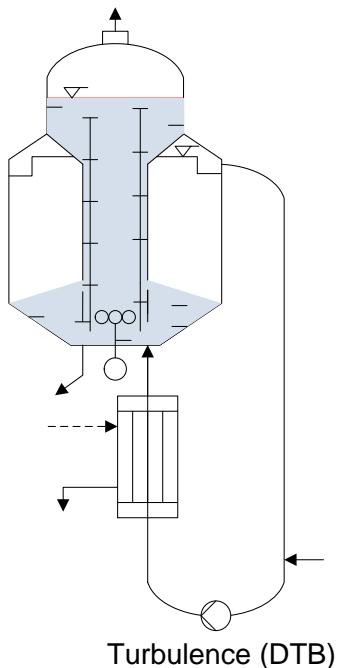
Figure 7.26
FORCED CIRCULATION (OSLO) CRYSTALLIZER



Source: www.niroinc.com

Nozzles locations for an Oslo crystallizer are shown in the figure below. A disengaging region near the top separates vacuum vapor from entrained droplets of solution. The feed location is just below the vapor disengaging section. Inlet and outlet nozzles to and from the external cooler are located in the solution's upper reservoir. Large adipic acid crystals that settle by gravity to the very bottom of the vessel are removed from the vessel using a nozzle near the bottom.

Figure 7.27
NOZZLE LOCATIONS FOR OSLO CRYSTALLIZER (DRAFT TUBE)



Source: Puren Technology

As the solution temperature drops, adipic acid begins to crystallize out of solution, and collects at the bottom center of the crystallizer vessel when the crystals grow to sufficient size. Care is taken to keep the crystallization solution temperature above 50°C, in order to avoid also crystallizing the succinic acid and glutaric acid components of the solution. Crystal slurry is discharged from the bottom center of the crystallization vessel. High liquid velocities within the crystallizer keep the solution well mixed, and eliminate the need for a mechanical agitator. Industrial suppliers of Oslo crystallizers include TSK, GEA/Niro, and Swenson.

Crystal Separation Using Pusher Centrifuge

The adipic acid crystal slurry discharged from the Oslo crystallizer is directed to a pusher centrifuge for the purpose of removing the adipic acid crystals, while recycling the nitric acid liquor back to the front of the nitric acid oxidation reactors.

Escher-Wyss Ferrum Corporation claims to have supplied 'pusher centrifuges' to the major producers of adipic acid, including Rhodia, DuPont, ICI, Monsanto, Bayer, BASF, Solutia, and several Chinese adipic acid producers. The Ferrum application list for pusher centrifuges is listed below.

Table 7.19
APPLICATIONS FOR FERRUM PUSHER CENTRIFUGES

Main Product Group	Products	Application	Reference Customers	Centrifuge Type
Basic products	Adipic acid	Polyamides	Rhodia/DuPont/ICI/Monsanto/Bayer	Pusher
		Nylon 66	BASF/Solutia/Various Chinese manufacturers	
	Bisphenol A	Polycarbonate, plexiglas, synthetic resins	DOW	Pusher
			Union Carbide	
			Toyo	
	Caprolactam	Nylon 6	TPL	Pusher
			GHCL	
			India	
	Paraxylene	Synthetic fibers	Exxon	Pusher
			Esso	
	ABS	Pure resins	Formosa Plastics	Pusher
			Marbon Chemicals	
	Polyethylene		Höchst	Pusher
	PP	Resins	ICI	Pusher

Other suppliers of industrial scale pusher centrifuges include TEMA Machinery, Alfa-Laval, GEA Westfalia, B&P, and Krauss-Maffei. Pusher centrifuges are useful in applications of suspended crystals that drain easily, and are granular and therefore resistant to filter plugging. Average particle diameter needs to be at least 0.1 mm. The overall configuration of a pusher consists of a filtration unit (at right) and a hydraulic drive unit (at left).

A pusher centrifuge is designed as a rotating filter screen within a cylindrical basket configured along a horizontal axis. Pressure within the basket pushes feed slurry within the basket to force free flowing liquid through the filter screen (mother liquor), while the concentrating solid crystals form on the inside surface of the filter screen. Pressure is created within the rotating horizontal basket by a rotating disk (the pusher) that moves by hydraulic pressure horizontally on the inside of the cylinder, and reciprocates back and forth as it traverses the basket from left to right. The action of the pusher forces liquid from the slurry through the screen while retaining the crystals on the inside of the screen. When the pusher moves its full distance from left to right, scraper knives remove the crystals from the inside surface of the screen, and discharge them as a solid cake from the unit.

Crude Adipic Acid Crystallization in Nitric Acid

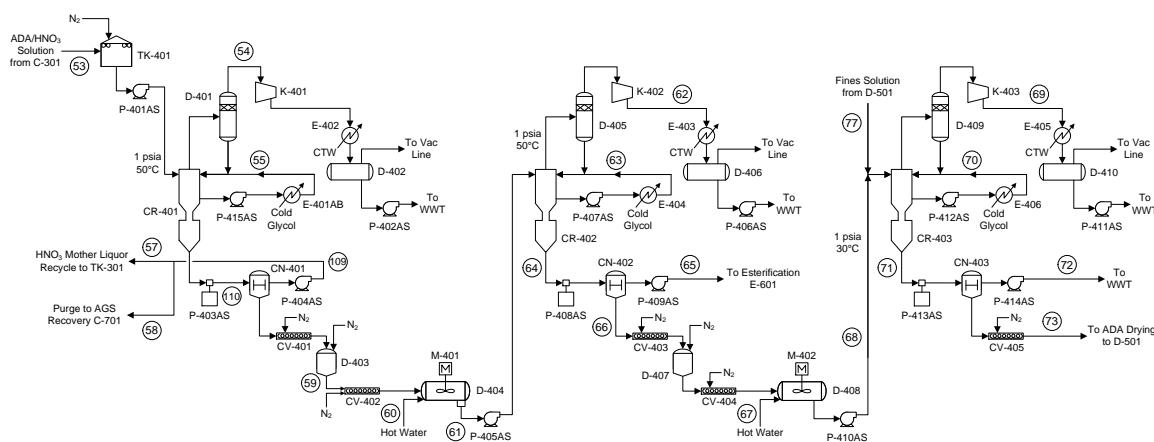
Nitric acid oxidation reactor product from the bottoms of the ADA concentrator, which is the feed to the crude crystallization unit, will have a concentration range (USP 6946572) as shown in the table below.

Table 7.20
CRYSTALLIZER FEED CONCENTRATION

Component	Weight %
Adipic acid	15–25
Nitric acid	25–45
Glutaric acid	5–15
Succinic acid	2–10
Water	Balance

The feed solution, stored in a day tank, is directed to the upper reservoir of an Oslo Crystallizer that is designed to operate continuously at a temperature of 50°C, and a pressure of 1–2 psia (0.07 atm, 52 mmHg). A centrifugal pump circulates crystallizer slurry from the upper reservoir through an external cooler using glycol refrigerant, and back to the crystallizer vessel. Vacuum condition is maintained by a vacuum pump and condenser, which principally removes water vapor from the slurry, and condenses it in a heat exchanger. The process configuration of the nitric acid crystallizer, pusher centrifuge, and ancillary equipment are shown in the process flow diagram below.

Figure 7.28



As water vapor is removed from the solution through the overhead vacuum pump system, and the solution is chilled, adipic acid crystallizes out of solution. Smaller crystals continue to circulate around the external pump around cooling loop, while larger size crystals drop into the bottom section of the Oslo crystallizer, and are removed as an adipic acid crystal in nitric acid slurry. The slurry is pumped using a Moyno pump to a pusher centrifuge. The centrifuge separates the nitric acid-rich bulk liquid (mother liquor) from the adipic acid crystals, which form a filter cake on the inside screen surface of the centrifuge.

The mother liquor is recycled to the nitric acid oxidation section recycle nitric acid feed tank. The adipic acid filter cake is discharged to a holding silo that is nitrogen blanketed, and transferred by conveyor (nitrogen blanketed) to a cold water washing tank. The cold water

washing tank is equipped with an overhead agitator, and a separate quiescent zone. Monocarboxylic acids contained in the adipic acid filter cake have a higher solubility in cold water than adipic acid, and then dissolve in the cold water. The cold water temperature should be below 30°C, or otherwise significant adipic acid will also dissolve in the solution and be lost to the process. The bulk of the adipic acid crystals remain as solids. The wash water, now containing monocarboxylic acids, is directed to the esterification section of the plant to recover economic value from the monocarboxylic acids. The washed crystals are conveyed to a hot water mixing tank, where they mix with hot water and low pressure steam, and redissolve in the hot water.

Adipic Acid 1st-Stage Aqueous Crystallization

The adipic acid solution in hot water is pumped to a 1st-stage aqueous crystallization unit that recrystallizes the now purer adipic acid solution using an Oslo crystallizer and pusher centrifuge. Crystallizer operating conditions are 50°C and 2 psia pressure. Vacuum conditions are maintained by an overhead vacuum pump and downstream condenser that are designed to remove most of the water in the solution. The Oslo crystallizer is equipped with a pump around loop using chilled glycol to reduce the solution temperature to 50°C. The combination of reduced temperature and water removal by evaporation causes adipic acid in solution to crystallize. The crystallized adipic acid aqueous slurry at the bottom of the Oslo crystallizer discharges through a Moyno pump to a pusher centrifuge that separates the crystals from the aqueous solution. The aqueous solution is pumped to wastewater treatment, or recycled to the dissolving tank. The crystals form a filter cake that is directed to a silo, and the filter cake is subsequently conveyed to a hot water mixing tank where the crystals redissolve to remove contaminants and improve product purity.

Adipic Acid 2nd-Stage Aqueous Crystallization

The adipic acid solution in hot water is pumped to a 2nd-stage aqueous crystallization unit that recrystallizes the now purer adipic acid using an Oslo crystallizer and pusher centrifuge. Additional quantities of water are added to the crystallizer solution to maintain the succinic acid concentration below 10% in water, and avoid crystallizing out succinic acid. The solubility in water of the AGS components at 30°C is shown in the table below.

Table 7.21
SOLUBILITY IN WATER OF AGS COMPONENTS AT 30°C

Component	Solubility Concentration
Glutaric acid	64%
Succinic acid	10%
Adipic acid	3%

Second-stage crystallizer operating conditions are 35°C and one psia pressure. Vacuum conditions are maintained by an overhead vacuum pump and downstream condenser that are designed to remove most of the water in the solution. The Oslo crystallizer is equipped with a pump around loop using chilled glycol to reduce the solution temperature to 35°C. The combination of reduced temperature and water removal causes adipic acid in solution to crystallize out of solution down to a concentration in water of 3%, while glutaric and succinic acids, having higher solubilities at this temperature, remain in solution. The crystallized adipic acid aqueous slurry at the bottom of the Oslo crystallizer discharges through a Moyno pump to a

pusher centrifuge that separates the crystals from the aqueous solution. The aqueous solution is pumped to wastewater treatment. The crystals form a filter cake that is directed to a silo, and subsequently conveyed to the crystal drying system.

Section 500—Adipic Acid Drying and Packaging

Adipic Acid Explosion Potential during Drying and Solids Transport

Once separated from its mother liquor via centrifugation, adipic acid filter cake proceeds to a two-stage drying system for the purpose of removing residual liquid, and then to solids product packaging. Adipic acid explosions have occurred on two occasions with 140°C hot air dryers used by DuPont in Texas in 1991 (284048, 248049). Based upon this experience, our design utilizes vacuum rotary dryers (rather than hot air dryers). Our design also incorporates the use of inert nitrogen blankets wherever there is a potential for adipic acid dust to otherwise mix with air and create the potential for an explosive mixture. In particular, our conveying systems are nitrogen inerted, as are adipic acid storage silos.

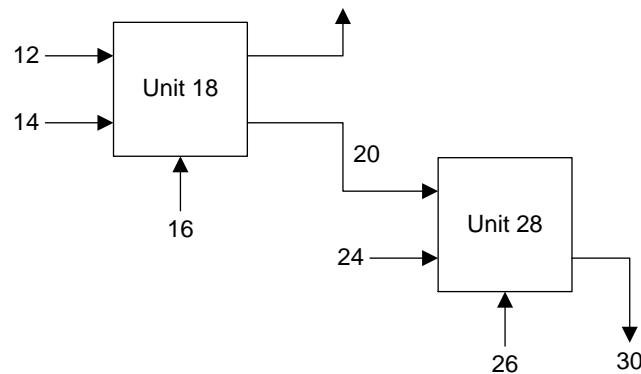
Adipic acid drying systems are still offered commercially using hot air rotary dryers. TianLi Drying Company of China uses a fluidized bed hot air dryer for adipic acid applications. The TianLi system blows hot air into the fluidized bed dryer to fluidize the adipic acid filter cake. An internal heat exchanger within the bed enhances drying time and efficiency. The system includes a downstream cooling section for discharge to a conveying system that will direct the dried adipic acid crystals to packaging. As the fluidizing air (hot air in front section: cold air in back section) leaves the top of the fluidized bed dryer, it contains entrained small particles of adipic acid. The stream is first directed to a cyclone to remove the bulk of the solid particles, and then to a filter to remove residual particulates. Adipic acid product exits the fluidized bed dryer and cyclone through rotary discharge valves. Nitrogen is used to inert the system, and to provide pneumatic conveying of adipic acid.

Proposed Adipic Acid Rotary Vacuum Drying System

To address the potential problem of air drying adipic acid, Invista US Patent 6946571 presents a two-stage process for adipic acid drying using inert gas rather than air. The process (see figure below) claims that the two-stage process reduces the production of 'fines' that occurs in a single, hot drying environment. The moisture content of adipic acid filter cake from the final centrifuge ranges from 3–12 weight %. The commercial sales specifications requires a moisture content of less than 0.2%. While surface moisture can be easily and quickly removed, moisture within the crystal is more difficult to remove, and takes higher temperatures and longer residence time. This more intense drying tends to cause physical degradation of the adipic acid, producing fine particles.

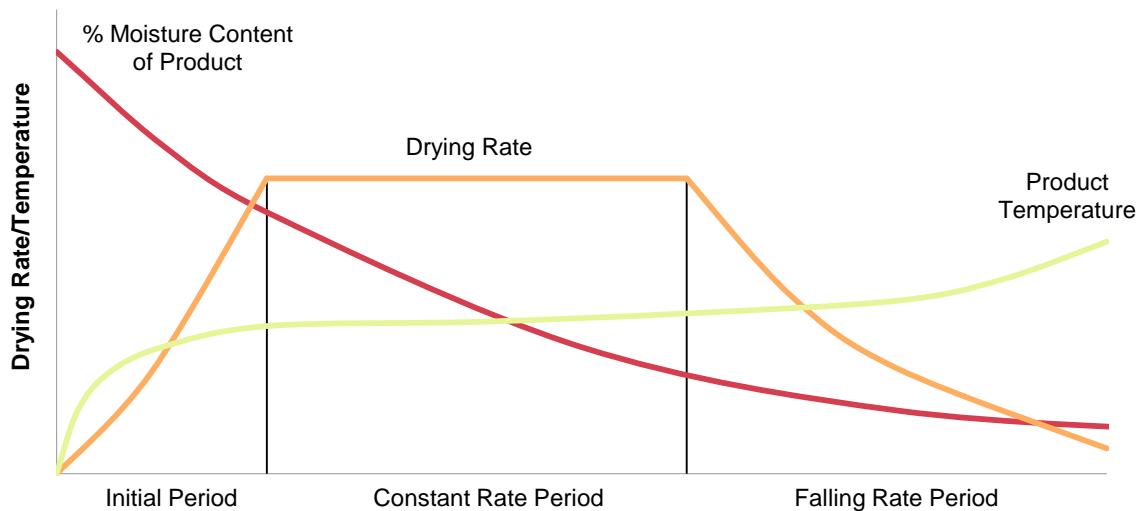
In the Invista patent, adipic acid filter cake from the centrifuge (#12) enters the 1st-stage dryer (#18) along with a hot and inert drying gas (#14). Heat (#16) is supplied via a heat exchanger. The temperature of the first-stage dryer is maintained between 90–110°C. The product adipic acid from the 1st-stage dryer (#20) has moisture content less than 1%. The partially dried adipic acid enters the 2nd-stage dryer (#28) along with inert drying gas (#24). Heat for drying (#26) is provided via a heat exchanger. The dryer operates at 100–150°C and produces a satisfactorily dried adipic acid (#30) with a moisture content less than 0.2%.

Figure 7.29
INVISTA 2-STAGE ADIPIC ACID DRYING (USP 6946571, 20-SEP-2005)



Our proposed drying system follows the Invista patent, and provides two stages of rotary vacuum dryers in series. Our design intent is to have the wet adipic acid crystals enter the rotary dryer and rapidly increase in temperature to the desired end point, and then hold that temperature for an extended period until nearly all of the moisture is removed from the crystals. The desired temperature profile and corresponding drying rate are shown in the figure below.

Figure 7.30
ROTARY DRYER TEMPERATURE PROFILE



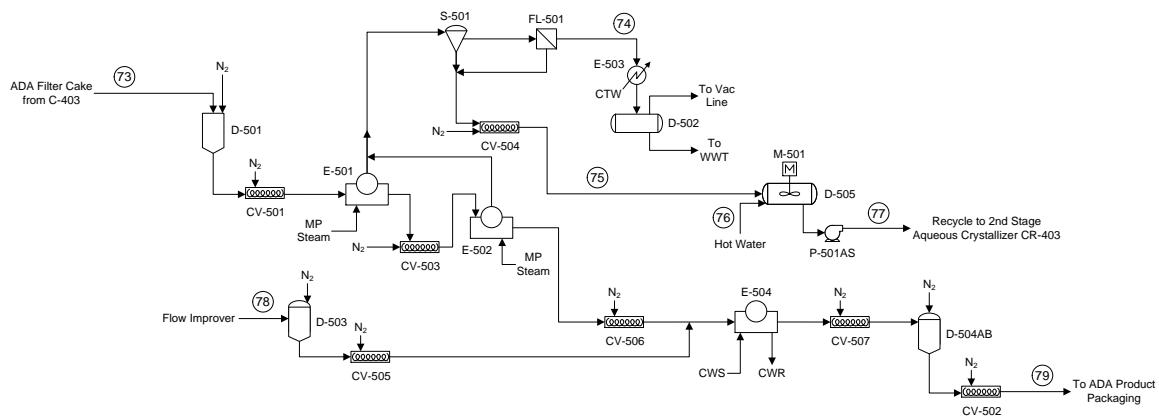
Source: Devki Energy Consultancy (2840500)

Adipic acid filter cake from the 2nd aqueous crystallization unit is conveyed to the first rotary vacuum dryer.

Our proposed configuration for a two-stage rotary vacuum drying system is shown in the process flow diagram below. Adipic acid filter cake enters the 1st-stage dryer, which is equipped with a horizontal axis drum that rotates slowly. An internal heat exchanger is supplied with

medium pressure (300 psia) saturated steam. The first-stage dryer operates at a temperature of 100°C, and the 2nd dryer operates at a temperature of 140°C.

Figure 7.31
ADIPIC ACID 2-STAGE ROTARY VACUUM DRYING



Both dryers are connected to a common overhead vacuum system operating at 7 psia. Hot water vapor removed from the adipic acid filter cake first passes through a cyclone separator, then a one micron fines filter (pulsed filter system), and into a heat exchanger cooled with cooling water. Steam condenses in the heat exchanger creating vacuum. Condensed steam is sent to the wastewater treatment plant for polishing and recycle.

Adipic acid dust particles caught by the overhead cyclone and filter are small in diameter, and unlikely to satisfy the sales specification for particle size distribution. They are conveyed to a hot water tank with a mixer, where they dissolve as an aqueous solution, and are then pumped to the feed of the 2nd-stage aqueous Oslo crystallizer for recovery of adipic acid as larger diameter crystals.

Addition of Adipic Acid Flow Improver

While in storage, adipic acid crystals have the propensity to agglomerate into large and hard chunks that are difficult to process. To overcome clumping, a number of approaches have been patented that use additives to reduce the adhesion of adjacent adipic acid crystals. The table below summarizes several approaches to the use of flow improvement chemical additives for this purpose.

Table 7.22
ADIPIC ACID FLOW IMPROVER APPROACHES

Assignee	US Patent	Flow Improver
Invista	2010/0025635	Monobasic acid
DuPont	3459798	Monobasic acid
DuPont	5025087	Dodecanedioic acid
BASF	6534680	Anionic polyelectrolyte

Our proposed system is to use dodecane dioic acid in solid form as the flow improving chemical. It is conveyed to the feed of the rotary cooler where it mixes with hot adipic acid crystals from the 2nd-stage rotary vacuum dryer discharge. Dosage rate is 250 ppm.

Discharged hot adipic acid crystals from the 2nd-stage rotary vacuum dryer are conveyed to a third rotary dryer for cooling. The dryer is equipped with an internal heat exchanger through which cooling tower water is pumped, which cools the adipic acid crystals down to near ambient temperature. The cooled crystals are discharged first to 2–12 hour silos. Upon satisfying product specifications, the adipic acid product crystals are transferred by conveyor to a packaging unit for 25-kg bagging, 1-metric ton palletizing with shrunk wrap polyethylene, and strapped for sales. Adipic acid crystals are also sent to bulk offsite silos for bulk product transfer by 20 and 40 metric ton bulk carriers. Additional capability is provided to produce adipic acid product in 500 kg and 1-mt iso containers.

Section 600—By-Product Recovery to Methyl Esters

NVR Composition and Source

The air oxidation of cyclohexane to KA oil using cobalt naphthenate catalyst results in the use or production of several high molecular weight by-products. These include the catalyst, formed oligomers and polymers, heavy tars, and oxygenated by-products such as acids, alcohols, ketones, lactones, and esters. The NVR stream also contains minor amounts of corrosion products from the process piping and vessels, primarily iron and chromium (from stainless steel), usually in quantities below 100 ppmw. These materials collectively are found in the air oxidation reactor product stream, and are processed through two stages of fractional distillation: 1) to recover and recycle unconverted cyclohexane, and 2) to purify KA oil (cyclohexanol + cyclohexanone) for further oxidation to adipic acid using nitric acid oxidation. What remains from the air oxidation reactor product stream after the cyclohexane and KA oil components are removed are high boiling point (greater than 160°C) components that leave the distillation train as the bottoms product stream from the KA oil distillation column.

Historically, this stream was burned as boiler fuel to produce process steam within the chemical plant. In the United States, use of hazardous materials as boiler fuel to recover energy is regulated under the portion of the Code of Federal Regulations applying to US EPA jurisdiction (40 CFR 266, Subpart D). With the high price of crude oil resulting in a high feedstock cost, efforts have been made to try to monetize some of the components of the NVR stream at a commercial value significantly higher than fuel value.

NVR Processing Options

Our approach to extracting economic value from the NVR stream follows a basic DuPont process (USP 3365490, 23-Jan-1968), while incorporating technology improvements to the basic

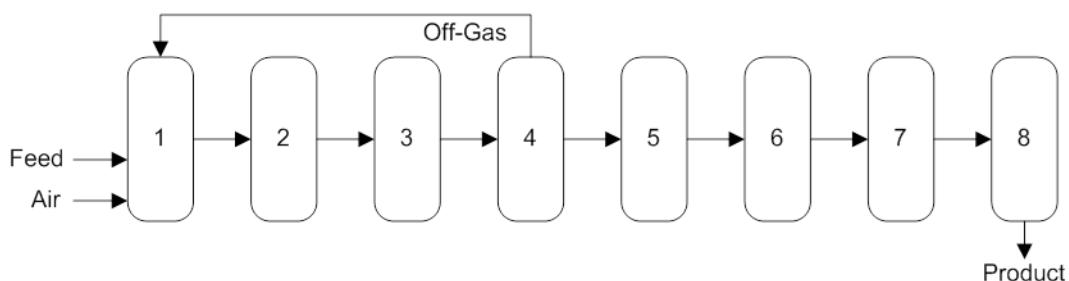
process that have been commercialized since then. Major improvements are documented in USP 6703529 (DuPont) and USPA 20120101009 (Invista).

The basic DuPont processing configuration for NVR recovery is similar to the configuration when KA oil instead is the feedstock (rather than NVR). NVR is subject to two-stage nitric acid oxidation. However, processing temperatures in the primary nitric acid oxidizing reactor are much lower when processing NVR than when processing KA oil. For NVR, the recommended temperature range in the DuPont patent is 35–60°C, while in DuPont patents for KA oil nitric acid oxidation, the recommended temperature range is 70–90°C. Nitric acid oxidation of NVR requires ammonium vanadate catalyst, but does not require copper catalyst as in the KA oil oxidation reaction.

Since the KA oil feed stream to nitric acid oxidation is a distillate product with no solids or high boiling material present, and at a very high concentration of KA oil, KA oil can be supplied directly to the nitric acid reactors. The NVR stream, containing many more contaminants, as well as solids and heavy ends, must be pretreated before nitric acid oxidation.

The basic processing scheme for DuPont USP 6703529 (9-Mar-2004) is shown in the figure below. Vessel #1 is the air oxidation reactor train, while vessel #2 is the oil:water separator. Vessel #3 is the CHHP converter, while vessel #4 is a distillation column taking unconverted cyclohexane feedstock overhead, and recycling it to the air oxidation reaction system. Vessel #5 is a second distillation column taking concentrated KA oil as the overhead product, for further processing in the nitric acid oxidation section. NVR is discharged as the bottoms product from the second distillation column (#5), and processed through an acid treatment reactor (#6), and mixed with an electrolyte solution allowing a phase separation between an oil phase and an aqueous phase. The chromium content of the NVR collects in the aqueous phase, allowing the NVR to be processed with the removal of chromium ions. The acid treatment reactor mixes NVR with dilute nitric acid (1–10%), followed by addition of an electrolyte solution that causes the liquid:liquid phase separation in a decanter (settling drum #8).

Figure 7.32
DUPONT NVR PROCESSING SCHEME (USP 6703529)



Our processing scheme for NVR uses the basic DuPont cyclohexane air oxidation process configuration which produces NVR as the distillation column bottoms product that also produces high concentration KA oil as the overhead distillate product. This differs from the earlier DuPont approach of processing the pretreated NVR stream via nitric acid oxidation.

Conversion of NVR to Methyl Esters

Our disposition for the NVR stream follows Invista USPA 20120101009 (26-Apr-2012) for pretreating the NVR stream to remove gross contaminants, and then esterifying the pretreated flow stream with methanol to form commercially salable polyester polyols useful in the

polyurethanes business. Other commercial uses for methyl esters formed from NVR (as documented in the Invista patent) include curing agents, drilling muds, paint removers, photoresist stripper, graffiti remover, and cleaner.

The ester product formed by reacting methanol with mixed acids will be a family of product grades sold on the basis of their boiling point ranges. Product acid value will be below 10 mg KOH/gm, and hydroxyl values will be between 100–250 mg KOH/gm. The ester product grades will be colorless liquids, with high boiling points (>150°C), and low viscosity (0.6–1.5 cSt). For safety reasons, the esters have high flash point (>93°C). Consisting primarily of monoesters, diesters, and hydroxyl-esters, the individual components with the highest concentration will be dimethyl adipate (derived from adipic acid), and methyl hydroxyl caproate (derived from caproic acid).

Some of the commercial applications listed for NVR-based methyl esters are due to the ability of such methyl esters to effectively dissolve other polymers. The table below lists polymers that will dissolve in methyl ester formulations.

Table 7.23
POLYMERS SOLUBLE IN METHYL ESTERS

Acrylic resin	Poly acrylonitrile	Polyvinylbutyral resin
Epoxy resins	Polyester resins	Polyvinylidene fluoride
Methacrylic resin	Polyurethane resins	Styrene/acrylonitrile copolymers
Phenolic resins	Polyvinyl acetate	Styrenic resins
Phenoxy resins	Polyvinyl chloride	Vinylidene halide resin

When methanol is used as the preferred alcohol for esterification, the family of methyl esters produced from NVR is shown in the table below.

Table 7.24
METHYL ESTERS PRODUCED FROM NVR (INVISTA USPA 20120101009)

Methyl hydroxycaprate	Cyclohexanediols
Dimethyl adipate	Methyl 5-hydroxyvalerate
Dimethyl glutarate	Gamma butyrolactone
Dimethyl succinate	Methyl leuliate

Invista NVR Processing Scheme

The processing scheme proposed by Invista for producing methyl esters has 5 primary steps, as described in the table below.

Table 7.25
NVR PROCESSING STEPS TO METHYL ESTERS

Step Activity

-
- | | |
|---|---|
| 1 | Remove water (dehydrate) and other low boiling point hydrocarbons |
| 2 | React carboxylic acids in NVR with methanol (or other alcohol) to form corresponding ester |
| 3 | More Methanol is added to formed oligomeric esters to convert them to monomeric esters via cleaving |
| 4 | Reactor product neutralization |
| 5 | Reactor production distillation to product grades |
-

Since the NVR stream is water free, step one is not required when processing only this stream. In the Invista patent, the 5 steps provided are used to co-treat the two major sources of by-products in the cyclohexane air oxidation section of the plant: water wash stream just after the oxidation reactors, and the NVR stream. If both streams are mixed in a common tank prior to processing, step one would be required, as the water wash stream contains upwards of 75% water content. If peroxides are present in the feedstock, the initial step is to heat soak the feed at 150°C to destroy the peroxides, which are detrimental to the esterification reaction.

Water dehydration is Step #1, and will also remove light hydrocarbons that boil at a temperature below the boiling temperature of water (100°C). Light boiling compounds include formic acid and acetic acid.

The Step #2 esterification with methanol or other light alcohol (ethanol, propanol, butanol) is a relatively simple reaction in which acid + alcohol yields ester + water. When conducted in the liquid phase, there are no phase changes, and low thermodynamic requirements. As such, the esterification reaction is equilibrium limited, such that as by-product water forms, it becomes progressively more difficult to drive the forward reaction. In some cases, a change in conditions can rapidly cause the reverse reaction to occur. The Invista patent presents esterification reactor conditions of 80–160°C, and sufficient pressure to maintain reactants and products in their liquid state (50–500 kPa, 7–73 psia).

Step #3 involves adding more methanol to the esterification reactor products in order to convert the roughly 20% of initial products that are formed as oligomers (esters reacting with other esters) back to monomeric esters via cracking of the oligomers. Reactor temperature conditions are 65–75°C, and sufficient pressure to maintain liquid conditions within the reactor. Although the principal alcohol used is methanol, other monohydric and poly-hydric alcohols (ethylene glycol, 1,4-butanediol) can also be used to crack oligomer esters back to monomeric form.

Once the ester product is formed and discharged from the reactor, Step #4 requires neutralization to prevent further reaction, and to reduce the acid number of unconverted carboxylic acids. The intent is to reduce the acid number to below 1 mg KOH/gm, which can be accomplished using sodium hydroxide.

Since the reactants are a multitude of individual oxygenated chemicals, the ester product will consist of a multitude of esters. Step #5 involves product distillation for the purpose of removing both light components (unconverted feedstock and water), and heavy polymer. The remaining mono- and diesters are distilled into product grades sold on the basis of boiling point range.

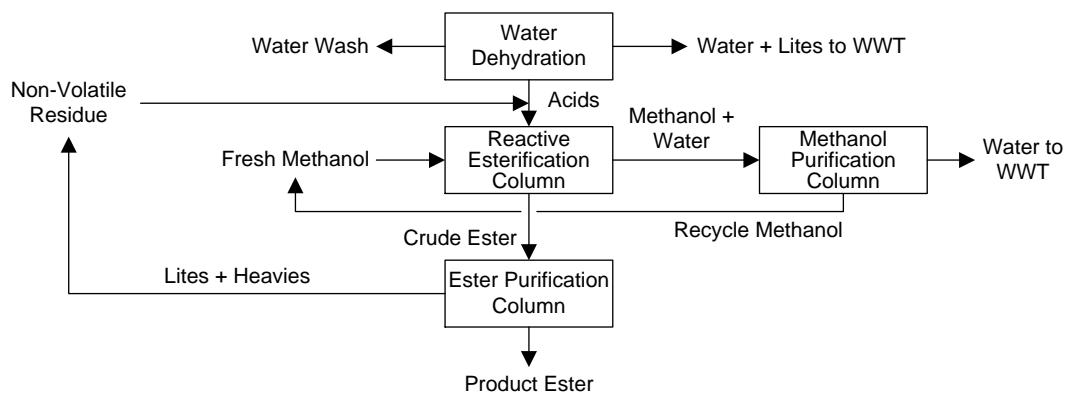
In other well commercial esterification reactions, the equilibrium concern has been overcome by conducting the reaction in a reactive distillation column, in which methanol is fed to the column at the bottom and migrates upward through trays containing beds of catalyst (usually cation ion

exchange resin), while the acid stream (NVR in our case) enters the column near the top and migrates downward through the catalyst beds. A large excess of methanol is used (5x stoichiometric) to maximize acid conversion and to minimize oligomerization of monomeric esters. As excess methanol sweeps through the reaction beds, the excess methanol moving upward in the column takes with it water formed by the esterification reaction. The overhead product stream from the reactive distillation column is water plus excess methanol, while the bottoms product stream is product ester. If a sufficient number of trays are provided in the design, intermediate product streams can be drawn off at different trays (and different temperatures) to provide a family of methyl ester product grades based upon boiling point.

Mixed Ester Production Process Description

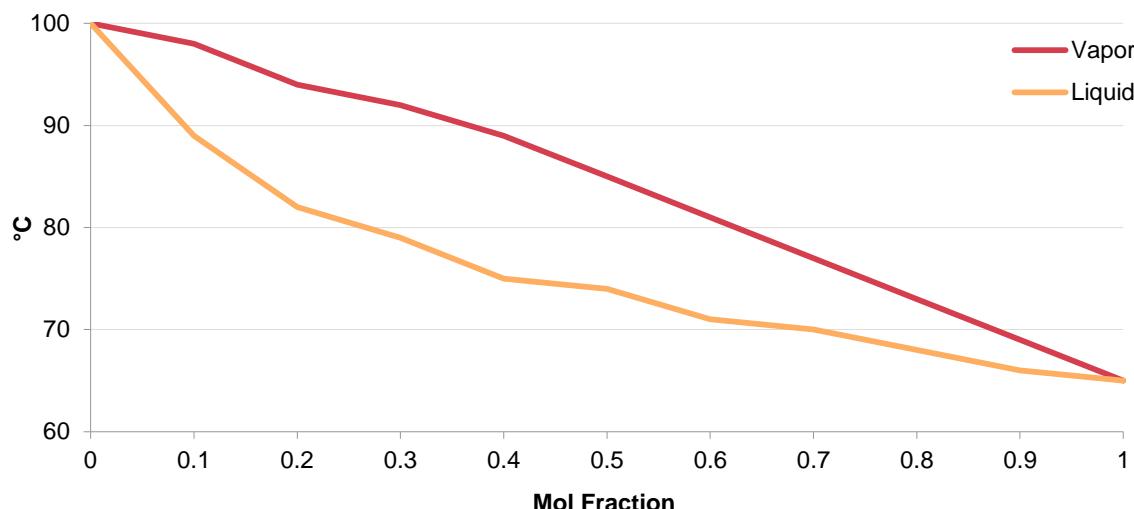
The overall processing scheme for proposed by-product recovery via esterification is shown in the block flow diagram below. Dilute water wash discharge from the oxidation section hydrolysis section is evaporated in a heat exchanger (using low pressure steam) to substantially remove the water content, and also light hydrocarbons that boil below 100°C. The resulting product is combined with non-volatile residue and directed to a reactive distillation column for the purpose of esterifying the acids to monoesters by reaction with vapor-phase methanol. NVR and concentrated water wash is fed to the top of the reactive distillation tower, while methanol is vaporized and enters the bottom of the column, flowing upward. Near the middle of the column are 6 trays loaded with esterification catalyst (cation exchange resin). Conventional distillation trays are located both above and below the trays dedicated to reaction service. A large excess of methanol is fed to the column (5x stoichiometric) for the purpose of both maximizing acid conversion to ester, and also minimizing the conversion of acid to oligomeric ester. As excess methanol vapor travels upward through the column, it sweeps away water vapor that is formed by the reaction. Methanol and water vapor exit the top of the tower and are fed directly to a methanol: water distillation column for the purpose of separating methanol from water.

**Figure 7.33
BY-PRODUCT RECOVERY VIA ESTERIFICATION BLOCK FLOW DIAGRAM**



Methanol and water do not form an azeotrope. Consequently, they can be separated via conventional fractional distillation. The distillation curve for methanol and water mixtures at atmospheric pressure is presented in the figure below.

Figure 7.34
**METHANOL: WATER DISTILLATION CURVE (284051)—METHANOL MOL FRACTION
 VERSUS TEMPERATURE (°C)**



Source: Luyben, WL, 'Distillation Design and Control Using Aspen Simulation,' John Wiley (2006)

Operating at atmospheric pressure, methanol can be distilled from water at high purity in a column with an overhead temperature at methanol's boiling point (337°K, 64°C), and a bottom temperature at water's boiling point (373°K, 100°C). The purified methanol overhead product stream is recycled to the esterification reactive distillation column, while the water is sent to wastewater treatment. Our design uses 54 trays at a reflux ratio = 4.

Esters produced in the reactive distillation column discharge from the bottom of the column, and are sent to a second distillation column (ester purification column) operating under vacuum conditions to produce product grades of ester differentiated by boiling point. The major components of esters formed are listed in the table below, with their boiling point at atmospheric pressure.

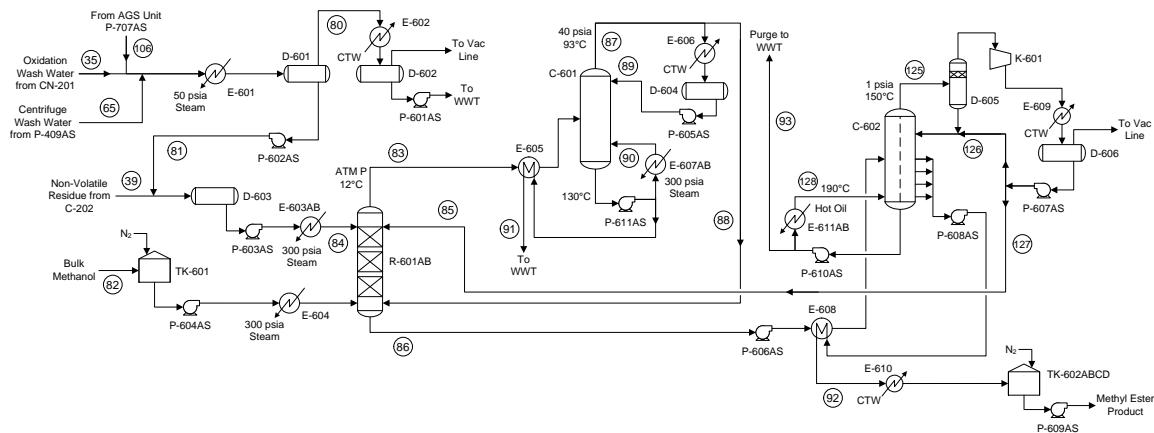
Table 7.26
BOILING POINT OF PRIMARY MONOESTER COMPONENTS

CAS Number	BP (°C)	Component
627-93-0	229	Dimethyl adipate
1119-40-0	214	Dimethyl glutarate
106-65-0	200	Dimethyl succinate
1792-81-0	237	Cyclohexanediol
24323-38-4	205	Methyl 5-hydroxyvalerate
96-48-0	204	Gamma butyrolactone
624-45-3	195	Methyl levulinate

Given the high boiling points of the major components, and the potential for them thermally degrading at boiling temperature, the ester product distillation column is designed to operate at deep vacuum (1 psia), in order to maintain distillation temperatures below 150°C. The distillation column is equipped with structured packing, rather than trays, and is designed as a divided wall distillation column, in order to produce reasonably pure ester-grade products in sidestream liquid draw off nozzles, rather than the conventional practice of taking product from either the overhead distillate or bottoms streams. For the ester purification column, unconverted acids are designed to be separated from product as the overhead distillate, and are recycled to the esterification reactive distillation column. A purge to wastewater treatment is also taken to prevent the build-up of light materials that do not form esters. The bottoms product stream from the ester purification column is expected to contain heavy material, primarily oligomeric esters, tars, solids, and polymer. This stream is also recycled to the ester reactive distillation column for the purpose of splitting the oligomers using the high excess concentration of methanol. A purge stream to wastewater treatment is also taken for this stream, to prevent the build-up of polymers and tar.

A process flow diagram for this section of the process plant is shown below.

Figure 7.35
BY-PRODUCT RECOVERY PROCESS FLOW DIAGRAM



One such composition of mixed methyl ester is listed in the table below.

Table 7.27
INVISTA METHYL ESTER PRODUCT COMPOSITION (INVISTA USPA 20120064252)

About 10 to 60 weight percent methyl hydroxycaproate
About 20 to 80 weight percent dimethyl adipate
About 1 to 15 wt% of dimethyl glutarate
About 0.1 to 5 wt% of dimethyl succinate
About 0.1 to 7 wt% of at least one cyclohexanediol
Less than about 20 wt% oligomeric esters.

Commercial applications identified in the Invista patent application for the methyl ester product stream are listed in the table below.

Table 7.28
ADIPIC ACID BY-PRODUCT END-USE APPLICATIONS (INVISTA USPA 2012/0064252)

Liquid solvents
Cleaning agents
Polymer curing agents
Foundry mold release agents
Polyols for polyurethane elastomers
Drilling muds and down-hole formulations
Photo-resist strippers

Witco Approach for Converting Non-Volatile Residue (NVR) Directly to Polyester Polyols

One approach, patented by Witco Chemical (USP 4233405) is to dehydrate/evaporate the NVR stream to minimize water concentration while also removing low boiling point components (that usually form color bodies), and reacting the entire concentrated NVR stream with a polyol to produce a polyurethane polyester. The NVR product stream directly discharged from the distillation column bottoms usually has a water content of up to 40%, due to the stream's acid content and the propensity of acids and water to form azeotropes rather than to distill in pure form. The Witco patent recommends reacting the dewatered NVR stream with pentaerythritol or trimethylolpropane. Patent examples showed that conducting the reaction at about 200°C removes all traces of water. Yield from the dried NVR feed was approximately 70%. The resulting polyester polyol had a viscosity of 13,800 cps, an acid number of 1.1, and a hydroxyl number just below 350. The polyol was then reacted with a polyisocyanate to form a polyurethane polymer which was blown to form a rigid foam.

Design Approach for this Project

The three remaining major process streams that contain dilute quantities of by-products that can be recovered, purified, and sold as commercial by-products: 1) a combined stream of adipic acid, glutaric acid, and succinic acid (AGS product) concentrated in the crude crystallization section of the plant as components in a nitric acid-rich mother liquor, and 2) a heavy hydrocarbon stream produced in the air oxidation section of the plant, and concentrated as the bottoms non-volatile residue (NVR) product stream from a distillation column designed to produce concentrated KA oil as the distillate, and 3) the water wash stream from the hydrolysis drum of the cyclohexane air oxidation section of the plant. The designs provided for recovering commercially valuable components within these streams are described below.

Section 700—AGS By-Product Production

Nitric Acid Mother Liquor Purge Stream from Crystallization

There is limited crystallization recovery of adipic acid possible from nitric acid solution without co-crystallizing succinic acid and/or glutaric acid. Once this limit has been reached,

additional adipic acid recovery at high purity is possible only by removing the nitric acid, replacing it with water, and recrystallizing additional amounts of adipic acid out of the aqueous solution. The improvement in recovery is due to the fact that adipic acid has a much higher solubility in nitric acid than it has in cold water. In cold water, adipic acid is much less soluble than either glutaric acid or succinic acid, providing an opportunity for additional adipic acid recovery without co-crystallizing either glutaric acid or succinic acid.

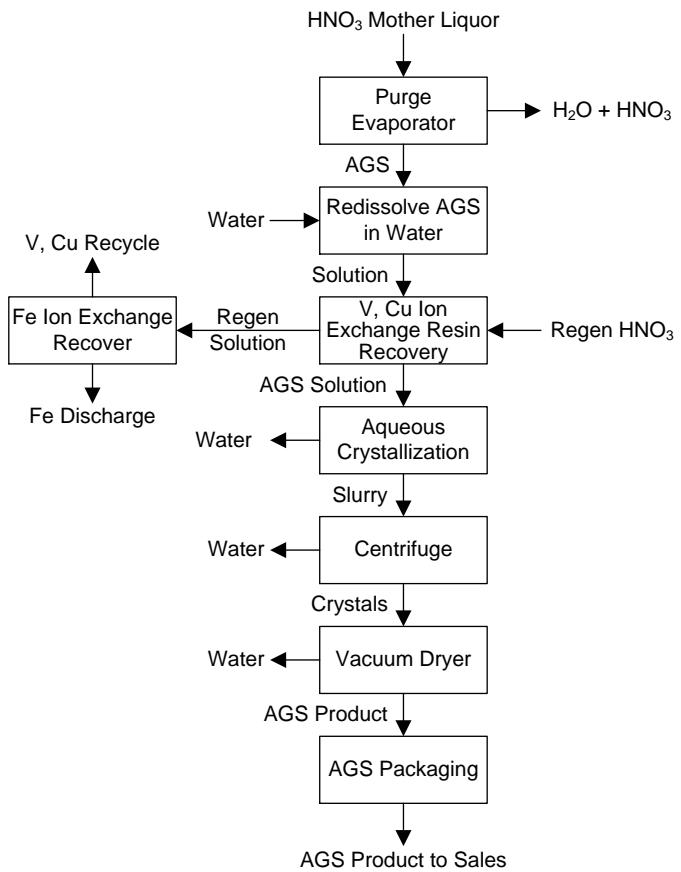
A nitric acid in water solution is used as solvent and reaction catalyst in the nitric acid oxidation reactors. The oxidation of KA oil to adipic acid produces water as a reaction by-product. The nitric acid oxidation reaction also produces thermal degradation products glutaric (C_5) acid, and succinic (C_4) acid, plus lesser quantities of monocarboxylic acids, hydroxyl carboxylic acids, and other oxygenated hydrocarbons (alcohols, aldehydes, ketones, lactones, esters). A representative composition of nitric acid mother liquor (after nitric acid crystallization and centrifugation of adipic acid crystals) was reported in Bayer USP 5587511 (24-Dec-1996), as shown in the table below.

Table 7.29
TYPICAL MOTHER LIQUOR COMPOSITION AFTER CRUDE ADIPIC ACID
CRYSTALLIZATION

Component	Weight %
Nitric acid	40–60%
Succinic acid	2–8%
Glutaric acid	4–10%
Adipic acid	2–25%
Water	Balance

If the nitric acid-rich mother liquor from crystallization is completely recycled, these di- and monocarboxylic acids will increase their concentration in the crystallization feed to a level that will contaminate adipic acid as it crystallizes out of solution. As a result, most adipic acid producers purge some of the recycle nitric acid solution mother liquor to a separate process unit that removes glutaric acid and succinic acid, and most of the monocarboxylic acids. Unfortunately, this process stream also contains residual quantities of adipic acid, which is removed at the same time. The result is a combined by-product stream of the three acids that can be sold as a single commercial product, principally to produce polyester polyols for elastomeric shoe soles. The nitric acid-rich mother liquor also contains the copper and vanadium oxidation catalyst for the nitric acid oxidation reaction, and most producers find it economically viable to recover these metals in the same process sequence as used to recover the AGS by-product acid stream. Depending on producer, the percentage of nitric acid mother liquor that is purged to the AGS recovery unit ranges between 10–30% of the mother liquor nitric acid recycle stream. Our design is based on 10% purge rate. The overall proposed process sequence for catalyst recovery and AGS purification is shown in the block flow diagram below.

Figure 7.36
AGS RECOVERY BLOCK FLOW DIAGRAM



Evaporation of Nitric Acid and Water from the Purge Stream

The first step in the proposed AGS by-product recovery scheme is to evaporate from the mother liquor purge stream both the nitric acid and the water content. Due to the nitric acid: water azeotrope, it is not possible to remove only the nitric acid. The purge stream is directed to a distillation column designed to operate with a bottom temperature of 140°C (overhead temperature = 60°C), and 2 psia (100 mmHg), which produces a molten product stream that is nearly free of nitric acid and water. The nitric acid and water can be evaporated at lower bottoms temperature (120°C) and lower corresponding pressure (1.5 psia, 80 mmHg).

An alternative approach to evaporating away the nitric acid and water for AGS by-product recovery is to instead dilute the mother liquor with an aqueous solution of low concentration (0.5–6%) adipic acid, and reduce the temperature of the resulting solution down to 30–60°C, which induces crystallization of the bulk of the remaining adipic acid in the solution. This approach was patented by Bayer in 1993 (USP 5264624). The abstract to the Bayer patent is presented below.

This invention relates to a process for the recovery of adipic acid from mother liquors collected during commercial production of adipic acid, wherein said mother liquors contain from 52 to 60% by weight of nitric acid calculated as HNO_3 , not taking into account the organic constituents, from 2 to 6% by weight of **succinic acid**, from 4 to 9%

by weight of **glutaric acid**, and from 5 to 10% by weight of adipic acid, by selective crystallization of the adipic acid dissolved in said mother liquors by (a) adding an aqueous adipic acid solution having an adipic acid content of from 0.5 to 6% by weight to said mother liquor in the temperature range of from 30° to 60°C. in such a quantity that the concentration of nitric acid in the mixture is reduced to 35 to 50% by weight; (b) cooling the mixture by at least 5 degrees Celsius within a period of from 0.5 to 5 hours to induce crystallization of the adipic acid; (c) isolating the crystallized adipic acid by filtration; and (d) transferring the filtrate obtained in step (c) to a distillation apparatus for distillative workup of the **glutaric acid** contained therein.

In our process, the purge stream mother liquor is directed to a distillation column operating under vacuum conditions (2 psia), with a design overhead temperature of 60°C, and a bottoms temperature of 140°C, which produces a molten residual bottom stream product containing primarily the AGS acids, plus less than 2% of water and nitric acid. The condensed water and nitric acid mixed overhead product stream are recycled to the nitric acid recycle tank. The column is designed to operate with 24 sieve trays, and a reflux ratio of 4.

Recovery of Vanadium and Copper Catalyst Metals

Once the molten dicarboxylic acid-rich molten solution is removed from the evaporator, and washed with hot water to redissolve the molten materials, the dilute aqueous stream containing catalyst and mixed acids is then processed through a Rohm and Haas Amberlyst-40™ wet cation exchange resin (sulfonated copolymer of divinyl benzene and styrene) at ambient conditions. The resin preferentially absorbs metal ions such as the dissolved vanadium and copper metals from the catalyst. Ion exchange design conditions are 40–70°C, and atmospheric pressure or above.

An alternative vendor to Rohm and Haas Amberlyst-40™ for supplying suitable cation ion exchange resin is Lanxess Lewatit MonoPlus SP112™ macroporous type strongly acid cation exchange resin (CAS 69011-20-7), which also consists of styrene-divinylbenzene copolymer.

The vanadium and copper ions are recovered from the cation exchange resin by regenerating the resin with diluted aqueous nitric acid (20–30% HNO₃).

Unfortunately, the ion exchange resin will also absorb other dissolved metals in the aqueous solution, principally small amounts of iron and chromium that become dissolved in the nitric acid solution via corrosion of the process piping and wetted process equipment. To separate the dissolved iron and chromium ions from the desired catalyst metal ions, the regeneration solution can be passed through a second ion exchange resin system consisting of aminophosphonic acid groups, which will selectively remove iron and chromium ions while leaving behind the vanadium and copper ions. This approach to iron removal was patented by Lanxess (USP 5723098) in 1998. The recommended ion exchange resin is Lanxess Lewatit MonoPlus SP112™ to which methylammonium phosphonic acid groups have been attached.

AGS Aqueous Crystallization and Centrifuging

The AGS aqueous solution, after being discharged from the ion exchange resin beds, is directed to an aqueous Oslo crystallizer for the purpose of crystallizing all three dicarboxylic acids together (adipic acid, glutaric acid, and succinic acid). At 5°C, adipic acid and succinic acid are nearly insoluble in water at atmospheric pressure. Suspension crystallization is performed at these conditions, eliminating the need for an overhead vacuum circuit. The residual glutaric acid remaining dissolved in the aqueous solution will be monetized by sending this stream to the esterification unit (after centrifuging), for conversion to the corresponding methyl ester.

The bottoms product discharge nozzle from the Oslo crystallizer is piped to a Moyno pump that discharges the slurry to a pusher centrifuge for the purpose of separating the AGS crystals, in the form of filter cake, from the aqueous liquor. The liquid discharge from the pusher centrifuge

is pumped to the esterification unit for the purpose of converting the organic acid content (primarily glutaric acid) to methyl esters.

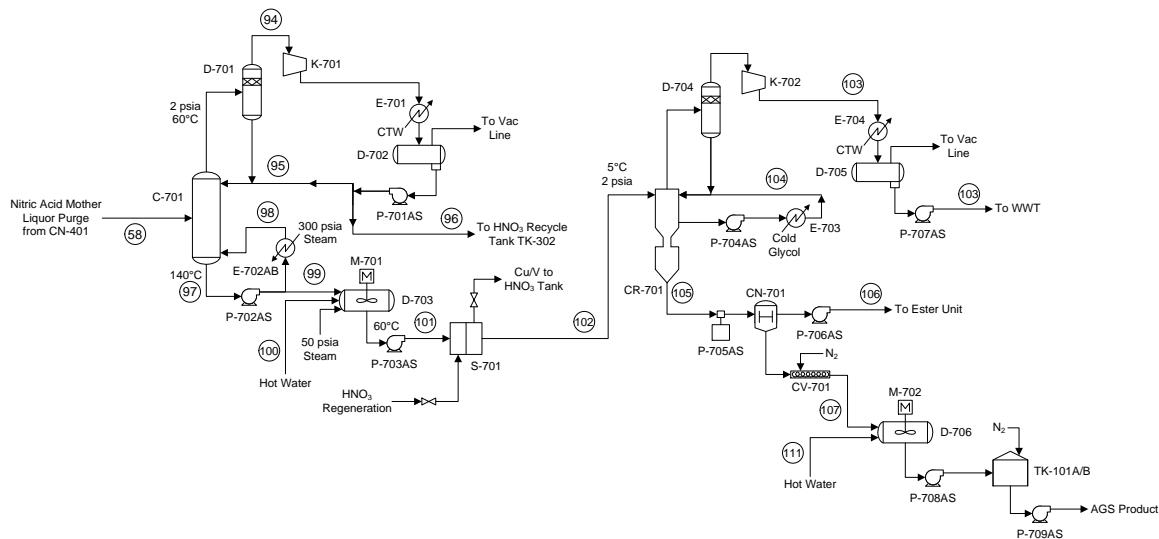
AGS Crystal Drying

The AGS aqueous filter cake from the pusher centrifuge is conveyed to a 1-stage rotary dryer for the purpose of removing sufficient water vapor from the crystals to produce a product with less than 0.5% moisture content. The crystals rotating in the dryer are heated by an internal heat exchange surface that is heated with low pressure saturated steam (50 psia). The rotary dryer is designed to operate at atmospheric pressure with an internal temperature of 115°C. Dried crystals are then conveyed to a rotary cooler that uses cooling water to cool the crystals down to a temperature of 60°C. Cooled and dried crystals are stored in several silos for subsequent packaging in palletized skids (25 kg bags), 500 kg and one mt iso containers, and 20 and 40 metric ton bulk containers.

The overhead moist vapors from the rotary dryer are directed through a 1-stage cyclone and 0.1 mm cartridge filter for removal of entrained dust. Collected dust from both the cyclone and filter are redissolved in hot water and directed to a small tank with a mixer to redissolve the dust. The solution formed is then recycled to the Oslo crystallizer for recrystallization at larger particle size. The moisture leaving the cartridge filter is condensed in a heat exchanger (using cooling water), and the condensate is pumped to the plant's wastewater treatment process unit.

A process flow diagram for the section of the plant treating nitric acid mother liquor purge is shown in the figure below.

Figure 7.37
NITRIC ACID MOTHER LIQUOR PURGE TREATMENT PROCESS FLOW DIAGRAM



Section 800—Nitrous Oxide Destruction

The nitric acid oxidation of KA oil produces a liquid stream rich in adipic acid, and a vapor stream containing steam and nitrogen oxide gases (NO₂, NO₃, N₂O, NO). Upon water scrubbing of this stream, NO oxidizes to NO₂, while the NO₂ and NO₃ vapors can be redissolved to form nitric acid. However, nitrous oxide (N₂O) passes through the water scrubber unaffected.

Rationale for Nitrous Oxide (N₂O) Destruction

Due to the extremely high greenhouse gas impact of nitrous oxide (N₂O) if vented to atmosphere, western governments require that N₂O not be discharged to atmosphere without some form of abatement. The Intergovernmental Panel of Climate Change (IPCC) claims that the N₂O impact as a greenhouse gas is 310 times higher than that of CO₂. The major industrial sources of potential N₂O atmospheric emissions are adipic acid plants and nitric acid plants. Several technologies are commercially available under process license for nitrous oxide destruction.

In the United States, regulations have been proposed (40 CFR Part 98—Subpart E) to require the submission of regular reports on N₂O production by adipic acid producers. In the absence of site-specific data, the guideline production value is 300 kg N₂O per metric ton of adipic acid produced. This is equivalent to one mol N₂O per mol of adipic acid produced. Plant operating performance at several sites has demonstrated an ability to eliminate 90%+ of the uncontrolled N₂O emissions using incineration technology.

In 1991, the US EPA published a document estimating the uncontrolled emissions of nitrogen oxides from US adipic acid plants (284052) as a function of production capacity, and also estimated the capital and annual operating costs for two approaches to reducing NOx emissions: improved absorption at lower temperatures by refrigerating the absorbing solvent, and thermal destruction of N₂O to nitrogen plus oxygen (see table below).

Table 7.30
US EPA ESTIMATE OF N₂O DESTRUCTION ECONOMICS

Plant Size, 10 ³ tons/yr	Uncontrolled NOx Emissions, tons/yr	Control Technique	NOx Removed, tons/yr	Capital Cost, \$10 ³	Annual Cost, \$10 ³	Effectiveness, \$/ton NOx Removed
190	5,040	Extended absorption	4,330	2,830	425	98
300	7,950	Thermal reduction	6,480	7,050	3,240	500
350	9,280	Thermal reduction	7,560	8,000	3,720	492

Source: US EPA

US EPA also identified the environmental impacts of employing both technologies (see table below). For extended absorption, operating at lower temperatures reduces NOx emissions at the expense of energy required to drive the refrigeration system. This approach, however, does not affect the more important emissions of nitrous oxide (N₂O). Thermal reduction can virtually eliminate N₂O emissions at the cost of energy required to create the high temperature environment required for thermal destruction.

Table 7.31
ENVIRONMENTAL IMPACT OF N₂O DESTRUCTION TECHNOLOGIES

Control Technique	Air Impact	Liquid Impact	Solid Impact	Energy Impact
Extended absorption	Reduces NOx, no abatement of N ₂ O	None	None	Pumps and refrigeration used
Thermal reduction	Reduces NOx, possible HC and CO emissions	None	None	Natural gas consumption; heat recovery possible

Source: US EPA

NITROUS OXIDE DESTRUCTION TECHNOLOGIES

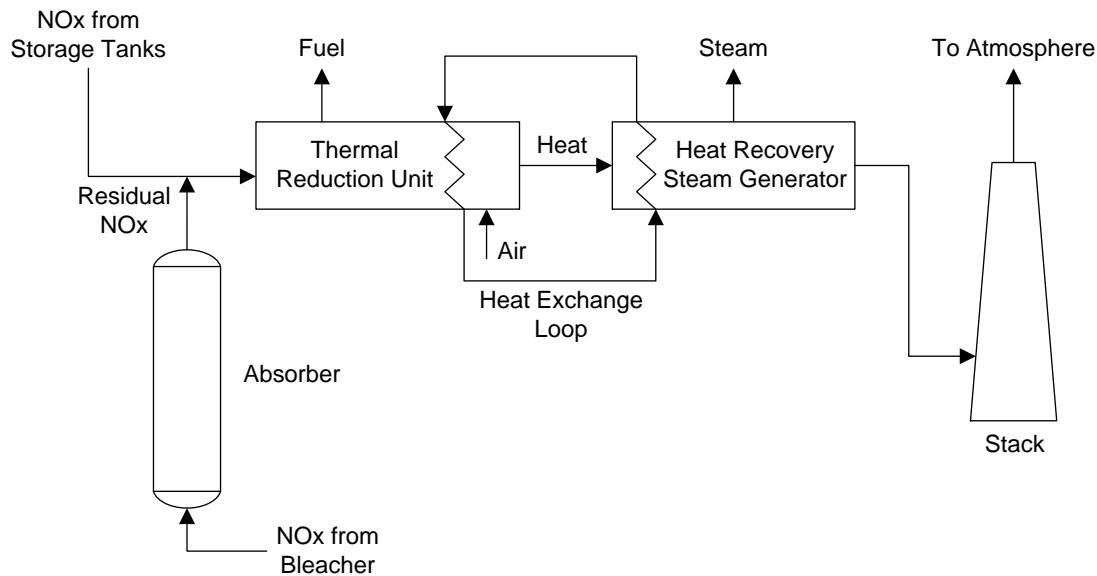
Four general technologies are applicable to substantially reduce atmospheric discharges of nitrous oxide:

1. Thermal reduction of N₂O
2. Two-stage catalytic reduction
3. UOP Pressure swing absorption for N₂O recovery
4. BASF N₂O reduction using ammonia (NH₃)

Thermal Reduction of Nitrous Oxide

It is believed that both Ascend (formerly Monsanto/Solutia) in the United States, Rhodia in South Korea and Brazil, Invista in Singapore, and Lanxess in Germany practice thermal destruction of N₂O via multi-stage incineration. Fuel gas and a small amount of air are combusted to raise the vapor temperature above 1,000°C. It is believed that 1,090°C is the optimum incineration temperature. At these conditions, the N₂O-rich stream will be reduced to a combination of nitrogen (N₂) and oxygen (O₂). The first step in the process is to combust natural gas in sufficient (but below stoichiometric ratio) air to raise the temperature to approximately 1,090°C. In the second stage, the nitrous oxide stream is injected, and reduced to nitrogen plus oxygen. The combustion and reduction reactions are conducted within a boiler fire box to use the heat of reaction to raise process steam. A generic block flow diagram for this process is presented below.

Figure 7.38
THERMAL REDUCTION OF NITROUS OXIDE BLOCK FLOW DIAGRAM (284052)

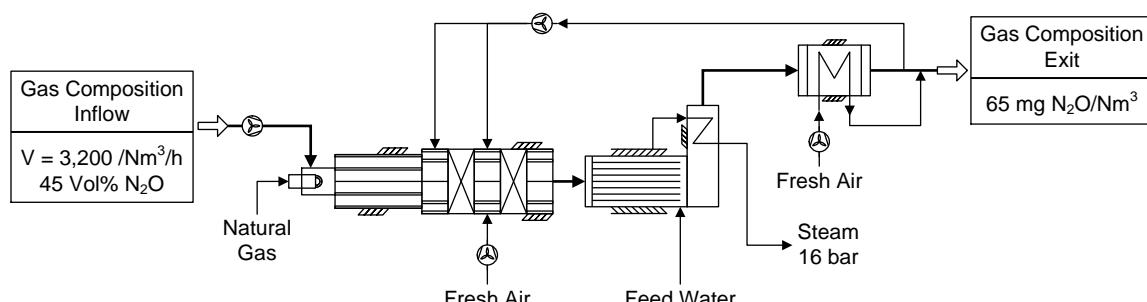


Source: US EPA (EPA-450/3-91-026)

Lanxess Thermal Decomposition of N₂O

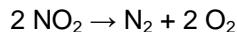
Lanxess operates the former Bayer adipic acid plant at Leverkusen (Krefeld-Uerdingen), Germany. Lanxess in 2006 planned the installation of a thermal decomposition facility for N₂O (284053), which involved two parallel trains of processing facilities to assure high reliability and high availability. Facility construction started in 2009, and was expected to be completed in three years. A schematic drawing of the facilities is presented below. The feed stream contains approximately 45% N₂O, and 1.0% nitric oxides. Both components are destroyed in a two-stage process. The components are first decomposed at very high temperature (approximately 1,500°C) using natural gas fuel, and then serve as the oxygen source for the combustion of an introduced air stream. The hot exhaust gases are passed through a boiler for the purpose of raising process steam.

Figure 7.39
LANXESS THERMAL DECOMPOSITION OF N₂O AT LEVERKUSEN



Source: Joint Implementation Project Design Document Form (UNFCCC), Lanxess Redundant Thermal Decomposition of N₂O (2006), Version 01

Residual NO_x components leaving the gas absorber can be further treated to increase the amount of residual NO_x that is removed. In two commercial adipic acid plants in the United States, the residual gas stream from the absorber is directed to a heat recovery boiler where natural gas and air are added at sub-stoichiometric ratios to create a reducing (rather than oxidizing) atmosphere. The reaction stoichiometry for reduction chemistry is presented below.



The prevalent reduction methodology is to direct the N₂O containing vapor stream through a fixed bed of cuprous oxide supported on alumina, which deoxidizes the N₂O back to nitrogen and oxygen (284054).

As an alternative to complete reduction, a two-step reaction scheme is used in a combined oxidation and reduction process, where the first reaction combines the vent gas, natural gas and air at 1,090°C to convert NO₂ to NO.



The product gases pass through the first section of the boiler for heat recovery, reducing the combined gas temperature to 760°C. At the lower temperature, additional natural gas is provided to reduce the NO to molecular nitrogen (N₂).



As an alternative to reducing NO to N₂, process technology exists from DuPont and Rhodia to catalytically oxidize NO to NO₂, which can then be combined with water for oxidation back to nitric acid.



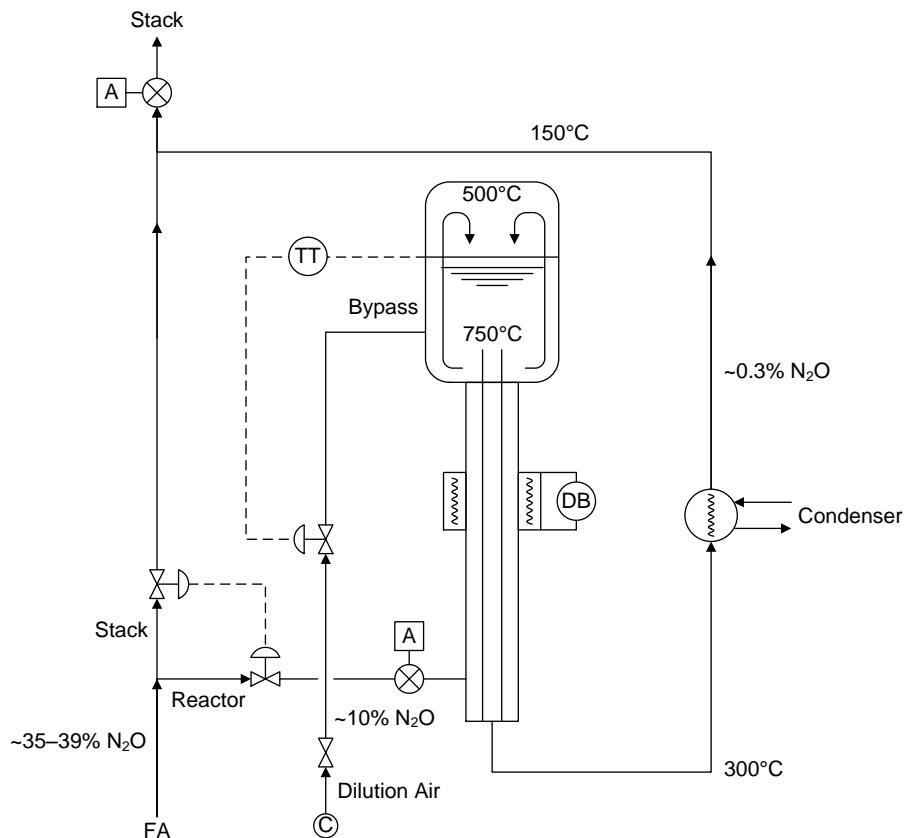
Catalytic Reduction of Nitrous Oxide

DuPont Canada Experience in Nitrous Oxide Reduction

In Canada during 2001, DuPont (former owner of the Maitland, Ontario adipic acid plant now shut down), applied to the Canadian government (Air Canada) for greenhouse gas credits associated with an existing (built in 1997) nitrous oxide reduction unit using catalytic incineration technology. The nitrous oxide containing gas was primarily off-gas from the nitric acid absorber, plus fumes from smaller nitric acid storage tank vent gas. The concentration of nitrous oxide in the stream is 35–39%. The DuPont process configuration passes the combined stream through a fume abatement column (caustic scrubber).

The DuPont process combines compressed air with the N₂O process stream to reduce the N₂O concentration to 10% by volume, and directs it to the shell side of a shell-and-tube reactor for heating followed by an adiabatic catalyst containing basket where the exothermic reaction proceeds, raising the gas by 23°C per 1% of nitrous oxide in the feed gas. The heated and reacted gas is directed back through the tube side of the reactor for the purpose of preheating the feed gas. Following discharge from the reactor at 300°C, the product gas passes through another heat exchanger that preheats condensate (for heat recovery), and eventually enters the discharge stack at a temperature of approximately 150°C. A schematic drawing of the DuPont process in Maitland is presented below.

Figure 7.40
DUPONT CANADA N₂O DESTRUCTION SCHEMATIC



Source: DuPont Submission to Air Canada for Greenhouse Gas Abatement Credits (2001)

The discharge concentration of N₂O to the discharge stack is 0.3% by volume. When compared to a feed concentration to the unit of 10%, the overall N₂O destruction efficiency is 97%. N₂O concentration is monitored in the stack with a Servomex (Norwood, Massachusetts, USA) Model Xendos 2500 continuous measuring instrument (single beam infrared gas analyzer). On cold start-up, electric induction heaters preheat the feed to the reactor.

BASF Approach to Nitrous Oxide Destruction

BASF in 2009 commercially implemented N₂O destruction at its 370 kty Ludwigshafen, Germany adipic acid plant (284055), and in 2011 contracted to license its N₂O destruction technology at PetroChina's adipic acid plant in China. As of 2012, German law requires the reduction of NO_x from manufacturing facilities, but does not specifically require N₂O destruction associated with greenhouse gas issues. The Ludwigshafen plant began commercial production of adipic acid in 1939 (284056), and the current manufacturing plant (as of 2012) was started up in 1965. The most recent adipic acid debottleneck was in 2007, resulting in a nameplate production capacity of 370 kty. Annual adipic acid production has averaged 300 kty. Recent adipic acid and N₂O production at Ludwigshafen is listed in the table below.

Table 7.32
ADIPIC ACID AND N₂O PRODUCTION AT BASF LUDWIGSHAFEN PLANT (284056)

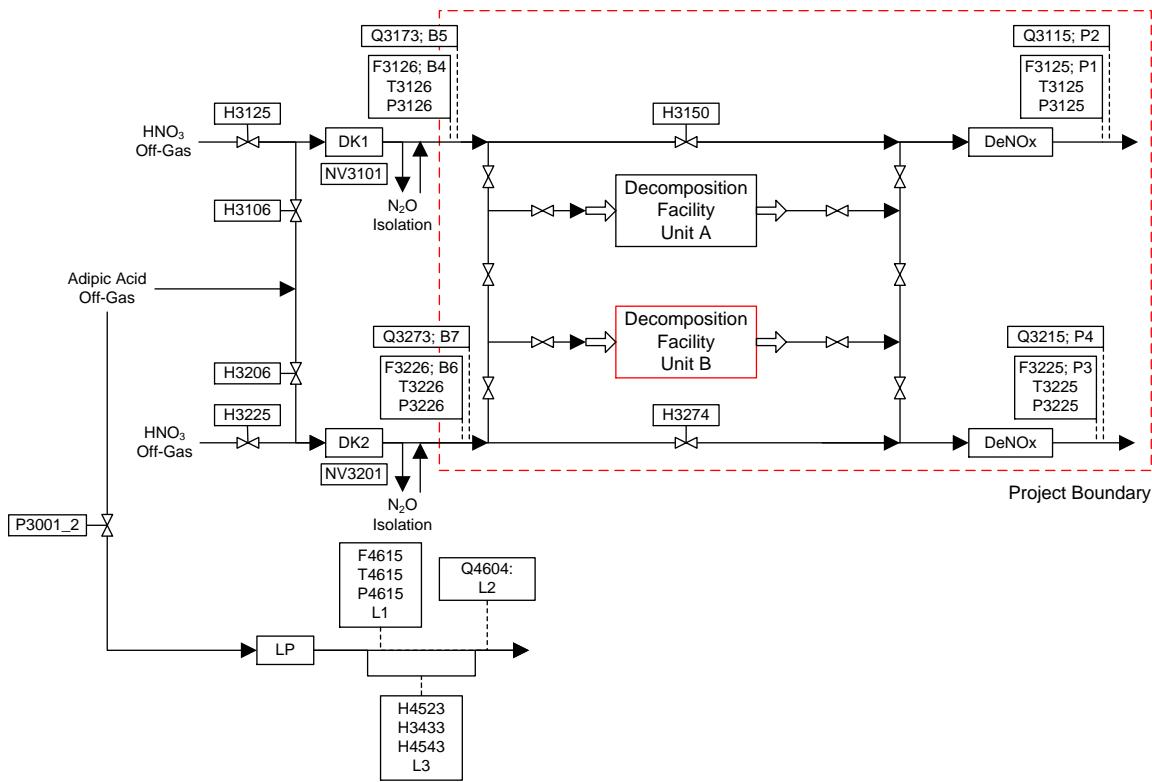
Year	Adipic Acid Production (kty)	N ₂ O Emissions (mty)
1998	238.9	17,845
1999	251.7	4,019
2000	285.7	3,000
2001	219.4	9,621
2002	232.8	9,637
2003	198.0	5,624
2004	240.0	11,391
2005	246.9	5,564
2006	290.5	7,000

Source: BASF SE

BASF employs two forms of NO_x abatement at Ludwigshafen: 1) selective catalytic reduction of NO_x, and 2) selective catalytic decomposition of N₂O. For N₂O abatement, BASF has installed two parallel (and redundant) processing trains. Average N₂O reduction has been 90%.

A schematic of the BASF process is presented in the figure below. The nitrous oxide decomposition reactor is located upstream of the NO_x reduction reactor.

Figure 7.41
BASF N₂O DESTRUCTION FACILITY IN GERMANY (284056)



Source: BASF SE

N₂O emissions are being measured online using an ABB AO2000 Uras-26 infrared photometer with an uncertainty of +/- 2%. Since the Ludwigshafen complex contains an onsite nitric acid manufacturing plant, the nitric acid reactor off-gas stream rich in N₂O is directed to the nitric acid plant for NO₂ and NO₃ recovery, rather than being processed through an absorber within the adipic acid plant. N₂O average concentration in the stream is 25–30%. The N₂O decomposition occurs inside the ammonia burners in the nitric acid plant. BASF also uses N₂O to produce cyclododecanone (for nylon-12) and cyclopentanone (for pharmaceutical intermediates) at the complex.

Invista N₂O Abatement Technology

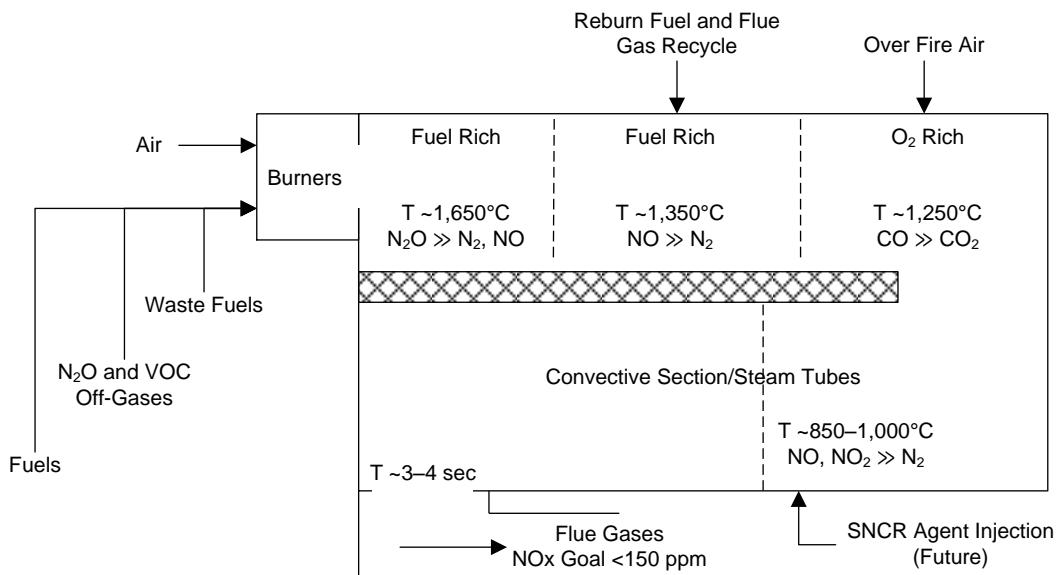
Invista offers three different process technologies for commercial license for N₂O abatement, as listed below, based upon commercial operating experience at 5 plants in Canada (former DuPont Maitland plant), the UK (former ICI plant at Wilton), and two former DuPont plants in the United States (Orange and Victoria, Texas).

1. High temperature thermal N₂O destruction using a specifically designed boiler
2. Catalytic N₂O destruction.
3. Thermal destruction of N₂O with HNO₃ recovery

Invista's thermal destruction technology incinerates N₂O in a high temperature firebox (1,200–1,700°C) such as a steam boiler, using low NO_x burners. Process steam production helps

offset the capital cost and energy cost for operating the system. The configuration of the firebox is shown in the figure below. In the first stage, N₂O containing gases are incinerated in the presence of fuel and sub-stoichiometric air at 1,650°C. The gas mixture then passes to the second stage where additional fuel is added to reduce the N₂O to nitrogen at 1,350°C. Once reduced, the gas stream passes through the third and final stage at even lower temperature (1,250°C), where additional air is injected to complete the combustion process and minimize the concentration of CO and unburned hydrocarbons.

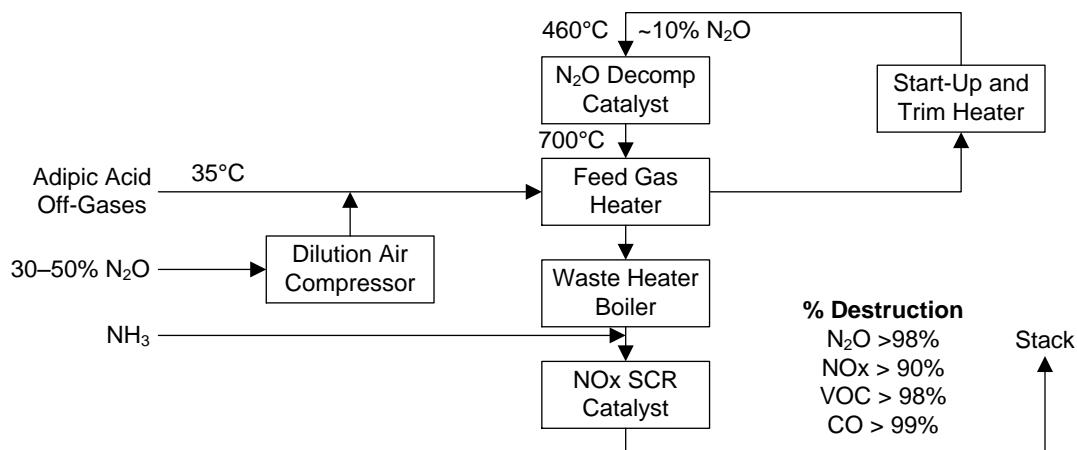
**Figure 7.42
INVISTA N₂O THERMAL DESTRUCTION SYSTEM**



Source: Invista N₂O Technology (284057)

Invista's catalytic N₂O destruction system uses a solid catalyst to operate at a much lower temperature (<700°C) than its thermal technology to avoid NO_x formation, as shown in the one-step process figure below. N₂O containing gases are mixed with compressed air, heated to reaction temperature, and passed through the decomposition reactor. The reaction is exothermic, and the reactor is operated under adiabatic conditions. To minimize energy consumption, reactor product gases are used to preheat reactor feed. The hot product gases are then directed to a heat recovery steam generator (boiler) to recover the enthalpy in the gas stream by producing process steam. Rhodium and nickel oxide or manganese oxide catalyst are used for N₂O reduction. Following reaction, the gas stream is passed through a conventional de-NOx system using selective catalyst reduction.

Figure 7.43
INVISTA N₂O CATALYTIC DESTRUCTION SYSTEM



Source: Invista N₂O Technology (284057)

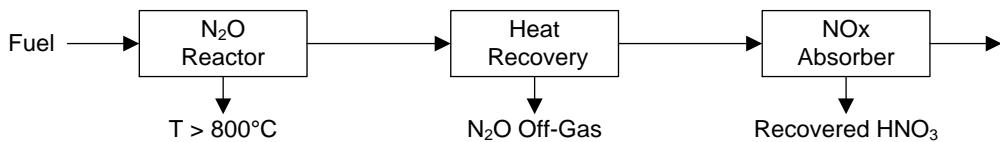
Three DuPont US patents presenting discoveries in nitrous oxide destruction processing, or the relevant catalysts used for nitrous oxide destruction, are listed below. The basic catalyst formulation is iron and a precious metal on a zirconia substrate.

Table 7.33
DUPONT N₂O CATALYTIC DESTRUCTION US PATENTS

Patent	Issue Date	Title
US6379640	30-Apr-2002	Process for the Decomposition of Nitrous Oxide
US6429168	6-Aug-2002	Catalyst for the Decomposition of Nitrous Oxide
US6710010	23-Mar-2004	Zirconia Catalysts for Nitrous Oxide Abatement

Invista's third N₂O destruction technology is high temperature ($T = 1,200\text{--}1,500^\circ\text{C}$) oxidation of N₂O to NO over a solid catalyst, followed by heat recovery. The NO can then be directed back to a nitric acid absorber in the plant, where counter-current contact with water oxidizes NO to NO₂, and then redissolves and further oxidizes the NO₂ in water to dilute nitric acid. A schematic of the third Invista technology is presented below. Natural gas and sub-stoichiometric air mix with preheated N₂O in a fixed bed catalyst reactor under adiabatic conditions. The heated product gas exchanges some of its heat with the feed gas, and is then directed back to the nitric acid absorber in the cyclohexane oxidation section of the adipic acid plant, which scrubs the NO containing stream with water in counter-current operation, oxidizing the NO to NO₂, and then converting the NO₂ to dilute nitric acid as the gas dissolves into the water stream.

Figure 7.44
INVISTA N₂O TO NO CATALYTIC OXIDATION SYSTEM



Source: Invista N₂O Technology (284057)

Performance of N₂O Destruction Systems

The IPCC has tabulated (284058) from published literature the estimated removal performance of several commercial N₂O destruction systems (see table below). Each of the systems has demonstrated better than 90% N₂O destruction. Thermal and catalytic destruction dominate the volume of commercially demonstrated technologies. The other technologies listed are site specific, and deal with non-conventional process technology.

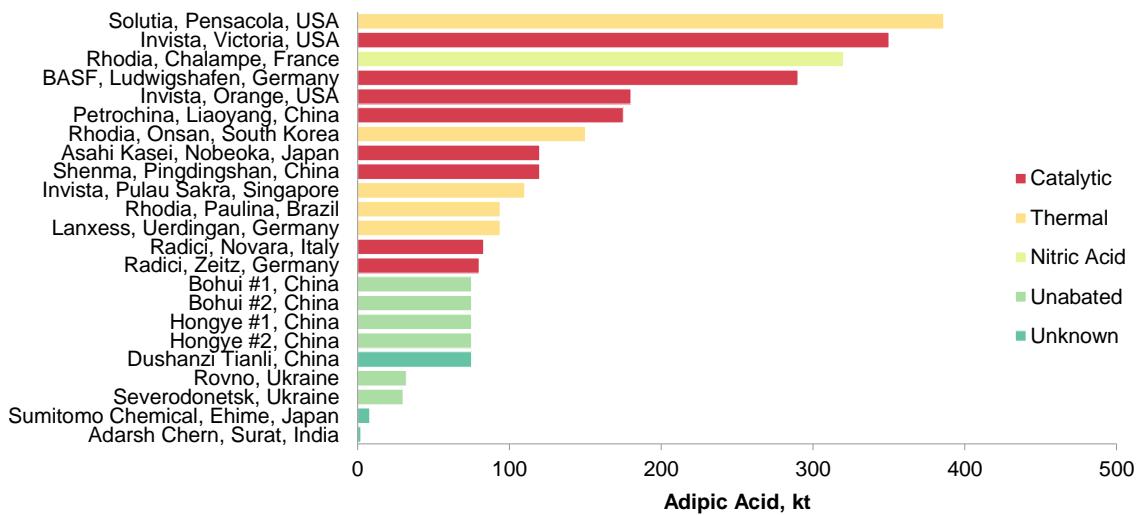
Table 7.34
IPCC TABULATION OF N₂O DESTRUCTION PERFORMANCE

Production Process	N ₂ O Generation Factor	Uncertainty Estimate
Nitric acid oxidation	300 kg/mt	+/-10%
Abatement Technology	N ₂ O Destruction Factor	Uncertainty Estimate
Catalytic destruction	92.50%	90–95%
Thermal destruction	98.50%	98–99%
Recycle to nitric acid	98.50%	98–99%
Recycle to feedstock for adipic acid	94%	90–98%
Abatement System	Utilization Factor	Uncertainty Estimate
Catalytic destruction	89%	80–98%
Thermal destruction	97%	95–99%
Recycle to nitric acid	94%	90–98%
Recycle to feedstock for adipic acid	89%	80–98%

Source: Intergovernmental Panel on Climate Change (IPCC) (284058)

The Stockholm Environment Institute (284059) has surveyed global adipic acid producers, and tabulated whether they have installed N₂O abatement facilities. If yes, they identified the technology used for abatement. This information is presented in the table below. The purpose of their study was to determine whether producers that have not installed abatement facilities were able to increase market share due to freedom from the cost of abatement.

Figure 7.45
STATUS OF N₂O ABATEMENT AT ADIPIC ACID PLANTS



Source: Stockholm Environment Institute (284059)

The Stockholm Institute tabulated the capital cost and performance of three N₂O abatement projects in Europe (see table below). Each plant was able to achieve 90%+ N₂O reduction, at capital costs below €15 MM.

Table 7.35
N₂O ABATEMENT PERFORMANCE AT THREE EUROPEAN ADIPIC ACID PLANTS

Plant	Chalampé	Ludwigshafen	Uerdingen
Country	France	Germany	Germany
Company	Rhodia	BASF	Lanxess
Adipic acid capacity (kty)	371	330	88
N ₂ O mitigation technology	Nitric acid	Redundant catalytic	Redundant thermal
Start of crediting period	11/2008	09/2009	03/2009
Abatement efficiency			
Historic level used as baseline	91%	89%	90%
Envisaged after project implementation	>97%	98%	100
Actually achieved	92–99%	NA	99.99999%
Baseline emission factor (kg N ₂ O/mt ADA)	27.7	33.0	29.8
Investment costs (€ MM)	13.9	13.4	10.0
Adipic acid production (kty)			
Assumed in the PDD	315	300	93
Actually achieved	236	NA	84
Historically before project implementation	288	245	75
Historical period considered	2002–2006	1998–2006	2002–2006

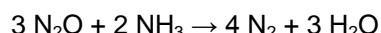
Source: Stockholm Environment Institute (284059)

UOP Pressure Swing Absorption

UOP has obtained a US patent (6080226) for using pressure swing absorption to concentrate N₂O from an adipic acid purge stream to high purity, for the purpose of recycling the N₂O for use in downstream processing

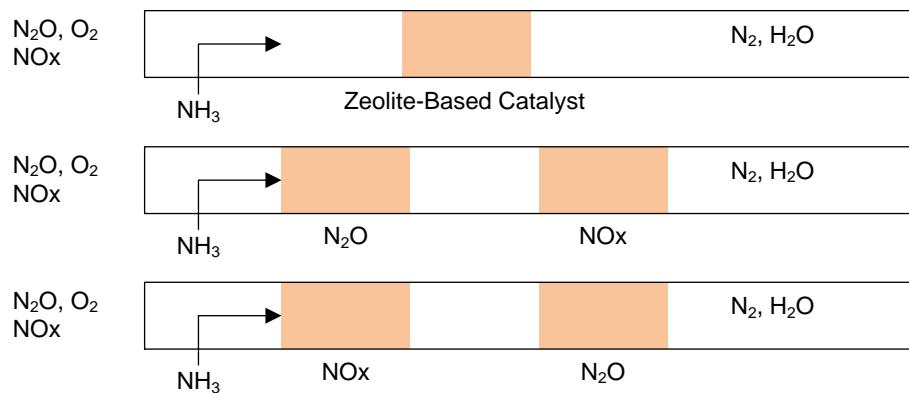
BASF Ammonia-Based N₂O Destruction Process

BASF has patented an alternative approach to N₂O destruction (USP 7951742) by reacting N₂O with ammonia (NH₃) over a zeolite-based catalyst (see figure below). The reaction stoichiometry is shown below.



In experiments, BASF recommends that the ammonia feed rate approximate the nitrous oxide feed rate on a weight basis. This approach allows the reaction to occur at much lower temperature (450–600°C) than incineration, but incurs a cost for ammonia consumption.

Figure 7.46
BASF N₂O DESTRUCTION VIA NH₃ REACTION OVER ZEOLITE (USP 7951742)



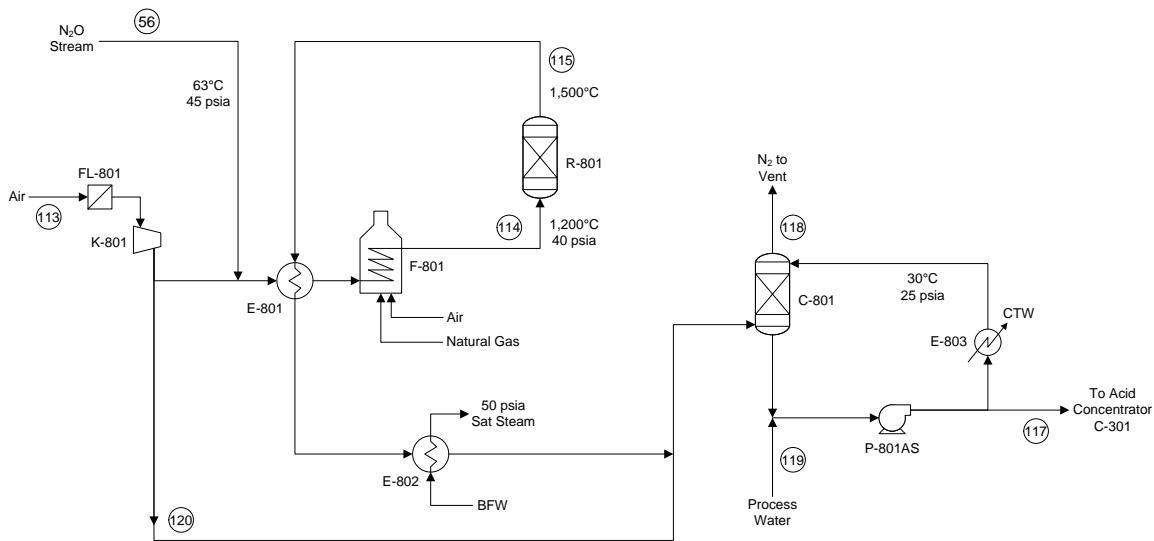
Other US patents that are similar in scope to the BASF approach are listed below:

- 5300472—Catalyst for selective reduction of nitrous oxides with ammonia
- 5198403—Process for producing a catalyst for selective reduction of nitrous oxides with ammonia
- 5140916—Staged combustion of fuel or sludge to reduce nitrous oxide emission
- 5048432—Process and apparatus for the thermal decomposition of nitrous oxide
- 4997631—Process for reducing nitrogen oxides without generating nitrous oxide

Proposed N₂O Destruction Processing Design

For this project, we have selected the Invista process for oxidizing N₂O to NO, for subsequent conversion back to nitric acid using a water absorber. A process flow diagram for this section of the plant is presented below.

Figure 7.47
N₂O CONVERSION TO NITROGEN OXIDE PROCESS FLOW DIAGRAM



PROCESS FLOW DIAGRAMS

Process flow diagrams have been prepared for each of the 8 sections of the plant, and are presented in the appendix (Figure 7.48).

MATERIAL BALANCE

A stream-by-stream material balance table is presented below. The key feeds and products are presented directly below. The KPIs (key performance indices) are a net cyclohexane feedstock consumption of 0.700 mt per mt of product adipic acid. This has been achieved via a combination of boric acid enhancement to air oxidation, 3-stage crystallization of crude adipic acid production, and long residence time at ambient temperature in the air oxidation scrubber. The net nitric acid consumption per unit of adipic acid production is 0.389, achieved primarily by converting nitrous oxide (N₂O) product from the nitric acid reactors back to NO in an on-purpose high temperature process unit for reconversion to nitric acid in the absorber section of the plant. In a grassroots plant, such a process unit reduces the capacity (and cost) of the attendant nitric acid plant. For an existing adipic acid production facility, a more likely option is to simply reduce the N₂O to molecular nitrogen.

The net production of mixed methyl ester is 0.90 mt/mt of adipic acid is achieved by collecting the miscellaneous aqueous streams that contain both low concentrations of monocarboxylic acids, and low concentrations of dicarboxylic acids. For the proposed grassroots plant, this approach reduces the cost that would otherwise be required to destroy these contaminants in the plant's wastewater treatment plant. For an existing plant, the cost of recovery might not be justified by ROI considerations. The overall unit raw materials consumptions are listed in the table below.

Table 7.36
MATERIAL BALANCE SUMMARY

Chemical	Stream #	mt/hr	qty	Key Performance Index
Fresh Cyclohexane Feed	1	14.21	112.0	0.700 Cyclohexane:Adipic Acid
Fresh Nitric Acid Feed	34	7.89	62.2	0.389 HNO ₃ Feed:Adipic Acid
Fresh Boric Acid Feed	4	0.09	0.7	0.0044 Boric Acid:Adipic Acid
Fresh Methanol Feed	82	0.7	5.5	0.0345 Methanol:Adipic Acid
Adipic Acid Product	79	20.29	160.0	
AGS Product (100% basis)	108	1.95	15.4	0.096 AGS:Adipic Acid
Mixed Ester Product	92	1.83	14.4	0.090 Mixed Ester:Adipic Acid

Table 7.37
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	1 Fresh Cyhex Feed	2 Recycle Cyhex	3 Cobalt Naphthenate Liq Catalyst	4 Fresh Boric Acid Addition	5 Recycle Boric Acid Slurry	6 Boric Acid Feed to Process	7 Vent from Scrubber	8 Scrubber B/S Stream
From	Tk-101	C-201	D-101	D-102	CN-201	P-103AS	V-101	V-101
To	V-101	E-105	E-105	D-103	E-105	E-105	ATM	D-104
Temperature (°C)	25	59	25	25	50	50	52	52
Pressure (psia)	150	50	150	150	150	150	20	20
Total Flow (mt/hr)	14.21	101.51	0.02	0.09	3.32	3.41	25.61	30.45
Components	MW	BP (°C)						
Water	18	100	0.01		1.66	1.66	0.66	5.94
Nitrogen	28	-210						20.36
Carbon Monoxide	28	-191						0.21
Oxygen	32	-218						2.71
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						1.57
N ₂ O	44	-88						
NO + NO ₂	46	21						
Boric Acid	62	300			0.09	1.66	1.75	
Nitric Acid	63	86						
Benzene	78	80	0.0003	0.0020			0.0003	0.0053
Cyclohexane	84	81	14.21	101.50	0.01		0.10	24.51
Cyclohexanone	98	156						
Cyclohexanol	100	161						
Monocarboxylic Acids	116	205						
Cyclohexyl Hydroperoxide	116	104						
Ammonium Vanadate	117	decomp						
Succinic Acid	118	235						
Glutaric Acid	132	303						
Adipic Acid	146	338						
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Copper Nitrate	188	170						
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324						
Cobalt Naphthenate	401	350		0.01				
Heavies, Tar and Polymer	na							

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	9	10	11	12	13	14	15	16
Oil Phase from Scrubber	Oil Phase from Scrubber	Water Phase from Scrubber	Carbon Filter Regen	Caustic Soln MakeUp	Oil Phase from Caustic Scrubber	Caustic Scrubber Circulation	Oil Layer from D-107	Catalyst + Oil Phase to Ox RXs
Decanter	Decanter	Steam			Scrubber			
From	D-104	D-104	OSBL	OSBL	D-106	P-106AS	D-107	D-107
To	P-107AS	P-108AS	V-102AB	D-106	D-104	V-101	E-105	E-105
Temperature (°C)	55	55	148	25	55	52	25	30
Pressure (psia)	150	150	50	50	50	50	150	150
Total Flow (mt/hr)	24.32	6.13	2.27	0.10	0.01	100.00	0.23	0.25
Components	MW	BP (°C)						
Water	18	100	0.06	5.88	2.27	0.09	0.00	90.00
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na				0.01		10.00
Carbon Dioxide	44	-79						
N ₂ O	44	-88						
NO + NO ₂	46	21						
Boric Acid	62	300						
Nitric Acid	63	86						
Benzene	78	80	0.0021	0.0032				0.0016
Cyclohexane	84	81	24.26	0.25		0.01		0.23
Cyclohexanone	98	156						
Cyclohexanol	100	161						
Monocarboxylic Acids	116	205						
Cyclohexyl Hydroperoxide	116	104						
Ammonium Vanadate	117	decomp						
Succinic Acid	118	235						
Glutaric Acid	132	303						
Adipic Acid	146	338						
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Copper Nitrate	188	170						
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324						
Cobalt Naphthenate	401	350					0.01	
Heavies, Tar and Polymer	na							

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	17	18	19	20	21	22	23	24
Water Layer from D-107	Feed to Oxidation RXs	Air to Ox Reactors	Steam Gen from Ox RXs	R-101 O/H Vapor Stream	Air Ox RX Liq Prod Stream	Process H ₂ O for Hydrolysis	Water Phase from D-108	Decanter
From	D-107	D-104	K-101	R-101ABCD	R-101ABCD	R-101ABCD	OSBL	D-108
To	D-108	R-101ABCD	R-101ABCD	D-109	V-101	D-108	M-105	FL-103
Temperature (°C)	25	165	150		165	165	30	120
Pressure (psia)	150	150	150		100	100	150	100
Total Flow (mt/hr)	5.91	129.49	25.77	42.63	41.85	119.97	27.12	35.18
Components	MW	BP (°C)						
Water	18	100	5.88	1.73	42.63	6.60	0.26	27.12
Nitrogen	28	-210		20.36		20.36		
Carbon Monoxide	28	-191				0.21		
Oxygen	32	-218		5.41		2.71		
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79				1.57		
N ₂ O	44	-88						
NO + NO ₂	46	21						
Boric Acid	62	300		1.75				1.75
Nitric Acid	63	86						
Benzene	78	80	0.0016	0.0023		0.0023		
Cyclohexane	84	81	0.03	126.00		10.40	101.50	
Cyclohexanone	98	156					1.52	
Cyclohexanol	100	161					4.75	
Monocarboxylic Acids	116	205					0.24	0.18
Cyclohexyl Hydroperoxide	116	104					2.06	
Ammonium Vanadate	117	decomp						
Succinic Acid	118	235					0.06	
Glutaric Acid	132	303					0.09	
Adipic Acid	146	338					0.62	
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)					0.01	
Copper Nitrate	188	170						
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324					8.66	
Cobalt Naphthenate	401	350		0.01			0.01	
Heavies, Tar and Polymer	na						0.19	

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	25	26	27	28	29	30	31	32
Hydrolysis Drum Oil Product	Crude KA Oil to C-201	C-201 O/H Vapor	C-201 Reflux	C-201 Reboil	C-201 B/S Product	Condensate from Boric Acid	Boric Acid Crystallizer B/S Slurry	
From	D-108	R-102AB	C-201	P-201AS	E-202	C-201	CR-201AB	CR-201
To	R-102AB	C-201	E-201	C-201	C-201	C-202	WWT	CN-201
Temperature (°C)	120	120	59	59	155	155	72	72
Pressure (psia)	100	100	8	50	50	50	50	50
Total Flow (mt/hr)	117.83	117.79	304.53	203.02	293.04	16.28	27.99	2.79
Components	MW	BP (°C)						
Water	18	100	0.01	0.01	0.03	0.02	27.99	0.86
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
N ₂ O	44	-88						
NO + NO ₂	46	21						
Boric Acid	62	300						1.75
Nitric Acid	63	86						
Benzene	78	80						
Cyclohexane	84	81	101.53	101.50	304.50	203.00		
Cyclohexanone	98	156	1.52	1.52			27.36	1.52
Cyclohexanol	100	161	11.66	13.72			246.96	13.72
Monocarboxylic Acids	116	205	0.06	0.06			1.08	0.06
Cyclohexyl Hydroperoxide	116	104	2.06					0.18
Ammonium Vanadate	117	decomp						
Succinic Acid	118	235	0.06	0.06			1.08	0.06
Glutaric Acid	132	303	0.09	0.09			1.62	0.09
Adipic Acid	146	338	0.62	0.62			11.16	0.62
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)	0.01	0.01			0.18	0.01
Copper Nitrate	188	170						
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324	0.01					
Cobalt Naphthenate	401	350	0.01	0.01			0.18	0.01
Heavies, Tar and Polymer	na		0.19	0.19			3.42	0.19

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	33	34	35	37	38	39	40	41
Steam to Boric Acid Crystallizer		Fresh HNO ₃ Feed	Boric Acid Centrifuge Liq to Ester Unit	C-202 O/H Vapor Stream	KA Oil Feed to HNO ₃ RXs	NVR to Methyl Ester Unit	C-202 Reboil	1st Acid Rx Prod Stream
From	OSBL	Tk-301	CN-201	C-202	D-204	C-202	E-206AB	R-301
To	CR-201AB	R-301	E-601	E-205	R-301	D-601	C-202	D-302
Temperature (°C)	138	25	72	135	135	282	282	70
Pressure (psia)	50	150	50	8	8	8	8	50
Total Flow (mt/hr)	26.65	13.27	0.47	15.53	15.53	0.75	14.90	91.99
Components	MW	BP (°C)						
Water	18	100	26.65	5.38	0.20			5.62
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
N ₂ O	44	-88						1.66
NO + NO ₂	46	21						14.92
Boric Acid	62	300		0.09				
Nitric Acid	63	86	7.89					26.94
Benzene	78	80						
Cyclohexane	84	81						
Cyclohexanone	98	156			1.52	1.52		1.74
Cyclohexanol	100	161			13.72	13.72		
Monocarboxylic Acids	116	205		0.18	0.02	0.02	0.04	0.76
Cyclohexyl Hydroperoxide	116	104						
Ammonium Vanadate	117	decomp						0.02
Succinic Acid	118	235			0.05	0.05	0.01	0.20
Glutaric Acid	132	303			0.07	0.07	0.02	0.40
Adipic Acid	146	338			0.15	0.15	0.47	9.40
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)					0.01	0.20
Copper Nitrate	188	170						0.20
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324						
Cobalt Naphthenate	401	350					0.007	0.14
Heavies, Tar and Polymer	na						0.19	3.80

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	42	43	44	45	46	47	48	49
O/H Vapor from Primary Acid Reactor	1st Stg Acid Rx Liq Prod	Secondary Acid Rx Liq Prod	O/H Vapor from Secondary Acid Reactor	Vapors from 2 Acid Reactors	Compressed Air to Bleacher	O/H Vapor from Bleacher	O/H Vapor from Bleacher	Liq B/S Prod
From	D-302	D-302	R-302	R-302	D-302	K-101	V-301	V-301
To	V-302	R-302	V-301	V-302	V-302	V-301	V-302	C-301
Temperature (°C)	70	70	110	110	80	150	110	110
Pressure (psia)	50	50	50	50	50	100	100	50
Total Flow (mt/hr)	16.58	75.41	73.30	2.10	21.04	5.34	6.52	72.12
Components	MW	BP (°C)						
Water	18	100	5.62	5.49				5.49
Nitrogen	28	-210				4.22	4.22	
Carbon Monoxide	28	-191						
Oxygen	32	-218				1.12		
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
N ₂ O	44	-88	1.66		0.18	1.84		
NO + NO ₂	46	21	14.92		1.92	19.20		2.30
Boric Acid	62	300						
Nitric Acid	63	86	26.94	23.70				22.52
Benzene	78	80						
Cyclohexane	84	81						
Cyclohexanone	98	156	1.74					
Cyclohexanol	100	161						
Monocarboxylic Acids	116	205	1.73	1.78				1.78
Cyclohexyl Hydroperoxide	116	104						
Ammonium Vanadate	117	decomp	0.02	0.02				0.02
Succinic Acid	118	235	4.69	4.83				4.83
Glutaric Acid	132	303	12.69	13.08				13.08
Adipic Acid	146	338	21.78	24.20				24.20
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Copper Nitrate	188	170	0.20	0.20				0.20
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324						
Cobalt Naphthenate	401	350						
Heavies, Tar and Polymer	na							

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	50 O/H Vapor from Acid Concent	51 O/H H ₂ O Prod from Acid Concent	52 Acid Reboil	53 Crystallizer Feed	54 Crystallizer Condensate	55 Vapors to Absorber	56 Acid Rich Stream	57 N ₂ O- Crystallization Liquor Recycle to RXs
From	C-301	C-301	E-309	C-301	D-402	D-302	V-302	CN-401
To	D-303	WWT	C-301	CR-401	WWT	V-302	E-801	Tk-302
Temperature (°C)	47	47	225	47	50	95	63	50
Pressure (psia)	2	2	2	50	50	50	45	50
Total Flow (mt/hr)	90.06	29.49	98.45	93.76	3.85	25.26	6.12	59.14
Components	MW	BP (°C)						
Water	18	100	90.06	29.49	9.98	9.50	3.85	3.68
Nitrogen	28	-210					4.22	4.22
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
N ₂ O	44	-88					1.84	1.84
NO + NO ₂	46	21					19.20	0.06
Boric Acid	62	300						
Nitric Acid	63	86		42.16	40.15			34.29
Benzene	78	80						
Cyclohexane	84	81						
Cyclohexanone	98	156						
Cyclohexanol	100	161						
Monocarboxylic Acids	116	205		1.87	1.78			1.44
Cyclohexyl Hydroperoxide	116	104						
Ammonium Vanadate	117	decomp		0.02	0.02			0.02
Succinic Acid	118	235		5.07	4.83			4.32
Glutaric Acid	132	303		13.73	13.08			11.70
Adipic Acid	146	338		25.41	24.20			3.51
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Copper Nitrate	188	170		0.21	0.20			0.18
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324						
Cobalt Naphthenate	401	350						
Heavies, Tar and Polymer	na							

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

	Label	Stream Number							
		58	59	60	61	62	63	64	65
	Nitric Purge Liquor to AGS Recovery	Crystal Filter Cake	Hot Water to Acid Filter Cake	1st Stage Aqueous Crystallizer Feed	CR-402 Condensate	CR-402 Circulating Loop	CR-402 Crystal Slurry	CR-402 Liquor to Esterification	
From	CN-401	CR-401	OSBL	D-404	D-406	CR-402	CR-402	CN-402	CN-402
To	C-701	D-404	D-404	CR-402	WWT	E-404	CN-402	E-601	
Temperature (°C)	50	50	80	50	50	50	50	50	50
Pressure (psia)	50	15	50	50	50	50	50	50	50
Total Flow (mt/hr)	6.57	24.20	76.88	101.08	60.55	297.09	40.53	15.09	
Components	MW	BP (°C)							
Water	18	100	0.41	1.56	76.88	78.44	58.50	235.32	19.94
Nitrogen	28	-210							14.85
Carbon Monoxide	28	-191							
Oxygen	32	-218							
Methanol	32	65							
Sodium Hydroxide	40	na							
Carbon Dioxide	44	-79							
N ₂ O	44	-88							
NO + NO ₂	46	21							
Boric Acid	62	300							
Nitric Acid	63	86	3.81	2.05		2.05	2.05		
Benzene	78	80							
Cyclohexane	84	81							
Cyclohexanone	98	156							
Cyclohexanol	100	161							
Monocarboxylic Acids	116	205	0.16	0.18		0.18		0.54	0.18
Cyclohexyl Hydroperoxide	116	104							0.15
Ammonium Vanadate	117	decomp	0.002						
Succinic Acid	118	235	0.48	0.03		0.03		0.09	0.03
Glutaric Acid	132	303	1.30	0.08		0.08		0.24	0.08
Adipic Acid	146	338	0.39	20.30		20.30		60.90	20.30
Mixed Methyl Ester	166	85 (vac)							
Dimethyl Adipate	174	109 (vac)							
Copper Nitrate	188	170	0.020						
Dodecanedioic Acid	230	250 (vac)							
Borate Ester	307	324							
Cobalt Naphthenate	401	350							
Heavies, Tar and Polymer		na							

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	66	67	68	69	70	71	72	73
1st Stage ADA Filter Cake	Hot Water to D-408	ADA Soln Feed to 2nd Stage	CR-403 O/H Condensate	CR-403 Circulating Loop	CN-403 B/S Slurry	Water from CN-403	ADA Filter Cake	
From	CN-402	OSBL	D-408	CR-403	CR-403	CR-403	CN-403	CN-403
To	D-407	D-408	CR-403	WWT	E-406	CN-403	WWT	D-501
Temperature (°C)	50	80	80	30	30	30	30	50
Pressure (psia)	15	50	50	50	50	50	50	15
Total Flow (mt/hr)	25.44	15.87	41.31	21.98	152.37	30.49	2.07	28.43
Components	MW	BP (°C)						
Water	18	100	5.09	15.87	20.96	21.98	91.32	9.13
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
N ₂ O	44	-88						
NO + NO ₂	46	21						
Boric Acid	62	300						
Nitric Acid	63	86						
Benzene	78	80						
Cyclohexane	84	81						
Cyclohexanone	98	156						
Cyclohexanol	100	161						
Monocarboxylic Acids	116	205	0.03		0.03		0.09	0.03
Cyclohexyl Hydroperoxide	116	104						0.01
Ammonium Vanadate	117	decomp						0.02
Succinic Acid	118	235	0.01		0.01		0.03	0.01
Glutaric Acid	132	303	0.02		0.02		0.06	0.02
Adipic Acid	146	338	20.29		20.29		60.87	21.30
Mixed Methyl Ester	166	85 (vac)						21.30
Dimethyl Adipate	174	109 (vac)						
Copper Nitrate	188	170						
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324						
Cobalt Naphthenate	401	350						
Heavies, Tar and Polymer	na							

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	74 Dryer Condensate	75 ADA Fines	76 Hot Water to Fines	77 ADA Fines Soln	78 Flow Improver	79 ADA Product	80 Condensate from D-602	81 D-601 B/S Product
From	D-502	CV-504	BL	P-501	BL	CV-508	D-602	D-601
To	WWT	D-501	D-501	CR-403	D-503	BL	WWT	D-603
Temperature (°C)	100	100	80	80	20	50	110	110
Pressure (psia)	15	15	75	75	15	15	15	50
Total Flow (mt/hr)	7.06	1.01	10.15	11.16	0.00	20.35	17.26	1.80
Components	MW	BP (°C)						
Water	18	100	7.06		10.15	10.15	0.04	17.26
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
N ₂ O	44	-88						
NO + NO ₂	46	21						
Boric Acid	62	300						0.09
Nitric Acid	63	86						
Benzene	78	80						
Cyclohexane	84	81						
Cyclohexanone	98	156						
Cyclohexanol	100	161						
Monocarboxylic Acids	116	205				0.02		0.49
Cyclohexyl Hydroperoxide	116	104						
Ammonium Vanadate	117	decomp						
Succinic Acid	118	235						0.07
Glutaric Acid	132	303						0.19
Adipic Acid	146	338	1.01		1.01	20.29		0.05
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Copper Nitrate	188	170						
Dodecanedioic Acid	230	250 (vac)			0.0002			
Borate Ester	307	324						
Cobalt Naphthenate	401	350						
Heavies, Tar and Polymer	na							

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	82	83	84	85	86	87	88	89
Fresh Methanol Feed		Ester RX O/H Stream	Combined Feed to Ester Reactor	Recycle Mono Acids	Ester Rx B/S Product	Methanol Column O/H Vapor	Recycle Methanol	Methanol Column Reflux
From	Tk-601	R-601AB	D-603	P-607AS	R-601AB	C-601	C-601	P-605AS
To	R-601AB	E-605	R-601AB	R-601AB	C-602	E-606	R-601AB	C-601
Temperature (°C)	35	120	198	150	120	93	93	93
Pressure (psia)	150	40	50	150	40	40	40	40
Total Flow (mt/hr)	0.70	2.64	2.55	0.05	2.09	7.15	1.43	5.72
Components	MW	BP (°C)						
Water	18	100	1.24	0.91		0.15	0.03	0.12
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65	0.70	1.40		7.00	1.40	5.60
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
N ₂ O	44	-88						
NO + NO ₂	46	21						
Boric Acid	62	300		0.09				
Nitric Acid	63	86						
Benzene	78	80						
Cyclohexane	84	81						
Cyclohexanone	98	156						
Cyclohexanol	100	161						
Monocarboxylic Acids	116	205		0.53	0.05	0.05		
Cyclohexyl Hydroperoxide	116	104						
Ammonium Vanadate	117	decomp						
Succinic Acid	118	235		0.08				
Glutaric Acid	132	303		0.21				
Adipic Acid	146	338		0.52				
Mixed Methyl Ester	166	85 (vac)			1.83			
Dimethyl Adipate	174	109 (vac)		0.01		0.01		
Copper Nitrate	188	170						
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324						
Cobalt Naphthenate	401	350		0.01		0.01		
Heavies, Tar and Polymer	na			0.19		0.19		

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	90	91	92	93	94	95	96	97
Methanol Column Reboil	Methanol Column B/S Product	Mixed Ester Product	Heavy Tar Product	C-701 O/H Vapor Stream	C-701 Reflux Stream	C-701 Distillate Product	C-701 Bottom Stream	
From	E-607AB	C-601	P-608AS	P-610AS	C0701	P-701AS	P-701AS	C-701
To	C-601	WWT	Tk-602ABCD	WWT	D-701	C-701	Tk-302	P-702AS
Temperature (°C)	130	130	50	190	60	60	60	140
Pressure (psia)	40	40	50	50	2	2	50	2
Total Flow (mt/hr)	1.72	1.21	1.84	0.20	12.12	8.08	4.04	27.85
Components	MW	BP (°C)						
Water	18	100	1.72	1.21		0.69	0.46	0.23
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
N ₂ O	44	-88						
NO + NO ₂	46	21						
Boric Acid	62	300						
Nitric Acid	63	86			11.43	7.62	3.81	
Benzene	78	80						
Cyclohexane	84	81						
Cyclohexanone	98	156						
Cyclohexanol	100	161						
Monocarboxylic Acids	116	205						1.76
Cyclohexyl Hydroperoxide	116	104						
Ammonium Vanadate	117	decomp						0.02
Succinic Acid	118	235						5.28
Glutaric Acid	132	303						14.30
Adipic Acid	146	338						4.29
Mixed Methyl Ester	166	85 (vac)		1.83				
Dimethyl Adipate	174	109 (vac)		0.01				
Copper Nitrate	188	170						0.22
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324						
Cobalt Naphthenate	401	350			0.01			
Heavies, Tar and Polymer	na				0.19			

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	98	99	100	101	102	103	104	105
	C-701 Reboil	C-701 B/S Product	Hot Water	Nitric Liquor to Ion Exchange	AGS Crystallizer Feed	AGS Crystallizer Condensate	AGS Crystallizer Circulating Loop	AGS Crystallizer Slurry
From	E-702	C-701	OSBL	D-703	S-110	P-707AS	CR-701	CR-701
To	C-701	D-703	D-703	S-110	CR-701	WWT	E-703	CN-701
Temperature (°C)	140	140	80	60	80	15	5	5
Pressure (psia)	2	50	50	50	50	20	50	2
Total Flow (mt/hr)	25.32	2.53	14.94	17.47	17.45	11.70	52.35	5.75
Components	MW	BP (°C)						
Water	18	100	1.80	0.18	14.94	15.12	15.12	11.70
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
N ₂ O	44	-88						
NO + NO ₂	46	21						
Boric Acid	62	300						
Nitric Acid	63	86						
Benzene	78	80						
Cyclohexane	84	81						
Cyclohexanone	98	156						
Cyclohexanol	100	161						
Monocarboxylic Acids	116	205	1.60	0.16	0.16	0.16	0.48	0.16
Cyclohexyl Hydroperoxide	116	104						
Ammonium Vanadate	117	decomp	0.02	0.002	0.002			
Succinic Acid	118	235	4.80	0.48	0.48	0.48	1.44	0.48
Glutaric Acid	132	303	13.00	1.30	1.30	1.30	3.90	1.30
Adipic Acid	146	338	3.90	0.39	0.39	0.39	1.17	0.39
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Copper Nitrate	188	170	0.20	0.020	0.020			
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324						
Cobalt Naphthenate	401	350						
Heavies, Tar and Polymer	na							

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	106	107	108	109	110	111	112	113
	AGS Centrifuge Liquor	AGS Filter Cake	AGS Product	Acid Centrifuge Liquor	Acid Crystallizer Slurry	Water for AGS	Fresh Cu/V Acid Catalyst	Fresh Air to N ₂ O Unit
From	CN-701	CN-701	P-709AS	CN-401	CR-401	OSBL	D-301	AMB
To	E-601	D-706	OSBL	Tk-302	CN-401	D-706	R-301	FL-801
Temperature (°C)	5	5	80	50	50	80	25	25
Pressure (psia)	50	15	50	50	50	50	150	15
Total Flow (mt/hr)	3.50	2.26	3.35	65.71	89.91	1.07	0.01	3.28
Components	MW	BP (°C)						
Water	18	100	3.12	0.30	1.37	4.09	5.65	1.07
Nitrogen	28	-210						2.59
Carbon Monoxide	28	-191						
Oxygen	32	-218						0.69
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
N ₂ O	44	-88						
NO + NO ₂	46	21						
Boric Acid	62	300						
Nitric Acid	63	86		0.03	38.10	40.15		
Benzene	78	80						
Cyclohexane	84	81						
Cyclohexanone	98	156						
Cyclohexanol	100	161						
Monocarboxylic Acids	116	205	0.16		1.60	1.78		
Cyclohexyl Hydroperoxide	116	104						
Ammonium Vanadate	117	decomp			0.02	0.02		0.0008
Succinic Acid	118	235	0.05	0.43	0.43	4.80	4.83	
Glutaric Acid	132	303	0.13	1.17	1.17	13.00	13.08	
Adipic Acid	146	338	0.04	0.35	0.35	3.90	24.20	
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Copper Nitrate	188	170			0.20	0.20		0.0081
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324						
Cobalt Naphthenate	401	350						
Heavies, Tar and Polymer	na							

Table 7.37 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number							
	114 N ₂ O Feed to Decomp	115 N ₂ O Unit Discharge	116 Compressed Air to Absorber	117 NO Solution to Acid Concentrator	118 N ₂ to Atmos Vent	119 Process Water to NO Absorber	120 Compressed Air to Absorber	121 Dilute Acid to HNO ₃ Concentrator
From	F-801	R-801	K-101	P-801AS	C-801	OSBL	K-101	V-302
To	R-801	E-801	V-302	C-301	ATM	P-801AS	C-801	C-301
Temperature (°C)	1200	1500	150	30	30	25	150	55
Pressure (psia)	40	35	100	75	50	75	125	75
Total Flow (mt/hr)	9.40	10.49	6.33	26.10	18.29	23.49	13.15	25.03
Components	MW	BP (°C)						
Water	18	100		23.49		23.49		10.01
Nitrogen	28	-210	6.81	7.90	5.00	18.29		10.39
Carbon Monoxide	28	-191						
Oxygen	32	-218	0.69		1.33		2.76	
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
N ₂ O	44	-88	1.84					
NO + NO ₂	46	21	0.06	2.59				
Boric Acid	62	300						
Nitric Acid	63	86			2.61			15.02
Benzene	78	80						
Cyclohexane	84	81						
Cyclohexanone	98	156						
Cyclohexanol	100	161						
Monocarboxylic Acids	116	205						
Cyclohexyl Hydroperoxide	116	104						
Ammonium Vanadate	117	decomp						
Succinic Acid	118	235						
Glutaric Acid	132	303						
Adipic Acid	146	338						
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Copper Nitrate	188	170						
Dodecanedioic Acid	230	250 (vac)						
Borate Ester	307	324						
Cobalt Naphthenate	401	350						
Heavies, Tar and Polymer		na						

Table 7.37 (Concluded)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number						
	122	123	124	125	126	127	128
V-302 B/S Product Liquid	Water to Absorber	Recycle H ₂ O to Absorber	C-602 O/H Vapor	C-602 Reflux	Recycle Mono Acids	C-602 Reboil Vapor	
From	V-302	OSBL	P-307AS	C-602	P-607AS	P-607AS	E-611AB
To	C-301	V-302	V-302	D-605	C-602	R-601AB	C-602
Temperature (°C)	55	25	55	150	150	150	190
Pressure (psia)	75	75	75	1	1	1	50
Total Flow (mt/hr)	100.12	4.82	75.09	0.25	0.20	0.05	0.24
Components	MW	BP (°C)					
Water	18	100	40.04	4.82	30.03		
Nitrogen	28	-210					
Carbon Monoxide	28	-191					
Oxygen	32	-218					
Methanol	32	65					
Sodium Hydroxide	40	na					
Carbon Dioxide	44	-79					
N ₂ O	44	-88					
NO + NO ₂	46	21					
Boric Acid	62	300					
Nitric Acid	63	86	60.08		45.06		
Benzene	78	80					
Cyclohexane	84	81					
Cyclohexanone	98	156					
Cyclohexanol	100	161					
Monocarboxylic Acids	116	205		0.25	0.20	0.05	
Cyclohexyl Hydroperoxide	116	104					
Ammonium Vanadate	117	decomp					
Succinic Acid	118	235					
Glutaric Acid	132	303					
Adipic Acid	146	338					
Mixed Methyl Ester	166	85 (vac)					
Dimethyl Adipate	174	109 (vac)					
Copper Nitrate	188	170					
Dodecanedioic Acid	230	250 (vac)					
Borate Ester	307	324					
Cobalt Naphthenate	401	350			0.01		
Heavies, Tar and Polymer	na				0.23		

EQUIPMENT LIST

Based on the process flow diagrams and stream-by-stream material balance, we have prepared the following equipment list with duty specifications.

Table 7.38
EQUIPMENT LIST WITH DUTY SPECIFICATIONS

Distillation Columns		# Installed	Materials of Construction	L x D (ft)	DesP (psia)	DesT (°F)	# of Trays	Internals Details
C-201	Cyhex Recycle Column	1	CS	92 x 15.3	Full Vac	350	36	Structured packing
C-202	KA Oil Column	1	CS	68 x 4	Full Vac	375	24	Structured packing
C-301	Nitric Acid Concentrator	1	310L SS	140 x 12	Full Vac	600	60	Ti sieve trays
C-601	Methanol Purification Column	1	CS	128 x 3	50	300	54	316L SS sieve trays
C-602	Ester Column	1	CS	84 x 4	Full Vac	450	32	Divided wall—struc packing
C-701	Drying Tower	1	Ti clad	68 x 6	Full Vac	350	24	Ti struc packing
C-801	NO Absorber	1	310L SS	24 x 6	50	1,500	na	18 ft packing
Centrifuges		# Installed	Materials of Construction	L x D (ft)	DesP (psia)	DesT (°F)	Duty (BHP)	Screen Opening (mils)
CN-201	Boric Acid 1st-Stage Centrifuge	1	304SS	4 x 1	100	250	2	Bowl
CN-401	Crude Acid Centrifuge	4	304SS	8 x 6	150	250	125	Pusher
CN-402	1st-Stage Centrifuge	4	304SS	8 x 6	150	250	125	Pusher
CN-403	2nd-Stage Centrifuge	4	304SS	8 x 6	150	250	125	Pusher
CN-701	AGS Centrifuge	1	304SS	2 x 1	150	250	15	Pusher
Crystallizers		# Installed	Materials of Construction	L x D (ft)	DesP (psia)	DesT (°F)	Duty (MM-btu/hr)	Surf Area (ft2)
CR-201AB	Boric Acid Crystallizer	2	304SS	6 x 6	Full Vac	250	36.4	Suspension
CR-401	Crude Acid Crystallizer	1	304SS	32 x 8	Full Vac	250	0	Suspension
CR-402	1st-Stage Aqueous Crystallizer	1	304SS	32 x 8	Full Vac	250	0	Suspension
CR-403	2nd-Stage Aqueous Crystallizer	1	304SS	32 x 8	Full Vac	250	0	Suspension
CR-701	AGS Crystallizer	1	304SS	24 x 6	Full Vac	200	0	Suspension
Solids Conveyors		# Installed	Materials of Construction	L x W (ft)	DesP (psia)	DesT (°F)	Mass Flow (lbs/hr)	Motor HP
CV-101	Boric Acid Conveyor	1	304SS	20 x 1	15	150	200	Closed Belt conveyor
CV-201	Boric Acid Filter Cake Conveyor	1	304SS	50 x 1	15	250	7,321	Closed Belt conveyor
CV-401	Crude Filter Cake Conveyor	1	304SS	50 x 4	15	150	53,361	Closed Belt conveyor
CV-402	Crude ADA Conveyor	1	304SS	50 x 4	15	150	53,361	Closed Belt conveyor
CV-403	1st-Stage Filter Cake Conveyor	1	304SS	50 x 4	15	150	56,095	Closed Belt conveyor
CV-404	D-407 Conveyor	1	304SS	50 x 4	15	150	56,095	Closed Belt conveyor
CV-405	CN-403 Filter Cake Conveyor	1	304SS	50 x 4	15	150	62,688	Closed Belt conveyor
CV-501	ADA Dryer Feed Conveyor	1	304SS	50 x 4	15	150	62,688	Closed Belt conveyor
CV-502	ADA Packaging Conveyor	1	304SS	50 x 4	15	250	44,871	Closed Belt conveyor
CV-503	Interstage Drying Conveyor	1	304SS	50 x 4	15	300	54,860	Closed Belt conveyor
CV-504	ADA Fines Conveyor	1	304SS	20 x 0.5	15	300	2,227	Closed Belt conveyor
CV-505	Flow Improver Conveyor	1	304SS	50 x 0.5	15	150	0.5	Closed Belt conveyor
CV-506	Dry ADA Conveyor	1	304SS	50 x 4	15	350	44,871	Closed Belt conveyor
CV-507	Cooled ADA Conveyor	1	304SS	50 x 4	15	250	44,871	Closed Belt conveyor
CV-701	AGS Filter Cake Conveyor	1	304SS	50 x 0.5	15	250	4,983	Closed Belt conveyor

Table 7.38 (Continued)
EQUIPMENT LIST WITH DUTY SPECIFICATIONS

Drums	# Installed	Materials of Construction	Vol (ft ³)	L x D (ft)	DesP (psia)	DesT (°F)	Orientation
D-101	Cobalt Naphthenate Feed Drum	1 304SS	25	8 x 2	15	150	Vertical-API 510
D-102	Boric Acid Feed Silo	1 304SS	106	13 x 3.2	15	150	Vertical-API 510
D-103	Boric Acid Mixing Drum	1 304SS	452	16 x 6	15	150	Vertical-API 510
D-104	Scrubber Decanter	1 304SS	1,075	28 x 7	150	400	Horiz-API 510
D-105	E-102 Receiver	1 304SS	56.5	8 x 3	150	400	Horiz-API 510
D-106	Scrubber Caustic Receiver	1 304SS	3,530	40 x 10.4	125	300	Horiz-API 510
D-107	P-108 Decanter	1 304SS	216	16 x 4	150	250	Horiz-API 510
D-108	Hydrolysis Drum	1 304SS	104	12 x 3	150	400	Horiz-API 510
D-109	R-101 Steam Drum	1 304SS	752	24 x 6	75	350	Horiz-API 510
D-201	C-201 Receiver	1 CS	2,687	86 x 21	15	175	Horiz-API 510
D-202	K-201 K/O Drum	1 CS	25	8 x 2	Full Vac	300	Horiz-API 510
D-203	C-202 Receiver	1 CS	274	18 x 4.5	Full Vac	300	Horiz-API 510
D-204	KA Oil Surge Drum	1 CS	1,100	28 x 7	15	300	Horiz-API 510
D-205	K-202 K/O Drum	1 CS	25	8 x 2	Full Vac	300	Horiz-API 510
D-301	HNO ₃ Catalyst Drum	1 CS	25	8 x 2	15	150	Vertical-API 510
D-302	R-301 Separator	1 304L SS	1,624	32 x 8	75	200	Horiz-API 510
D-303	C-301 Receiver	1 310L SS	1,590	32 x 8	Full Vac	200	Horiz-API 510
D-304	K-301 K/O Drum	1 304L SS	25	8 x 2	Full Vac	150	Vertical-API 510
D-401	K-401 K/O Drum	1 304L SS	25	8 x 2	Full Vac	150	Vertical-API 510
D-402	E-402 Receiver	1 304L SS	67.9	10 x 2.5	Full Vac	250	Horiz-API 510
D-403	Crude Filter Cake Silo	1 304L SS	854	25.9 x 6.4	15	150	Vertical
D-404	Crude ADA Dissolving Drum	1 304L SS	893	26.3 x 6.5	50	250	Horiz-API 510
D-405	K-402 K/O Drum	1 304L SS	25	8 x 2	Full Vac	150	Vertical-API 510
D-406	E-403 Receiver	1 304L SS	67.9	10 x 2.5	Full Vac	250	Horiz-API 510
D-407	1st-Stage Filter Cake Silo	1 304L SS	450	20.9 x 5.2	15	150	Vertical
D-408	1st-Stage Dissolving Drum	1 304L SS	893	26.3 x 6.5	50	250	Horiz-API 510
D-409	K-403 K/O Drum	1 304L SS	25	8 x 2	Full Vac	150	Vertical-API 510
D-410	E-405 Receiver	1 304L SS	67.9	10 x 2.5	Full Vac	250	Horiz-API 510
D-501	ADA Drying Silo	1 304L SS	8,140	55 x 14	15	250	Vertical
D-502	E-503 Receiver	1 304L SS	127	12 x 3	25	250	Horiz-API 510
D-503	Flow Improver Silo	1 304L SS	3	4 x 1	25	150	Vertical
D-504AB	ADA Product Silos	2 304L SS	2,873	40 x 10	15	250	Vertical
D-505	Fines Dissolving Drum	1 304L SS	35.6	9 x 2	15	300	Horiz-API 510
D-601	Wash Water Separator	1 304 SS	412	20 x 5	50	400	Horiz-API 510
D-602	E-602 Receiver	1 304 SS	412	20 x 5	50	400	Horiz-API 510
D-603	NVR Feed Drum	1 304 SS	90	12 x 3	75	600	Horiz-API 510
D-604	E-606 Receiver	1 CS	101	12 x 3	75	250	Horiz-API 510
D-605	K-601 K/O Drum	1 CS	25	8 x 1	Full Vac	400	Vert-API 510
D-606	E-609 Receiver	1 CS	4.4	4 x 1	Full Vac	400	Horiz-API 510
D-701	K-701 K/O Drum	1 SiFe	25	8 x 1	Full Vac	400	Vert-API 510
D-702	E-701 Receiver	1 SiFe	212	16 x 4	50	200	Horiz-API 510
D-703	AGS Mixing Drum	1 304 SS	309	16 x 4	75	350	Horiz-API 510
D-704	K-702 K/O Drum	1 304 SS	25	8 x 2	75	200	Vert-API 510
D-705	E-704 Receiver	1 304 SS	373	20 x 5	75	250	Horiz-API 510
D-706	AGS Mixing Drum	1 304 SS	59	10 x 2.5	75	250	Horiz-API 510

Table 7.38 (Continued)
EQUIPMENT LIST WITH DUTY SPECIFICATIONS

Heat Exchangers	# Installed	Materials of Construction Shell Side/ Tube Side	Duty (MM- btu/hr)	Surf Area (ft ²)	DesP (psia) Tube/ Shell	DesT (°F) Tube/ Shell	HX Configuration
E-101AB	Cyhex Tank Feed Heaters	2	CS/CS	2.5	250	75/15	300/150 Bayonet tank heater
E-102	Carbon Filter Condenser	1	304L SS/304L SS	5	500	100/50	350/150 Finned tube
E-103AB	Caustic Coolers	2	304L SS/304L SS	2.6	258	200/100	250/150 S&T—API660
E-104	P-108 Glycol Cooler	1	CS/304L SS	1.4	203	200/100	200/150 S&T—API660
E-105	Cyhex Trim Heater	1	CS/304L SS	11.4	1,150	350/200	400/350 S&T—API660
E-201	C-201 Condenser	1	CS/304SS	181.6	31,900	15/75	175/100 S&T—API660
E-202AB	C-201 Reboilers	2	304SS/304SS	86.8	8,690	350/15	475/150 S&T—API660
E-204	K-201 Condenser	1	304SS/304SS	61.7	6,170	15/75	250/150 S&T—API660
E-205	C-202 Condenser	1	CS/304SS	10.3	1,025	15/75	300/150 S&T—API660
E-206AB	C-202 Reboilers	2	CS/304SS	4.9	493	15/75	600/700 S&T—API660
E-307	R-302 Heater	1	304SS/304SS	16.2	1,575	75/75	250/350 S&T—API660
E-308	C-301 Condenser	1	304LSS/Ti	199	18,500	15/75	150/150 S&T—API660
E-309AB	C-301 Reboilers	2	304LSS/Ti	76	8,295	15/350	600/450 S&T—API660
E-310	K-301 Condenser	1	304SS/304SS	8.5	825	50/75	250/150 S&T—API660
E-311AB	Absorber Cooler	2	304SS/304SS	4.49	460	75/75	300/150 S&T—API660
E-312	R-301 Pumparound Cooler	1	304SS/Ti	158	17,464	75/75	200/150 S&T—API660
E-401AB	CR-401 Coolers	2	304L SS/Ti	3.12	785	75/75	250/150 S&T—API660
E-402	K-401 Condenser	1	304SS/304SS	8.5	934	15/75	250/150 S&T—API660
E-403	K-401 Condenser	1	304SS/304SS	8.5	934	15/75	250/150 S&T—API660
E-404	CR-402 Cooler	1	304L SS/Ti	6.24	1,570	75/75	250/150 S&T—API660
E-405	K-403 Condenser	1	304SS/304SS	8.5	934	15/75	250/150 S&T—API660
E-406	CR-403 Cooler	1	304L SS/Ti	6.24	1,570	75/75	250/150 S&T—API660
E-501	1st-Stage Rotary Dryer	1	304SS	21.98	2,250	350	450 Rotary Dryer (Atm P)
E-502	2nd-Stage Rotary Dryer	1	304SS	9.42	975	350	450 Rotary Dryer (Atm P)
E-503	Dryer O/H Condenser	1	304SS/304SS	15.65	1,520	15/75	250/150 S&T—API660
E-504	ADA Rotary Cooler	1	304SS	4.5	550	50	250 Rotary Dryer (Atm P)
E-601	Wash Water Evaporator	1	CS/304SS	51.5	4,950	50/75	300/400 Kettle Boiler
E-602	Wash Water Condenser	1	304SS/304SS	46.4	4,455	50/75	300/150 S&T—API660
E-603AB	R-601 Feed Heaters	2	304SS/304SS	0.45	51	150/350	400/600 S&T—API660
E-604AB	Methanol Feed heaters	2	CS/CS	0.3	24	150/325	300/600 S&T—API660
E-605	C-601 Feed Heater	1	304SS/304SS	0.6	87	50/150	300/500 S&T—API660
E-606	C-601 Condenser	1	304SS/304SS	4.1	420	75/75	250/150 S&T—API660
E-607AB	C-601 Reboiler	2	304SS/304SS	2.2	225	75/325	300/450 S&T—API660
E-608	C-602 Feed Heater	1	304SS/304SS	1.01	152	75/75	450/500 S&T—API660
E-609	C-602 Condenser	1	304SS/304SS	0.22	33	15/75	400/150 S&T—API660
E-610	Ester Product Cooler	1	CS/CS	0.81	101	75/75	400/150 S&T—API660
E-611AB	C-602 Reboilers	2	CS/CS	0.22	32	75/75	400/600 S&T—API660
E-701	C-701 Condenser	1	SiFe/Ti	13.2	1,852	75/75	200/150 S&T—API660
E-702AB	C-701 Reboilers	1	304SS/304SS	8.4	1,172	75/325	350/450 S&T—API660
E-703	CR-701 Cooler	1	304SS/304SS	3.85	770	75/75	250/150 S&T—API660
E-704	K-702 Condenser	1	304SS/304SS	25.8	1,806	75/75	250/150 S&T—API660
E-801	Feed/Product Heater	1	CS/304SS	11	5,400	50/50	3,000/500 Gas/Gas finned tube
E-802	N2O Steam Generator	1	304SS/304SS	11	2,950	75/50	1,500/350 S&T—API660
E-803	NO Absorber Cooler	1	304SS/304SS	2.3	148	75/75	150/150 S&T—API660

Table 7.38 (Continued)
EQUIPMENT LIST WITH DUTY SPECIFICATIONS

Fired Heaters		# Installed	Materials of Construction	Duty (MM-btu/hr)	DesP (psia) Tubes	DesT (°F) Tubes	Fuel
F-801 N2O Furnace		1	304SS	22.05	50	3,000	CH4
Filters	# Installed	Materials of Construction	Flow Rate (lbs/hr)	DesP (psia)	DesT (°F)	Opening Size (microns)	
FL-101 Compressed Air Filter	1	CS	56,800	Full Vac	150	0.05	Pulsed air baghouse
FL-102 R-101 Liq Filter	1	304L SS	265,000	150	400	0.5	Dual basket, 3way valve
FL-201 Boric Acid Filter	1	304SS	77,600	100	300	0.5	Dual basket, 3way valve
FL-202 C-202 Bottoms filter	1	304L SS	34,839	Full Vac	600	0.5	Dual basket, 3way valve
FL-301 Bleacher Filter	1	304L SS	271,987	75	300	0.5	Dual basket, 3way valve
FL-501 ADA Drying Filter	1	304 SS	15,435	15	250	0.05	Pulsed air baghouse
FL-801 K-801 Air Filter	1	CS	7,232	15	150	0.05	Pulsed air baghouse
Compressors	# Installed	Fluid/Type Machine	BHP	SCFM	Pin (psia)	Pout (psia)	Materials of Construction/Design Details
K-101 Air Compressor	1	Air/Centrif	3,922	12,380	15	150	CS/Centrifugal
K-201 Boric Acid Compressor	1	H2O/Centrif	2,037	21,430	5	15	304 SS/Centrifugal
K-202 C-202 Vacuum Pump	1	Cyhex/Liq Ring	15	249	8	15	CS/Liquid Ring
K-301 C-301 Vacuum Pump	1	H2O/Liq Ring	700	2,948	2	15	304SS/Liquid Ring
K-401 CR-401 Vacuum Pump	1	H2O/centrif	1,401	2,948	1	15	Ti/3-stage Centrifugal
K-402 CR-402 Vacuum Pump	1	H2O/centrif	11,014	46,359	2	15	304SS/3-stage Centrifugal
K-403 CR-403 Vacuum Pump	1	H2O/centrif	7,997	16,828	1	15	304SS/3-stage Centrifugal
K-601 C-602 Vacuum Pump	1	MCA/screw	14	30	1	15	304SS/twin screw vac pump
K-701 C-701 Vacuum Pump	1	HNO3/screw	928	3,907	2	15	Ti/twin screw vac pump
K-702 CR-701 Vacuum Pump	1	H2O/Liq Ring	2,128	8,958	2	15	304SS/twin screw vac pump
K-801 N2O Compressor	1	CO+Air/Centrif	161	1,698	15	45	CS/1-stg centrif
Mixers and Agitators	# Installed	Materials of Construction	BHP	DesT (°F)	Liquid	Viscosity (cs)	Mixer Type
M-101AB Cyhex Tank Mixer	2	CS	25	150	Cyhex	1	Side entering
M-102 Cobalt Napthenate Feed Tank Mixer	1	304L SS	1	150	Co Naphten- ate	15	Top Vertical
M-103 Boric Acid Drum Mixer	1	304L SS	5	150	Boric Acid	5	Top Vertical
M-104ABCD Oxidation Rx Mixers	4	304L SS	50	400	Cyhex	1	Top Vertical
M-105 R-101 Liq Static Mixer	1	304L SS	0	400	Cyhex	1	8 " Kenics Static Mixer
M-106 Hydrolysis Drum Mixer	1	304L SS	2	400	Cyhex	1	Top Vertical
M-201AB E-203 Agitators	2	304L SS	35	250	BA + H2O	2.5	Top Vertical
M-301 R-302 Agitator	1	304L SS	25	300	HNO3	2.5	Top Vertical
M-401 D-404 Agitator	1	304L SS	25	250	H2O	1.3	Top Vertical
M-402 D-408 Agitator	1	304L SS	25	250	H2O	1.3	Top Vertical
M-501 D-501 Agitator	1	304L SS	1	300	H2O	1	Top Vertical
M-701 D-703 Agitator	1	304L SS	10	350	AGS Soln	3.8	Top Vertical
M-702 D-706 Agitator	1	304L SS	4	250	AGS Soln	3.8	Top Vertical

Table 7.38 (Continued)
EQUIPMENT LIST WITH DUTY SPECIFICATIONS

Pumps	# Installed	Materials of Construction	gpm x hd (ft)	Liquid	DesP (psia)	DesT (°F)	Type Pump	Pump HP	
P-101AS	Cyhex Tank Feed Pumps	2	CS	75 x 350	Cyhex	150	150	API 610—Horiz	11.1
P-102AS	Cobalt Naphthenate Feed Pumps	2	CS	0.1 x 350	Co Naphthenate	150	150	Metering	0.01
P-103AS	Boric Acid Feed Pumps	2	304 SS	12 x 350	Boric Acid	150	150	API 610—Horiz	1.8
P-104AS	Carbon Filter Condensate Pumps	2	304 SS	10 x 150	Condensate	150	400	API 610—Horiz	0.65
P-105AS	Caustic Oil Pumps	2	304 SS	0.04 x 150	Cyhex	150	200	Metering	0.003
P-106AS	Caustic Water Pumps	2	304 SS	450 x 50	Water	150	300	ANSI—Horiz	9.5
P-107AS	D-104 Oil Pumps	2	304 SS	110 x 150	Cyhex	150	300	API 610—Horiz	7
P-108AS	D-104 Water Pumps	2	CI/CS	27 x 300	Water	150	300	ANSI—Horiz	3.4
P-109AS	D-107 Oil Pumps	2	CI/CS	2.7 x 300	Cyhex	150	300	API 610—Horiz	0.34
P-110ABCD	Cyhex Rx Pumps	4	304 SS	530 x 75	Cyhex	150	400	API 610—Horiz	16.8
P-111AS	Hydrolysis Water Pumps	2	304 SS	155 x 75	BA + H ₂ O	150	400	API 610—Horiz	4.9
P-201AS	C-201 Reflux Pumps	2	CI/CS	1,343 x 75	Cyhex	15	175	API 610—Horiz	42.6
P-202AS	C-201 Bottoms Pumps	2	304L SS	1,390 x 75	KA Oil	15	350	API 610—Horiz	44.1
P-203AS	Boric Acid Condensate Pumps	2	304 SS	123 x 75	H ₂ O	75	250	ANSI—Horiz	3.9
P-204AS	Boric Acid Slurry Pumps	2	304 SS	12.3 x 75	BA Slurry	100	300	Moyno	0.4
P-205AS	C-202 Reflux Pumps	2	CI/CS	68.5 x 75	KA Oil	75	300	API 610—Horiz	2.2
P-206AS	C-202 Bottoms Pumps	2	304L SS	69.7 x 150	NVR	75	600	API 610—Horiz	4.4
P-301AS	HNO ₃ Fresh Feed Pumps	2	304L SS	46.8 x 150	HNO ₃	75	150	API 610—Horiz	3
P-302AS	HNO ₃ Recycle Feed Pumps	2	304L SS	233 x 150	HNO ₃	75	250	API 610—Horiz	14.8
P-303AS	HNO ₃ Catalyst Feed Pumps	2	CI/CS	0.3 x 150	Catalyst	75	150	API 610—Horiz	0.02
P-304AS	Bleacher Pumps	2	304L SS	324 x 50	HNO ₃	75	300	API 610—Horiz	6.8
P-305AS	C-301 Reflux Pumps	2	304L SS	374 x 75	H ₂ O	75	150	ANSI—Horiz	11.9
P-306AS	C-301 Bottoms Pumps	2	304L SS	847 x 75	HNO ₃ +ADA	75	600	API 610—Horiz	26.9
P-307AS	Absorber Pumps	2	304L SS	441 x 75	HNO ₃	75	300	API 610—Horiz	14
P-308AS	HNO ₃ Rx Recycle Pumps	2	304L SS	406 x 75	HNO ₃ Rx Recycle	75	250	API 610—Horiz	12.9
P-401AS	TK-401 Feed Pumps	2	304 SS	413 x 75	HNO ₃ +ADA	75	600	API 610—Horiz	13.1
P-402AS	K-401 Condensate Pumps	2	304 SS	17 x 75	HNO ₃ +ADA	75	250	API 610—Horiz	0.54
P-403AS	CR-401 Slurry Pumps	2	304 SS	396 x 75	HNO ₃ +ADA	75	250	Moyno	12.6
P-404AS	Mother Liquor Recycle Pumps	2	304 SS	290 x 75	HNO ₃ +ADA	75	250	API 610—Horiz	9.2
P-405AS	CR-402 Feed Pumps	2	304 SS	446 x 75	H ₂ O	75	250	ANSI—Horiz	14.1
P-406AS	D-406 Condensate Pumps	2	304 SS	267 x 75	H ₂ O	75	250	ANSI—Horiz	8.5
P-407AS	CR-402 Circulating Pumps	2	304 SS	1,310 x 75	H ₂ O+ADA	75	250	API 610—Horiz	41.5
P-408AS	CR-402 Slurry Pumps	2	304 SS	179 x 75	H ₂ O+ADA	75	250	Moyno	5.7
P-409AS	CN-402 Liquor Pumps	2	304 SS	67 x 150	H ₂ O	100	250	ANSI—Horiz	4.2
P-410AS	D-408 Pumps	2	304 SS	182 x 75	H ₂ O	100	250	ANSI—Horiz	5.8
P-411AS	D-410 Pumps	2	304 SS	97 x 75	H ₂ O	100	250	ANSI—Horiz	3.1
P-412AS	CR-403 Circulating Pumps	2	304 SS	1,310 x 75	H ₂ O+ADA	75	250	API 610—Horiz	41.5
P-413AS	CR-403 Slurry Pumps	2	304 SS	134 x 75	H ₂ O+ADA	75	250	Moyno	4.2
P-414AS	CN-403 Discharge Pumps	2	304 SS	9 x 75	H ₂ O+ADA	75	250	API 610—Horiz	0.3
P-415AS	CR-401 Recycle Pumps	2	304LSS	111 x 75	HNO ₃ +ADA	75	600	API 610—Horiz	3.5
P-501AS	Fines Solution Pumps	2	304LSS	45 x 125	H ₂ O Soln	50	300	API 610—Horiz	2.4
P-601AS	D-602 Pumps	2	304SS	76 x 75	H ₂ O	75	300	centrif-ANSI	0.23
P-602AS	D-601 Pumps	2	304SS	8 x 75	Org Acid	75	300	API 610—Horiz	0.25
P-603AS	NVR Feed Pumps	2	304SS	11 x 75	NVR	75	600	API 610—Horiz	0.35
P-604AS	Methanol Feed Pumps	2	CS	3.1 x 75	Methanol	75	150	Diaphragm	0.1

Table 7.38 (Continued)
EQUIPMENT LIST WITH DUTY SPECIFICATIONS

Pumps	# Installed	Materials of Construction	gpm x hd (ft)	Liquid	DesP (psia)	DesT (°F)	Type Pump	Pump HP	
P-605AS	C-601 Reflux Pumps	2	CS	25 x 75	Methanol	75	250	API 610—Horiz	0.8
P-606AS	R-601 Bottoms Pumps	2	304SS	9.2 x 75	Ester	75	500	API 610—Horiz	0.3
P-607AS	C-602 Reflux Pumps	2	CI/CS	1.1 x 75	Ester	75	400	Gear pump	0.35
P-608AS	Ester Product Pumps	2	CI/CS	7.2 x 75	Ester	75	400	Gear pump	0.23
P-609AS	TK-602 pumps	2	CI/CS	16.2 x 150	Ester	100	400	API 610—Horiz	0.39
P-610AS	C-602 Bottoms pumps	2	CI/CS	1.65 x 75	Ester	75	400	Gear pump	0.05
P-611AS	C-601 Bottoms Pumps	2	304SS	11.4 x 75	H2O	75	325	API 610—Horiz	0.36
P-701AS	C-701 Reflux Pumps	2	SiFe	53 x 75	HNO3	75	200	API 610—Horiz	1.7
P-702AS	C-701 Bottoms Pumps	2	SiFe	12 x 75	Org Acid	75	350	API 610—Horiz	0.38
P-703AS	AGS Solution Pumps	2	304SS	77 x 75	Org Acid	75	350	API 610—Horiz	2.44
P-704AS	CR-701 Circulating Pumps	2	304SS	231 x 75	AGS Soln	75	150	API 610—Horiz	7.33
P-705AS	AGS Slurry Pumps	2	304SS	25 x 75	AGS Slurry	75	150	Moyno	0.79
P-706AS	CN-701 Liquid Pumps	2	304SS	16 x 75	H2O	75	150	API 610—Horiz	0.51
P-707AS	D-705 Pumps	2	304SS	52 x 75	H2O	75	150	API 610—Horiz	1.64
P-708AS	AGS Product Pumps	2	304SS	20 x 75	AGS Vолн	75	150	API 610—Horiz	0.63
P-709AS	AGS Rundown Pumps	2	304SS	20 x 150	AGS Soln	150	150	API 610—Horiz	1.27
P-801AS	NO Absorber Pumps	2	CI/CS	80 x 75	H2O	75	150	API 610—Horiz	2.54
Reactors	# Installed	Materials of Construction	Vol (ft³)	L x D (ft)	DesP (psia)	DesT (°F)	Internals		
R-101ABCD	Cyhex Oxidation Reactors	4	304L SS	1,428	12 x 12	150	400	Baffling + Stm jacket	
R-102AB	CHHP Reactors	2	304L SS	520	22 x 5.5	150	400	Catalyst bed supports	
R-301	1st-Stage HNO3 Reactor	1	310L SS	1,675	12 x 13.3	75	200	Shell & tube, 14,500 1/2 inch Titanium tubes	
R-302	2nd-Stage HNO3 Reactor	1	310L SS	1,060	12 x 10.6	75	250	Autoclave w CWS jacketing	
R-601AB	Ester Reactors	2	304SS	150	48 x 3	50	400	8 RX zones, w 6 trays above and below beds	
R-801	N2O Reactor	1	304SS	1,206	24 x 8	50	3,000	2 fixed cat beds	
Specially Packaged Equipment	# Installed	Duty	Details						
S-101	Process Flare System	2	100 MM Btu/hr each	250 ft x 24 inch				John Zink or equiv auto stm inject	
S-102	Vapor Waste Incinerator	1	50 MM Btu/hr at 1,200°C					Vapor, liq and solid waste handling	
S-103	Process Computer Control System	1	1,200 loops Honeywell Experion					Honeywell Experion or equiv	
S-104	Vacuum Line Compression System	1	5 psia x 50 MM scf/hr						
S-105	N2 PSA System		10 MM-scfh at 99% N2						
S-106	Packaged Glycol Refrigeration System		20 MM Btu/hr at 0°C						
S-501	ADA Drying Cyclone	1	4.5L x 3D					500 lb solids/hr of 1% solids in steam	
S-108	ADA & AGS Computerized Modular Packaging System	1	25 mt/day, 20 & 25 kg bagging on 1 mt strapped & wrapped pallets	500 kg & 1 mt iso containers, 20 & 40 mt bulk containers blown					
S-109	Dowtherm Hot Oil System		10 MM Btu/hr at 325°C						
S-701	Rohm&Haas Ion Exchange System	1	40 k lb/hr of 1,000 ppm Cu + V						

Table 7.38 (Concluded)
EQUIPMENT LIST WITH DUTY SPECIFICATIONS

Steam Turbine Drivers		# Installed	Mechanical or Electrical?	BHP	KW	Inlet Steam (Pres/Temp)	Outlet Steam (Pres/Temp)	Steam Turbine Details
ST-401	K-402 Driver	1	Mechanical	22,000	16,500	1,200/800	50/375	Horiz Split-Centrif
ST-402	K-403 Driver	1	Mechanical	8,000	6,000	1,200/800	50/375	Horiz Split-Centrif
Storage Tanks		# Installed	Materials of Construction	Vol (ft3)	H x D (ft)	DesP (psia)	DesT (°F)	Type Tank w Details (API?)
TK-101AB	Cyhex Day Feed Tank	2	CS	4,013	10.8 x 21.6	15	150	Floating Roof-API650
TK-301	Nitric Acid Feed Day Tank	1	304L SS	468	5.3 x 10.6	15	150	Floating Roof-API650
TK-302	Nitric Acid Recycle Tank	1	304L SS	26,763	20.3 x 40.6	15	250	Floating Roof-API650-insulate
TK-401	Crystallization Feed Tank	1	304L SS	39,700	23.2 x 46.4	15	250	Floating Roof-API650-insulate
TK-601	Methanol Feed Tank	1	CS	588	10 x 10	15	150	Floating Roof-API650
TK-602ABCD	Ester Product Grade Tanks	4	CS	1,560	12 x 12	15	400	API 650
TK-701AB	AGS Rundown Tanks	2	304 SS	1,428	12 x 12	15	150	API 650
Pressure Vessels		# Installed	Materials of Construction	Vol (ft3)	L x D (ft)	Orientat ion	DesP (psia)	DesT (°F)
V-101	Cyhex Scrubber	1	304 SS	7,912	70 x 12	Vert	125	600
V-102AB	Cyhex Activated Carbon Filters	2	304 SS	2,713	24 x 12	Vert	125	600
V-301	Bleacher	1	304L SS	678	24 x 6	Vert	75	300
V-302	Nitric Acid Absorber	1	304L SS	1,017	36 x 6	Vert	75	250

Itemized Capital Cost Estimate

Combining the process equipment duty specifications with data from the PEPCOST computer program, we have generated the following estimated FOB and installation costs for each tagged piece of equipment at a PEP Cost index of 795, and location factor of 1.0

Table 7.39
ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Distillation Columns					
C-201	Cyhex Recycle Column	424.2	424.2	506.6	506.6
C-202	KA Oil Column	77.1	77.1	311.3	311.3
C-301	Nitric Acid Concentrator	2,178.3	2,178.3	610.7	610.7
C-601	Methanol Purification Column	217.3	217.3	362.3	362.3
C-602	Ester Column	122.0	122.0	330.7	330.7
C-701	Drying Tower	373.4	373.4	366.8	366.8
C-801	NO Absorber	111.5	111.5	209.7	209.7
Centrifuges					
CN-201	Boric Acid 1st-Stage Centrifuge	258.5	258.5	68.5	68.5
CN-401	Crude Acid Centrifuge	505.6	2,022.4	95.5	382.0
CN-402	1st-Stage Centrifuge	505.6	2,022.4	95.5	382.0
CN-403	2nd-Stage Centrifuge	505.6	2,022.4	95.5	382.0
CN-701	AGS Centrifuge	85.5	85.5	35.6	35.6
Crystallizers					
CR-201AB	Boric Acid Crystallizer	345.0	690.0	52.3	104.6
CR-401	Crude Acid Crystallizer	3,128.0	3,128.0	414.0	414.0
CR-402	1st-Stage Aqueous Crystallizer	3,128.0	3,128.0	414.0	414.0
CR-403	2nd-Stage Aqueous Crystallizer	3,128.0	3,128.0	414.0	414.0
CR-701	AGS Crystallizer	470.0	470.0	68.5	68.5
Solids Conveyors					
CV-101	Boric Acid Conveyor	28.5	28.5	38.2	38.2
CV-201	Boric Acid Filter Cake Conveyor	62.5	62.5	75.0	75.0
CV-401	Crude Filter Cake Conveyor	125.0	125.0	185.0	185.0
CV-402	Crude ADA conveyor	125.0	125.0	185.0	185.0
CV-403	1st-Stage Filter Cake Conveyor	125.0	125.0	185.0	185.0
CV-404	D-407 Conveyor	125.0	125.0	185.0	185.0
CV-405	CN-403 Filter Cake Conveyor	125.0	125.0	185.0	185.0
CV-501	ADA Dryer Feed Conveyor	125.0	125.0	185.0	185.0
CV-502	ADA Packaging Conveyor	125.0	125.0	185.0	185.0
CV-503	Interstage Drying Conveyor	125.0	125.0	185.0	185.0
CV-504	ADA Fines Conveyor	25.5	25.5	36.2	36.2
CV-505	Flow Improver Conveyor	48.5	48.5	62.7	62.7
CV-506	Dry ADA Conveyor	125.0	125.0	185.0	185.0
CV-507	Cooled ADA Conveyor	125.0	125.0	185.0	185.0
CV-701	AGS Filter Cake Conveyor	48.5	48.5	62.7	62.7

Table 7.39 (Continued)
ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Drums					
D-101	Cobalt Naphthenate Feed Drum	17.8	17.8	33.8	33.8
D-102	Boric Acid Feed Silo	27.9	27.9	36.5	36.5
D-103	Boric Acid Mixing Drum	46.0	46.0	41.6	41.6
D-104	Scrubber Decanter	92.8	92.8	46.6	46.6
D-105	E-102 Receiver	17.6	17.6	36.3	36.3
D-106	Scrubber Caustic Receiver	155.7	155.7	53.4	53.4
D-107	P-108 Decanter	30.2	30.2	39.4	39.4
D-108	Hydrolysis Drum	23.9	23.9	37.8	37.8
D-109	R-101 Steam Drum	49.4	49.4	43.6	43.6
D-201	C-201 Receiver	62.3	62.3	49.5	49.5
D-202	K-201 K/O Drum	12.5	12.5	34.5	34.5
D-203	C-202 Receiver	23.5	23.5	38.9	38.9
D-204	KA Oil Surge Drum	42.1	42.1	44.6	44.6
D-205	K-202 K/O Drum	12.5	12.5	34.5	34.5
D-301	HNO ₃ Catalyst Drum	15.6	15.6	33.0	33.0
D-302	R-301 Separator	78.3	78.3	47.9	47.9
D-303	C-301 Receiver	73.0	73.0	47.6	47.6
D-304	K-301 K/O Drum	17.6	17.6	33.8	33.8
D-401	K-401 K/O Drum	17.6	17.6	33.8	33.8
D-402	E-402 Receiver	18.8	18.8	36.7	36.7
D-403	Crude Filter Cake Silo	63.0	63.0	46.6	46.6
D-404	Crude ADA Dissolving Drum	52.7	52.7	44.4	44.4
D-405	K-402 K/O Drum	17.6	17.6	33.8	33.8
D-406	E-403 Receiver	18.8	18.8	36.7	36.7
D-407	1st-Stage Filter Cake Silo	49.4	49.4	42.7	42.7
D-408	1st-Stage Dissolving Drum	53.8	53.8	44.6	44.6
D-409	K-403 K/O Drum	17.6	17.6	33.8	33.8
D-410	E-405 Receiver	19.2	19.2	36.8	36.8
D-501	ADA Drying Silo	241.5	241.5	86.9	86.9
D-502	E-503 Receiver	23.9	23.9	38.0	38.0
D-503	Flow Improver Silo	11.9	11.9	32.2	32.2
D-504AB	ADA Product Silos	122.4	244.8	61.8	123.6
D-505	Fines Dissolving Drum	16.5	16.5	36.0	36.0
D-601	Wash Water Separator	38.2	38.2	41.4	41.4
D-602	E-602 Receiver	38.2	38.2	41.4	41.4

Table 7.39 (Continued)
ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Drums					
D-603	NVR Feed Drum	21.7	21.7	37.4	37.4
D-604	E-606 Receiver	18.2	18.2	36.8	36.8
D-605	K-601 K/O Drum	15.6	15.6	33.0	33.0
D-606	E-609 Receiver	8.9	8.9	32.8	32.8
D-701	K-701 K/O Drum	19.1	19.1	33.9	33.9
D-702	E-701 Receiver	34.2	34.2	39.3	39.3
D-703	AGS Mixing Drum	34.1	34.1	40.5	40.5
D-704	K-702 K/O Drum	17.6	17.6	33.8	33.8
D-705	E-704 Receiver	37.2	37.2	41.1	41.1
D-706	AGS Mixing Drum	19.1	19.1	36.7	36.7
Heat Exchangers					
E-101AB	Cyhex Tank Feed Heaters	21.4	42.8	33.6	67.2
E-102	Carbon Filter Condenser	23.3	23.3	41.4	41.4
E-103AB	Caustic Coolers	28.3	56.6	40.3	80.6
E-104	P-108 Glycol Cooler	22.8	22.8	39.9	39.9
E-105	Cyhex Trim Heater	92.2	92.2	44.6	44.6
E-201	C-201 Condenser	1,153.0	1,153.0	147.5	147.5
E-202AB	C-201 Reboilers	446.4	892.8	60.0	120.0
E-204	K-201 Condenser	341.0	341.0	55.7	55.7
E-205	C-202 Condenser	79.9	79.9	43.2	43.2
E-206AB	C-202 Reboilers	44.9	89.8	41.2	82.4
E-307	R-302 Heater	115.5	115.5	44.9	44.9
E-308	C-301 Condenser	2,505.0	2,505.0	59.0	59.0
E-309AB	C-301 Reboilers	1,502.0	3,004.0	59.5	119.0
E-310	K-301 Condenser	69.7	69.7	42.5	42.5
E-311AB	Absorber Cooler	45.5	91.0	41.7	83.4
E-312	R-301 Pumparound Cooler	2,505.0	2,505.0	88.5	88.5
E-401AB	CR-401 Coolers	189.8	379.6	42.4	84.8
E-402	K-401 Condenser	76.8	76.8	42.8	42.8
E-403	K-401 Condenser	76.8	76.8	42.8	42.8
E-404	CR-402 Cooler	353.1	353.1	44.9	44.9
E-405	K-403 Condenser	76.8	76.8	42.8	42.8
E-406	CR-403 Cooler	353.1	353.1	44.9	44.9

Table 7.39 (Continued)
ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Heat Exchangers					
E-501	1st-Stage Rotary Dryer	317.6	317.6	48.1	48.1
E-502	2nd-Stage Rotary Dryer	165.6	165.6	43.9	43.9
E-503	Dryer O/H Condenser	117.2	117.2	45.9	45.9
E-504	ADA Rotary Cooler	105.4	105.4	42.3	42.3
E-601	Wash Water Evaporator	273.1	273.1	52.1	52.1
E-602	Wash Water Condenser	257.2	257.2	51.2	51.2
E-603AB	R-601 Feed Heaters	13.4	26.8	38.2	76.4
E-604AB	Methanol Feed Heaters	11.0	22.0	31.4	62.8
E-605	C-601 Feed Heater	14.4	14.4	38.9	38.9
E-606	C-601 Condenser	42.9	42.9	41.8	41.8
E-607AB	C-601 Reboiler	25.6	51.2	40.3	80.6
E-608	C-602 Feed Heater	18.0	18.0	39.1	39.1
E-609	C-602 Condenser	12.3	12.3	37.5	37.5
E-610	Ester Product Cooler	12.5	12.5	32.4	32.4
E-611AB	C-602 Reboilers	10.9	21.8	31.3	62.6
E-701	C-701 Condenser	407.8	407.8	45.7	45.7
E-702AB	C-701 Reboilers	95.5	95.5	44.6	44.6
E-703	CR-701 Cooler	68.6	68.6	43.1	43.1
E-704	K-702 Condenser	128.5	128.5	45.6	45.6
E-801	Feed/Product Heater	146.0	146.0	52.8	52.8
E-802	N ₂ O Steam Generator	187.6	187.6	48.3	48.3
E-803	NO Absorber Cooler	17.7	17.7	39.0	39.0
Fired Heaters					
F-801	N ₂ O Furnace	653.7	653.7	283.6	283.6
Filters					
FL-101	Compressed Air Filter	1,250.0	1,250.0	258.0	258.0
FL-102	R-101 Liq Filter	325.6	325.6	158.2	158.2
FL-201	Boric Acid Filter	85.2	85.2	45.3	45.3
FL-202	C-202 Bottoms filter	39.7	39.7	28.1	28.1
FL-301	Bleacher Filter	342.8	342.8	176.5	176.5
FL-501	ADA Drying Filter	458.0	458.0	106.0	106.0
FL-801	K-801 Air Filter	56.5	56.5	29.6	29.6

Table 7.39 (Continued)
ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Compressors					
K-101	Air Compressor	3,470.0	3,470.0	7,062.0	7,062.0
K-201	Boric Acid Compressor	1,695.0	1,695.0	3,218.0	3,218.0
K-202	C-202 Vacuum Pump	40.6	40.6	203.8	203.8
K-301	C-301 Vacuum Pump	752.7	752.7	1,176.0	1,176.0
K-401	CR-401 Vacuum Pump	1,275.0	1,275.0	2,084.0	2,084.0
K-402	CR-402 Vacuum pump	11,360.0	11,360.0	27,360.0	27,360.0
K-403	CR-403 Vacuum pump	4,794.0	4,794.0	10,910.0	10,910.0
K-601	C-602 Vacuum Pump	38.5	38.5	156.8	156.8
K-701	C-701 Vacuum Pump	932.5	932.5	1,613.0	1,613.0
K-702	CR-701 Vacuum Pump	1,752.0	1,752.0	3,169.0	3,169.0
K-801	N ₂ O Compressor	246.3	246.3	414.3	414.3
Mixers and Agitators					
M-101AB	Cyhex Tank Mixer	28.3	56.6	7.4	14.7
M-102	Cobalt Naphthenate Feed Tank Mixer	1.8	1.8	0.5	0.5
M-103	Boric Acid Drum Mixer	7.1	7.1	1.8	1.8
M-104ABCD	Oxidation Rx Mixers	51.3	205.3	13.3	53.4
M-105	R-101 Liq Static Mixer	8.3	8.3	2.1	2.1
M-106	Hydrolysis Drum Mixer	3.2	3.2	0.8	0.8
M-201AB	E-203 Agitators	37.8	75.5	9.8	19.6
M-301	R-302 Agitator	28.3	28.3	7.4	7.4
M-401	D-404 Agitator	28.3	28.3	7.4	7.4
M-402	D-408 Agitator	28.3	28.3	7.4	7.4
M-501	D-501 Agitator	1.8	1.8	0.5	0.5
M-701	D-703 Agitator	12.9	12.9	3.3	3.3
M-702	D-706 Agitator	5.8	5.8	1.5	1.5
Pumps					
P-101AS	Cyhex Tank Feed Pumps	8.3	16.6	47.8	67.6
P-102AS	Cobalt Naphthenate Feed Pumps	2.8	5.6	11.4	16.1
P-103AS	Boric Acid Feed Pumps	7.7	15.4	17.5	24.7
P-104AS	Carbon Filter Condensate Pumps	7.1	14.2	16.7	23.6
P-105AS	Caustic Oil Pumps	1.6	3.2	3.5	4.9
P-106AS	Caustic Water Pumps	7.8	15.6	65.8	93.1
P-107AS	D-104 Oil Pumps	9.3	18.6	32.6	46.1
P-108AS	D-104 Water Pumps	2.8	5.6	21.8	30.8
P-109AS	D-107 Oil Pumps	3.4	6.8	13.4	19.0

Table 7.39 (Continued)
ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Pumps					
P-110ABCD	Cyhex Rx Pumps	20.2	80.8	96.4	192.8
P-111AS	Hydrolysis Water Pumps	12.2	24.4	38.2	54.0
P-201AS	C-201 Reflux Pumps	17.2	34.4	96.2	136.0
P-202AS	C-201 Bottoms Pumps	33.9	67.8	105.1	148.6
P-203AS	Boric Acid Condensate Pumps	5.6	11.2	34.0	48.1
P-204AS	Boric Acid Slurry Pumps	13.4	26.8	15.6	22.1
P-205AS	C-202 Reflux Pumps	4.9	9.8	24.8	35.1
P-206AS	C-202 Bottoms Pumps	11.5	23.0	34.4	48.6
P-301AS	HNO ₃ Fresh Feed Pumps	10.2	20.4	31.9	45.1
P-302AS	HNO ₃ Recycle Feed Pumps	18.3	36.6	63.8	90.2
P-303AS	HNO ₃ Catalyst Feed Pumps	2.8	5.6	11.6	16.4
P-304AS	Bleacher Pumps	13.0	26.0	59.3	83.9
P-305AS	C-301 Reflux Pumps	8.0	16.0	55.8	78.9
P-306AS	C-301 Bottoms Pumps	23.6	47.2	89.9	127.1
P-307AS	Absorber Pumps	17.3	34.6	54.7	77.4
P-308AS	HNO ₃ Rx Recycle Pumps	16.7	33.4	56.3	79.6
P-401AS	TK-401 Feed Pumps	16.8	33.6	56.6	80.0
P-402AS	K-401 Condensate Pumps	7.0	14.0	16.2	22.9
P-403AS	CR-401 Slurry Pumps	33.0	66.0	73.2	103.5
P-404AS	Mother Liquor Recycle Pumps	14.5	29.0	52.5	74.2
P-405AS	CR-402 Feed Pumps	8.7	17.4	58.6	82.9
P-406AS	D-406 Condensate Pumps	7.2	14.4	51.6	73.0
P-407AS	CR-402 Circulating Pumps	29.9	59.8	108.3	153.2
P-408AS	CR-402 Slurry Pumps	24.4	48.8	38.1	53.9
P-409AS	CN-402 Liquor Pumps	5.6	11.2	32.2	45.5
P-410AS	D-408 Pumps	6.1	12.2	42.2	59.7
P-411AS	D-410 Pumps	5.1	10.2	33.9	47.9
P-412AS	CR-403 Circulating Pumps	29.9	59.8	118.0	166.9
P-413AS	CR-403 Slurry Pumps	22.2	44.4	36.9	52.2
P-414AS	CN-403 Discharge Pumps	6.4	12.8	15.3	21.6
P-415AS	CR-401 Recycle Pumps	10.4	20.8	38.9	55.0
P-501AS	Fines Solution Pumps	9.4	18.8	30.2	42.7

Table 7.39 (Continued)
ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Pumps					
P-601AS	D-602 Pumps	9.4	18.8	31.2	44.1
P-602AS	D-601 Pumps	6.4	12.8	15.3	21.6
P-603AS	NVR Feed Pumps	6.6	13.2	15.9	22.5
P-604AS	Methanol Feed Pumps	4.5	9.0	12.8	18.1
P-605AS	C-601 Reflux Pumps	3.8	7.6	9.0	12.7
P-606AS	R-601 Bottoms Pumps	6.4	12.8	15.7	22.2
P-607AS	C-602 Reflux Pumps	4.6	9.2	12.2	17.3
P-608AS	Ester Product Pumps	4.6	9.2	13.5	19.1
P-609AS	TK-602 Pumps	3.6	7.2	14.8	20.9
P-610AS	C-602 Bottoms Pumps	4.6	9.2	12.3	17.4
P-611AS	C-601 Bottoms Pumps	6.6	13.2	15.9	22.5
P-701AS	C-701 Reflux Pumps	8.6	17.2	31.1	44.0
P-702AS	C-701 Bottoms Pumps	6.6	13.2	15.6	22.1
P-703AS	AGS Solution Pumps	9.4	18.8	33.0	46.7
P-704AS	CR-701 Circulating Pumps	13.3	26.6	47.2	66.8
P-705AS	AGS Slurry Pumps	7.4	14.8	24.7	34.9
P-706AS	CN-701 Liquid Pumps	6.9	13.8	16.8	23.8
P-707AS	D-705 Pumps	8.6	17.2	31.0	43.8
P-708AS	AGS Product Pumps	7.1	14.2	16.7	23.6
P-709AS	AGS Rundown Pumps	8.1	16.2	18.8	26.6
P-801AS	NO Absorber Pumps	4.9	9.8	26.2	37.1
Reactors					
R-101ABCD	Cyhex Oxidation Reactors	109.5	438.0	211.5	1,752.0
R-102AB	CHHP Reactors	59.6	119.2	164.9	238.4
R-301	1st-Stage HNO ₃ Reactor	3,392.0	3,392.0	120.5	3,392.0
R-302	2nd-Stage HNO ₃ Reactor	70.2	70.2	192.2	70.2
R-601AB	Ester reactors	32.1	64.2	138.7	128.4
R-801	N ₂ O Reactor	78.0	78.0	204.9	78.0

Table 7.39 (Concluded)
ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Specially Packaged Equipment					
S-101	Process Flare System	5,600.0	11,200.0	3,800.0	7,600.0
S-102	Vapor Waste Incinerator	1,800.0	1,800.0	1,250.0	1,250.0
S-103	Process Computer Control System	16,200.0	16,200.0	8,400.0	8,400.0
S-104	Vacuum Line Compression System	8,500.0	8,500.0	9,620.0	9,620.0
S-105	N ₂ PSA System	2,400.0	2,400.0	1,600.0	1,600.0
S-106	Packaged Glycol Refrigeration System	1,600.0	1,600.0	1,850.0	850.0
S-501	ADA Drying Cyclone	20.4	20.4	10.8	10.8
S-108	ADA & AGS Computerized modular packaging system	8,400.0	8,400.0	4,700.0	4,700.0
S-109	Dowtherm Hot Oil System	3,500.0	3,500.0	1,875.0	1,875.0
S-701	Rohm&Haas Ion Exchange System	850.0	850.0	750.0	750.0
Steam Turbine Drivers					
ST-401	K-402 Driver	2,550.0	2,550.0	2,784.0	2,784.0
ST-402	K-403 Driver	1,024.0	1,024.0	1,264.0	1,264.0
Storage Tanks					
TK-101AB	Cyhex Day Feed Tank	73.3	146.6	34.5	69.0
TK-301	Nitric Acid Feed Day Tank	109.4	109.4	16.1	16.1
TK-302	Nitric Acid Recycle Tank	553.7	553.7	147.1	147.1
TK-401	Crystallization Feed Tank	720.7	720.7	191.4	191.4
TK-601	Methanol Feed Tank	37.0	37.0	17.4	17.4
TK-602ABCD	Ester Product Grade Tanks	52.1	208.4	24.5	98.0
TK-701AB	AGS Rundown Tanks	161.6	323.2	23.7	47.4
Pressure Vessels					
V-101	Cyhex Scrubber	391.8	391.8	97.4	97.4
V-102AB	Cyhex Activated Carbon Filters	169.3	338.6	66.0	132.0
V-301	Bleacher	60.2	60.2	46.4	46.4
V-302	Nitric Acid Absorber	72.2	72.2	50.0	50.0

Segmentation of Itemized Capital Costs

There are several ways to segment the itemized capital costs in order to get a better understanding of where the majority of the capital cost is required within the process area. One approach is segmenting the capital cost between the FOB purchase price of tagged process equipment, and the cost to install the equipment. This data is presented in the table below. As shown in the table, costs are nearly split even between the FOB purchase cost, and the cost to install the process equipment.

Table 7.40
ITEMIZED CAPITAL COST SEGMENTATION BY FOB AND INSTALLATION COST

US\$-MM

FOB Purchased Cost	135,356.5
Installation Cost	121,114.0
Installed Cost	256,470.5

A different way to segment the capital cost is by the kind of equipment required. This segmentation of tagged process equipment is presented below. The largest single cost element is specially packaged equipment, which for this process is primarily inside battery limits facilities that are shared throughout the different sections of the plant. These facilities include the process flare system, incinerators, process computer control system, vacuum line compression network, nitrogen PSA supply, glycol refrigeration, dust cyclones, the solids packaging systems for products and by-products, hot oil system, and the ion exchange system for recovering vanadium and copper oxidation catalysts.

The second highest cost category of equipment is process compressors, which are used both to supply air to the air oxidation reactors and nitric acid bleacher, and to also provide vacuum for both the three stages of crystallizers and for those distillation columns designed to operate under vacuum in order to minimize process temperatures and avoid product thermal degradation. The segmentation of itemized FOB and installation costs by equipment type is presented in the table below.

Table 7.41
ITEMIZED CAPITAL COST SEGMENTATION BY FOB EQUIPMENT TYPE

	FOB	Installation	Installed
Distillation Columns	3,503.8	2,698.1	6,201.9
Centrifuges	6,411.2	1,250.1	7,661.3
Crystallizers	10,544.0	1,415.1	11,959.1
Solids Conveyors	1,463.5	2,124.8	3,588.3
Process Drums	1,967.9	1,888.0	3,855.9
Heat Exchangers	14,910.3	2,537.5	17,447.8
Fired Heaters	653.7	283.6	937.3
Filters	2,557.8	801.7	3,359.5
Compressors	26,356.6	57,366.9	83,723.5
Mixers and Agitators	463.1	120.3	583.4
Pumps	1,356.8	3,352.9	4,709.7
Reactors	4,161.6	5,659.0	9,820.6
Specially Packaged Equipment	54,470.4	36,655.8	91,126.2
Steam Turbine Drivers	3,574.0	4,048.0	7,622.0
Storage Tanks	2,099.0	586.4	2,685.4
Pressure Vessels	862.8	325.8	1,188.6
Total	135,356.5	121,114.0	256,470.5

If the itemized capital cost of FOB + installation is segmented by section of the plant, the results are reported in the table below. The crystallization process unit has the highest capital cost, and requires three stages of suspension crystallization, all operating under vacuum conditions. The next highest cost section of the plant is nitric acid oxidation of KA oil, where the high cost is associated with the significant use of titanium heat exchanger tubes in the nitric acid primary reactor, due to the combination of high nitric acid concentration, and high operating temperature.

Table 7.42
ITEMIZED CAPITAL COST SEGMENTED BY SECTION OF PLANT

Section	US\$-MM
100 Air Oxidation of Cyclohexane to Crude KA Oil	18,790.3
200 Purification of Crude KA Oil	11,850.9
300 Nitric Acid Oxidation of KA Oil to Crude Adipic Acid	21,019.3
400 Adipic Acid Crystallization	92,069.7
500 Adipic Acid Drying and Packaging	3,794.0
600 By-Product Recovery to Methyl Esters	3,832.8
700 AGS By-Product Production	11,114.9
800 Nitrous Oxide Destruction	2,699.5
Special Equipment	91,126.2
Total	256,297.6

TOTAL FIXED CAPITAL COST ESTIMATE

When incorporating the itemized capital cost items within the larger cost framework for building the entire plant, other major cost items occur, principally offsite battery limits facilities. In addition, for this Class-3 capital cost estimate, we add a 25% contingency factory to our cost estimate. The final capital cost estimate for the entire plant is \$667 MM, segmented between \$453 MM for ISBL facilities, plus \$215 MM for OSBL facilities. The detailed cost estimate is presented in the table below.

Table 7.43
ADIPIC ACID VIA TWO-STAGE OXIDATION OF CYCLOHEXANE—TOTAL FIXED CAPITAL COST

CAPACITY: 160,000 MT/YR AT 0.90 STREAM FACTOR

PEP COST INDEX: 795

	COST (\$US-MM)	CAPACITY EXPONENT	
		UP	DOWN
BATTERY LIMITS EQUIPMENT, FOB			
DISTILLATION COLUMNS	3,504	0.55	0.53
CENTRIFUGES	6,411	0.70	0.60
CRYSTALLIZERS	10,544	0.61	0.58
SOLIDS CONVEYORS	1,464	0.67	0.62
PROCESS DRUMS	1,968		
HEAT EXCHANGERS	14,910	0.65	0.63
FIRED HEATERS	654	0.63	0.60
FILTERS	2,558	0.62	0.60
COMPRESSORS	26,357	0.69	0.60
MIXERS & AGITATORS	463	0.67	0.62
PUMPS	1,357	0.85	0.85
REACTORS	4,162	0.65	0.65
SPECIALLY PACKAGED EQUIPMENT	54,470	0.70	0.70
STEAM TURBINE DRIVERS	3,574	0.85	0.85
STORAGE TANKS	2,099	0.55	0.53
PRESSURE VESSELS	863	0.65	0.65
TOTAL BLE	135,356		
DIRECT INSTALLATION COSTS	121,114	0.66	0.62
INDIRECT COSTS	90,836	0.63	0.59
UNSCHEDULED EQUIPMENT, 20%	24,223	0.65	0.62
BATTERY LIMITS, INSTALLED	371,529	0.65	0.62
BLI CONTINGENCY, 25%	92,882	0.65	0.62
BATTERY LIMITS INVESTMENT	464,411	0.65	0.62
OFF-SITES, INSTALLED			
COOLING WATER	23,070	0.65	0.62
PROCESS WATER	2,563	0.65	0.62
BOILER FEEDWATER	7,431	0.65	0.62
PROCESS STEAM	53,470	0.55	0.53
FUEL GAS SYSTEM	1,858	0.55	0.53
INERT GAS & INSTRUMENT AIR	1,226	0.55	0.53
OFFSITES TANKAGE	20,500	0.55	0.53
UTILITIES & STORAGE	110,117	0.65	0.62
GENERAL SERVICE FACILITIES	7,431	0.65	0.62
WASTEWATER TREATMENT	55,729	0.65	0.62
TOTAL OFFSITES	173,277	0.65	0.62
OFFSITES CONTINGENCY 25%	43,319	0.65	0.62
OFFSITES CAPITAL INVESTMENT	216,596	0.65	0.62
TOTAL FIXED CAPITAL	681,007	0.65	0.62

PRODUCTION COST ESTIMATE

Combining the capital cost information with material balance requirements for feedstock and energy components allows us to develop and production cost estimate for the plant at the base production capacity of 160 kty, plus factored sensitivities for capacities of 80 kty and 320 kty.

Variable Cost of Adipic Acid Production via Cyclohexane

We have estimated the variable cost of adipic acid production in the table below. The primary raw material cost element in feedstock cyclohexane, and to a lesser extent nitric acid required for the 2nd-stage oxidation reaction. A significant by-product credit (\$117.2/mt) is recognized for producing AGS mixture and for producing mixed methyl esters from the monocarboxylic acids made in the process.

The adipic acid process is also highly energy intensive. A large amount of energy is used to recover the non-reacted cyclohexane, given the low (14%) conversion per pass in the air oxidation reactors. Large amounts of steam are also required to remove water from dilute adipic acid aqueous solutions during two stages of aqueous suspension crystallization. Conducting the crystallizations under vacuum conditions, and the subsequent distillations also under vacuum conditions, requires a large amount of compressor horsepower.

**Table 7.44
VARIABLE COST OF ADIPIC ACID PRODUCTION VIA CYCLOHEXANE**

	Unit Cost	Consumption	\$/mt
Raw Materials			
Cyclohexane	1,250 \$/mt	0.7003 mt/mt	875.4
Nitric Acid	250 \$/mt	0.3889 mt/mt	97.2
Caustic Soda (100 %)	300 \$/mt	0.005 mt/mt	1.5
Boric Acid	1,050 \$/mt	0.0044 mt/mt	4.6
Methanol	360 \$/mt	0.0345 mt/mt	12.4
Cobalt Naphthenate	4,200 \$/mt	0.00049 mt/mt	2.1
Ammonium Vanadate	12,700 \$/mt	0.00098 mt/mt	12.4
Copper Nitrate	2,500 \$/mt	0.00986 mt/mt	24.7
AGS By-Product	750 \$/mt	-0.0961 mt/mt	-72.1
Mixed Methyl Ester By-Product	500 \$/mt	-0.0902 mt/mt	-45.1
Net Raw Material Cost			913.1
Utilities			
Process Water	0.2803 \$/m ³	0.205 m ³ /mt	0.1
Cooling Water	0.0187 \$/m ³	45.6 m ³ /mt	0.9
Electricity	60 \$/mwh	0.409 mwh/mt	24.5
Process Steam	8.28 \$/mt	15.8 mt/mt	130.8
Fuel Gas	3.05 \$/MM-Btu	0.495 MM-Btu/mt	1.5
Glycol Refrigeration	0.18 \$/ton	18.3 ton/mt	3.3
Net Utility Cost			161.1
Variable Cost			1,074.2

Total Cost of Adipic Acid Production via Cyclohexane

We have estimated the total production cost of adipic acid production in the table below, for three production capacities: 80 kty, 160 kty (base case), and 320 kty. Given the large capital cost for building and operating a grassroots adipic acid plant (using the two-stage cyclohexane oxidation process), our analysis shows a reasonable cash cost margin for production, but not sufficient margin to provide acceptable return on investment for a grassroots adipic acid plant. This result might explain why there have been no grassroots adipic acid plants built in industrial countries for the last 10+ years.

Table 7.45
ADIPIC ACID TOTAL PRODUCTION COST ESTIMATE FROM CYCLOHEXANE

Capacity	MT/Y	80,000	160,000	320,000
Production	MT/Y	<u>80,000</u>	<u>160,000</u>	<u>320,000</u>
Investment (US\$ millions)				
Battery Limits		289.9	(0.68)	464.4
Off-Sites		<u>154.2</u>	(0.49)	<u>216.6</u>
Total Fixed Capital		444.1		681.0
				1,048.2
Production Cost (\$/MT)				
Net Raw Materials		913.1		913.1
Net Utilities		<u>161.1</u>		<u>161.1</u>
Variable Costs		1,074.2		1,074.2
Direct Costs				
Maintenance Materials		54.3		43.5
Operating Supplies		2.7		1.3
Operating Labor		26.9		13.5
Maintenance Labor		54.3		43.5
Control Laboratory		<u>5.4</u>		<u>2.7</u>
Total Direct Costs		1,217.9		1,178.8
				1,152.7
Plant Overhead		52.0		35.8
Taxes & Insurance		111.0		85.1
Depreciation		<u>555.1</u>		<u>425.6</u>
Plant Gate Cost		1,936.0		1,725.3
G&A, Sales, R&D		48.0		48.0
Total Production Cost				
At 100% Capacity		1,984.0		1,773.3
At 75% Capacity		2,287.3		2,006.4
At 50% Capacity		2,893.9		2,472.5
Product Value (Cost + 25%/Yr ROI Before Taxes)				
At 100% Capacity		3,426.6		2,875.7
At 75% Capacity		3,675.1		3,070.4
At 50% Capacity		4,281.6		3,536.5
Cash Cost		1,428.94		1,347.72
Cash Cost Profitability		171.06		252.28
Total Cost Profitability		-384.04		-173.34
				-19.56

Table 7.46
SECTION 7 APPENDIX: GLOBAL CYCLOHEXANE PRODUCERS

Producer	Location	qty
Chevron-Phillips	Port Arthur, TX, USA	481
Citgo	Corpus Christi, TX, USA	88
Conoco-Phillips	Sweeny, TX, USA	272
ExxonMobil	Beaumont, TX, USA	191
Flint Hills Resources	Port Arthur, TX, USA	265
Repsol-YPF	Buenos Aires, Argentina	95
Braskem	Camacari, Bahia, Brazil	72
Ecopetrol	Barrancabermeja, Colombia	38
Fina	Antwerp, Belgium	90
BASF	Ludwigshafen, Germany	130
BP	Gelsenkirchen, Germany	150
BP	Lingen, Germany	270
Holborn Europa	Hamburg, Germany	60
ExxonMobil	Rotterdam, Netherlands	280
Cepsa	Palos de la Frontera, Spain	185
Sabic	Wilton, UK	300
Grodno Azot	Grodno, Belarus	145
Zaklady Azotowe Pulawy	Pulawy, Poland	70
Zaklady Azotowe w Tarnowie	Tarnow, Poland	100
Kemerovskoe Azot	Kemerovo, Russia	155
Kuybyshevazot	Tol'yatti, Russia	170
Norsi	Nizhniy Novgorod, Russia	80
SJSC Shchokinoazot	Shchokino, Russia	51
Ufaorgsyntez	Ufa, Russia	50
OJSC Azot	Cherkassy, Ukraine	60
Obedanenie Azot	Severodonetsk, Ukraine	20
Rovno Azot	Rivne, Ukraine	21
Idemitsu Kosan	Chiba and Shunan City, Japan	240
Japan Energy	Aichi, Japan	220
Kanto Denka Kogyo	Mizushima, Japan	18
Nippon Steel Chemical	Hyogo, Japan	36
Ube Industries	Sakai City, Japan	100
DSM Nanjing	Nanjing, China	100
Fujian Dongxin	Fujian, China	75

Table 7.46 (Concluded)
SECTION 7 APPENDIX: GLOBAL CYCLOHEXANE PRODUCERS

Henan Shenma Group	Henan, China	19
Jiangsu Jurong	Jiangsu, China	5
Jiangsu Yangnong	Jiangsu, China	3
Juhua Group	Quzhou, Zhejiang, China	80
Neijiang Tianke	Sichuan, China	10
PetroChina Jinxi	Liaoning, China	7
PetroChina Liaoyang	Liaoyang, China	110
Shandong Fangming	Shandong, China	110
Shandong Haili	Shandong, China	120
Shandong Hongye	Shandong, China	160
Shijiazhuang Coking and Chemical	Hebei, China	25
Sinopec Baling	Hunan, China	85
Sinopec Nanjing	Nanjing, China	60
Taiyuan Chemical Industry Group	Shanxi, China	40
Xinjiang Dushanzi Tianli	Xinjiang, China	55
Fertilisers and Chemicals Travancore	Kerala, India	65
Reliance Industries	Gujarat, India	40
Gujarat State Fertilizers	Gujarat, India	110
Capro Corp	Ulsan, S Korea	190
SK Energy	Ulsan, S Korea	160
ExxonMobil	Singapore	227
CPDC	Miaoli Hsien, Taiwan	54
PTT Aromatics and Refining	Rayong, Thailand	200

8 VERDEZYNE FERMENTATION PROCESS FOR MAKING ADIPIC ACID FROM GLUCOSE

VERDEZYNE TECHNOLOGY

Based upon our understanding of the various technologies developed by Verdezyne for adipic acid production, we have selected for our design basis their use of candida yeast as the preferred enzyme and glucose as the feedstock of choice. The fact that BP and DSM have invested in Verdezyne suggests that a comprehensive due diligence assessment of the Verdezyne technology has already been completed to the satisfaction of the investors. Our review of Verdezyne's major patent claims (see table below) suggests that converting C₆ glucose to C₆ adipic acid is likely to result in higher feedstock selectivity and yield than using other Verdezyne technology that is based on vegetable oil, paraffin, and/or C₅ xylase as feedstock.

Table 8.1
VERDEZYNE MAJOR PATENTS

Verdezyne Relevant Patents and Applications

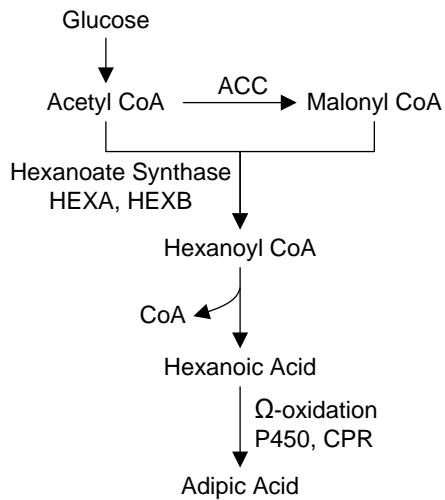
US	8227236	Engineered Microorganisms with Enhanced Fermentation Activity
US	8114974	Engineered Microorganisms with Enhanced Fermentation Activity
US	8093037	Engineered Microorganisms with Enhanced Fermentation Activity
US	20120077252	Combinatorial Methods for Optimizing Engineered Microorganism Function
US	20120184465	Combinatorial Methods for Optimizing Engineered Microorganism Function
US	20120184020	Engineered Microorganisms with Enhanced Fermentation Activity
US	20120156761	Biological Methods for Preparing Adipic Acid
US	20120077252	Biological Methods for Preparing Adipic Acid
US	20120077237	Biological Methods for Preparing Adipic Acid
US	20120021474	Biological Methods for Preparing Adipic Acid
US	20110229959	Biological Methods for Preparing Adipic Acid
US	20110224416	Engineered Microorganisms with Enhanced Fermentation Activity
US	20110165661	Engineered Microorganisms with Enhanced Fermentation Activity
US	20110165660	Engineered Microorganisms with Enhanced Fermentation Activity
EP	2451960	Engineered Microorganisms with Enhanced Fermentation Activity
EP	2449091	Biological Methods for Preparing Adipic Acid
WO	2011/006136	Engineered Microorganisms with Enhanced Fermentation Activity
WO	2011/011292	Combinatorial Methods for Optimizing Engineered Microorganism Function
WO	2011/006126	Engineered Microorganisms with Enhanced Fermentation Activity
WO	2011/003034	Biological Methods for Preparing Adipic Acid

BioAmber Relevant Patent Applications

US	20110266133	Processes for Producing Monoammonium Adipate from Fermentation Broths Containing Diammonium Adipate, Monoammonium Adipate and/or Adipic Acid, and Conversion of Monoammonium Adipate to Adipic Acid
US	20110269993	Processes for Producing Adipic Acid from Fermentation Broths Containing Diammonium Adipate

The most economically viable Verdezyne pathway from glucose to adipic acid appears to be hexanoate synthesis, in which hexanoic acid is the intermediate product (see pathway diagram below). Hexanoic acid is then preferentially oxidized to adipic acid.

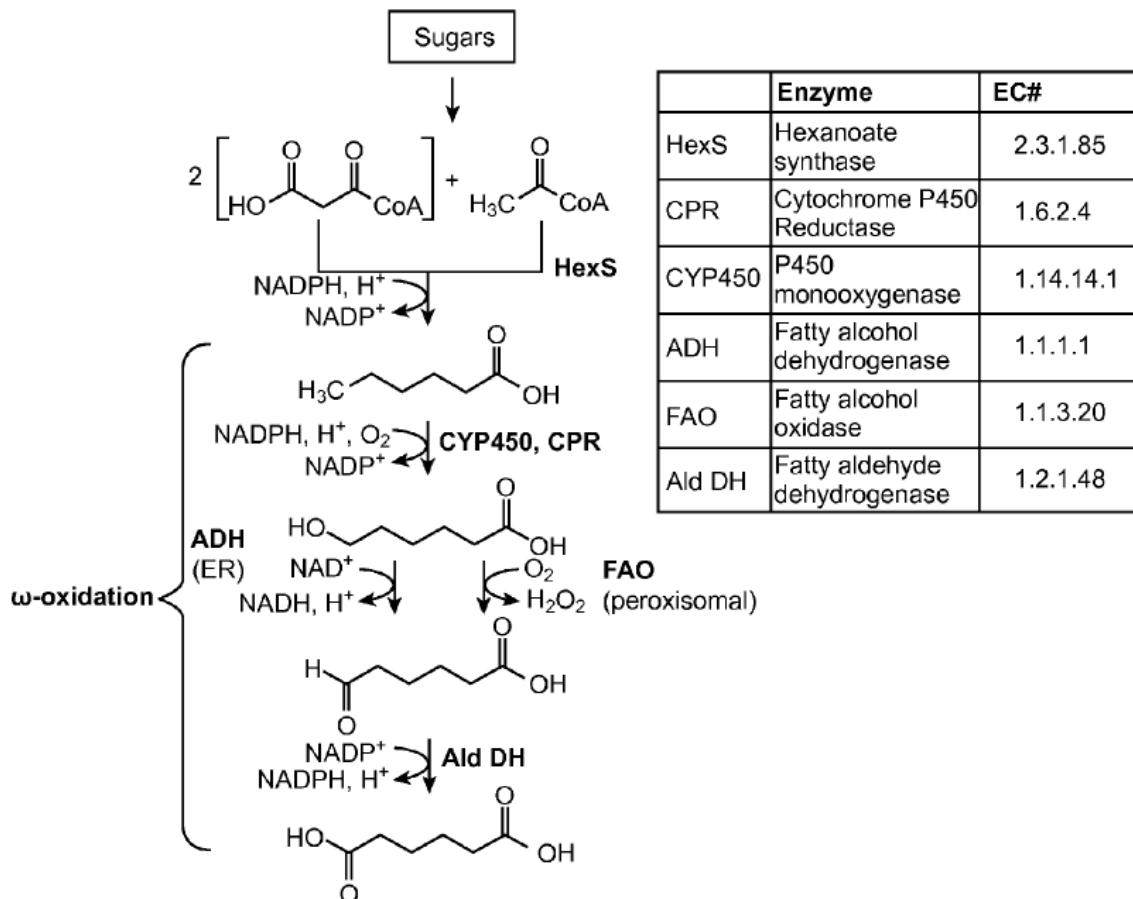
Figure 8.1
VERDEZYNE PATHWAY TO ADIPIC ACID FROM GLUCOSE (USPA 2012 0156761)



Verdezyne Metabolic Pathway (USPA 2012 0156761)

Genetically modified enzymes developed by Verdezyne develop chemical pathways to sustain growth and metabolism. Verdezyne's pathways inhibit cell growth, but promote the production of chemicals such as adipic acid. The three chemical reactions that Verdezyne's yeast promote are hexanoate synthesis, mono-oxygen activity, and finally mono-oxygen reduction. This produces a di-acid from glucose, where the acid groups are on the terminal carbon atoms. Verdezyne's *Candida* yeast encodes a polypeptide producing a polynucleotide with the desired chemical activity. The first chemical reaction (hexanoate synthesis) is provided by a heterologous polypeptide derived from an *Aspergillus parasiticus* fungus. The mono-oxygenate functionality is developed by encoding the yeast with an endogenous polynucleotide (CYP52A15, CYP52A16 or CYP52A19). The oxygen reduction activity is promoted by combining an endogenous polynucleotide with a heterologous promoter. The enzymes used to create the desired chemical reactions are shown in the figure below.

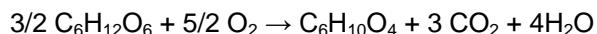
Figure 8.2
VERDEZYNE GLUCOSE PATHWAY TO ADIPIC ACID (USPA 2012 0156761)



PROCESS YIELD AND SELECTIVITY

To be economically viable, we believe that the scale-up to commercial production would require adipic acid productivity rates of at least 5 gm/l-hr of solution medium. To produce approximately 20 mt of adipic acid per hour (equivalent to 160 kty at 90% capacity utilization), the volume of aqueous fermentation solution required is 4 million liters (25,000 barrels). Patent examples indicate that when operated in batch mode, product concentration can approach 100 g/l after 70–90 hours of fermentation.

A viable fermentation route producing CO₂ and H₂O as respiration products, in addition to the desired adipic acid, would have the theoretical stoichiometry shown in the equation below.



The theoretical molar conversion of glucose to adipic acid would require 1.5 mols glucose to produce 1.0 mols adipic acid. When converted to a mass basis, the corresponding conversion would require 1.849 mt glucose to produce 1.0 mt adipic acid. If we add to this the consumption of glucose to sustain enzyme metabolism, and factor in 3–4% loss of produced adipic acid to by-product streams in the crystallization purification sequence, the molar conversion is likely to be

approximately 2.0, corresponding to a mass consumption of 2.466 mt glucose per mt of adipic acid product.

We believe that Verdezyne can or shortly will be able to develop an enzyme strain capable of 55–60% molar selectivity to adipic acid from glucose, with major by-products being monocarboxylic acids (15%), lower carbon number dicarboxylic acid (primarily C₄ succinic acid) at 15%, plus 10% carbon feedstock loss to combustion products (CO₂ + CO). A 60% molar selectivity is equivalent to 49% weight selectivity (0.48667) of product from glucose.

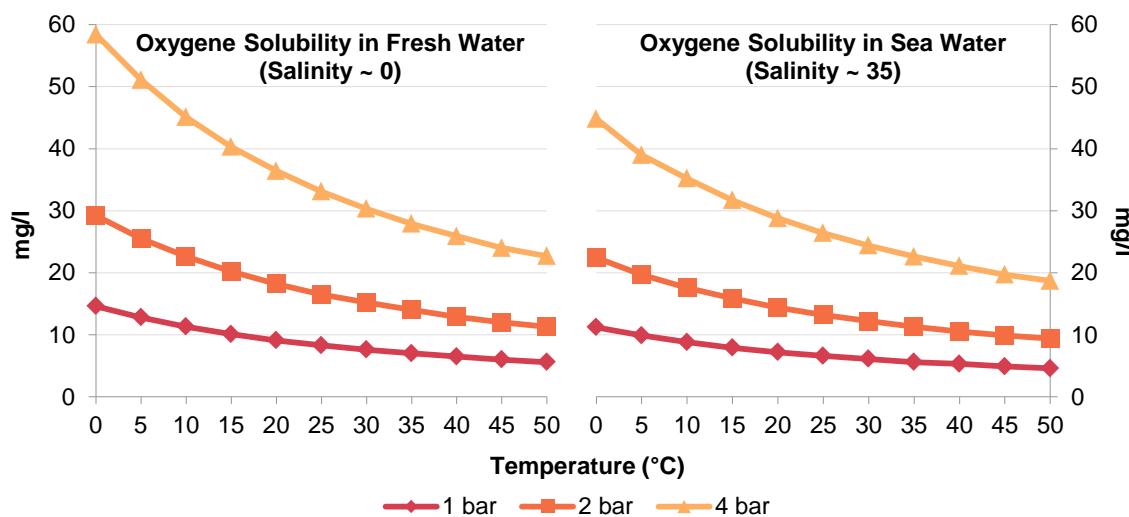
Titer is expected to be 5 gm adipic acid per liter of solution, above which the acidity of the solution would adversely affect the productivity of the enzymes. Verdezyne's patents claim yields as high as 80%, but we believe that these claims are associated with using paraffin (normal hexane) as feedstock. Conceptually, the removal of hydroxyl groups from glucose backbone carbon atoms is expected to result in the fracture of some carbon-carbon bonds, resulting in the formation of C₄ and C₅ acid by-products (both monocarboxylic and dicarboxylic), as well as the production of combustion products. Paraffins are derived from crude oil, as are the cyclohexane used in the conventional two-stage oxidation process for producing adipic acid. Consequently, the economic benefits of using a claimed low cost feedstock source (such as glucose) rather than a higher cost crude oil derivative feedstock (paraffin) sacrifices yield in order to obtain low net cost feedstock. The price margin between paraffin (in 2012 \$950/mt) and cyclohexane (in 2012 \$1,250/mt) does not provide a significant feedstock cost advantage over the conventional crude oil derived process.

COMMERCIAL DESIGN CONSIDERATIONS

Fermentation Conditions

Fermentation of Verdezyne genetically modified Candida yeast to crude adipic acid can be accomplished by creating a fermentation broth containing approximately 1% dissolved feedstock (glucose in this case), 10,000 ppm of enzyme yeast, and sufficient air to maintain oxygen in a saturated state (8 ppm at 25°C and one atmosphere), as shown in the figure below.

Figure 8.3
OXYGEN SATURATED IN FRESH AND SEA WATER



Source: The Engineering Toolbox.com

Growth promoters (ammonium phosphate monobasic, potassium phosphate monobasic, potassium phosphate dibasic, magnesium sulfate heptahydrate) need to be provided. Growth promoter properties are listed in the table below.

Table 8.2
FERMENTATION BROTH GROWTH PROMOTERS

	Ammonium Phosphate Monobasic	Potassium Phosphate Monobasic	Potassium Phosphate Dibasic	Magnesium Sulfate Heptahydrate
Formula	$\text{NH}_4\text{H}_2\text{PO}_4$	KH_2PO_4	K_2HPO_4	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
CAS Number	7722-76-1	7778-77-0	7758-11-4	10034-99-8
Form	White solid	Crystal or powder	Crystal solid	Solid
Solubility	in cold water	in cold water	in cold water	in cold water
Molecular weight	115	136	174	246
Boiling point (°C)	na	na	na	na
Melting point (°C)	190	253	465 decomposes	1,124
Specific gravity	1.803	2.34	2.3	2.66
Broth concentration (ppmw)	3,000	2,000	1,000	500

Requirement for Aqueous Crystallization

To satisfy commercial production specifications for nylon polymer-grade adipic acid product, we believe that a commercial design for an adipic acid plant capable of producing polymer-grade adipic acid will require purification via two-stage aqueous crystallization. The requirement for crystallization is driven by relatively close boiling points of by-products to adipic acid, and the reality of thermal product degradation if distillation is attempted at temperatures above 250°C. Adipic acid's boiling point at atmospheric pressure is 338°C. When processed through a single stage of aqueous crystallization (under reduced pressure), the formed adipic acid crystals tend to coat their outer surfaces with other acid components (both monocarboxylic and dicarboxylic acids), requiring that 1-stage crystalline adipic acid be redissolved in distilled water to dilute the by-product content such that a second stage of aqueous crystallization will produce an adipic acid crystal of acceptable purity.

By-Product Monetization

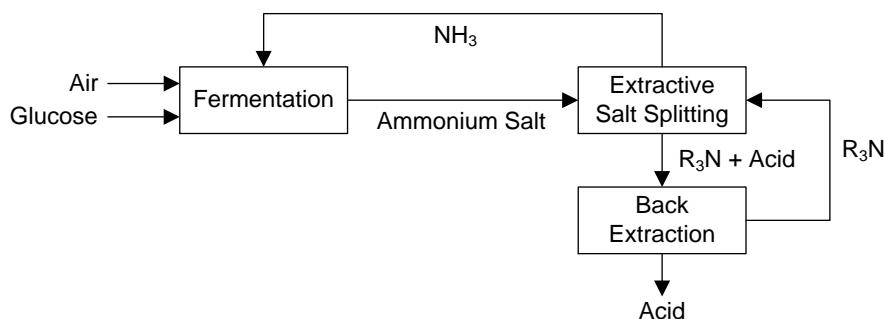
Given the relatively low (55–60% molar) selectivity of glucose to adipic acid, the commercial process developed should be able to recover purified by-products succinic acid and hexanoic acid in some manner that provides a reasonable by-product credit. We believe that the most convenient method for accomplishing this objective is to process the aqueous solutions of by-products through a methanol esterification process unit, which would allow easy separation and purification, and a ready market for the mixed methyl esters into the polyol polyurethanes business.

Direct Formation of Diammonium Adipate Salt

In order to avoid the adverse reaction of enzyme catalyst to high levels of acidity created by adipic acid production, our design provides for the reaction of adipic acid, as it is produced, with ammonia injected into the fermentation reactors to produce diammonium adipate salt, which can be easily concentrated for back salt splitting to recover adipic acid and recycle the ammonia. As documented by DSM (WO 2010/003728), conventional bacteria require maintaining a fermentation broth pH of 6–7, in order to avoid productivity degradation and acid toxicity toward the bacteria.

Cargill has patented an extractive salt splitting process for recovery of carboxylic acids from fermentation broth (WO 2002/090312, USP 7186856). By using an ammonium salt to control fermentation pH, no calcium sulfate is generated during the recovery process. Carboxylic acid (adipic acid) is recovered by heating an ammonium salt of the acid in the presence of an organic solvent. The resulting ammonia or amine by-products can be recycled to the fermentation reactor.

**Figure 8.4
CARGILL USP 7186856 PRODUCING AMMONIUM SALT OF PRODUCED ACID**



As adipic acid is produced by the enzyme catalyst, it will lower the pH of the fermentation broth, and become toxic to the enzyme. To avoid acidification of the fermentation broth, the conventional approach is to add a mild alkaline agent to the fermentation broth to maintain near neutral pH. The chemical used most often is calcium hydroxide. To recover adipic acid from the dicalcium adipate, dilute sulfuric acid is generally used, forming calcium sulfate as undesired by-product. The separation and removal of calcium sulfate (gypsum) increases the cost and complexity of the recovery step. Use of ammonia rather than a hydroxide eliminates the issues of sulfate separation and sulfate sludge disposition.

To separate the diammonium adipate from the fermentation broth, liquid-liquid extraction is used employing a liquid organic solvent that is both insoluble in water, and of a light viscosity comparable to water. When added to the fermentation broth, the mixture separates into two immiscible liquid phases that can be separated in a decanter, with the organic phase containing diammonium adipate at the top, and the aqueous fermentation broth below. An organic solvent family with these attributes are amines, specifically trimethylamine, triethylamine, and dibutylamine. Higher molecular weight amines (and more expensive to purchase) that also work well include trioctyl amine, tridecyl amine, and tridodecyl amine. Tertiary amines are preferred, due to their relatively high boiling point, relatively low viscosity, and high affinity for diammonium adipate salt. Alamine 336 (from Cognis/BASF, CAS 57176-40-6) specifically is mentioned in the trade literature as an extracting solvent.

Salt Splitting to Recover Adipic Acid from Diammonium Salt

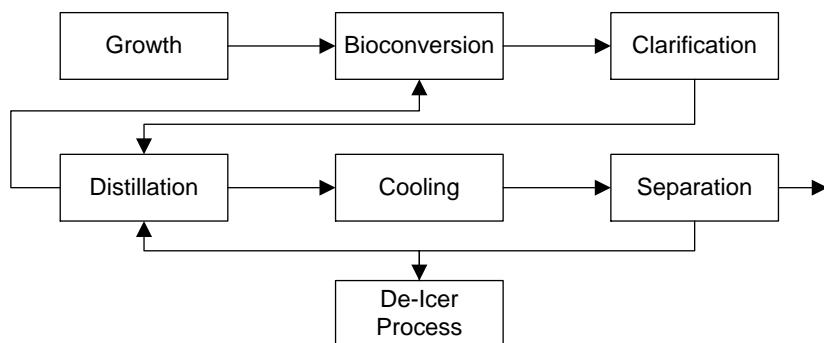
In theory, simple heating of diammonium salt in a water solution will split the salt back into components ammonia and adipic acid. Verdezyne appears to prefer to adopt the method presented by BioAmber in two US patent applications (USPA 2011/0266133, 2011/026993) published in 2011.

Heating the amine solvent containing diammonium salt will split the salt back into adipic acid plus ammonia. One desirable characteristic of trimethyl amines is their relatively high boiling point, such that the heating process does not cause them to vaporize. Suitable heating temperature ranges for salt splitting are 40–120°C at atmospheric pressure. Operating at subambient temperature is preferred because it allows the salt splitting to occur at lower design pressure.

The BioAmber approach is based on converting diammonium adipate salt (DAA) from the fermentation broth to monoammonium adipate (MAA) via heating and use of an anti-solvent, and then heating the MAA to produce crude adipic acid. The adipic acid is then purified by conventional crystallization. Although the BioAmber patent applications are not specific as to the crystallization methodology, it appears that the conventional (cyclohexane process) approach of aqueous suspension crystallization in an Oslo Crystallizer, followed by separation in a pusher centrifuge, will work adequately to produce polymer-grade purity adipic acid crystal product. An overall block flow diagram from the BioAmber patent applications appears in the figure below.

In the figure below, vessel #12 is a steam sterilizable fermenter used to produce the genetically modified yeast enzymes that will catalyze glucose to adipic acid using Verdezyne technology. Note that an organic solvent is *not* used to concentrate DAA and MAA from the fermentation broth. The enzyme catalyst is introduced into a fermentation vessel along with feedstock (glucose), air for aerobic fermentation, ammonia for acidic pH control, dilute sulfuric acid for alkaline pH control, and lower concentration components (vitamins, phosphates, salts) that promote cell growth and product formation. If the oxygen-rich gas is turned off and replaced by an oxygen deficient gas, adipic acid can be produced directly from the fermentation broth. Long-term fermentation to adipic acid and then its ammonium salt occurs in vessel #16, in which the genetically modified enzymes produced in vessel #12 are transferred via transfer line #14. The presence of ammonia or ammonium hydroxide will cause the formed adipic acid to convert to diammonium adipate (DAA), which remains in solution as a salt.

Figure 8.5
BIOAMBER ADA RECOVERY FROM DAA AND MAA (USPA 2011/0266133 A1)



Once fermentation is completed in batch reactors, transfer line #18 directs the mixture to clarification vessel #20 for removal of suspended solids such as cell debris, and other insoluble

solid products of fermentation. Alternative methods of clarification include gravity settlers, centrifuges, solid surface filters, and membrane filters such as microfiltration and ultrafiltration organic membranes. The BioAmber patent applications mention specifically Koch Membranes SelRO MPS-U20P membrane, which is made from polyethersulfone, and has a filtration cut-off capability of 25,000 Dalton molecular weight. Soluble materials can be removed by ion exchange resin columns or physical adsorbing solvents.

Once both the insoluble and soluble materials have been filtered out of the fermentation broth, the broth is distilled in unit #24 for the purpose of concentrating the diammonium adipate and monoammonium adipate by removing lower boiling water and ammonia as overhead distillate products. The formation of ammonia indicates that some of the DAA and MAA are splitting back to ammonia and adipic acid. The water and ammonia distillate is recycled to the fermentation vessel. The column bottoms product will be water rich, and include primarily DAA and MAA, plus smaller concentrations of ammonium acetate, ammonium formate, ammonium lactate, and related color bodies.

Given the low level of separation in this column, we believe an evaporator will perform acceptably at much lower capital and operating cost than a fractional distillation column.

The bottoms product from distillation is expected to contain at least 40% water by weight (per the BioAmber patent applications), in order to provide a boiling medium in the bottom of the column at modest temperature. Diammonium adipate boils at a high enough temperature to cause thermal degradation of the product. As a result, diluting the diammonium adipate in a 40% water solution substantially reduces the boiling point to an acceptable temperature in the bottom of the distillation column. The BioAmber patent applications prefer a distillation column bottoms temperature in the range of 110–140°C. Physical properties of diammonium adipate are listed in the table below.

Table 8.3
DIAMMONIUM ADIPATE PROPERTIES

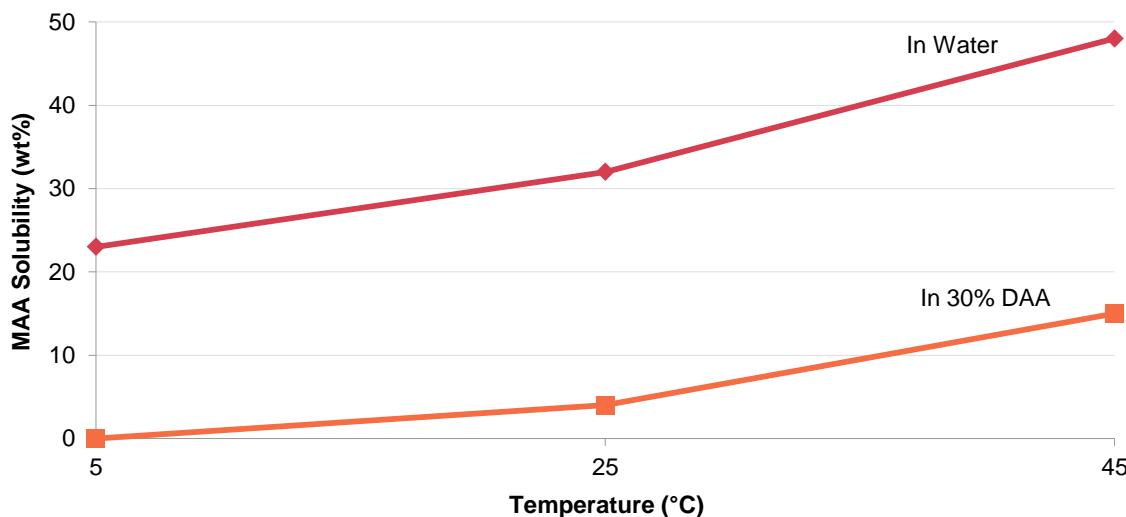
CAS Number	Formula	Molecular Weight	Boiling Point	Flash Point
3385-41-9	C ₆ H ₁₀ O ₄ ·2NH ₃	180	338.5°C at 760 mmHg	172.7°C

The BioAmber patent applications also introduce the use of adding an organic agent to the distillation column feedstock for the purpose of improving ammonia removal. Suggested organic solvents include DMSO, DMF, dimethyl sulfone, sulfolane, NMP and MEK. However, an organic solvent is not required, nor is it presented in the preferred process sequence.

Following distillation, the bottoms product is cooled in a heat exchanger (equipment #30) to approximately 15°C. This will require either a modest mechanical refrigeration unit (glycol or ammonia), or operation of the cooler under deep vacuum conditions using a process compressor and downstream condenser. Cooling causes the monoammonium adipate (MAA) to crystallize out of solution. The solubility of MAA is shown in the figure below as a function of temperature. As shown, the solubility of MAA is much lower in a 30% solution of DAA than it is in water.

Crystallization can be accomplished under conventional conditions that both evaporate water using a vacuum pump, and maintain a cold temperature for the purpose of minimizing the solubility of MAA in the solution. In a downstream centrifuge, the crystals can be separated from the solution, and the solution recycled to distillation or evaporation for the purpose of recovering more MAA. The BioAmber patent applications recommend the use of Nutsche or Rosenmond pressure filters. The temperature of the distillation or evaporation section will also promote the conversion of DAA to MAA.

Figure 8.6
MONOAMMONIUM ADIPATE SOLUBILITY (USPA 2011/0266133 A1)



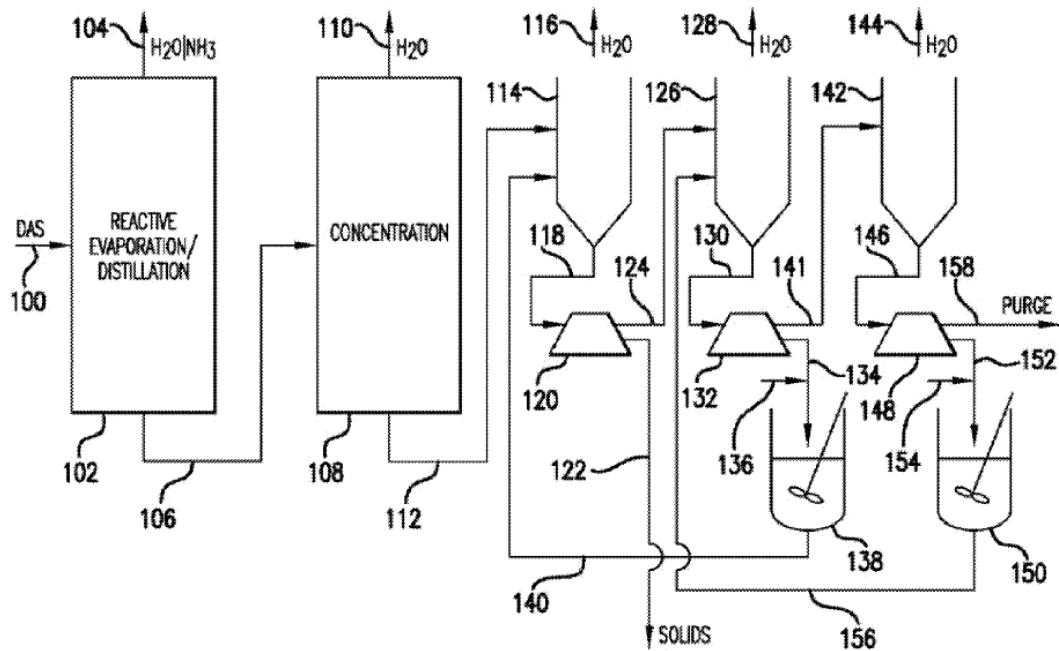
The BioAmber figure also shows the use of a de-icer (equipment #40) to treat the mother liquor from crystallization with potassium hydroxide for the purpose of releasing ammonia (from DAA and MAA) by converting the ammonium salts to potassium salts.

Solid MAA crystal product is then converted to adipic acid by dissolving MAA in water, and distilling the mixture. The heat of distillation will split the salt back into adipic acid plus ammonia. The distillate product from the column is ammonia (which readily dissolves in water) and water. Adipic acid and water are the bottoms product from the distillation column. The adipic acid can be purified from water via conventional suspension crystallization at 50°C.

Taking these production features into consideration, BioAmber proposes in the figure below its overall process for producing adipic acid from DAA and MAA. Fermentation broth is distilled following removal of both suspended and dissolved solids in equipment #102. The temperature of distillation (135°C at the bottom at 3.5 atmospheres pressure) causes the conversion of some DAA to MAA, releasing ammonia. Ammonia, which readily dissolves in water, exits the distillation column in the overhead distillate product in water. A typical bottoms composition is 80% water, almost 20% MAA, and the balance (1–3%) DAA. The pH of the bottoms stream ranges between 4.6 and 5.6.

Figure 8.7

BIOAMBER ADIPIC ACID PURIFICATION FROM DAA AND MAA (USPA 2011/0266133 A1)

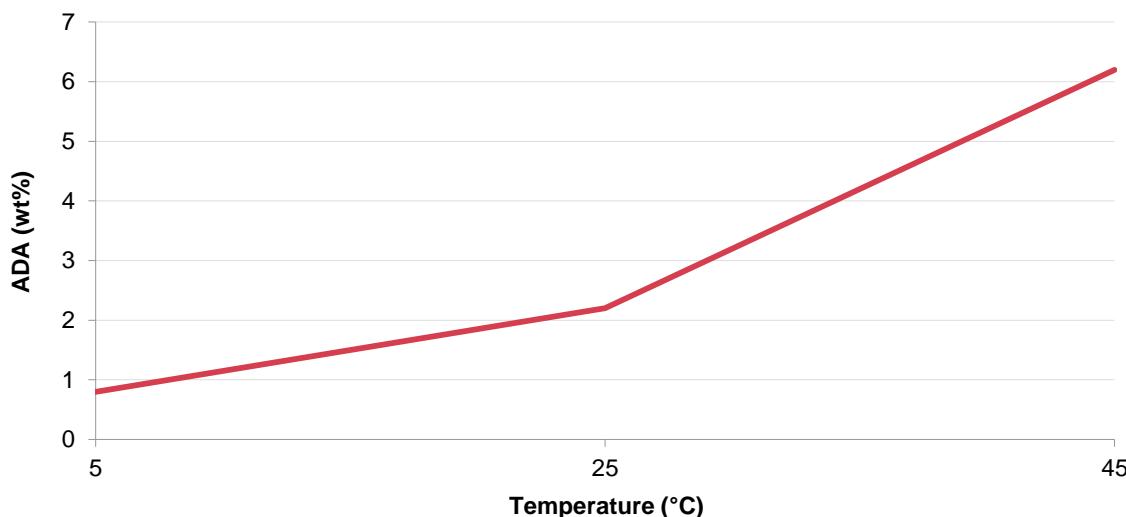


The bottoms product from distillation is sent to an evaporator (equipment #108) to remove additional quantities of water. Preferred evaporator operating conditions are 100°C and 1.1 bar. The evaporator produces a concentrated MAA stream that is 55% MAA in water.

The concentrated MAA stream is then sent to a 3-stage crystallizer (equipment 114, 126, and 142). Preferred operating conditions are 60°C in the first stage, 40°C in the second stage, and 20°C in the third stage. The crystal slurry bottoms stream from the first crystallizer is sent to a centrifuge (#120) for production of a solid MAA cake that is sent to drying for subsequent conversion to adipic acid. The second and third-stage centrifuges (#132 and #148) produce solid cakes that are redissolved in water (equipment #138 and #150), and recycled to the previous crystallizers.

A streamlined approach in the BioAmber patent applications involves distilling the fermentation broth at a much higher temperature (170–230°C) than previously documented (120°C). At the higher operating temperature in the distillation column, virtually all of the DAA decomposes to ADA, as does most of the MAA. Consequently, the downstream cooling and crystallization of the distillation bottoms produces substantially pure adipic acid crystals, which can be subsequently recrystallized to produce product specification adipic acid. This alternative eliminates the complications associated with producing crystallized solid MAA as an intermediate product stream, and then having to separately convert MAA to adipic acid. BioAmber USPA 2011/0269993 presents the following solubility curve showing the ease by which adipic acid can be purified from an aqueous solution by suspension crystallization, in which the combination of water removal (by evaporation) at modest temperature (<50°C) quickly reduces the solubility of adipic acid in an aqueous solution, producing an adipic acid crystal precipitate.

Figure 8.8
BIOAMBER SOLUBILITY CURVE FOR ADIPIC ACID IN WATER (USPA 2011/0269993)



DSM Alternative Approach to Salt Formation

DSM has patented (WO 2010/003728) an alternative approach to bio-based carboxylic acid production that does not require conversion of acid formed to salt for the purpose of avoiding pH problems. Adipic acid is specifically mentioned in the patent as suitable for the proposed process, and *Candida* yeast is specifically mentioned as a bio-organism capable of producing high rates of adipic acid at low pH values in the absence of salt forming agents (ammonia or a hydroxide). Differences between fermentation conditions for the DSM approach versus conventional approach are listed below.

- The DSM approach requires modifying the yeast by encoding a nucleotide sequence using phosphoenolpyruvate carboxykinase.
- Aerobic fermentation operates at an intentionally low level of oxygen addition, up to 90% below conventional oxygen addition rates.
- The acid is produced in fermentation broth at a pH of 4–5.

Water Solution Purification and Recycle

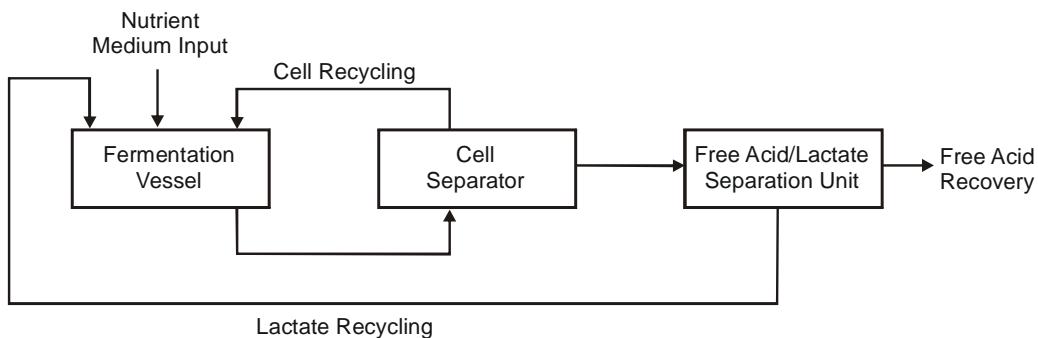
At the low concentration of adipic acid or its ammonium salts in the aqueous solution, a commercial method needs to also be developed to treat the wastewaters produced so that they can be recycled back to the front of the process as fresh solution. Given the environmental concerns over any process using genetically modified enzymes, we would expect that water pollution discharge criteria will be so stringent that recycling will be a lower cost approach than treating the wastewater with the intent to discharge back to the environment or to a public owned treatment works.

Enzyme Catalyst Recycle

Given our expectation of relatively high cost to produce the desired genetically modified enzyme catalyst, compared to low cost natural or ‘wild’ enzymes, the commercial design process needs to recover and recycle the enzymes from the process, rather than disposing of the enzyme

along with cell debris. This approach has been used in other IHS bio-processing designs for bio-lactic acid, which faces the same economic concerns. The recycling approach suggested is shown schematically in the figure below.

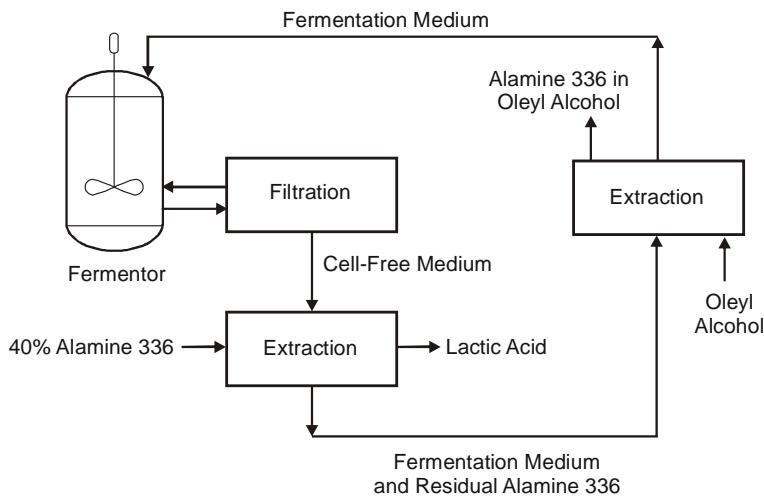
**Figure 8.9
ENZYME RECYCLING REQUIREMENT FOR BIO-LACTIC ACID**



Source: IHS Chemical PEP Report 259, Bio-Based C₃s

Another design issue is the requirement for a mechanism for separating useful enzyme catalyst (immobilization by encapsulation), so that it can be separated from cell debris and recycled, while the cell debris to be discarded is dried and incinerated. Other approaches for separating useful enzyme from undesirable fermentation products include filtration, membrane separation, desalting electro-dialysis, and liquid-liquid extraction using higher molecular amines (Alamine 336 is a favorite by Archer Daniels Midland). The extraction approach for lactic acid production is shown in the figure below.

**Figure 8.10
ENZYME RECOVERY VIA AMINE EXTRACTION**



Source: IHS Chemical PEP Report 259, Bio-Based C₃s

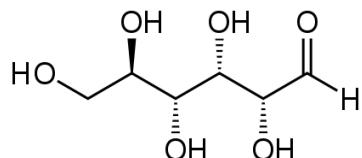
Continuous versus Batch Fermentation

Historically, fermentation has been practiced as a batch operation for producing alcoholic beverages, pharmaceuticals, and food components. These products are generally characterized as low volume and relatively high price. For industrial chemicals production, cost competitiveness dictates the migration to continuous processing for a variety of reasons. Continuous processing generally has lower capital and operating costs per unit of product made. Continuous processing also tends to have more uniform product characteristics, due to elimination of process variability between batches. The process dilemma associated with migrating from batch to continuous processing for fermentation is the very high required residence time, and the reality that some fermentations require 100% conversion per pass, with no feasible way to recycle intermediate products. It appears from the Verdezyne patent estate that their process can be adapted to operate on a continuous fashion, using 2–3 stages of CSTR reactors in series so that fresh and recycled enzyme can avoid being shocked by a fermentation broth operating at 100% conversion composition.

FEEDSTOCK GLUCOSE PROPERTIES

As discussed above, glucose was selected among the adipic acid feedstocks developed by Verdezyne because we believe that it combines low acquisition cost, easy processability in fermentation, and likely high selectivity. Glucose is a simple sugar with an aldehyde group (CHO) on a terminal carbon atom, and an alcohol group on the other terminal carbon atom. The internal carbon atoms each have a hydroxyl (-OH) group attached. At room temperature, glucose is a white crystalline powder solid that is odorless and colorless.

Figure 8.11
GLUCOSE CHEMICAL STRUCTURE



Principal physical and thermodynamic properties of glucose are presented in the table below.

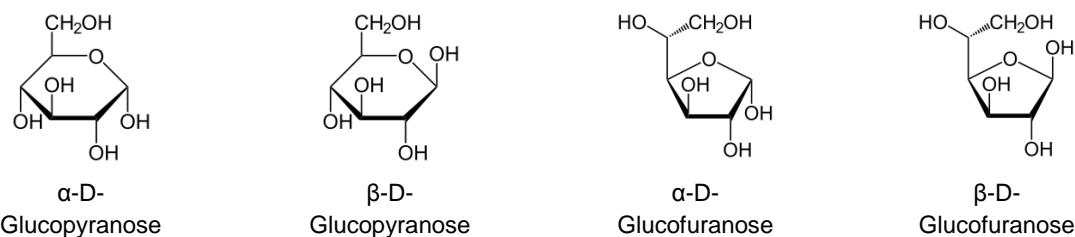
Table 8.4
GLUCOSE PROPERTIES

Formula	C ₆ H ₁₂ O ₆
CAS number	50-99-7
Physical form	Viscous liquid
Molecular weight	180
Density (liquid)	1.54 gm/cm ³
Boiling point (°C)	Degrades
Melting point (°C)	146
Solubility in water g/100 ml	91
Enthalpy of formation (kJ/mol)	-1,271
Standard enthalpy of combustion (kJ/mol)	-2,805
Standard molar entropy (kJ/mol)	209
Solvents	Water, acetic acid

Open and Cyclic Molecular Structure

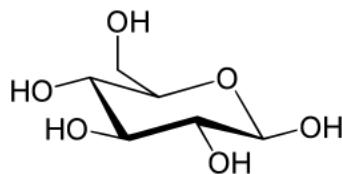
Although the glucose molecular structure is usually shown as an open molecule with a 6 carbon backbone, the aldehyde functional group on one terminal carbon atom causes the molecule to be more thermodynamically stable if it forms a ringed structure with 5 carbon atoms when in an aqueous solution. An oxygen atom is incorporated in the ring, and a methyl alcohol group is branched to one of the carbon ring atoms that is adjacent to the oxygen ring atom. Various isomers of the 5-atom ring configuration are shown in the figure below. When dissolved in water, glucose molecules dissolve primarily as ringed compounds.

Figure 8.12
RING STRUCTURE OF GLUCOSE



The existence of (OH-) hydroxyl groups on adjacent carbon atoms in the ring causes the entire ring to deform such that it is not on a flat plane. Instead, the three-dimensional form of the glucose has a high and low point above and below a flat plane, as shown in the figure below.

Figure 8.13
STRESSED THREE-DIMENSIONAL CONFIGURATION OF RINGED GLUCOSE STRUCTURE

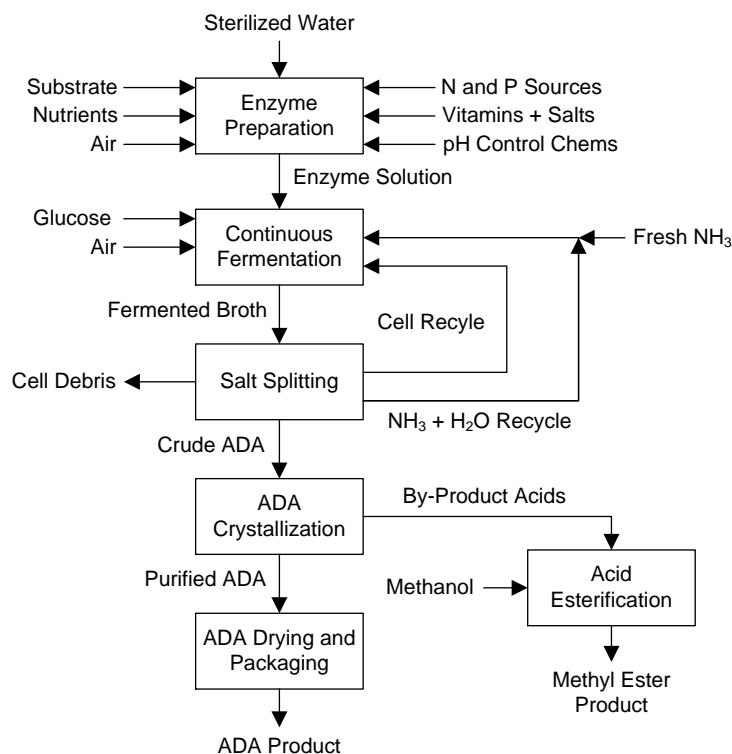


PROPOSED COMMERCIAL PROCESS SEQUENCE AND DESCRIPTION

Our commercial design approach for a 160 kty adipic acid plant employing fermentation via genetically modified Verdezyne enzymes is based on a combination of Verdezyne's patent estate plus BioAmber's technology for salt splitting (DAA + MAA) and adipic acid purification. To convert the adipic acid as it is produced to a corresponding salt, the Cargill approach using ammonia was chosen over alternative hydroxide precursors (sodium hydroxide, potassium hydroxide, calcium hydroxide).

The following is a block flow diagram representing our processing scheme.

Figure 8.14
VERDEZYNE FERMENTATION PROCESS BLOCK FLOW DIAGRAM



Our plant design consists of several processing sections:

- Section 100—Enzyme preparation
- Section 200—Product fermentation
- Section 300—Salt splitting of diammonium adipate and monoammonium adipate
- Section 400—Two-stage aqueous crystallization of adipic acid
- Section 500—Adipic acid crystal drying and product packaging
- Section 600—Methyl ester production

Key elements of the design basis are presented in the table below.

**Table 8.5
ADIPIC ACID VIA VERDEZYNE FERMENTATION DESIGN BASIS**

Verdezyne Design Basis	Value
Production capacity (kty)	160
Capacity utilization factor (%)	90
ADA recovery factor from crystallization (%)	95
Process approach	Continuous
Overall ADA mass selectivity from glucose (mt/mt)	0.4056
Fermenter productivity (grams/liter-hr)	5
Molar fermentation selectivity	
to ADA (%)	60
to monocarboxylic acids (%)	15
to dicarboxylic acids (%)	15
to combustion losses ($\text{CO}_2 + \text{CO}$)	10
Fermentation temperature (°C)	34–38
Fermentation pressure (psia)	14.7
Average fermentation residence time (hrs)	72
ADA crystallizer temperature (°C)	50 and 35
Salt splitting reactor temperature (°C)	240
Salt splitting reactor pressure (psia)	375
Salt splitting reactor residence time (minutes)	10
Fermenter salt concentration (gm/liter)	100

Section 100—Enzyme Preparation

Genetically modified *Candida* yeast using Verdezyne technology is prepared in commercial quantities at the plant site in two parallel (50% capacity each) stainless steel fermenters equipped with a vessel jacket capable of both warming (with low pressure steam) or cooling (with refrigerated glycol) the contents of each vessel to produce and maintain the active enzymes at desired temperatures at atmospheric pressure. Each fermenter is equipped with an overhead hung agitator designed to operate at low rpm (direct drive via VFD). Both fermenters can be

sterilized and are covered, such that the atmosphere above the liquid level is swept away by a low pressure vacuum blower that discharges to two parallel (50% capacity each) activated carbon beds for removal of particulate matter and organic species. The activated carbon beds are regenerated with low pressure saturated steam. Vapor discharge from the beds is vented to atmosphere.

Facilities are provided to inject both liquid and solid components into the fermenters. Listed below are the additives that are supplied to the enzyme preparation fermenters.

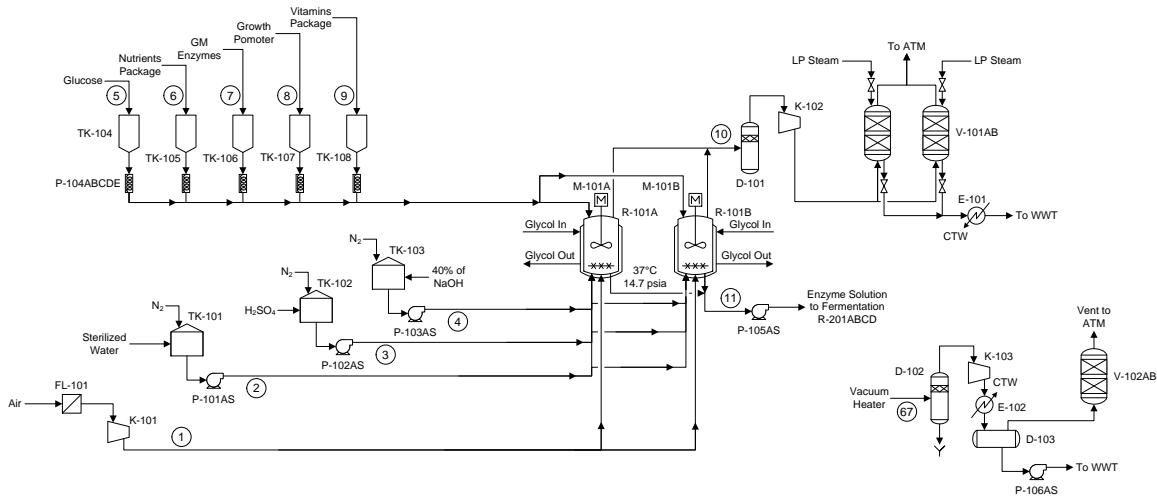
Table 8.6
MATERIALS SUPPLY TO ENZYME PREPARATION FERMENTERS

Sterilized water	Liquid
Sulfuric acid	Liquid for pH control
40% caustic solution	Liquid for pH control
Glucose	Solid transferred by rotary airlock screw
Air	Via blower and fermenter bottoms sparger
Nutrients package	Solid transferred by rotary airlock screw
Genetically modified Verdezyne enzymes	Solid transferred by rotary airlock screw
Growth promoter package	Solid transferred by rotary airlock screw
Vitamins package	Solid transferred by rotary airlock screw

The mixture of components is gently agitated in an aqueous solution for an average residence time in each preparation fermenter of 48 hours. Temperature control via the fermenter jacketing maintains the mixture at a temperature range of 32–38°C. The fermenters operate at atmospheric pressure. A low pressure air blower provides oxygen to the bottom of each preparation fermenter through a sparger manifold. Sterilized water is continuously fed to the preparation fermenters. Sulfuric acid (to address an alkaline pH condition) and 40% caustic soda (to address an acidic pH condition) are mixed with the incoming sterilized water, rather than being pumped directly into the preparation fermenters.

A screw conveyor injects into the preparation fermenters solid materials from storage silos, through a rotary airlock valve near the reactor nozzles. Silos with screw feeders are provided for glucose, a nutrients package specifically tailored by Verdezyne, Verdezyne's genetically modified *Candida* yeast enzymes, a growth promoter package of nitrogen and phosphorus containing salts, and a vitamins package. The figure below presents the process flow diagram for this section of the plant.

Figure 8.15
SECTION 100—ENZYME PREPARATION



Section 200—Product Fermentation

At the design product make of 5 grams per liter per hour, producing 160 kty of adipic acid at a 90% capacity utilization and 95% recovery level requires a fermentation volume of 4.06 million liters (25,800 barrels). Once adipic acid is produced in the production fermenters, we believe that a reasonable recovery across the balance of the process unit is 95%, with most of the balance of the adipic acid being lost in crystallization/centrifuges as spent liquor. Most of the adipic acid in the spent liquor (75%) will be recovered as mixed methyl ester by-product.

Verdezyne enzyme solution (1% active yeast concentration) from the preparation fermenters is pumped into four parallel, production fermenters operated in parallel. Each fermenter has a capacity of 8,000 barrels. Each fermenter is equipped with an overhead mixer (slow speed direct drive motor via VFD), and is jacketed to either modestly heat or cool the fermenter. Each fermenter is insulated and covered (air sealed). A low pressure blower pulls vapors from the top of the fermenters, and directs them through a two-bed pressure vessel designed to remove particulates (inert media) and organics (activated carbon media) from vapors generated in the fermenters. Discharge from the filters is directed to a vapor incinerator discharging to atmosphere. The filters are regenerated with low pressure saturated steam.

Ammonia gas is held in a day sphere within the process unit, and flows to the fermenters for the purpose of quickly converting formed adipic acid to preferentially diammonium adipate salt, which remains in solution. A small portion of the adipic acid is converted to monoammonium adipate salt. Also fed to the production fermenters is recycled distilled ammonia in water solution from the downstream evaporator.

Anaerobic fermentation is practiced. Enzyme solution is diluted to 10,000 ppm for feed to the production fermenters. The production fermenters have cone bottoms designed to concentrate formed solid cell debris. Fermentation broth is discharged from the bottom center of each fermenter, and directed to a coarse, precoat diatomaceous earth rotary filter for the purpose of removing gross solids produced in the fermenters.

Verdezyne enzyme is designed to pass through the coarse filter, but be removed by a downstream combination of microfilters followed by ultrafiltration filters. Removed enzymes from the MF-UF unit are recycled back to the production fermenters. Solid cell debris removed from

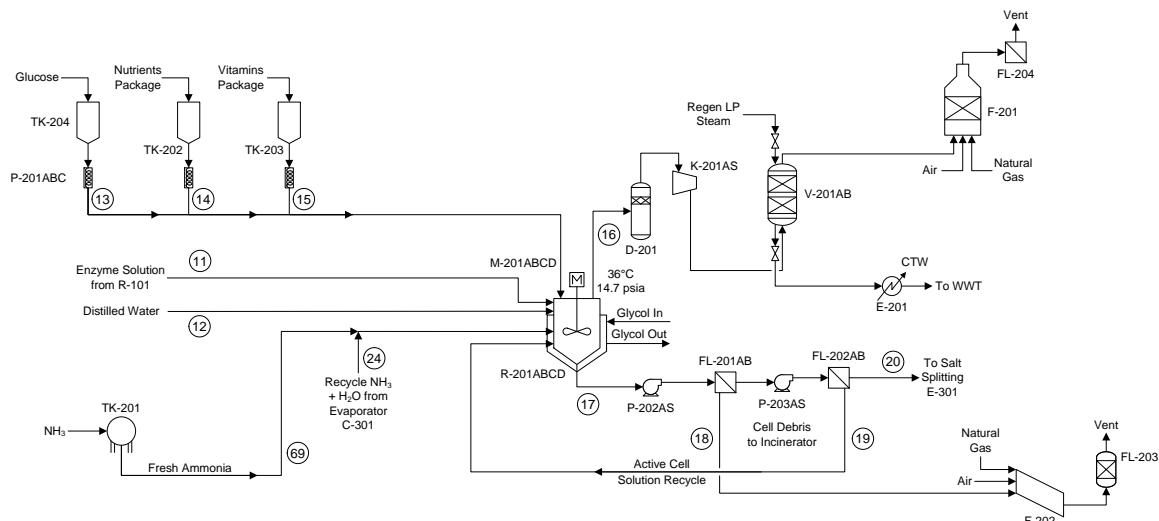
the precoat diatomaceous earth rotary filter is directed to a rotary, horizontal solids incinerator. Exhaust gas from the incinerator passes through a high temperature ceramic filter designed to remove particulates, and is discharged to atmosphere. A typical production broth concentration is presented in the table below.

**Table 8.7
TYPICAL PRODUCTION FERMENTER BROTH COMPOSITION (WO 2010/003728)**

Raw Material	Formula	Concentration (g/l)
Ammonium sulphate	$(\text{NH}_4)_2\text{SO}_4$	2.5
Potassium dihydrogen phosphate	KH_2PO_4	3.0
Magnesium sulphate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.5
Trace element solution		1.0
Vitamin solution		1.0

The figure below presents the process flow diagram for this section of the plant.

**Figure 8.16
SECTION 200—GLUCOSE FERMENTATION**



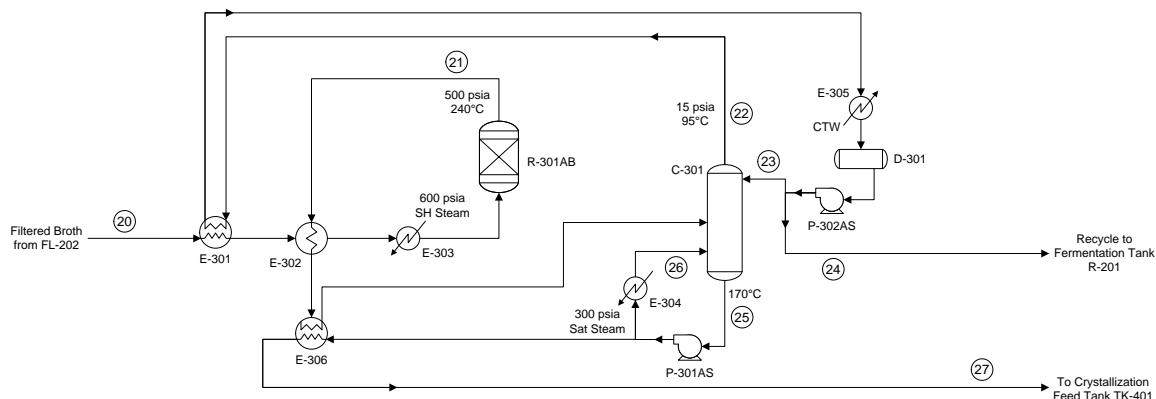
Section 300—Salt Splitting of Diammonium Adipate and Monoammonium Adipate

Filtered fermentation broth contains adipic acid salt in a concentration of approximately 100 grams per liter. This solution is heated to 240°C and 500 psia, and passes through a reactor designed to heat soak (for 10 minutes) the broth for the purpose of splitting the di- and monoammonium adipate salt back to a combination of free ammonia and adipic acid. Since ammonia is readily soluble in water, it will dissolve in the water phase. The flow stream is preheated with distillation bottoms product, passes through a feed/product exchanger, and then a trim heater bringing the temperature to 240°C. The discharge from the reactor is then directed to

a distillation column designed to take all of the ammonia and most of the water as an overhead product, leaving a bottoms product containing 70% water and approximately 30% adipic acid, with minor amounts of mono- and dicarboxylic acids. The bottoms product is then directed to the two-stage aqueous crystallization unit that is designed to produce on-spec, polymer-grade adipic acid.

The figure below presents the process flow diagram for this section of the plant.

Figure 8.17
SECTION 300—SALT SPLITTING AND CONCENTRATION



Section 400—Two-Stage Aqueous Crystallization of Adipic Acid

Distillation product is first directed to a day tank for storage of dilute adipic acid, prior to crystallization. The first step in crystallization is to process the feed stream through an Oslo crystallizer designed to effect suspension crystallization. The inventory of solution is maintained at 50°C by an external pump-around loop through an external cooler. Water in the solution is evaporated at this temperature by pulling vacuum (2 psia) through an overhead vacuum pump, with the compressed discharge from the vacuum pump directed to a condenser. The combination of water removal (to concentrate the adipic acid) plus cooling causes the adipic acid in solution to saturate and then precipitate as crystal slurry. Large diameter crystal particles drop to the bottom of the Oslo crystallizer, and are processed through a pusher centrifuge for additional water removal. Small diameter crystals are unable to precipitate, and circulate around the pump-around loop until they grow to sufficient diameter to fall to the bottom of the crystallizer for discharge. The slurry discharge contains approximately 20% adipic acid crystal by weight. It is processed through a pusher centrifuge to form a crystal cake with an adipic acid concentration of approximately 80% by weight. The liquid filtrate from the centrifuge is recycled to the crystallizer.

As the adipic acid crystals are being formed in the first crystallizer, they tend to be surrounded by other miscellaneous by-products acids (both monocarboxylic and dicarboxylic), and miscellaneous other oxygenated products from fermentation. These include low concentrations of aldehyde, ketones, and alcohols.

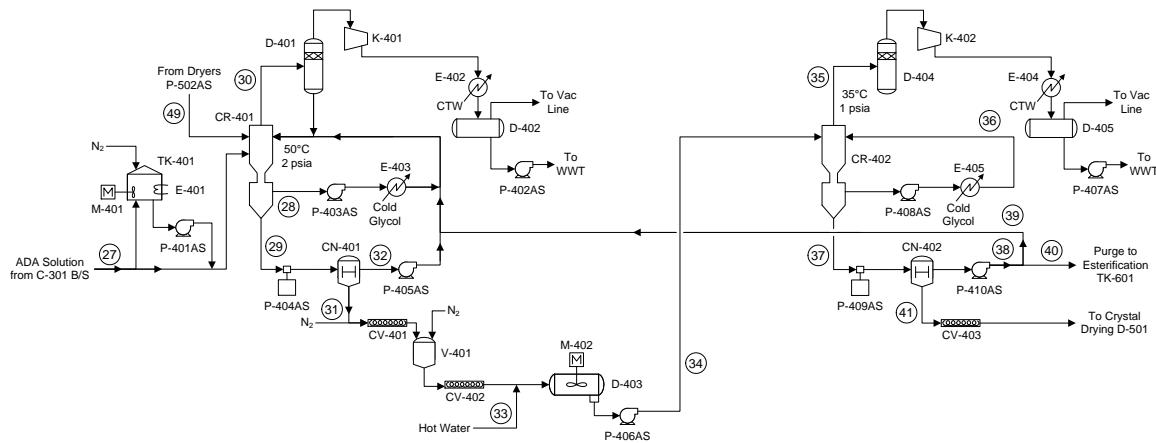
To remove these miscellaneous contaminants, the filter cake from the first pusher centrifuge is redissolved in distilled water and processed through a second stage of Oslo crystallizer that operates at 35°C and one psia pressure. The crystal slurry discharged from the 2nd-stage crystallizer is passed through a 2nd-stage pusher centrifuge to produce an 80% adipic acid filter

cake. The filter cake from the second-stage centrifuge is directed to the adipic acid drying and packaging unit.

The figure below presents the process flow diagram for this section of the plant.

Figure 8.18

SECTION 400—AQUEOUS CRYSTALLIZATION



Section 500—Adipic Acid Crystal Drying and Product Packaging

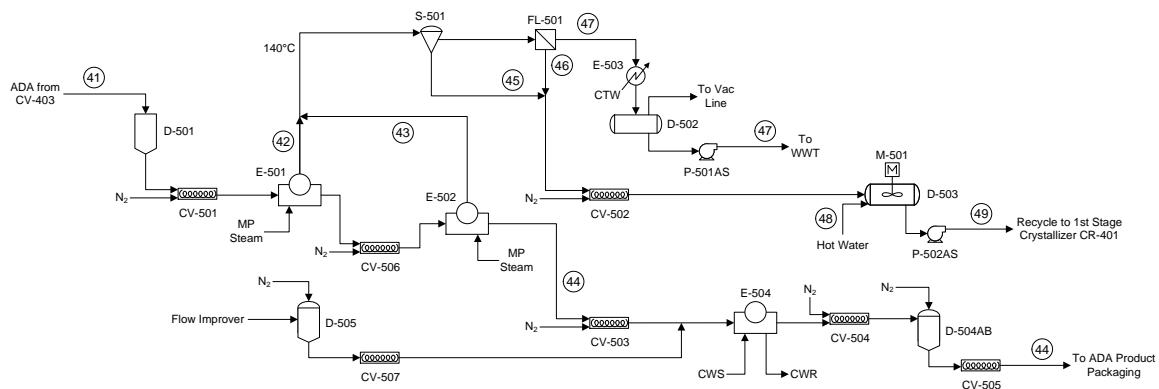
Filter cake from the 2nd-stage pusher centrifuge is conveyed to a two-stage rotary dryer designed to remove residual quantities of water from the adipic acid crystal product. A steam heated heat exchanger within the rotary dryer drives off water vapor, but also drives off small dust particles of adipic acid.

The overhead vapor stream from the rotary dryers, containing primarily water vapor but also small diameter particles of adipic acid, is passed through one stage of cyclone and then one stage of filter screen (0.05 micron) to remove adipic acid dust. The adipic acid dust particles are redissolved in hot distilled water, and recycled to the first stage of crystallization for recrystallization into acceptable diameter particles (>100 microns).

Hot and dry adipic acid crystals from the 2nd-stage rotary dryer are passed through a rotary cooler containing a heat exchanger using cooling water, and are reduced in temperature to near ambient temperature. The adipic acid is then conveyed to product silos for the purpose of packaging into both palletized bags (20 and 25 kg), iso containers (500 kg and one metric ton), and bulk shipping containers (20 and 40 metric ton parcels).

The figure below presents the process flow diagram for this section of the plant.

Figure 8.19
SECTION 500—ADA DRYING AND PACKAGING



Section 600—Methyl Ester Production

A slip stream of the filtrate from the second stage of aqueous pusher centrifuge is passed through a separate section of the plant that is designed to concentrate miscellaneous mono- and dicarboxylic acid by converting them to the corresponding methyl esters using a methanol reactor to effect esterification. The methyl ester product stream can then be used as feed to a polyester polyol unit (not within the scope of work) that can produce polyols for the polyurethane industry. If the slipstream were not taken, the miscellaneous oxygenated by-products formed by fermentation would concentrate in the aqueous stream to unacceptable concentrations, and eventually precipitate out with the adipic acid, producing off-spec adipic acid. An alternative disposition for the miscellaneous oxygenates could be to traditional wastewater treatment using conventional tertiary biological treatment, but the relatively high concentration of oxygenates justifies recovery to salable by-product.

The slipstream from the 2nd-stage pusher centrifuge filtrate is stored in a day tank within section 600 of the plant. This feed stream is combined with a recycle stream from purification and fed to the top of a reaction distillation column (R-601), which the liquid flow downward through several beds containing acidic ion exchange catalyst beds that enhance esterification.

Fresh methanol from tankage (TK-602) is vaporized and combined with recycle methanol vapor from the purification distillation column (C-601) and directed to the bottom of the reactive distillation column where the vapor flows upward, and reacts with liquid containing acid flowing downward through the ion exchange resin catalyst beds. Monomethyl and dimethyl ester is formed by the reaction of methanol with both monocarboxylic acid and dicarboxylic acid. Reaction conditions are 120°C and atmospheric pressure.

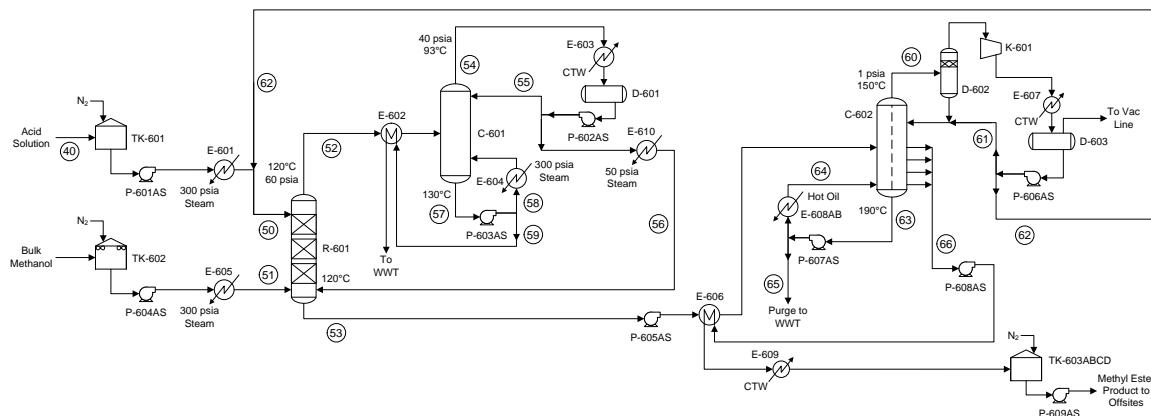
The overhead vapor leaving the top of the reaction distillation column (R-601) is a combination of excess methanol (to promote conversion of the acid) plus water formed by the esterification reaction. This vapor stream is directed to a distillation column (C-601) designed to separate and purify methanol from the water. Water is distilled as the overhead distillate product from C-601, while water is the bottoms product. The column is designed to operate at 40 psia with a top temperature of 95°C, and a bottoms temperature of 130°C. The water stream is sent to wastewater treatment while the overhead methanol vapor stream (prior to the condenser) is recycled back to the reactive distillation column.

The bottoms product stream from the reactive distillation column is crude methyl ester. It is directed to a fractional distillation column operating under vacuum conditions (1 psia). Column

internals are structured packing designed to provide divided wall distillation. The overhead distillate product from the column is unconverted acids, which are recycled to the top of the reactive distillation column. The bottoms product from the divided wall column is heavy tar and polymer from the reaction. Several sections of the column near the bottom have liquid collection trays in which nearly pure methyl ester can be removed from the right side of the divided wall. Different nozzle locations at various heights along the column provide a range of methyl ester grades based upon boiling point.

The figure below presents the process flow diagram for this section of the plant.

Figure 8.20
SECTION 600—BY-PRODUCT ESTERIFICATION SECTION



STREAM-BY-STREAM MATERIAL BALANCE

A stream-by-stream material balance was prepared for the overall process in units of metric tons per hour. Based upon the material balance, we summarized in the table below the major by-product and feedstock unit consumptions as a function of the amount of adipic acid product recovered from the process as salable adipic acid.

Table 8.8
UNIT FEEDSTOCK AND BY-PRODUCT CONSUMPTION
 (METRIC TONS PER METRIC TON OF ADIPIC ACID PRODUCT)

Material	mt/mt
By-product methyl ester production	0.66
Glucose feedstock consumption	2.466
Methanol consumption for esterification	0.15
Ammonia consumption for adipate salt production	0.0074

The stream-by-stream material balance is presented in the table below.

Table 8.9
STREAM-BY-STREAM MATERIAL BALANCE

	Label	Stream Number						
		1 Air	2 Sterile H ₂ O	3 Sulfuric Acid	4 Caustic Soda	5 Glucose	6 Nutrients Pkg	7 GM Enzymes
	From	Atm	BL	BL	BL	BL	BL	BL
	To	R-101AB	R-101AB	R-101AB	R-101AB	R-101AB	R-101AB	R-101AB
Temperature (°C)		50	25	25	25	25	25	25
Pressure (psia)		20	20	20	20	20	20	20
Total Flow (mt/hr)		0.15	28.47	0.01	0.01	4.78	0.00	1.09
Components	MW	BP (°C)						
Ammonia	17	-33						
Water	18	100		28.47		0.01		
Nitrogen	28	-210	0.12					
Carbon Monoxide	28	-191						
Oxygen	32	-218	0.03					
Methanol	32	65						
Sodium Hydroxide	40	na			0.00			
Carbon Dioxide	44	-79						
Sulfuric Acid	98	337			0.01			
Monocarboxylic Acids	116	205						
Succinic Acid	118	235						
Glutaric Acid	132	303						
Adipic Acid	146	338						
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Dodecanedioic Acid	230	250 (vac)						
Ammonium Salts	169	306						
Heavies, Tar & Polymer	na	na						
Verdezyne Enzymes	na	na					1.09	
Cell Debris	na	na						
Vitamins Pkg	na	na						
Nutrients Pkg	na	na				0.00		
Glucose	180	degrades				4.78		
Growth Promoter	na	na						

Table 8.9 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

Label	Stream Number						
	8	9	10	11	12	13	14
	Growth Promoter	Vitamins Pkg	Enzyme Prep Vent Gas	Enzyme Prep Solution	Distilled Water	Glucose	Nutrients Pkg
From	BL	BL	R-101AB	R-101AB	BL	BL	BL
To	R-101AB	R-101AB	K-102	R-201ABCD	R-201ABCD	R-201ABCD	R-201ABCD
Temperature (°C)	25	25	36	36	36	36	36
Pressure (psia)	20	20	15	50	50	15	15
Total Flow (mt/hr)	0.00	0.00	1.44	32.64	10.54	45.28	0.05
Components	MW	BP (°C)					
Ammonia	17	-33					
Water	18	100		1.28	27.20	10.54	
Nitrogen	28	-210		0.12			
Carbon Monoxide	28	-191		0.00			
Oxygen	32	-218		0.02			
Methanol	32	65					
Sodium Hydroxide	40	na					
Carbon Dioxide	44	-79		0.02			
Sulfuric Acid	98	337					
Monocarboxylic Acids	116	205					
Succinic Acid	118	235					
Glutaric Acid	132	303					
Adipic Acid	146	338					
Mixed Methyl Ester	166	85 (vac)					
Dimethyl Adipate	174	109 (vac)					
Dodecanedioic Acid	230	250 (vac)					
Ammonium Salts	169	306					
Heavies, Tar & Polymer	na	na					
Verdezyne Enzymes	na	na		5.44			
Cell Debris	na	na					
Vitamins Pkg	na	na	0.00				
Nutrients Pkg	na	na				0.05	
Glucose	180	degrades				45.28	
Growth Promoter	na	na	0.00				

Table 8.9 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

	Label	Stream Number						
		15	16	17	18	19	20	21
	Vitamins Pkg	Fermenter O/H Vapor	Fermenter Broth	Fermenter Cell Debris	Recycle Enzymes	Filtered Broth	R301 Product Stream	
From	BL	R-201	R-201	R-201	FL-202	FL-202	R-301	
To	R-201ABCD	K-201	FL-201	F-202	R-201	E-301	E-302	
Temperature (°C)	36	36	36	36	36	36	240	
Pressure (psia)	15	15	50	50	250	50	500	
Total Flow (mt/hr)	0.02	13.51	506.64	8.54	60.07	438.03	438.03	
Components	MW	BP (°C)						
Ammonia	17	-33		0.09	4.53	0.06	0.50	3.97
Water	18	100		0.36	450.43	6.08	49.75	394.60
Nitrogen	28	-210						
Carbon Monoxide	28	-191		0.78				
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79		12.28				
Sulfuric Acid	98	337						
Monocarboxylic Acids	116	205					5.08	
Succinic Acid	118	235					4.07	
Glutaric Acid	132	303					1.02	
Adipic Acid	146	338					21.35	
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Dodecanedioic Acid	230	250 (vac)						
Ammonium Salts	169	306		45.03	0.61	4.96	39.46	
Heavies, Tar & Polymer	na	na						
Verdezyne Enzymes	na	na		5.44	0.58	4.86		
Cell Debris	na	na		1.21	1.21			
Vitamins Pkg	na	na	0.02					
Nutrients Pkg	na	na						
Glucose	180	degrades						
Growth Promoter	na	na						

Table 8.9 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

		Stream Number						
		22	23	24	25	26	27	28
Label		C-301 O/H Stream	C-301 Reflux Stream	C-301 O/H Stream	C-301 B/S Distillate Product	C-301 Reboil	C-301 B/S Product	1st Stage Pump- Around
From		C-301	P-302	P-302	C-301	E-304	P-301	CR-401
To		E-305	C-301	R-201	P-301	C-301	TK-401	E-403
Temperature (°C)		95	95	95	170	170	170	50
Pressure (psia)		100	125	125	100	125	125	2
Total Flow (mt/hr)		772.93	397.72	375.21	502.54	439.72	62.82	161.39
Components	MW	BP (°C)						
Ammonia	17	-33	24.53	12.62	11.91			
Water	18	100	748.40	385.10	363.30	250.40	219.10	31.30
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
Sulfuric Acid	98	337						
Monocarboxylic Acids	116	205			40.64	35.56	5.08	44.77
Succinic Acid	118	235			32.54	28.47	4.07	33.96
Glutaric Acid	132	303			8.16	7.14	1.02	7.96
Adipic Acid	146	338			170.80	149.45	21.35	27.78
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Dodecanedioic Acid	230	250 (vac)						
Ammonium Salts	169	306						
Heavies, Tar & Polymer	na	na						
Verdezyne Enzymes	na	na						
Cell Debris	na	na						
Vitamins Pkg	na	na						
Nutrients Pkg	na	na						
Glucose	180	degrades						
Growth Promoter	na	na						

Table 8.9 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

		Stream Number						
		29	30	31	32	33	34	35
Label		1st Stage Crystal Slurry	1st Stage O/H Vapor	1st Stage Filter Cake	1st Stage Centrifuge Filtrate	Re- dissolving Hot Water	Re- dissolved ADA Solution	2nd Stage O/H Vapor
From		CR-401	CR-401	CN-401	CN-401	BL	D-403	CR-402
To		CN-401	D-401	V-401	CR-401	D-403	CR-402	K-402
Temperature (°C)		50	50	50	50	90	85	35
Pressure (psia)		2	2	15	50	50	50	1
Total Flow (mt/hr)		147.62	34.66	65.84	81.78	33.65	99.49	31.29
Components	MW	BP (°C)						
Ammonia	17	-33						
Water	18	100	42.65	34.66	10.89	31.76	33.65	44.54
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
Sulfuric Acid	98	337						
Monocarboxylic Acids	116	205	40.70		15.22	25.48		15.22
Succinic Acid	118	235	30.87		12.19	18.68		12.19
Glutaric Acid	132	303	7.24		3.06	4.18		3.06
Adipic Acid	146	338	26.16		24.48	1.68		24.48
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Dodecanedioic Acid	230	250 (vac)						
Ammonium Salts	169	306						
Heavies, Tar & Polymer	na	na						
Verdezyne Enzymes	na	na						
Cell Debris	na	na						
Vitamins Pkg	na	na						
Nutrients Pkg	na	na						
Glucose	180	degrades						
Growth Promoter	na	na						

Table 8.9 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

		Stream Number						
		36	37	38	39	40	41	42
Label		2nd Stage Pump Around	2nd Stage ADA Slurry	2nd Stage Centrifuge Filtrate	2nd Stage Centrifuge Filtrate Recycle	2nd Stage Centrifuge Filtrate	2nd Stage ADA Filter Purge	1st Stage Dryer O/H Cake
From	CR-402	CR-402	CN-402	CN-402	CN-402	CN-402	CN-402	E-501
To	E-405	CN-402	P-401	CR-401	TK-601	D-501	S-501	
Temperature (°C)	35	35	35	35	35	35	35	140
Pressure (psia)	1	1	1	1	1	1	1	15
Total Flow (mt/hr)	150.04	68.20	39.78	26.52	13.26	28.42	5.65	
Components	MW	BP (°C)						
Ammonia	17	-33						
Water	18	100	29.15	13.25	6.15	4.10	2.05	7.10
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
Sulfuric Acid	98	337						
Monocarboxylic Acids	116	205	33.48	15.22	15.21	10.14	5.07	0.01
Succinic Acid	118	235	26.82	12.19	12.18	8.12	4.06	0.01
Glutaric Acid	132	303	6.73	3.06	3.06	2.04	1.02	
Adipic Acid	146	338	53.86	24.48	3.18	2.12	1.06	21.30
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Dodecanedioic Acid	230	250 (vac)						
Ammonium Salts	169	306						
Heavies, Tar & Polymer	na	na						
Verdezyne Enzymes	na	na						
Cell Debris	na	na						
Vitamins Pkg	na	na						
Nutrients Pkg	na	na						
Glucose	180	degrades						
Growth Promoter	na	na						

Table 8.9 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

	Label	Stream Number						
		43	44	45	46	47	48	49
	2nd Stage Dryer O/H	Dry ADA Crystals	ADA Cyclone Dust	ADA Filter Dust	Dryer Condensate Dust	Dust Dissolving Water	ADA Dust Solution	
From	E-502	E-502	S-501	FL-501	D-502	BL	D-503	
To	S-501	E-504	D-503	D-503	WWT	D-503	CR-401	
Temperature (°C)	140	140	140	140	65	90	80	
Pressure (psia)	15	15	15	15	15	15	50	
Total Flow (mt/hr)	2.42	20.35	0.50	0.51	7.06	10.15	11.16	
Components	MW	BP (°C)						
Ammonia	17	-33						
Water	18	100	2.12	0.04		7.06	10.15	10.15
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
Sulfuric Acid	98	337						
Monocarboxylic Acids	116	205		0.01				
Succinic Acid	118	235		0.01				
Glutaric Acid	132	303						
Adipic Acid	146	338	0.30	20.29	0.50	0.51		1.01
Mixed Methyl Ester	166	85 (vac)						
Dimethyl Adipate	174	109 (vac)						
Dodecanedioic Acid	230	250 (vac)		0.00				
Ammonium Salts	169	306						
Heavies, Tar & Polymer	na	na						
Verdezyne Enzymes	na	na						
Cell Debris	na	na						
Vitamins Pkg	na	na						
Nutrients Pkg	na	na						
Glucose	180	degrades						
Growth Promoter	na	na						

Table 8.9 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

		Stream Number						
		50	51	52	53	54	55	56
Label		Ester Reactor Feed	Methanol Feed	Ester Rx O/H Stream	Ester Rx B/S Stream	Methanol Column O/H Vapor	Methanol Column Reflux	Methanol Column Distillate Product
From		E-601	TK-602	R-601	R-601	C-601	P-602	P-602
To		R-601	R-601	C-601	C-602	E-603	C-601	R-601
Temperature (°C)		120	120	120	120	93	93	93
Pressure (psia)		75	75	60	60	40	75	75
Total Flow (mt/hr)		14.29	3.05	3.60	15.29	7.65	6.12	1.53
Components	MW	BP (°C)						
Ammonia	17	-33						
Water	18	100	2.77		2.07	0.72	0.10	0.08
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65	0.31	3.05	1.53	0.31	7.55	6.04
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
Sulfuric Acid	98	337						
Monocarboxylic Acids	116	205	5.07			0.01		
Succinic Acid	118	235	4.06			0.03		
Glutaric Acid	132	303	1.02					
Adipic Acid	146	338	1.06					
Mixed Methyl Ester	166	85 (vac)				13.51		
Dimethyl Adipate	174	109 (vac)						
Dodecanedioic Acid	230	250 (vac)						
Ammonium Salts	169	306						
Heavies, Tar & Polymer	na	na			0.71			
Verdezyne Enzymes	na	na						
Cell Debris	na	na						
Vitamins Pkg	na	na						
Nutrients Pkg	na	na						
Glucose	180	degrades						
Growth Promoter	na	na						

Table 8.9 (Continued)
STREAM-BY-STREAM MATERIAL BALANCE

	Label	Stream Number						
		57	58	59	60	61	62	63
	Methanol Column B/S	Methanol Column Reboil	Methanol Column B/S Product	C-602 O/H Vapor	C-602 Reflux	C-602 O/H Distillate	C-602 B/S	
From	C-601	E-604	P-603	C-602	P-606	P-606	C-602	
To	P-603	C-601	WWT	K-601	C-602	R-601	P-607	
Temperature (°C)	130	130	130	150	150	150	190	
Pressure (psia)	40	75	75	1	60	60	1	
Total Flow (mt/hr)	6.42	4.35	2.07	2.26	1.23	1.03	2.13	
Components	MW	BP (°C)						
Ammonia	17	-33						
Water	18	100	6.36	4.31	2.05	1.58	0.86	0.72
Nitrogen	28	-210						
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65	0.06	0.04	0.02	0.68	0.37	0.31
Sodium Hydroxide	40	na						
Carbon Dioxide	44	-79						
Sulfuric Acid	98	337						
Monocarboxylic Acids	116	205						
Succinic Acid	118	235						
Glutaric Acid	132	303						
Adipic Acid	146	338						
Mixed Methyl Ester	166	85 (vac)						0.34
Dimethyl Adipate	174	109 (vac)						
Dodecanedioic Acid	230	250 (vac)						
Ammonium Salts	169	306						
Heavies, Tar & Polymer	na	na						1.79
Verdezyne Enzymes	na	na						
Cell Debris	na	na						
Vitamins Pkg	na	na						
Nutrients Pkg	na	na						
Glucose	180	degrades						
Growth Promoter	na	na						

Table 8.9 (Concluded)
STREAM-BY-STREAM MATERIAL BALANCE

	Label	Stream Number					
		64 C-602 Reboil	65 C-602 B/S Product	66 Ester Product	67 Vacuum Line Flow	68 Flow Improver	69 Fresh Ammonia Feed
From	E-608	C-602	C-602	Plant	BL	TK-201	
To	C-602	WWT	TK-603	D-201	D-505	R-201	
Temperature (°C)	190	190	175	100	25	25	
Pressure (psia)	15	15	50	8	15	25	
Total Flow (mt/hr)	1.29	0.84	13.42	6.38	0.00	0.15	
Components	MW	BP (°C)					
Ammonia	17	-33					0.15
Water	18	100					5.06
Nitrogen	28	-210					0.37
Carbon Monoxide	28	-191					
Oxygen	32	-218					0.10
Methanol	32	65					
Sodium Hydroxide	40	na					
Carbon Dioxide	44	-79					0.85
Sulfuric Acid	98	337					
Monocarboxylic Acids	116	205					0.01
Succinic Acid	118	235					0.03
Glutaric Acid	132	303					
Adipic Acid	146	338					
Mixed Methyl Ester	166	85 (vac)	0.21	0.13	13.38		
Dimethyl Adipate	174	109 (vac)					
Dodecanedioic Acid	230	250 (vac)					0.00
Ammonium Salts	169	306					
Heavies, Tar & Polymer	na	na	1.08	0.71			
Verdezyne Enzymes	na	na					
Cell Debris	na	na					
Vitamins Pkg	na	na					
Nutrients Pkg	na	na					
Glucose	180	degrades					
Growth Promoter	na	na					

EQUIPMENT LIST

Based upon the process flow diagram and corresponding material balance, we have prepared the following equipment list with duty specifications for tagged items.

Table 8.10
EQUIPMENT LIST WITH DUTY SPECIFICATIONS

Distillation Columns	# Installed	Materials of Construction	L x D (ft)	DesP (psia)	DesT (°F)	# of Trays	Internals Details		
C-301	Adipic Acid Concentrator	1	304SS	40 x 25	125	550	12	316L SS sieve trays	
C-601	Methanol Column	1	CS	128 x 3	50	300	54	316L SS sieve trays	
C-602	Ester Column	1	CS	84 x 4	Full Vac	450	32	Divided wall—struc packing	
Centrifuges	# Installed	Materials of Construction	L x D (ft)	DesP (psia)	DesT (°F)	Duty (BHP)	Screen Opening (mils)		
CN-401	1st-Stage Centrifuge	4	304SS	8 x 6	150	250	125	Pusher	0.1
CN-402	2nd-Stage Centrifuge	4	304SS	8 x 6	150	250	125	Pusher	0.1
Crystallizers	# Installed	Materials of Construction	L x D (ft)	DesP (psia)	DesT (°F)	Duty (MM-btu/hr)	Suspension or Draft Tube?	Surf Area (ft2)	
CR-401	1st-Stage Crystallizer	1	304SS	32 x 8	Full Vac	250	0	Suspension	0.0
CR-402	2nd-Stage Crystallizer	1	304SS	32 x 8	Full Vac	250	0	Suspension	0.0
Solids Conveyors	# Installed	Materials of Construction	L x W (ft)	DesP (psia)	DesT (°F)	Mass flow (lbs/hr)	Belt, Pneumatic, or Screw?	Motor HP	
CV-402	1st-Stage Conveyor-1	1	304SS	50 x 4	15	150	53,361	Closed Belt conveyor	45.0
CV-403	1st-Stage Conveyor-2	1	304SS	50 x 4	15	150	56,095	Closed Belt conveyor	45.0
CV-403	2nd-Stage Conveyor	1	304SS	50 x 4	15	150	56,095	Closed Belt conveyor	45.0
CV-501	Drying Feed Conveyor	1	304SS	50 x 4	15	150	56,095	Closed Belt conveyor	45.0
CV-502	Dust Conveyor	1	304SS	20 x 0.5	15	300	2,227	Closed Belt conveyor	5.0
CV-503	Hot ADA Conveyor	1	304SS	50 x 4	15	150	56,095	Closed Belt conveyor	45.0
CV-504	Cool ADA Conveyor	1	304SS	50 x 4	15	150	56,095	Closed Belt conveyor	45.0
CV-505	Final ADA Conveyor	1	304SS	50 x 4	15	150	56,095	Closed Belt conveyor	45.0
CV-506	Inter-Dryer Conveyor	1	304SS	50 x 4	15	150	56,095	Closed Belt conveyor	45.0
CV-507	Flow Improver Conveyor	1	304SS	50 x 0.5	15	150	0.5	Closed Belt conveyor	0.3
Drums	# Installed	Materials of Construction	Vol (ft3)	L x D (ft)	DesP (psia)	DesT (°F)	Orientation		
D-101	K-102 K/O Drum	1	304SS	25	8 x 2	50	200	Vertical-API510	
D-102	Vacuum Line K/O Drum	1	304SS	200	16 x 4	50	200	Vertical-API510	
D-103	Vacuum Line Receiver	1	304SS	510	18 x 6	50	200	Horizontal-API510	
D-201	K-201 K/O Drum	1	304SS	85	12 x 3	50	200	Vertical-API510	
D-301	C-301 Receiver	1	304SS	1,205	24 x 8	125	400	Horizontal-API510	
D-401	K-401 K/O Drum	1	304SS	25	8 x 2	Full Vac	150	Vertical-API 510	
D-402	E-402 Receiver	1	304SS	67.9	10 x 2.5	Full Vac	250	Horiz-API 510	
D-403	Re-dissolving Drum	1	304SS	893	26.3 x 6.5	50	250	Horiz-API 510	
D-404	K-402 K/O Drum	1	304SS	25	8 x 2	Full Vac	150	Vertical-API 510	
D-405	E-404 Receiver	1	304SS	67.9	10 x 2.5	Full Vac	250	Horiz-API 510	
D-501	Drying Feed Silo	1	304SS	8,140	55 x 14	15	250	Vertical	
D-502	E-501 Receiver	1	304SS	127	12 x 3	25	250	Horiz-API 510	
D-503	Dust Solution Drum	1	304SS	35.6	9 x 2	15	300	Horiz-API 510	
D-504AB	ADA Product Silos	2	304L SS	2,873	40 x 10	15	250	Vertical	
D-505	Flow Improver Silo	1	304L SS	3	4 x 1	25	150	Vertical	
D-601	E-603 Receiver	1	CS	101	12 x 3	75	250	Horiz-API 510	
D-602	K-601 K/O Drum	1	CS	25	8 x 1	Full Vac	400	Vert-API 510	
D-603	E-607 Receiver	1	CS	4.4	4 x 1	Full Vac	400	Horiz-API 510	

Table 8.10 (Continued)
EQUIPMENT LIST WITH DUTY SPECIFICATIONS

Heat Exchangers	# Installed	Materials of Construction Shell Side/Tube Side	Duty (MM-btu/hr)	Surf Area (ft ²)	DesP (psia) Tube/Shell	DesT (°F) Tube/Shell	HX Configuration
E-101	Regen Steam Condenser	1 CS/304SS	3.0	295	75/75	350/150	S&T—API660
E-102	Vacuum Line Condenser	1 CS/304SS	15.0	1,475	75/75	350/150	S&T—API660
E-201	Regen Steam Condenser	1 CS/304SS	3.0	295	75/75	350/150	S&T—API660
E-301	C-301 O/H Cooler	1 304SS/304SS	53.1	2,656	75/125	250/250	S&T—API660
E-302	R-301 Feed/Product HX	1 304SS/304SS	208.6	10,450	600/75	600/600	S&T—API660
E-303	R-301 Trim Heater	1 304SS/304SS	43.5	2,473	600/75	600/600	S&T—API660
E-304	C-301 Reboiler	1 304SS/304SS	717.4	28,696	325/50	600/600	S&T—API660
E-305AB	C-301 Condenser	2 304SS/304SS	825.6	33,023	75/75	250/250	S&T—API660
E-306	C-301 B/S Cooler	1 304SS/304SS	25.8	1,032	600/125	600/600	S&T—API660
E-401	TK-401 Tank Heater	1 304SS	5.0	50	50	400	Bayonet insertion heater
E-402	K-401 Condenser	1 304SS/304SS	8.5	934	15/75	250/150	S&T—API660
E-403	Recycle Cooler	1 304SS/304SS	6.24	1,570	75/75	250/150	S&T—API660
E-404	K-402 Condenser	1 304SS/304SS	8.5	934	15/75	250/150	S&T—API660
E-405	2nd-Stage Recycle Cooler	1 304SS/304SS	6.24	1,570	75/75	250/150	S&T—API660
E-501	1st-Stage ADA Dryer	1 304SS	21.98	2,250	350	450	Rotary Dryer (Atm P)
E-502	2nd-Stage ADA Dryer	1 304SS	9.42	975	350	450	Rotary Dryer (Atm P)
E-503	ADA Dust Condenser	1 304SS/304SS	15.65	1,520	15/75	250/150	S&T—API660
E-504	ADA Rotary Cooler	1 304SS	4.5	550	50	250	Rotary Dryer (Atm P)
E-601	Ester Feed Heater	1 304SS/304SS	0.9	102	150/350	400/600	S&T—API660
E-602	C-601 Feed Heater	1 304SS/304SS	0.6	87	50/150	300/500	S&T—API660
E-603	C-601 Condenser	1 304SS/304SS	4.1	420	75/75	250/150	S&T—API660
E-604AB	C-601 Reboiler	2 304SS/304SS	2.2	225	75/325	300/450	S&T—API660
E-605AB	Methanol Heater	2 CS/CS	0.3	24	150/325	300/600	S&T—API660
E-606	Crude Ester Heater	1 CS/CS	0.9	89	50/50	400/400	S&T—API660
E-607	C-602 Condenser	1 304SS/304SS	0.22	33	15/75	400/150	S&T—API660
E-608AB	C-602 Reboiler	2 CS/CS	0.22	32	75/75	400/600	S&T—API660
E-609	Ester Cooler	1 CS/CS	2.4	237	15/75	400/150	S&T—API660
E-610	Methanol Vaporizer	1 CS/CS	1.4	105	75/75	250/350	S&T—API660
Fired Heaters	# Installed	Materials of Construction	Duty (MM-btu/hr)	DesP (psia) Tubes	DesT (°F) Tubes	Fuel	
F-201	Off-Gas Incinerator	1 Monel tubes	15	50	2,500	CH4	Gas fired furnace
F-202	Solids Incinerator	1 Refractory lined CS	79	na	2,500	CH4	Rotary tilt gas fired
Filters	# Installed	Materials of Construction	Flow Rate (lbs/hr)	DesP (psia) Tubes	DesT (°F) Tubes	Opening Size (microns)	Details
FL-101	Pulsed Air Blower Filter	1 CS w glass fiber bags	330.8	Atm	Amb	0.05	Pulsed automatic bag filter
FL-201AB	Cell Debris Coarse Filters	2 304SS	558,500	Atm	Amb	0.25	Rotary precoat DE
FL-202AB	MF-UF Filters	2 304SS	965,860	250	na	0.01	12 inch Koch spiral wound
FL-203AB	Rotary Incinerator Ceramic Filter	2 304SS	23,150	30	2,500	0.05	Honeycomb ceramic matrix
FL-204	Gas Incineration Filter	1 304SS	29,800	30	2,500	0.05	Honeycomb ceramic matrix
FL-501	ADA Dust Pulse Filter	1 304SS	15,600	30	250	0.1	304SS screen

Table 8.10 (Continued)
EQUIPMENT LIST WITH DUTY SPECIFICATIONS

Compressors		# Installed	Fluid/Type Machine	BHP	SCFM	Pin (psia)	Pout (psia)	Material of Construction/ Design Details	
K-101	Enzyme Prep Air Blower	1	Air-centrifugal	3.6	76	15	20	304SS-1-stage API-617 centrifugal	
K-102	Induced Air Blower	1	Air-centrifugal	3.6	76	15	20	304SS-1-stage API-617 centrifugal	
K-103	Vacuum Line Compressor	1	Water Vapor-centrifugal	307	3,235	7.5	22.5	304SS-1-stage API-617 centrifugal	
K-201AB	Fermenter Induced Blowers	2	Air + CO ₂ -centrifugal	217	3,424	15	30	304SS-1-stage API-617 centrifugal	
K-401	1st-Stage Vacuum Pump	1	H ₂ O /centrif	22,029	46,359	1	15	304SS/3-stage Centrifugal	
K-402	2nd-Stage Vacuum Pump	1	H ₂ O /centrif	7,997	16,828	1	15	304SS/3-stage Centrifugal	
K-601	Ester Vacuum Pump	1	H ₂ O/screw	14	30	1	15	304SS/twin screw vac pump	
Mixers and Agitators		# Installed	Materials of Construction	BHP	DesT (°F)	Liquid	Viscosity (cs)	Mixer Type	
M-101AB	Growth Fermenter Mixers	2	304SS	35	150	Water	1	Top entering-propeller	
M-201ABCD	Fermenter Mixers	4	304SS	175	150	Water	1	Top entering-propeller	
M-401	TK-401 Mixer	1	304SS	25	400	H ₂ O+ADA	1	Side entering-propeller	
M-402	D-403 Mixer	1	304SS	12.5	250	H ₂ O+ADA	1	Top entering-propeller	
M-501	D-503 Mixer	1	304SS	2.5	250	H ₂ O+ADA	1	Top entering-propeller	
Pumps		# Installed	Materials of Construction	gpm x hd (ft)	Liquid	DesP (psia)	DesT (°F)	Type Pump	Pump HP
P-101AS	Distilled Water Pumps	2	304 SS	125 x 75	H ₂ O	50	150	ANSI—Horiz	4.8
P-102AS	Sulfuric acid pumps	2	316L SS	0.04 x 75	H ₂ SO ₄	50	150	Metering	0.002
P-103AS	Caustic Pumps	2	304 SS	0.04 x 75	40% NaOH	50	150	Metering	0.002
P-104ABCDE	Nutrients Screw Feeders	5	304 SS	11,000 lbs/hr	Dry powder	Atm	Amb	Solids screw feeder	1.2
P-105A/B	Enzyme Slurry Pumps	2	304 SS	145 x 75	H ₂ O	50	150	ANSI—Horiz	5.4
P-106A/B	Vacuum Line Condensate Pumps	2	304 SS	28 x 75	H ₂ O	50	300	ANSI—Horiz	1.0
P-201ABC	Nutrient Screw Feeders	3	304 SS	93,000 lbs/hr	Dry powder	Atm	Amb	Solids screw feeder	10.0
P-202AS	Fermenter Pumps	2	304 SS	2,234 x 75	H ₂ O	50	150	ANSI—Horiz	84.6
P-203AS	MF-UF HP Pumps	2	304 SS	2,234 x 460	H ₂ O	50	150	ANSI—Horiz	519.0
P-301AS	C-301 B/S Pumps	2	304 SS	2,216 x 75	H ₂ O	150	400	ANSI—Horiz	84.0
P-302AS	C-301 Reflux Pumps	2	304 SS	3,410 x 75	H ₂ O	150	300	ANSI—Horiz	129.5
P-401AS	Crystallization Feed Pumps	2	304 SS	277 x 75	H ₂ O	150	400	ANSI—Horiz	10.4
P-402AS	1st-Stage Wastewater Pumps	2	CI/CS	153 x 75	H ₂ O	50	200	ANSI—Horiz	5.8
P-403AS	1st-Stage Recycle Pumps	2	304 SS	711 x 75	H ₂ O	50	200	ANSI—Horiz	26.0
P-404AS	1st-Stage Slurry Pumps	2	304 SS	651 x 75	H ₂ O	50	200	Moyno	24.6
P-405AS	1st-Stage Filtrate Pumps	304 SS	361 x 75	H ₂ O	50	200	API 610—Horiz	13.6	
P-406AS	ADA Re-dissolved Solution Pumps	2	304 SS	439 x 75	H ₂ O	50	300	ANSI—Horiz	16.6
P-407AS	2nd-Stage Wastewater Pumps	2	CI/CS	138 x 75	H ₂ O	50	300	ANSI—Horiz	5.2
P-408AS	2nd-Stage Recycle Pumps	2	304 SS	662 x 75	H ₂ O	50	200	API 610—Horiz	25.0
P-409AS	2nd-Stage Slurry Pumps	2	304 SS	301 x 75	H ₂ O	50	200	Moyno	11.4
P-410AS	2nd-Stage Filtrate Pumps	2	304 SS	175 x 75	H ₂ O	50	200	API 610—Horiz	6.6
P-501AS	Drying Wastewater Pumps	2	CI/CS	31 x 75	H ₂ O	50	300	ANSI—Horiz	1.2
P-502AS	Dust Solution Pumps	2	304 SS	49 x 75	H ₂ O	50	200	API 610—Horiz	1.8
P-601AS	Ester Feed Pumps	2	304 SS	58 x 75	Ester	50	200	API 610—Horiz	2.2
P-602AS	C-601 Reflux Pumps	2	CS	38 x 75	Methanol	75	250	API 610—Horiz	1.4
P-603AS	C-601 B/S Pumps	2	304SS	28 x 75	Water	75	325	API 610—Horiz	1.0
P-604AS	Methanol Feed Pumps	2	CS	13.5 x 75	Methanol	75	150	Diaphragm	0.6
P-605AS	Crude Ester Pumps	2	304SS	67.4 x 75	Ester	75	500	API 610—Horiz	2.4
P-606AS	C-602 Reflux Pumps	2	304 SS	10 x 75	H ₂ O	75	300	Diaphragm	0.4
P-607AS	C-602 B/S Pumps	2	CI/CS	9.4 x 75	Ester	75	400	Diaphragm	0.4
P-608AS	Ester Pumps	2	CI/CS	9.4 x 75	Ester	75	400	Diaphragm	0.4
P-609AS	TK-603 Pumps	2	CI/CS	59.2 x 75	Ester	75	400	API 610—Horiz	2.2

Table 8.10 (Concluded)
EQUIPMENT LIST WITH DUTY SPECIFICATIONS

Reactors		# Installed	Materials of Construction	Vol (ft3)	L x D (ft)	DesP (psia)	DesT (°F)	Internals	
R-101AB	Enzyme Growth Fermenters	2	304 SS	41,076	57.2 x 16	15	150	Cooling/Warming jacket	
R-201ABCD	Production Fermenters	4	304 SS	319,158	50 x 90	15	150	Cooling/Warming jacket	
R-301AB	Salt Splitting Reactors	2	304 SS	16,278	36 x 24	550	500	Fixed cat bed-insulated	
R-601	Ester Reactor	1	CS	450	40 x 4	75	250	8 RX zones, w 6 trays above and below beds	
Specially Packaged Equipment		# Installed	Duty						
S-101	Process Flare System	1	50 MM Btu/hr each	250 ft x 16 inch					
S-103	Process Computer Control System	1	1,200 loops Honeywell Experion						
S-105	N2 PSA System	1	5 MM-scfh at 99% N2						
S-106	Packaged Glycol Refrigeration System	1	15 MM Btu/hr at 0°C						
S-501	ADA Drying Cyclone	1	4.5L x 3D						
S-108	ADA & AGS Computerized Modular Packaging System	1	25 mt/day, 20 & 25 kg bagging on 1 mt strapped & wrapped pallets	500 kg & 1 mt iso containers, 20 & 40 mt bulk containers blown					
S-109	Dowtherm Hot Oil System	1	10 MM Btu/hr at 325°C						
Steam Turbine Drivers		# Installed	Mechanical or Electrical?	BHP	KW	Inlet Steam (Pres/Temp)	Outlet Steam (Pres/Temp)	Steam Turbine Details	
ST-401	K-401 Driver	1	Mechanical	22,000	16,500	1,200/800	50/375	Horiz Split-Centrif	
ST-402	K-402 Driver	1	Mechanical	8,000	6,000	1,200/800	50/375	Horiz Split-Centrif	
Storage Tanks		# Installed	Materials of Construction	Vol (ft3)	L x D (ft)	DesP (psia)	DesT (°F) (API?)	Type Tank w Details (API?)	
TK-101	Distilled Water Tank	1	304 SS	12,000	25 x 25	15	150	Heat trace & insulate	
TK-102	Sulfuric Acid Tank	1	304 SS	16.6	4.4 x 2.2	15	150	Heat trace & insulate	
TK-103	40% Caustic Tank	1	304 SS	16.6	4.4 x 2.2	15	150	Heat trace & insulate	
TK-104	Glucose Silo	1	CS	4,015	70 x 8.6	15	150	Epoxy internal lining	
TK-105	Nutrients Silo	1	CS	6.3	8 x 1	15	150	Epoxy internal lining	
TK-106	Enzymes Silo	1	CS	916	42 x 5.2	15	150	Epoxy internal lining	
TK-107	Growth Promoter Silo	1	CS	6.3	8 x 1	15	150	Epoxy internal lining	
TK-108	Vitamins Silo	1	CS	6.3	8 x 1	15	150	Epoxy internal lining	
TK-201	Ammonia Sphere	1	304 SS	1,485	8 ft radius	300	150	ANSI K61.1-Insulate	
TK-202	Nutrients Silo	1	CS	42	16 x 2	15	150	Epoxy internal lining	
TK-203	Vitamins Silo	1	CS	16.8	12 x 2	15	150	Epoxy internal lining	
TK-204AB	Glucose Silo	2	CS	17,741	70 x 17	15	150	Epoxy internal lining	
TK-401	Crystallization Feed Tank	1	CS	17,590	18 x 36	15	250	API 650	
TK-601	Ester Feed Tank	1	CS	3,713	10.5 x 21	15	150	API 650	
TK-602	Methanol Feed Tank	1	CS	2,562	9 x 18	15	150	Floating Roof-API650	
TK-603ABCD	Ester Product Tanks	4	CS	2,818	10 x 20	15	150	API 650	
Pressure Vessels (API 510-ASME BPVC)		# Installed	Materials of Construction	Vol (ft3)	L x D (ft)	Orientation	DesP (psia)	DesT (°F)	
V-101AB	Air Filter Beds	2	CS-epoxy lined	707	25 x 6	vertical	30	150	
V-102AB	Vacuum Line Filters	2	CS-epoxy lined	3,390	30 x 12	vertical	30	250	
V-201AB	Fermenter Off-Gas Filters	2	CS-epoxy lined	707	25 x 6	vertical	30	150	
V-401	1st-Stage Filter Cake Silo	1	CS	18,435	114 x 14	vertical	30	150	

ITEMIZED CAPITAL COST ESTIMATE

We prepared an itemized capital cost estimate for the equipment on the tagged equipment list, using the duty specifications and the PEP Cost index of 795, and location factor of 1.00 (US Gulf Coast). The details are provided in the table below.

Table 8.11
ITEMIZED CAPITAL COST INDEX
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Distillation Columns					
C-301	Adipic Acid Concentrator	1,243.4	1,243.4	890.8	890.8
C-601	Methanol Column	217.3	217.3	362.3	362.3
C-602	Ester Column	122.0	122.0	330.7	330.7
Centrifuges					
CN-401	1st-Stage Centrifuge	505.6	2,022.4	95.5	382.0
CN-402	2nd-Stage Centrifuge	505.6	2,022.4	95.5	382.0
Crystallizers					
CR-401	1st-Stage Crystallizer	3,128.0	3,128.0	414.0	414.0
CR-402	2nd-Stage Crystallizer	3,128.0	3,128.0	414.0	414.0
Solids Conveyors					
CV-402	1st-Stage Conveyor-1	125.0	125.0	185.0	185.0
CV-403	1st-Stage Conveyor-2	125.0	125.0	185.0	185.0
CV-403	2nd-Stage Conveyor	125.0	125.0	185.0	185.0
CV-501	Drying Feed Conveyor	125.0	125.0	185.0	185.0
CV-502	Dust Conveyor	25.5	25.5	36.2	36.2
CV-503	Hot ADA Conveyor	125.0	125.0	185.0	185.0
CV-504	Cool ADA Conveyor	125.0	125.0	185.0	185.0
CV-505	Final ADA Conveyor	125.0	125.0	185.0	185.0
CV-506	Inter-Dryer Conveyor	125.0	125.0	185.0	185.0
CV-507	Flow Improver Conveyor	25.5	25.5	36.2	36.2
Drums					
D-101	K-102 K/O Drum	17.8	17.8	33.8	33.8
D-102	Vacuum Line K/O Drum	30.8	30.8	34.7	34.7
D-103	Vacuum Line Receiver	50.6	50.6	45.8	15.8
D-201	K-201 K/O Drum	23.9	23.9	37.8	37.8
D-301	C-301 Receiver	84.2	84.2	89.2	89.2

Table 8.11 (Continued)
ITEMIZED CAPITAL COST INDEX
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Drums					
D-401	K-401 K/O Drum	17.6	17.6	33.8	33.8
D-402	E-402 Receiver	18.8	18.8	36.7	36.7
D-403	Re-dissolving Drum	53.8	53.8	44.6	44.6
D-404	K-402 K/O Drum	17.6	17.6	33.8	33.8
D-405	E-404 Receiver	18.8	18.8	36.7	36.7
D-501	Drying Feed Silo	241.5	241.5	86.9	86.9
D-502	E-501 Receiver	23.9	23.9	38.0	38.0
D-503	Dust Solution Drum	16.5	16.5	36.0	36.0
D-504AB	ADA Product Silos	122.4	244.8	61.8	123.6
D-505	Flow Improver Silo	11.9	11.9	32.2	32.2
D-601	E-603 Receiver	18.2	18.2	36.8	36.8
D-602	K-601 K/O Drum	15.6	15.6	33.0	33.0
D-603	E-607 Receiver	8.9	8.9	32.8	32.8
Heat Exchangers					
E-101	Regen Steam Condenser	34.0	34.0	48.4	48.4
E-102	Vacuum Line Condenser	136.0	136.0	121.0	121.0
E-201	Regen Steam Condenser	34.0	34.0	48.4	48.4
E-301	C-301 O/H Cooler	282.7	282.7	56.3	56.3
E-302	R-301 Feed/Product HX	1,130.8	1,130.8	225.2	225.2
E-303	R-301 Trim Heater	226.2	226.2	45.1	45.1
E-304	C-301 Reboiler	3,392.4	3,392.4	675.6	675.6
E-305AB	C-301 Condenser	3,902.9	7,805.8	777.4	1,554.8
E-306	C-301 B/S Cooler	141.4	141.4	28.2	28.2
E-401	TK-401 Tank Heater	53.8	53.8	30.0	30.0
E-402	K-401 Condenser	76.8	76.8	42.8	42.8
E-403	Recycle Cooler	98.4	98.4	44.9	44.9
E-404	K-402 Condenser	76.8	76.8	42.8	42.8
E-405	2nd-Stage Recycle Cooler	98.4	98.4	44.9	44.9
E-501	1st-Stage ADA Dryer	317.6	317.6	48.1	48.1
E-502	2nd-Stage ADA Dryer	165.6	165.6	43.9	43.9
E-503	ADA Dust Condenser	117.2	117.2	45.9	45.9
E-504	ADA Rotary Cooler	105.4	105.4	42.3	42.3

Table 8.11 (Continued)
ITEMIZED CAPITAL COST INDEX
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Heat Exchangers					
E-601	Ester Feed Heater	26.8	26.8	76.4	76.4
E-602	C-601 Feed Heater	14.4	14.4	38.9	38.9
E-603	C-601 Condenser	42.9	42.9	41.8	41.8
E-604AB	C-601 Reboiler	25.6	51.2	40.3	80.6
E-605AB	Methanol Heater	11.0	22.0	31.4	62.8
E-606	Crude Ester Heater	27.4	27.4	76.1	76.1
E-607	C-602 Condenser	12.3	12.3	37.5	37.5
E-608AB	C-602 Reboiler	10.9	21.8	31.3	62.6
E-609	Ester Cooler	28.2	28.2	44.3	44.3
E-610	Methanol Vaporizer	16.5	16.5	25.8	25.8
Fired Heaters					
F-201	Off-Gas Incinerator	1,680.0	1,680.0	875.0	875.0
F-202	Solids Incinerator	8,750.0	8,750.0	6,500.0	6,500.0
Filters					
FL-101	Pulsed Air Blower Filter	56.4	56.4	39.6	39.6
FL-201AB	Cell Debris Coarse Filters	1,012.2	2,024.4	727.4	1,454.8
FL-202AB	MF-UF Filters	7,600.0	15,200.0	3,850.0	7,700.0
FL-203AB	Rotary Incinerator Ceramic Filter	285.0	570.0	215.0	430.0
FL-204	Gas Incineration Filter	76.4	76.4	58.6	58.6
FL-501	ADA Dust Pulse Filter	156.0	156.0	205.5	205.5
Compressors					
K-101	Enzyme Prep Air Blower	11.9	11.9	48.4	48.4
K-102	Induced Air Blower	11.9	11.9	48.4	48.4
K-103	Vacuum Line Compressor	492.6	492.6	828.6	828.6
K-201AB	Fermenter Induced Blowers	344.8	689.6	580.0	1,160.0
K-401	1st-Stage Vacuum Pump	11,360.0	11,360.0	27,360.0	27,360.0
K-402	2nd-Stage Vacuum Pump	4,794.0	4,794.0	10,910.0	10,910.0
K-601	Ester Vacuum Pump	38.5	38.5	156.8	156.8

Table 8.11 (Continued)
ITEMIZED CAPITAL COST INDEX
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Mixers and Agitators					
M-101AB	Growth Fermenter Mixers	45.5	91.0	9.1	18.2
M-201ABCD	Fermenter Mixers	227.5	910.0	45.5	182.0
M-401	TK-401 Mixer	32.5	32.5	6.5	6.5
M-402	D-403 Mixer	16.3	16.3	3.3	3.3
M-501	D-503 Mixer	3.3	3.3	0.7	0.7
Pumps					
P-101AS	Distilled Water Pumps	5.4	10.8	35.0	21.6
P-102AS	Sulfuric Acid Pumps	0.6	1.2	2.3	4.6
P-103AS	Caustic Pumps	0.6	1.2	2.3	4.6
P-104ABCDE	Nutrients Screw Feeders	28.7	143.5	71.8	359.0
P-105A/B	Enzyme Slurry Pumps	21.3	42.6	93.8	187.6
P-106A/B	Vacuum Line Condensate Pumps	22.8	45.6	67.5	135.0
P-201ABC	Nutrient Screw Feeders	172.2	516.6	430.8	1,292.4
P-202AS	Fermenter Pumps	100.3	200.6	379.8	759.6
P-203AS	MF-UF HP Pumps	401.2	802.4	1,519.2	3,038.4
P-301AS	C-301 B/S Pumps	99.7	199.4	379.1	758.2
P-302AS	C-301 Reflux Pumps	141.2	282.4	479.2	958.4
P-401AS	Crystallization Feed Pumps	28.2	56.4	123.6	247.2
P-402AS	1st-Stage Wastewater Pumps	22.9	45.8	94.1	188.2
P-403AS	1st-Stage Recycle Pumps	46.2	92.4	167.7	335.4
P-404AS	1st-Stage Slurry Pumps	174.6	349.2	165.4	330.8
P-405AS	1st-Stage Filtrate Pumps	64.0	128.0	127.0	254.0
P-406AS	ADA Re-dissolved Solution Pumps	35.4	70.8	151.6	303.2
P-407AS	2nd-Stage Wastewater Pumps	21.0	42.0	93.5	187.0
P-408AS	2nd-Stage Recycle Pumps	44.3	88.6	165.8	331.6
P-409AS	2nd-Stage Slurry Pumps	116.3	232.6	124.6	249.2
P-410AS	2nd-Stage Filtrate Pumps	46.1	92.2	95.0	190.0
P-501AS	Drying Wastewater Pumps	13.0	26.0	67.7	135.4
P-502AS	Dust Solution Pumps	29.6	59.2	72.0	144.0

Table 8.11 (Continued)
ITEMIZED CAPITAL COST INDEX
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Pumps					
P-601AS	Ester Feed Pumps	31.1	62.2	73.3	146.6
P-602AS	C-601 Reflux Pumps	20.3	40.6	53.7	107.4
P-603AS	C-601 B/S Pumps	25.4	50.8	67.5	135.0
P-604AS	Methanol Feed Pumps	31.8	63.6	45.4	90.8
P-605AS	Crude Ester Pumps	32.5	65.0	73.7	147.4
P-606AS	C-602 Reflux Pumps	40.0	80.0	49.9	99.8
P-607AS	C-602 B/S Pumps	29.6	59.2	44.7	89.4
P-608AS	Ester Pumps	29.6	59.2	44.7	89.4
P-609AS	TK-603 Pumps	23.1	46.2	56.3	112.6
Reactors					
R-101AB	Enzyme Growth Fermenters	733.1	1,466.2	194.7	389.4
R-201ABCD	Production Fermenters	3,275.0	13,100.0	869.8	3,479.2
R-301AB	Salt Splitting Reactors	2,520.0	5,040.0	901.4	1,802.8
R-601	Ester Reactor	33.1	33.1	157.2	157.2
Specially Packaged Equipment					
S-101	Process Flare System	3,500.0	3,500.0	2,350.0	2,350.0
S-103	Process Computer Control System	2,500.0	2,500.0	1,400.0	1,400.0
S-105	N2 PSA System	2,100.0	2,100.0	1,250.0	1,250.0
S-106	Packaged Glycol Refrigeration System	1,200.0	1,200.0	1,825.0	1,825.0
S-501	ADA Drying Cyclone	20.4	20.4	10.8	10.8
S-108	ADA & AGS Computerized Modular Packaging System	8,400.0	8,400.0	4,700.0	4,700.0
S-109	Dowtherm Hot Oil System	3,500.0	3,500.0	1,875.0	1,875.0
Steam Turbine Drivers					
ST-401	K-401 Driver	2,550.0	2,550.0	2,784.0	2,784.0
ST-402	K-402 Driver	1,024.0	1,024.0	1,264.0	1,264.0

Table 8.11 (Concluded)
ITEMIZED CAPITAL COST INDEX
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Storage Tanks					
TK-101	Distilled Water Tank	329.5	329.5	87.5	87.5
TK-102	Sulfuric Acid Tank	24.1	24.1	3.5	3.5
TK-103	40% Caustic Tank	24.1	24.1	3.5	3.5
TK-104	Glucose Silo	72.5	72.5	34.1	34.1
TK-105	Nutrients Silo	5.6	5.6	2.6	2.6
TK-106	Enzymes Silo	43.2	43.2	20.3	20.3
TK-107	Growth Promoter Silo	5.6	5.6	2.6	2.6
TK-108	Vitamins Silo	5.6	5.6	2.6	2.6
TK-201	Ammonia Sphere	346.2	346.2	59.4	59.4
TK-202	Nutrients Silo	9.9	9.9	4.7	4.7
TK-203	Vitamins Silo	7.6	7.6	3.4	3.4
TK-204AB	Glucose Silo	132.5	265.0	112.7	225.4
TK-401	Crystallization Feed Tank	131.8	131.8	112.0	112.0
TK-601	Ester Feed Tank	70.6	70.6	33.2	33.2
TK-602	Methanol Feed Tank	62.0	62.0	29.1	29.1
TK-603ABCD	Ester Product Tanks	64.1	256.4	30.1	120.4
Pressure Vessels (API 510-ASME BPVC)					
V-101AB	Air Filter Beds	39.7	79.4	43.6	87.2
V-102AB	Vacuum Line Filters	84.7	169.4	62.3	124.6
V-201AB	Fermenter Off-Gas Filters	39.7	79.4	43.6	87.2
V-401	1st-Stage Filter Cake Silo	231.4	231.4	124.1	124.1

In examining the distribution of itemized capital costs, we segmented the data in the table above in two ways: 1) by type of equipment, and 2) by section of plant. The table below summarizes the segmentation of tagged process equipment by type of equipment. The major cost categories are process compressors, special packaged equipment, filters, and reactors. The purification of adipic acid to polymer quality specifications requires crystallization under high vacuum conditions, in order to conduct the crystallization at a low enough temperature to avoid precipitating other contaminants in the crystal slurry (principally other mono- and dicarboxylic acids). Due to the high flow rates and low concentration of adipic acid in the feed stream, very large process compressors are required to create the vacuum conditions for effective subambient temperature and pressure crystallization. The most expensive component of specialized package equipment is the automated system for packaging producing adipic acid crystals in a combination of palletized shrink-wrapped and strapped 1-metric ton pallets, 500 kg and 1,000 kg iso containers, and 20 and 40 metric ton bulk containers. The most expensive filtration equipment required for this process is the combination of microfiltration and ultrafiltration membrane systems.

(Koch Membranes or equivalent) necessary to separate and recycle active enzymes from the fermentation broth (free of enzymes) that will undergo purification via a combination of vacuum distillation and vacuum crystallization. Without the separation and recycle of genetically modified enzymes, the cost of supplying adequate enzymes to the production fermenters would be prohibitively expensive.

Table 8.12
SEGMENTED TAGGED EQUIPMENT CAPEX BY TYPE OF EQUIPMENT

Category	FOB	Installation	Installed
Distillation Columns	1,582.7	1,583.8	3,166.5
Centrifuges	4,044.8	764.0	4,808.8
Crystallizers	6,256.0	828.0	7,084.0
Solids Conveyors	1,051.0	1,552.4	2,603.4
Drums	915.2	816.2	1,731.4
Heat Exchangers	14,556.8	3,735.4	18,292.2
Fired Heaters (incinerators)	10,430.0	7,375.0	17,805.0
Filters	18,083.2	9,888.5	27,971.7
Compressors	17,398.5	40,512.2	57,910.7
Mixers and Agitators	1,053.0	210.6	1,263.6
Pumps	4,056.3	11,433.8	15,490.1
Reactors	19,639.3	5,828.6	25,467.9
Special Packaged Equipment	21,220.4	13,410.8	34,631.2
Steam Turbine Drivers	3,574.0	4,048.0	7,622.0
Storage Tanks (ISBL)	1,659.7	744.3	2,404.0
Pressure Vessels	559.6	423.1	982.7
Total	126,080.5	103,154.7	229,235.2

In the table below, we have segmented the capital cost by section of the plant. The sections of the plant requiring the greatest capital cost are the two-stage aqueous crystallization section, and the production fermentation section. The high cost of crystallization is due to the requirement to concentrate adipic acid from dilute but filtered fermentation broth at both low temperature and high vacuum pressure. Refrigeration is required for maintaining a low enough temperature to prevent other contaminants in the broth (primarily other acids) from also crystallizing, while low vacuum conditions (1 and 2 psia) require large process compressors with large steam turbine drivers.

Table 8.13
SEGMENTED TAGGED EQUIPMENT CAPEX BY SECTION OF PLANT

Section		US\$-MM
100	Enzyme Preparation	6,110.3
200	Production Fermentation	72,682.3
300	Salt Splitting	26,913.3
400	Two-Stage ADA Crystallization	80,263.0
500	ADA Drying and Packaging	4,144.7
600	Methyl Ester Production	4,490.4
Special Equipment		34,631.2
Total		229,235.2

TOTAL FIXED CAPITAL COST

We have incorporated the itemized tagged equipment capital costs into a standardized PEPCOST total capital cost build-up, as presented in the table below. The total fixed capital cost is estimated to be \$545.2 million, segmented by \$409.0 million for inside battery limits process facilities, plus \$136.2 million for offsite battery limits facilities. The principal offsite capital cost elements are for wastewater treatment, steam generation, and cooling water. These are all driven by the highly dilute nature of fermentation in water, and requirements for downstream processing to concentrate adipic acid from the dilute solution, and then to treat the residual water that constitutes the fermentation broth.

Table 8.14
TOTAL FIXED CAPITAL COST ESTIMATE

CAPACITY: 160,000 MT/YR AT 0.90 STREAM FACTOR

PEP COST INDEX: 795

	COST (\$US-MM)	CAPACITY EXPONENT	
	-----	UP	DOWN
BATTERY LIMITS EQUIPMENT, FOB			
CONVEYING SYSTEMS	1,051	0.55	0.53
REACTORS	19,639	0.70	0.60
DISTILLATION COLUMNS	1,583	0.61	0.58
DRUMS	915	0.67	0.62
FILTERS	18,083		
HEAT EXCHANGERS	14,557	0.65	0.63
PUMPS	4,056	0.63	0.60
COMPRESSORS	17,399	0.62	0.60
TANKS	1,660	0.69	0.60
PRESSURE VESSELS	560	0.67	0.62
FIRED HEATERS	10,430	0.85	0.85
MIXERS & AGITATORS	1,053	0.65	0.65
SPECIAL PACKAGED EQUIPMENT	21,220	0.65	0.65
CENTRIFUGES	4,045	0.65	0.65
CRYSTALLIZERS	6,256	0.65	0.65
STEAM TURBINE DRIVERS	3,574	0.75	0.75
 TOTAL BLE	 126,081		
DIRECT INSTALLATION COSTS	103,155	0.66	0.62
INDIRECT COSTS	77,366	0.63	0.59
UNSCHEDULED EQUIPMENT, 20%	20,631	0.65	0.62
 BATTERY LIMITS, INSTALLED	 327,233	0.65	0.62
BLI CONTINGENCY, 25%	81,808	0.65	0.62
 BATTERY LIMITS INVESTMENT	 409,042	0.65	0.62
OFF-SITES, INSTALLED			
COOLING WATER	14,355	0.65	0.62
PROCESS WATER	5,650	0.65	0.62
BOILER FEEDWATER	4,772	0.65	0.62
PROCESS STEAM	14,240	0.55	0.53
FUEL GAS SYSTEM	1,636	0.55	0.53
INERT GAS & INSTRUMENT AIR	281	0.55	0.53
OFFSITES TANKAGE	12,400	0.55	0.53
 UTILITIES & STORAGE	 53,334	0.65	0.62
GENERAL SERVICE FACILITIES	6,545	0.65	0.62
WASTEWATER TREATMENT	49,085	0.65	0.62
 TOTAL OFFSITES	 108,964	0.65	0.62
OFFSITES CONTINGENCY 25%	27,241	0.65	0.62
 OFFSITES CAPITAL INVESTMENT	 136,205	0.65	0.62
 TOTAL FIXED CAPITAL	 545,246	0.65	0.62

PRODUCTION COST ESTIMATE

By combining the capital cost estimate with the variable costs associated with feedstock and utility consumptions driven by the stream-by-stream material balance, we have developed in the table below our estimate of the variable production cost for producing adipic acid using Verdezyne genetically modified enzyme fermentation technology. The major feedstock components are glucose feed, and the cost that Verdezyne will charge others to buy its genetically modified enzymes for production of adipic acid on a licensed basis. We have estimated a unit cost for genetically modified Verdezyne enzymes of \$4,000/mt, but the range of competitive costs is very wide, as practiced by other producers of genetically modified enzymes (Genencor, Novozymes, Syngenta). The high unit production of undesirable by-product acids (primarily succinic, glutaric, 3-hydroxypropionic) is monetized in the process for converting them to their respective methyl esters, which can be sold at high volume into the polyester polyols market.

Our design of a commercially viable Verdezyne-based fermentation process also shows relatively high unit costs for utilities, especially process steam. This is due to the requirement for concentrating the adipic acid in fermentation broth via fractional distillation and suspension crystallization, plus the large horsepower requirement to drive the crystallization vacuum compressors with steam turbines.

Table 8.15
ADIPIC ACID VIA VERDEZYNE FERMENTATION
VARIABLE COST ESTIMATE

	Unit Cost	Consumption	\$/mt
Raw Materials			
Glucose	300 \$/mt	2.466 mt/mt	739.8
Methanol	360 \$/mt	0.1503 mt/mt	54.1
Verdezyne Enzymes	4,000 \$/mt	0.0537 mt/mt	214.8
Ammonia	750 \$/mt	0.0074 mt/mt	5.6
Vitamins	3,500 \$/mt	0.001 mt/mt	3.5
Other nutrients	600 \$/mt	0.0025 mt/mt	1.5
Mixed Methyl Ester By-Product	500 \$/mt	-0.66 mt/mt	<u>-330.0</u>
Net Raw Material Cost			689.3
Utilities			
Process Water	0.2803 \$/m ³	13.5 m ³ /mt	3.8
Cooling Water	0.0187 \$/m ³	38.5 m ³ /mt	0.7
Electricity	60 \$/mwh	0.258 mwh/mt	15.5
Process Steam	8.28 \$/mt	22.6 mt/mt	187.1
Fuel Gas	3.05 \$/MM-Btu	2.55 MM-Btu/mt	7.8
Glycol Refrigeration	0.18 \$/ton	12.8 ton/mt	<u>2.3</u>
Net Utility Cost			217.2
Variable Cost			906.5

We have incorporated the unit variable costs for feedstocks, materials and utilities with the estimated capital costs developed above, and used standardized pep factors for estimating the

fixed costs of production. These are presented in the table below at three different production capacities, with the base case being 160 kty, and alternative cases of 80 kty and 320 kty estimated via factoring. On this basis, the total (all in) production cost for a 160 kty plant using our understanding of the Verdezyne fermentation technology is \$1,437 per metric ton, compared to an average adipic acid selling price of \$1,600/mt. The estimated cash cost of production is \$1,097 per metric ton. At these costs, a 160 kty capital project with these economic factors would experience a positive ROI, but only a 5% ROI.

Table 8.16
ADIPIC ACID VIA VERDEZYNE FERMENTATION
PRODUCTION COST ESTIMATE

Capacity	MT/Y	80,000	160,000	320,000
Production	MT/Y	<u>80,000</u>	<u>160,000</u>	<u>320,000</u>
Investment (US\$ millions)				
Battery Limits		260.7	(0.65)	409.0
Off-Sites		<u>97.0</u>	<u>(0.49)</u>	<u>136.2</u>
Total Fixed Capital		357.7		545.2
				860.4
Production Cost (\$/MT)				
Net Raw Materials		689.3		689.3
Net Utilities		<u>217.2</u>	<u>217.2</u>	<u>217.2</u>
Variable Costs		906.5		906.5
Direct Costs				
Maintenance Materials		48.9		31.4
Operating Supplies		1.8		0.4
Operating Labor		18.0		4.5
Maintenance Labor		48.9		31.4
Control Laboratory		<u>3.6</u>	<u>1.8</u>	<u>0.9</u>
Total Direct Costs		1,027.5		975.0
Plant Overhead		42.3		22.1
Taxes & Insurance		89.4		53.8
Depreciation		<u>447.1</u>	<u>340.8</u>	<u>268.9</u>
Plant Gate Cost		1,606.3		1,319.7
G&A, Sales, R&D		48.0		48.0
Total Production Cost				
At 100% Capacity		1,654.3		1,367.7
At 75% Capacity		1,903.6		1,521.5
At 50% Capacity		2,402.1		1,829.0
Product Value (Cost + 25%/Yr ROI Before Taxes)				
At 100% Capacity		2,808.2		2,053.5
At 75% Capacity		3,021.2		2,193.6
At 50% Capacity		3,519.8		2,501.2
Cash Cost		1,207.22		1,098.84
Cash Cost Profitability		392.78		501.16
Total Cost Profitability		-54.28		232.29

9 RENNOVIA PROCESS FOR MAKING ADIPIC ACID

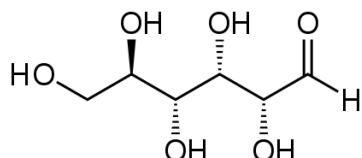
Rennovia (Menlo Park, California, USA) is different from most bio-based chemical technology firms because its process avoids fermentation (284035). Instead, Rennovia uses catalytic oxidation and hydrogenation technology platforms (284034) to convert low cost bio-based materials (glucose in the case of producing adipic acid). Of Rennovia's two process technology routes to adipic acid, 1) glucose via glucaric acid, and 2) carbohydrates via furans, we believe that the glucose to glucaric acid route has the greatest near term potential for commercial success. Glucose is sourced commercially from corn starch via corn wet milling.

To address the 'food versus fuel' social issue of using glucose from corn, significant efforts are being developed by others to convert nonfood biomass sources (lignocelluloses) to glucose and other sugars (monosaccharides) that represent the basic feedstock for the Rennovia adipic acid process.

FEEDSTOCK AND PRODUCT MOLECULAR STRUCTURE

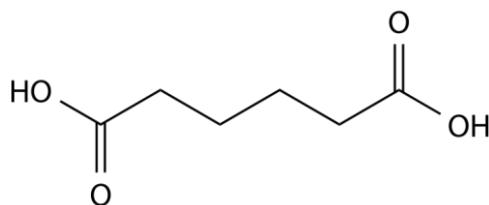
The molecular structure of glucose is remarkably similar to the desired adipic acid end product. Both molecules have linear C₆ backbones. Glucose has an aldehyde radical on one terminal carbon atom (CHO-), and a CH₂OH group at the terminal carbon atom. Adipic acid has acid groups (COOH-) on both terminal carbon atoms. The molecular structure of glucose is shown in the figure below.

Figure 9.1
GLUCOSE MOLECULAR STRUCTURE



As shown above, glucose also has hydroxyl groups (OH-) on each of the internal carbon atoms. Adipic acid internal carbon atoms are fully saturated, as shown in the figure below.

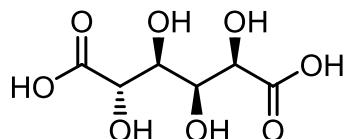
Figure 9.2
ADIPIC ACID MOLECULAR STRUCTURE



RENNOVIA TECHNOLOGY APPROACH

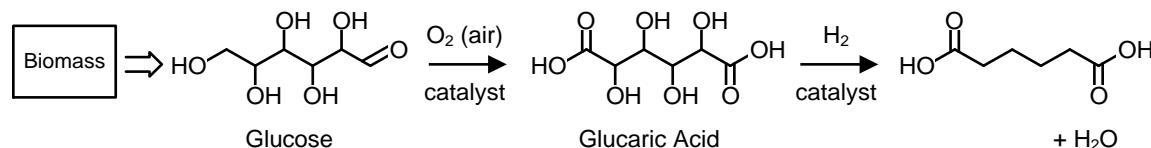
The Rennovia technology approach (284060) is to first oxidize the glucose terminal carbon atoms to form acid groups at both ends of the molecule, producing glucaric acid as an intermediate product. The molecular structure of glucaric acid is shown below.

Figure 9.3
GLUCARIC ACID MOLECULAR STRUCTURE



The glucaric acid is then hydrogenated selectively to replace the internal hydroxyl groups with fully saturated carbon atoms, without disturbing the terminal carboxylic acid groups. The hydrogenation replaces each internal oxygen atom with a hydrogen atom. The released oxygen atom combines with excess hydrogen atoms in the reactor to form water and release heat. The overall stoichiometric pathway is shown in the figure below.

Figure 9.4
RENNOVIA TWO-STAGE OXIDATION CHEMISTRY



Source: Rennovia (284035)

The major properties of each molecule are shown in the table below.

Table 9.1
PROPERTIES OF RENNOVIA FEED, INTERMEDIATE AND FINAL PRODUCT

Property	Glucose	Glucaric Acid	Adipic Acid
CAS Number	50-99-7	87-73-0	124-04-9
Formula	C ₆ H ₁₂ O ₆	C ₆ H ₁₀ O ₈	C ₆ H ₁₀ O ₄
Molecular Weight	180	210	146
Physical form	White powder	White powder	White crystals
Boiling Point °C	decomp	766	337.5
Melting Point °C	146	131	152
Water Solubility gm/100 ml	91	63	2
Density gm/cm ³	1.54	1.94	1.36

As shown in the above table, feedstock glucose is highly soluble in water at standard conditions, while intermediate product glucaric acid is less so, and adipic acid nearly insoluble in water. This property affects options for the design of how to process the feed and intermediate products, and how to purify the end product. To process the feed glucose, which in its natural state is a white powder, a fluid should be created in order to provide ease of handling and transport. Given the high solubility of glucose in water, it would seem convenient to use water as the dissolving solvent, and then process the resulting aqueous solution through the required reaction steps.

The high boiling points of each component mitigate against fractional distillation as a means of product purification. The relatively high solubility of glucose and glucaric acid in water, combined with the very low solubility of adipic acid in water, suggests that crystallization (as practiced in the conventional cyclohexane oxidation process) is likely to be a successful way to produce high-purity adipic acid product.

From a process safety perspective, the sugar processing industry, which employs unit operations similar to glucose processing, has a history of experiencing dust explosions. For this reason, solids storage and conveying equipment in this design are entirely enclosed and covered with an inert nitrogen blanket.

RENNOVIA PATENT PORTFOLIO

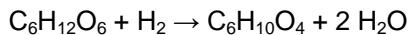
Rennovia's patents and applications for its processes to make adipic acid are listed below.

Table 9.2
RENNOVIA PATENTS AND APPLICATIONS

Patent Number	Title
US 20110306790	Oxidation Catalysts
US 20110218318	Composition of Matter
US 20100317825	Production of Glutaric Acid and Derivatives from Carbohydrate-Containing Materials
US 20100317823	Production of Adipic Acid and Derivatives from Carbohydrate-Containing Materials
US 20100317822	Production of Adipic Acid and Derivatives from Carbohydrate-Containing Materials
EP 2440514	Production of Glutaric Acid and Derivatives from Carbohydrate-Containing Materials
EP 2440515	Production of Glutaric Acid and Derivatives from Carbohydrate-Containing Materials
EP 2440513	Production of Adipic Acid and Derivatives from Carbohydrate-Containing Materials
WO 2011/1455964	Catalyst Comprising Platinum and Gold Nano-Particles and its use for Oxidation of Glucose and Preparation Method of Such a Catalyst
WO 2011/109051	Adipic Acid Composition
WO 2010/144862	Production of Adipic Acid and Derivatives from Carbohydrate-Containing Materials
WO 2010/144871	Production of Glutaric Acid and Derivatives from Carbohydrate-Containing Materials
WO 2010/144873	Production of Adipic Acid and Derivatives from Carbohydrate-Containing Materials

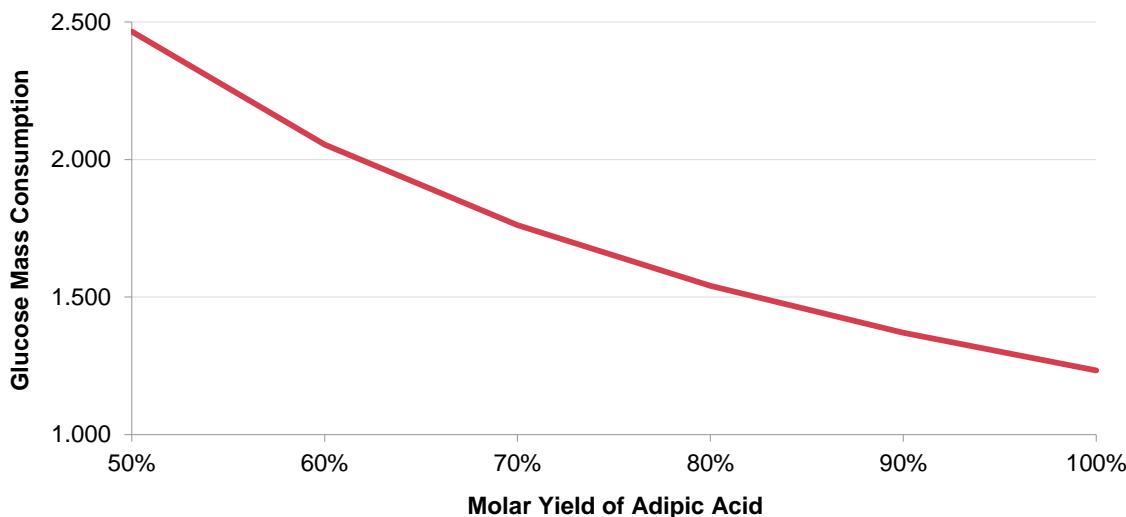
Overall Process Yield and Feedstock Consumption

On a theoretical basis, if one could convert a single mol of glucose to a single mol of adipic acid, the mass consumption of glucose would be 1.233 metric tons of glucose to produce 1.000 metric tons of adipic acid.



From Rennovia's patent literature, it is expected that the molar conversion of glucose to glucaric will be approximately 80% for the first-stage oxidation, while the molar conversion of glucaric acid to adipic acid via hydrodeoxygenation will be approximately 90%. Combining the two stages leads to a 72% molar conversion from glucose to adipic acid. If we assume that about 5% of produced adipic acid will be lost in the purification process, the overall molar yield on that basis drops to 68.4%. This is equivalent to a mass requirement of 1.802 metric tons of glucose per metric ton of product adipic acid. The graph below plots the overall mass consumption of glucose to produce 1.000 metric ton of adipic acid as a function of the molar yield across the entire process.

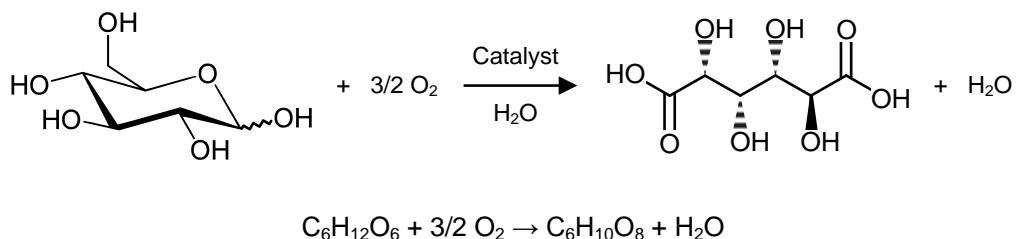
Figure 9.5
RENNOVIA FEED CONSUMPTION VERSUS YIELD



Rennovia 1st-Stage Oxidation of Glucose to Glucaric Acid

Rennovia has developed proprietary heterogeneous multi-component catalyst formulations via high throughput screening that are designed to optimized yield, kinetics, and productivity. The conventional oxidation of glucose to glucaric acid in the literature uses platinum catalyst with oxygen, or nitric acid catalysis with air as the oxidant. The Rennovia process relies on a combined platinum and gold catalyst at prevailing pH conditions in which glucose is dissolved in water as solvent, and uses air as the oxidant. The reaction mechanism is shown in the figure below.

Figure 9.6
RENNOVIA OXIDATION OF GLUCOSE TO GLUCARIC ACID



Based upon the stoichiometric equation shown above, one can calculate the theoretical yield from glucose (both molar and mass) to produce glucaric acid and water, and also calculate the theoretical yield to glucaric acid (both molar and mass) from glucose and from oxygen. This calculation is presented in the table below.

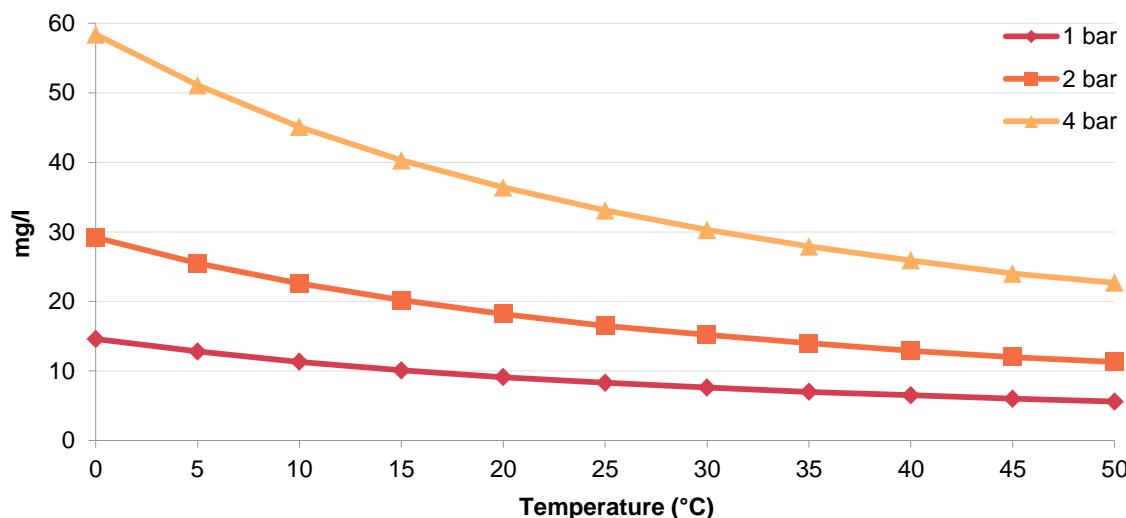
Table 9.3
THEORETICAL YIELDS OF GLUCOSE OXIDATION REACTION

	Molar	Mass
Yield from Glucose		
To Glucaric acid	1.0	1.167
To Water	1.0	0.100
Yield to Glucaric acid		
From Glucose	1.0	0.857
From Oxygen	1.5	0.229

Rennovia US patent application 20110306790 A1 (15-December-2011) provides details on their catalysts used for glucose oxidation to glucaric acid. The Rennovia preferred oxidation catalyst is a combination of nano-dispersed (2 to 50 nm) gold and platinum particles on an inorganic titanium oxide substrate (Saint Gobain Norpro ST3119) in which the ratio of gold to platinum ranges between 100:1 and 4:1. The platinum is in the zero valence state Pt(0). Further embodiments include adding a third active catalyst metal (palladium), and a fourth metal (tungsten) to the catalyst formulation. Total active catalyst loading on the titania substrate ranges from 1 to 4% by weight.

Rennovia's patent application uses water as a reaction solvent for glucose, and uses air as the oxidant. Both glucose and intermediate product glucaric acid are highly soluble in water. Air is not, as shown in the figure below with oxygen's solubility below 10 ppm at atmospheric pressure. For this reason, a commercial design will require operation at elevated air pressure to maximize oxygen solubility in the aqueous glucose solution.

Figure 9.7
OXYGEN SOLUBILITY IN WATER



Source: engineeringtoolbox.com

When glucaric acid is dissolved in a water solution, the open ring form of the molecule exists in equilibrium with two closed-ring forms created by either hydration or dehydration: monolactones (C=O bond) D-glucaro-6,3-lactone and D-glucaro-1,4-lactone, also forming dilactone D-glucaro-1,4:6,3-dilactone (284061). As the concentration of acid increases, the proportion of molecules converting from open form to closed ring form increases. Each form reacts essentially the same to downstream processing conditions for either oxidations or hydrogenations.

Two of the commercial design considerations driven by the use of proposed precious metal catalyst formulations are deactivation and physical loss. Precious metal catalysts require unusually pure feedstocks (often reagent-grade feedstocks), and have a propensity to deactivate in the presence of sulfur, nitrogen, and coke particles. Given the high cost of precious metal catalyst, catalyst reactor design should guard against the physical abrasion/erosion that produces fines which leave the reactor in reactor product, and also highly acidic or alkaline process conditions that can cause the active catalyst metals to dissolve in the process fluid, and be lost from the system.

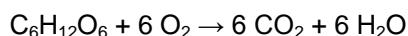
The Rennovia patent applications provide nearly 100 examples of glucose conversion and glucaric acid yield from various catalyst formulations. A subset of these from a Rennovia US patent application is shown in the table below. Independent published data on oxidation product formation exist in a 1977 paper published by Dirkx, van der Baan and Van den Broek (284062). The published data, combined with Rennovia's patent disclosures, indicate that for the design conditions glucose conversion should be virtually 100%. Molar conversion to glucaric acid should be approximately 80%, corresponding to a mass consumption of 1.071 mt of glucose consumed per mt of glucaric acid produced.

Table 9.4
RENNOVIA USPA 2011/0306790 PARTIAL YIELD TABLE

Run #	Catalyst wt (mg)	Au wt%	Pt wt%	Glucose Conversion %	Glucaric Acid Yield %
72	7.8	1.6	2.4	100%	36
73	8.2	2.0	2.0	100%	36
74	8.0	2.4	1.6	100%	32
75	7.5	2.4	5.6	100%	58
76	8.1	2.8	1.2	100%	26
77	7.9	3.2	0.8	100%	19
78	7.9	3.2	4.8	100%	58
79	8.0	3.6	0.4	100%	7
80	8.5	4.0	0.0	100%	3
81	8.0	4.0	4.0	100%	57
82	8.0	4.8	3.2	100%	47
83	7.6	5.6	2.4	100%	31
84	7.7	6.4	1.6	100%	16

Glucose Oxidation Intermediate Products

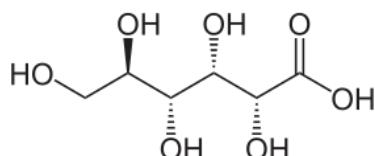
We expect that the oxidation of glucose will produce a wide variety of oxidation intermediate and final by-products, beside the desired glucaric acid. Complete oxidation of glucose results in combustion products carbon dioxide plus water, via the following equation:



It is doubtful that the stoichiometric mechanism for oxidizing glucose to hydroxy dicarboxylic acid (glucaric acid) involves the instantaneous oxidation of both terminal carbon atoms to carboxylic acid groups. It is more likely that the aldehyde group on one terminal carbon atom is first oxidized (forming gluconic acid), or that the CH_2OH group on the opposite carbon atom is first oxidized (forming glucuronic acid). Subsequent oxidation at the other end of the molecule will complete the conversion to hydroxyl dicarboxylic acid (glucaric acid).

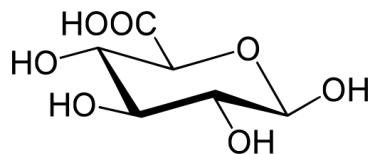
Gluconic acid is a linear C_6 monocarboxylic acid formed when glucose is oxidized such that the aldehyde group on a terminal carbon atom is converted into a carboxylic acid, with no other chemical changes to the glucose molecule. Gluconic acid (CAS 526-95-4) has a formula of $\text{C}_6\text{H}_{12}\text{O}_7$, and a molecular weight of 196. The molecular structure of the molecule is shown below.

Figure 9.8
GLUCONIC ACID MOLECULAR STRUCTURE



Glucuronic acid (CAS 6556-12-3) is a C_6 monocarboxylic acid having the chemical formula $\text{C}_6\text{H}_{10}\text{O}_7$ (molecular weight 194, melting temperature 160°C). If glucose is oxidized so that the CH_2OH terminal carbon atom (at the opposite end of the molecule) is converted to a monocarboxylic acid (with no other changes to the molecule), the product formed is glucuronic acid. Its molecular structure is shown in the figure below.

Figure 9.9
GLUCURONIC ACID MOLECULAR STRUCTURE



In aqueous solution, the intermediate products of glucose oxidation will be observed as a combination of open ring and closed ring C_6 compounds. C_6 Keto aldehydes are formed when glucose is oxidized such that one or more hydroxyl groups on the internal carbon atoms have their hydrogen atom removed, and the remaining oxygen atom forms a double bond with the carbon atom to which it is bonded. In this structure, the terminal carbon atoms are not oxidized, such that the terminal aldehyde group on the glucose molecule is not disturbed. Some keto aldehydes represent the ring form in solution of conventional monosaccharide molecules, and will participate in chemical reactions designed to either oxidize or hydrogenate the molecule.

Glucose Oxidation By-Products

Hydroxy mono- and dicarboxylic acids of lower carbon number than C₆ are formed when glucose is oxidized such that one or more carbon atoms on the backbone of the glucose molecule are stripped away as CO₂/CO, with either or both remaining terminal carbon atoms converted to a carboxylic acid group. Hydroxy monocarboxylic acids include glycolic acid (C₂), glyceric acid (C₃), erythronic acid (C₄), and arabinonic acid (C₅). Hydroxy dicarboxylic acids include oxalic acid (C₂), tartronic acid (C₃), tartaric acid (C₄), arabinonic, and xylaric acid (C₅).

We expect the commercial yield pattern from glucose oxidation to be consistent with the table below. The primary by-products are combustion oxidation products (CO₂ + CO), lower molecular weight dicarboxylic acids (C₄ and C₅), and monocarboxylic acids.

**Table 9.5
EXPECTED GLUCOSE OXIDATION YIELD PATTERN**

Product	Molar Yield %
Glucaric acid	80
C ₆ Hydroxy Keto aldehydes	1
C ₂ -C ₆ Hydroxy monocarboxylic acid	6
C ₂ -C ₅ Hydroxy dicarboxylic acid	3
Carbon dioxide	9.5
Carbon monoxide	0.5

Comparing the expected actual yield of the glucose oxidation reaction to glucaric acid with the stoichiometric yield, we have estimated the overall mass consumption and feedstock, and mass production of products and products per metric ton of glucaric acid produced. These values are listed in the table below.

Table 9.6
EXPECTED MASS YIELD FOR GLUCARIC ACID PRODUCTION FROM GLUCARIC ACID AIR
VIA OXIDATION

Feedstock Consumed	Yield %
Glucose	-1.0713
Oxygen	-0.2863
Total	-1.3575
Product Produced	
Glucaric acid	1.0000
C ₆ Keto aldehydes	0.0125
C ₂ –C ₆ Hydroxy monocarboxylic acid	0.1050
C ₂ –C ₅ Hydroxy dicarboxylic acid	0.0524
Carbon dioxide	0.0352
Carbon monoxide	0.0011
Water	0.1513
Total	1.3575

Experimental results reported in the patent application at a variety of temperatures and residence time show that at temperatures in the range of 100°C, and residence times in the range of 3–5 hours, high yield of glucaric acid can be achieved. We believe that for a commercial system the oxidation reactor can be designed for 15 minutes residence time and provide equivalent yield. Representative results from Rennovia's patent applications are shown in the table below.

Table 9.7
RENNOVIA USPA 2011/0306790 TEMPERATURE AND RESIDENCE TIME RESULTS

Run #	Temperature (°C)	Reaction time (hrs)	Glucose Conversion (%)	Glucaric Acid Yield (%)
1	91	5	100	51
2	98	3	100	52
3	98	5	100	59
4	105	3	100	58
5	112	3	100	68
6	119	2	100	69
7	119	3	100	71
8	126	2	100	70

Intermediate ring-form products from an air oxidation step include monolactones (D-glucaro-1,4-lactone, D-glucaro-6,3-lacone) and dilactones (D-glucaro-1,4:6,3-dilactone), most of which will also be converted to adipic acid when subjected to downstream hydrodeoxygenation.

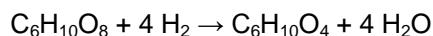
Preferred reaction conditions are a temperature range between 80–140°C, and a pressure range from atmospheric up to 500 psia. Higher pressure increases the solubility of oxygen in the aqueous glucose solution, increasing reaction kinetics.

An alternative approach to sugar oxidation was patented (EP 798310) by Freres Roquette in 1997 using nitroxyl catalysis, but yield and selectivity were far lower than reported by Rennovia. Another approach using chlorine as the oxidant was patented by the University of Connecticut (USP 6498269).

Rennovia 2nd-Stage Hydrodeoxygenation of Glucaric Acid to Adipic Acid

The aqueous solution of glucaric acid and by-products is dried to solid form to remove water, and then is processed through a sequence of operations to produce adipic acid. A solvent mixture containing hydrogen bromide (HBr) at 2% solution weight is mixed in acetic acid solvent. HBr acts as an intermediate catalyst in that the initial reaction at the hydroxyl (OH-) site on the internal carbon atoms is to replace the oxygen atom with a bromine atom. Hydrogen subsequently replaces the bromine atom to saturate the internal carbon atom with hydrogen, while restoring the HBr. Consequently, there is no net consumption of hydrogen bromide in the reaction.

The dried glucaric acid product is dissolved in the acetic acid solvent at elevated temperature 90°C at a concentration of approximately 20% glucaric acid in the acetic acid solvent containing hydrogen bromide. The hydrodeoxygenation reaction converting glucaric acid to adipic acid (284035) is shown below:

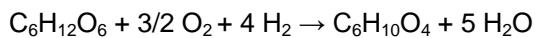


From a theoretical perspective, we can calculate the molar and mass yield from the primary feedstock (glucaric acid), and to the primary product (adipic acid), assuming stoichiometric conversion of feedstock to product. This calculation is shown in the table below.

Table 9.8
THEORETICAL YIELDS OF GLUCARIC ACID HYDRODEOXYGENATION REACTION

	Molar	Mass
Yield from Glucaric Acid		
To Adipic Acid	1.0	0.695
To Water	4.0	0.343
Yield to Adipic Acid		
From Glucaric Acid	1.0	1.438
From Hydrogen	4.0	0.0548

We can combine the glucose oxidation reaction with the glucaric acid hydrogenation reaction for the purpose of calculating the overall yield to adipic acid product from starting feedstock glucose, and the yield from glucose to produce adipic acid. The overall stoichiometric equation is presented below.



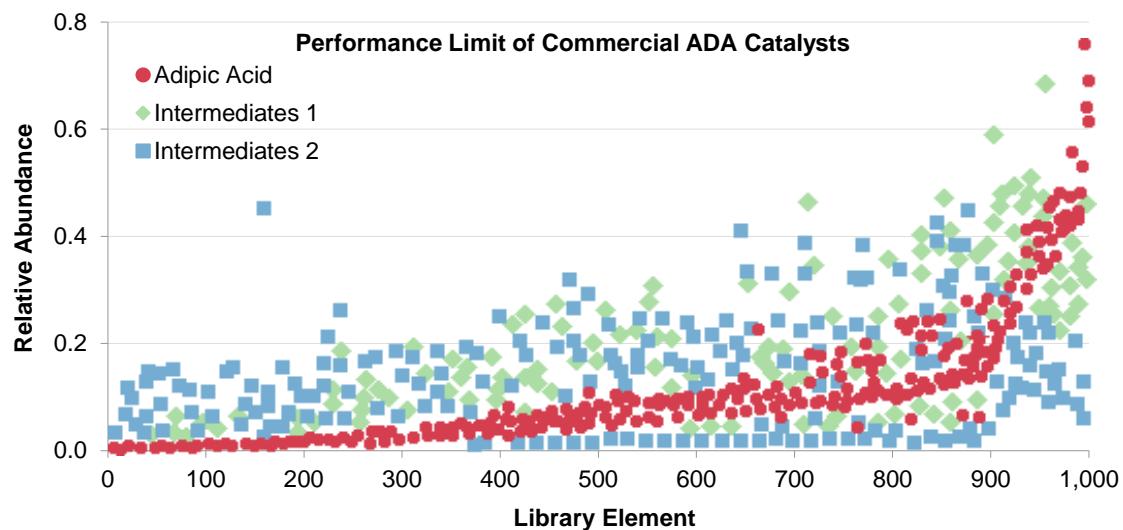
The overall yield can be calculated from the above equation, and is presented in the table below.

**Table 9.9
THEORETICAL YIELDS OF OVERALL GLUCOSE TO ADIPIC ACID REACTION**

	Molar	Mass
Yield from Glucose		
To Adipic Acid	1.0	0.811
To Water	5.0	0.500
Yield to Adipic Acid		
From Glucose	1.0	1.233
From Oxygen	1.5	0.329
From Hydrogen	4.0	0.0548

By conducting high throughput screening through many fixed bed reactors in parallel, Rennovia was able to compare the yield of adipic acid from each set of experimental conditions to the by-product and intermediate product make from each individual catalyst formulation. A visual depiction of ADA yield to other reactor by-products is shown in the figure below, which suggested the types of catalysts and catalyst conditions most likely to maximize conversion and yield during the early development of Rennovia's technology.

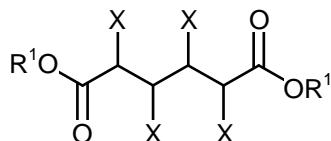
**Figure 9.10
RENNOVIA HIGH THROUGHPUT SCREENING RESULTS**



Source: Rennovia (284060)

The generalized structure of the intermediate product of glucose oxidation is shown in the figure below, where the terminal carbon atoms have carboxylic acid groups, while the internal carbon atoms contain oxygenated radicals.

**Figure 9.11
STRUCTURE OF INTERMEDIATE C₆ OXIDIZED PRODUCT**



Although the desired intermediate contains four hydroxyl (-OH) groups on the internal carbon atoms, some intermediate products will be in the various equilibrium forms of aliphatic internal ketone groups (2-ketoglucaric acid, 3-ketoglucaric acid) and ringed aliphatic lactone groups (C=O) rather than hydroxyl groups (D-glucaro-1,4-lactone, D-glucaro-6,3-lactone, D-glucaro-1,4:6,3-dilactone).

Once glucaric acid is produced at a molar yield of about 80%, a second reaction step of hydrodeoxygenation strips the oxygen atoms from the four hydroxyl groups off the internal carbon atoms to yield adipic acid. The reaction is dramatically enhanced by the presence of a halogen (HI, HBr) promoter. Our design incorporates HBr at a 2% concentration in acetic acid solution.

In Rennovia USPA 2011/0218318, Rennovia presents results for converting glucaric acid to adipic acid in high yield and nearly 100% conversion. The aqueous glucaric acid solution from the oxidation step is dried to a solid residue, and redissolved in a solvent containing HBr at a weight ratio of 2% HBr with contained acetic acid. The concentration of glucaric acid in the mixed HBr/acetic acid solution in our design is 20%.

The preferred hydrodeoxygenation catalyst is a formulation of platinum and rhodium at a ratio between 5:1 and 1:1. The active metal is deposited on a silica substrate at an active metal concentration of 4 weight percent.

A large excess of hydrogen was added to the experimental apparatus at a pressure of 710 psia. The Rennovia patent application recommends a hydrogen pressure between 800–1,300 psia. Reaction temperature ranges between 100–180°C (preferred 160°C), with a residence time of three hours in the laboratory experiments. Commercial design is expected to use a hydrogen trickle bed reactor with a glucaric acid residence time of 60 seconds. Adipic acid is formed directly in the reactor at nearly 90% molar yield from glucaric acid, as shown in the table below. This molar yield corresponds to a weight yield of 73%.

**Table 9.10
RENNOVIA CONVERSION OF GLUCARIC ACID TO ADIPIC ACID (USPA 2011/0218318)**

Catalyst	M1 Precursor	M2 Precursor	Catalyst Amount	Adipic Acid Yield
1.65% Rh 4.7% Pt/Silica Davisil 635	Pt(NO ₃) ₂	Rh(NO ₃) ₃	8 mg	89%

For an expected commercial yield of 90 molar % to adipic acid from glucaric acid via hydrogenation, the expected yield pattern is provided in the table below. As is typical of

hydrogenations, the by-products are primarily saturated hydrocarbons created by the over-hydrogenation of the feedstock to lower carbon number fully saturated molecules.

**Table 9.11
EXPECTED COMMERCIAL YIELD FOR GLUCARIC ACID HYDROGENATION**

Product	Molar Yield %
Adipic acid	90
Methane	4%
Propane	6%

Comparing the expected actual yield of the glucaric acid hydrogenation reaction with the stoichiometric yield, we have estimated the overall mass consumption and feedstock, and mass production of products and products per metric ton of adipic acid produced. These values are listed in the table below.

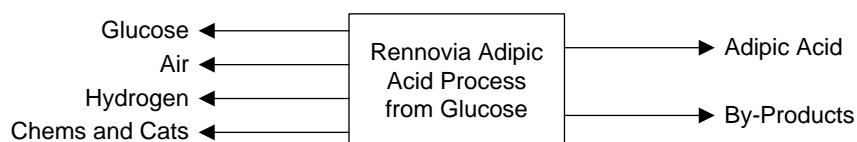
**Table 9.12
EXPECTED MASS YIELD FOR ADIPIC ACID PRODUCTION FROM GLUCARIC ACID VIA HYDRODEOXYGENATION**

Product Produced	(mt)	Feedstock Consumed	(mt)
Adipic Acid	1.000	Glucaric Acid	1.5987
Water	0.4935	Hydrogen	0.08219
Propane	0.16243		
Methane	0.02496		

COMMERCIAL PLANT DESIGN BASIS

Given the patent information developed above, we have prepared a commercial design around the Rennovia patent literature, consistent with what we believe to be reasonable business and engineering judgments. The overall requirements for the process are shown in the input/output diagram below.

**Figure 9.12
INPUT/OUTPUT DIAGRAM FOR RENNOVIA PROCESS**



The primary design criteria for the two desired reactions, 1) oxidizing glucose to glucaric acid, and then 2) hydro-deoxygenating glucaric acid to adipic acid, is presented in the table below.

**Table 9.13
RENNOVIA DESIGN BASIS**

Parameter	Oxidation of Glucose	Hydrogenation of Glucaric Acid
Feedstock	Glucose + air	Glucaric acid + H ₂
Desired product	Crude glucaric acid	Crude adipic acid
Reactor design	Continuous plug flow	Hydrogen trickle bed
Reaction thermodynamics	Moderate exothermic	Exothermic
Reactor heat removal	Internal cooling coils + dilute feedstock	Internal cooling coils + external pump around loop
Reactor thermal protection	Steam deluge	Steam deluge + depressurize H ₂
Type catalyst	Heterogeneous pellets	Heterogeneous pellets
Primary active catalyst metals	Nano-dispersed Au/Pt(0)	Pt/Rh
Ratio of active metals	10:1	5:3
Secondary active catalyst metals	Pd/W	None
Catalyst substrate	Titanium oxide	Silicon oxide
Active metal ratio on substrate	4%	5%
Solvent	Water	Acetic acid
Solvent Promoter	None	HBr
Feedstock concentration wt%	20%	20%
Rx design temperature °C	100	160
Rx design pressure psia	400 (Air)	1,000 (H ₂)
Residence time	15 minutes	60 seconds
Feedstock conversion %	100	100
Product yield molar %	80%	90%
Product yield mass (mt/mt)	0.9336	0.626

COMMERCIAL PROCESS DESIGN

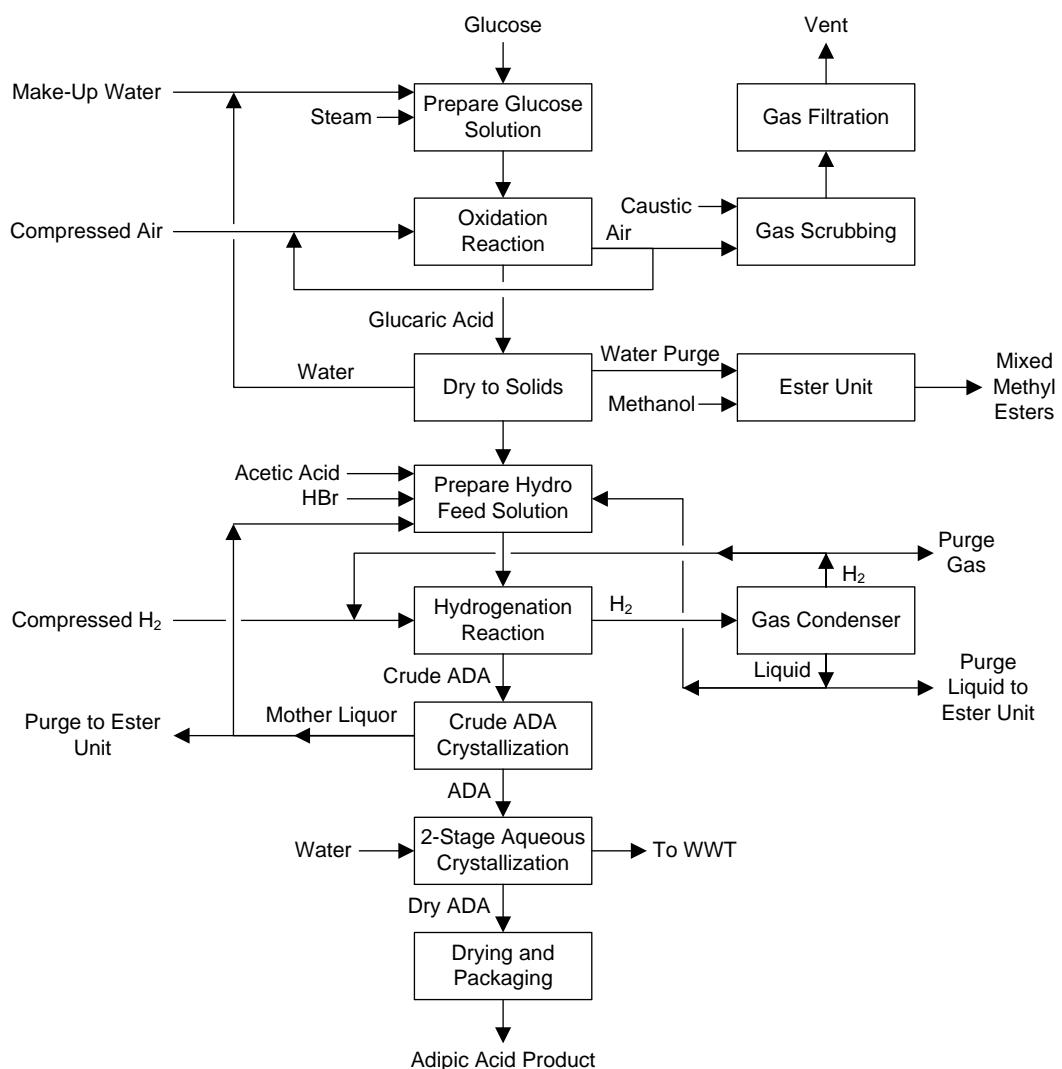
We have prepared a continuous process for the preparation of polymer-grade adipic acid from glucose using our understanding of Rennovia process technology, as reported in the patent data presented in tables above. A block flow diagram of the process is presented in the figure below.

Glucose powder feedstock is prepared by dissolving it in an aqueous solution in hot water (heated by direct steam injection). Recycle water from the downstream glucaric acid product stream drying operation is recycled to the mixing tank for preparing the glucose aqueous solution. The liquid solution is then pumped into one or more oxidation reactors for the purpose of

converting the glucose to crude glucaric acid. The reactors are heterogeneous fixed bed catalyst reactors into which compressed air is pumped for the oxidation reaction. Liquid feed flow is from top to bottom. Air flow is from bottom to top.

A high level of excess air is pumped through the oxidation reactors (excess ratio 10:1). Most of the discharge air is recycled back to the feed air compressor. To avoid the build-up of vapor impurities, approximately 10% of the air product gas from the oxidation reactors is purged first through a caustic/water scrubber to remove acids and organics, and then through a mixed media filtration system containing beds of activated carbon, followed by a bag-house filtration unit for fine particulate removal prior to atmospheric venting.

Figure 9.13
RENNOVIA ADIPIC ACID BLOCK FLOW DIAGRAM



The hydrocarbon content of the aqueous liquid product stream leaving the oxidation reactors is approximately 80 molar % glucaric acid, mixed with oxidation products and acid by-products

such as lower molecular weight mono- and dicarboxylic acids, lactones, ketones, and aldehydes. This stream is dried to remove the water, which is recycled back to the glucose solution preparation tank. The dry residue solid is mostly glucaric acid.

The dry residue is redissolved in a solution of acetic acid and hydrogen bromide. The concentration of glucaric acid in the acetic acid solution is approximately 20%. The dissolved glucaric acid solution is then directed to the hydrodeoxygenation reactor, which is a trickle bed hydrogenation reactor similar to those used in refinery heavy oil hydro-desulfurization. High pressure hydrogen (1,000 psia) reacts with the glucaric acid over a Pt/Rh fixed bed catalyst, and selectively removes the oxygen atoms from the hydroxyl (OH-) groups of the internal carbon atoms without appreciably affecting the carboxylic acid groups on the two terminal carbon atoms, producing adipic acid. This reaction has a feedstock conversion of 100%, and an adipic acid molar yield of 90%. A large excess of hydrogen is used to drive glucaric acid feedstock to 100% conversion, with the off-gas being primarily hydrogen plus miscellaneous light hydrocarbon by-product gases and slight liquid carry-over. The hydrogen-rich product gas is passed through a water-cooled condenser to remove condensables, with the hydrogen recycled back to the reactor. Most of the liquid condensed can be recycled to the hydrogenation preparation tank, with about 10% discharged to the ester unit to recover valuable by-products and to avoid the build-up of contaminants in the acetic acid solvent.

The Rennovia patent portfolio claims that the hydrodeoxygenation reactor liquid product stream, which is approximately 20% adipic acid in a solution rich in acetic acid, with some hydrogen bromide, can be cooled to room temperature from reaction temperature (160°C) to selectively precipitate out adipic acid. Our process design accomplishes this by cooling the solution in a suspension Oslo crystallizer, recovering crude adipic acid crystals as 20% solids slurry. The slurry is further concentrated to an 80% adipic acid filter cake in one or more pusher centrifuges. The filter cake is further dried to 98% solids content in a rotary dryer, for the purpose of recovering contained acetic acid for recycle.

The dried adipic acid is not yet adequately pure for polymer-grade adipic acid sales. It is further processed through two more stages of suspension crystallization using water as the solvent. The first stage of crystallization operates at 50°C, and the final stage of crystallization operates at 35°C. Both stages are conducted under high vacuum. Filter cake from the final crystallization sequence is dried in two stages of rotary dryer, cooled to ambient conditions in another rotary cooler, and directed to a modular process unit for packaging into a combination of 1-mt palletized 25kg bags (LLDPE vacuum shrunk and strapped), 500 and 1,000 kg iso containers, and 20 and 40 mt bulk product containers.

The oxygenated by-products of the process, which are primarily mono- and dicarboxylic acids, have economic value if converted to methyl esters. The aqueous process stream purged from the first stage of glucose oxidation is reacted directly in the methyl ester reactor, with grades of methyl ester product purified by fractional distillation. The acetic acid purge stream containing both water and mixed acids is first distilled to recover and recycle acetic acid, with the aqueous product stream containing most of the acid components then directed to the methyl ester reactor.

PROCESS DESCRIPTION

The process plant is segmented into the following sections, as listed below:

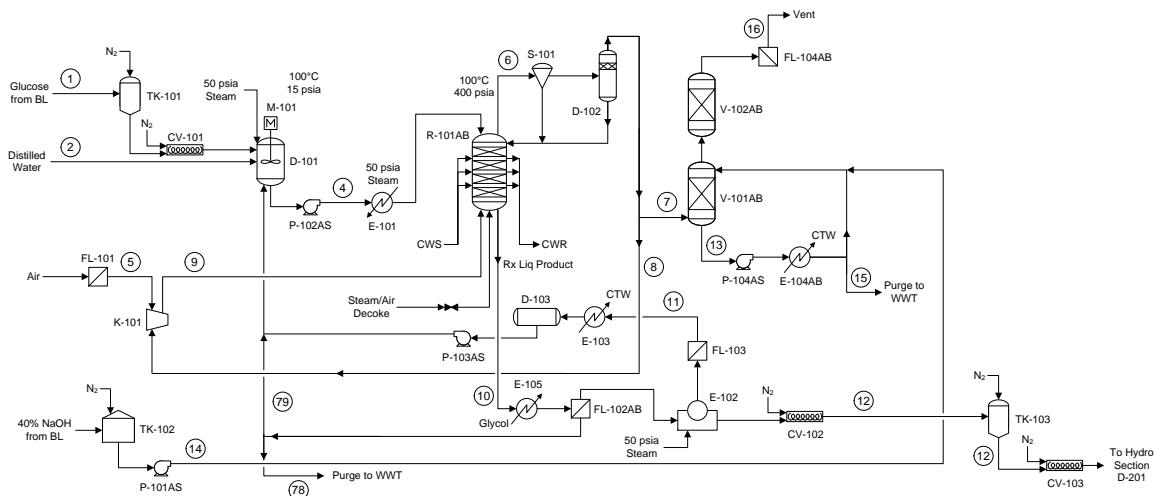
- Section 100—Glucose oxidation with air
- Section 200—Glucaric acid hydrodeoxygenation to adipic acid
- Section 300—Adipic acid crystallization
- Section 400—Adipic acid drying and packaging
- Section 500—Acetic acid recovery

- Section 600—Mixed methyl ester production

Section 100—Glucose Oxidation with Air

Glucose in the form of a dry solid is stored in a day silo within battery limits, and conveyed to a mixing tank to be dissolved in warm water down to a 20% feed concentration. A process flow diagram for section 100 is presented in the figure below.

Figure 9.14
GLUCOSE AIR OXIDATION PROCESS FLOW DIAGRAM



Glucose in the form of commercial dextrose powder and/or syrup is available from many agricultural products companies, including Cargill, ADM, and Corn Products in the United States. Typical solids content is over 99% glucose (also called dextrose), with the remaining components being small quantities of fructose, maltose, maltotriose, and higher saccharides. Syrup commercial specific gravity is 1.3. We have designed our process around Cargill's ClearSweet® 99% Refined Liquid Dextrose Corn Syrup. The commercial product Cargill spec is shown in the figure below.

Table 9.14
CARGILL GLUCOSE SYRUP SPECIFICATION

Clearsweet® 99% Refined Liquid Dextrose Corn Syrup Product Information

Chemical and Physical Properties				
Fermentables (%)	99.5			
Refractive Index (20°C)	1.4629–1.4653			
Refractive Index (45°C)	1.4581–1.4604			
Total Solids (%)	70.5–71.5			
Moisture (%)	28.5–29.5			
Sulfated Ash (%)	0.05 max			
pH (1:1)	3.5–5.0			
pH (1:10)	4.0–6.0			
Sulfur Dioxide (ppm)	2 max			
Conductivity (30% DS)	65 micromhos			
Calories/100 g	284			
Typical Carbohydrate Profile (% Dry Basis)				
Dextrose	99			
Fructose	0.1			
Maltose	0.6			
Maltotriose	0.2			
Higher Saccharides	0.1			
Microbiological Limits				
Mesophilic Bacteria	1,000 cfu/10 g max			
Yeast	100 cfu/10 g max			
Mold	100 cfu/10 g max			
Sensory Characteristics				
Appearance	Clear Liquid			
Taste	Sweet, Bland			
Odor	Characteristic			
Density and Viscosity Factors				
Temp (°F)	Specific Gravity (Temp °F/ 60°F)	Pounds/ Gallon (Temp °F)	Pounds/ Gallon (DSB)	Viscosity (cP)
130	1.3239	11.04	7.84	41
140	1.3205	11.01	7.82	34
150	1.3170	10.98	7.8	28

Table 9.14 (Concluded)
CARGILL GLUCOSE SYRUP SPECIFICATION

Clearsweet® 99% Refined Liquid Dextrose Corn Syrup Product Information

Regulatory/Labeling Data	
United States GRAS Affirmation	CFR 21 184.1865
Labeling	Corn Syrup; Dextrose
Canada FDR	B.18.016
Labeling	Glucose Syrup; Glucose
Shelf Life and Storage	The recommended storage temperature range is 130–140°F. Syrups stored for extended periods (over 6 months) should be evaluated periodically for fitness of use. At below normal storage temperatures, e.g., room temperature, this product may be in a crystallized or “solid” state. It can be returned to its liquid form by applying heat.

Source: Cargill

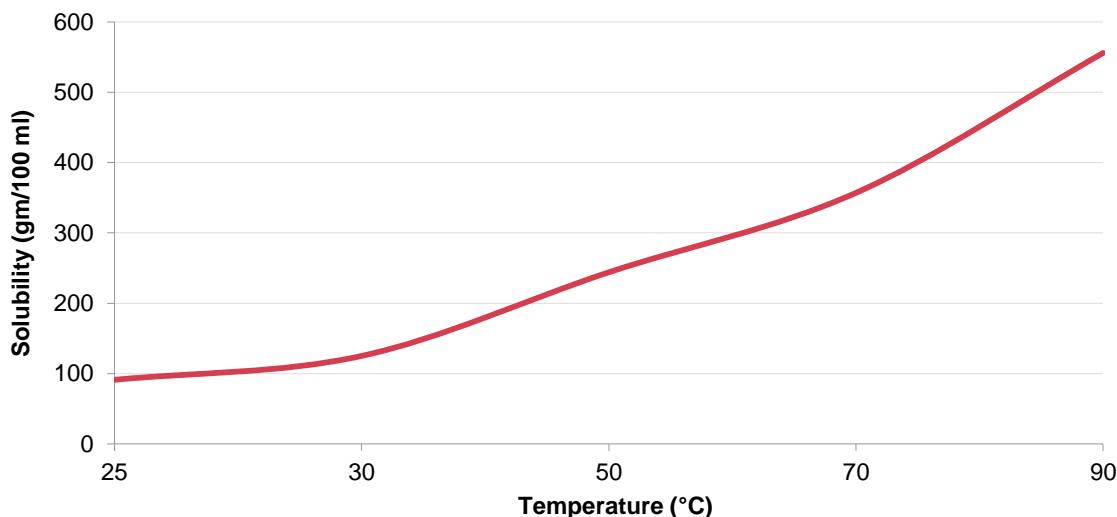
The principal properties of the feedstock components are shown in the table below. All decompose before reaching a boiling temperature at atmospheric pressure.

Table 9.15
COMMERCIAL FEEDSTOCK COMPONENTS

Component	CAS Number	Formula	Mol Wt
Glucose/dextrose	50-99-7	C ₆ H ₁₂ O ₆	180
Fructose	57-48-7	C ₆ H ₁₂ O ₆	180
Maltose	69-79-4	C ₁₂ H ₂₂ O ₁₁	342
Maltotriose	1109-28-0	C ₁₈ H ₃₂ O ₁₆	504

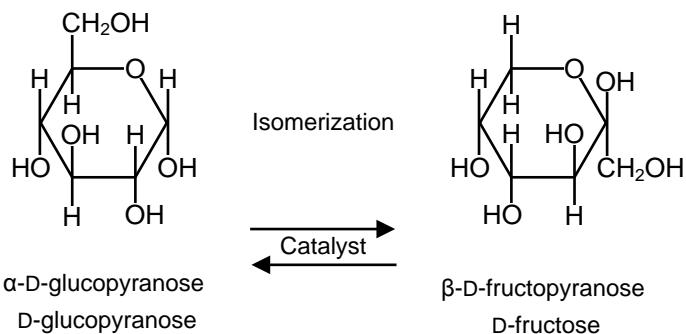
Glucose is highly soluble in water, as shown by the figure below. Recycle water from glucaric acid drying is returned to the mixing tank, as is fresh make-up water. Glucose is dissolved to produce a solution containing 20% glucose by weight in the total solution. The solution is heated by direct steam injection of 50 psia saturated steam.

Figure 9.15
GLUCOSE SOLUBILITY IN WATER



Glucose and fructose are structural isomers, with their structure as shown in the diagram below.

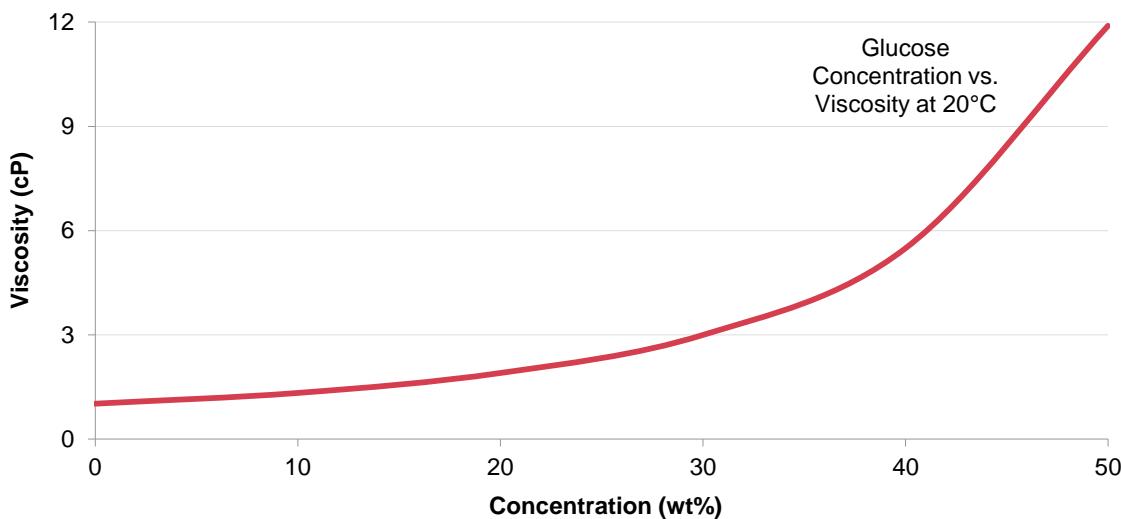
Figure 9.16
GLUCOSE AND FRUCTOSE MOLECULAR STRUCTURE



Source: Corn Refiners Association

At the relatively low concentration of glucose in water (approximately 20%), glucose is not only easily dissolved, but as a Newtonian fluid does not significantly increase the viscosity of the resulting solution. The graph below provides viscosity data for glucose aqueous solutions at 20°C.

Figure 9.17
GLUCOSE VISCOSITY IN WATER



The glucose solution is preheated to 100°C in a heat exchanger, and pumped into two parallel, 50% capacity each down-flow oxidation reactors packed with gold/platinum/palladium/tungsten active metal catalyst on a titanium oxide support. Each reactor contains four beds of catalyst. Between catalyst beds are both redistribution plates and cooling water heat exchanger manifolds to remove the exothermic heat of reaction. The reactors operate at 100°C and 400 psia. Filtered and compressed air is distributed to the bottom section of each reactor, and flows upward through the beds of catalyst. The reactors convert 100% of the glucose to oxidation products, 80% being glucaric acid. The balance of the oxidation products are combustion degradation gases ($\text{CO} + \text{CO}_2$), lower molecular weight mono- and dicarboxylic acids, and solution equilibrium mono- and dilactones, ketones and aldehydes.

The overhead vapor stream product from the oxidation reactors is mostly unconverted excess air, but also contains combustion degradation products ($\text{CO} + \text{CO}_2$), and carried over mist containing water vapor, organic acids, ketones, lactones, and aldehydes. The vapor stream product is passed through a cyclone separator and knock-out drum to separate out liquid components, with most of the vapor stream primarily recycled back to the inlet air compressor. About 25% of the vapor stream is purged to prevent the build-up of vapor-phase contaminants. To meet atmospheric discharge emission limits, the purged vapor stream is processed first through a caustic scrubber, then activated carbon filter, and finally a pulse air bag house. The cleaned stream is then suitable for discharge venting to atmosphere.

The liquid product stream exiting the oxidation reactors is primarily water solvent, includes glucaric acid product (80% molar yield), and also contains miscellaneous oxygenated organic by-products.

The liquid stream is chilled in a glycol heat exchanger to precipitate preferentially glucaric acid, which is the least soluble hydrocarbon component. At ambient temperature, the solubility of glucaric acid in water is 63 mg/l (284064), compared to a concentration of nearly 200 mg/l in the liquid product stream from the oxidation reactors at the 100°C reactor temperature. The liquid stream is filtered, with the filtered solids directed to a rotary bed dryer containing a heat exchanger that is designed to dry the glucaric acid and by-products to a solid residue, while discharging as a vapor the water for recycle. The vapor from the dryer is condensed, and pumped

back to the glucose solution preparation tank. The filtrate from the filter is recycled back to the mixing tank.

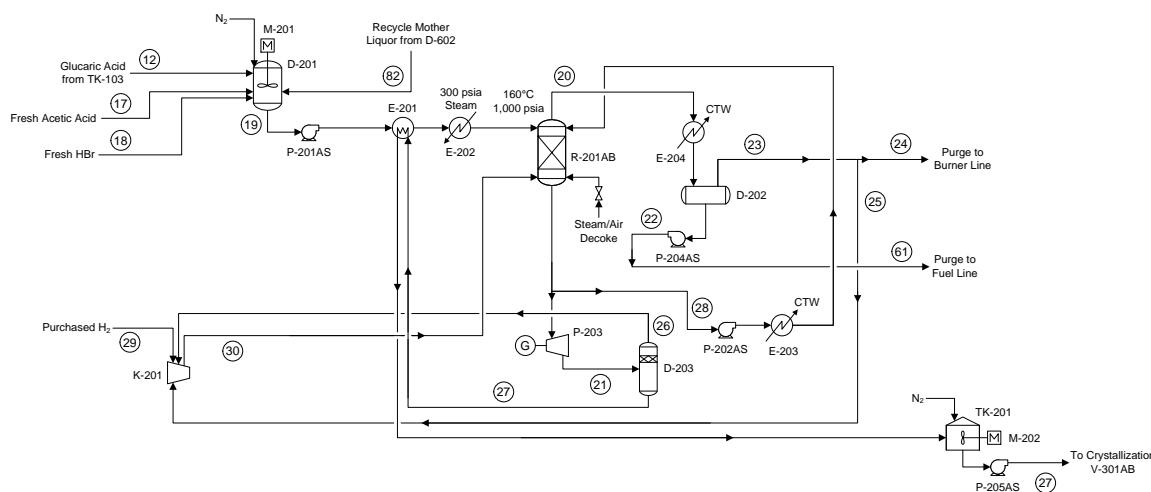
At atmospheric pressure, the water solvent boils at 100°C. Operating the rotary dryer at 40 psia will provide sufficient vapor pressure to discharge the water back to the oxidation preparation tank in the liquid phase. 50 psia saturated steam is suitable for use as the heating medium in the dryer, and will condense as a liquid within the indirect heat exchange surface inside the dryer.

The dried glucaric acid residue is conveyed to an intermediate storage silo prior to being processed to the hydrodeoxygénéation reaction.

Section 200—Glucaric Acid Hydrodeoxygénéation to Adipic Acid

The dried glucaric acid residue is redissolved in a solution containing acetic acid and 2% hydrogen bromide (HBr) promoter. The overall concentration of dissolved glucaric acid within the mixed solvent is 20 weight %. The solution mixing tank also receives recycle mother liquor from the crude adipic acid crystallization section. A process flow diagram for section 200 is presented in the figure below.

**Figure 9.18
GLUCARIC ACID HYDRODEOXYGENATION PROCESS FLOW DIAGRAM**



Hydrogen bromide is a gas at atmospheric conditions, and readily dissolves in the acetic acid solution at the design concentration of 2 weight %. Once dissolved, hydrogen bromide converts to hydrobromic acid. Its molecular weight is 81.

The glucaric acid solution first passes through a reactor feed/product heat exchanger, then a trim heat exchanger to increase its temperature to reactor design temperature (160°C). The hydrodeoxygénéation reactor is designed to operate adiabatically. A solution pump around loop through an external heat exchanger cooled by cooling tower water absorbs the exothermic heat of reaction.

The hydrodeoxygénéation reactor is protected from thermal runaways by a combination of hydrogen depressurization to the process flare header system, dilute feedstock concentration of 20%, and a network of snuffing steam nozzles contained throughout the inside walls of the reactor. For high temperature excursions, a higher proportion of liquid product would be recycled through the external pump around cooling loop. For an emergency shutdown, the reactor would

first be depressured to the process flare header. If that is not effective in killing the reaction, the snuffing steam system would then be activated.

The reactor is designed with a feed rate of high excess hydrogen (10:1 by weight) at 1,000 psia. Hydrogen is fed to a distribution header at the bottom of the reactor and flows upward, while the liquid glucaric acid in acetic acid liquid solution flows downward through a fixed bed of Pt/Rh catalyst on alumina substrate. The reactor is designed for trickle bed operation.

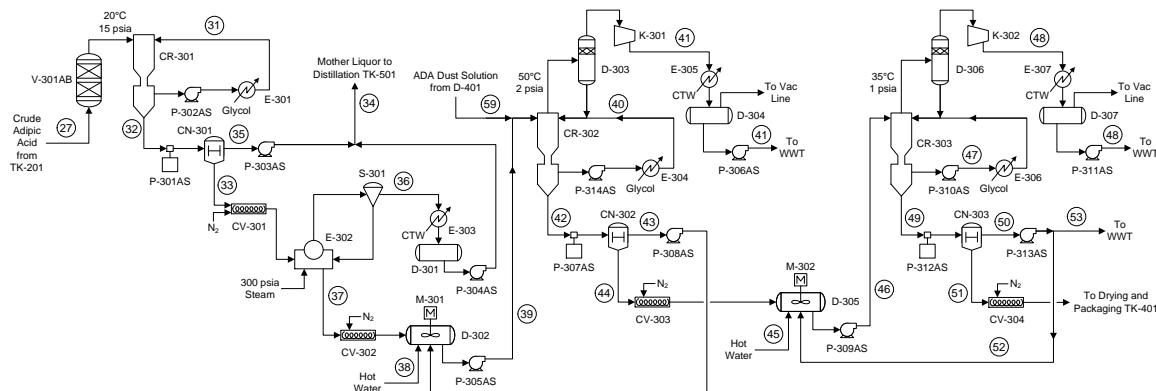
Overhead vapor product from the reactor is passed first through a condenser to remove condensable liquids, and then recycled back to the hydrogen feed compressor. About 1% of the overhead gas is purged to the burner line to prevent the build-up of vapor-phase contaminants, which are principally light hydrocarbon gases. The reactor product gases, after passing through the condenser, are directed to a knock-out drum to remove the condensables. The condensable liquid is pumped back to the solution mixing tank, while a small percentage is purged to the esterification unit to prevent the build-up of impurities, and to recover in ester form the by-product acids contained in the vapor mist.

Liquid hydrodeoxygenation reactor product at 1,000 psia is directed through a two-phase hydraulic turbine generator for the purpose of depressuring the 1,000 psia liquid down at near atmospheric pressure (50 psia). The turbine generator makes electric power from the depressuring of the liquid, and is designed as a twin screw progressive cavity pump run in reverse direction. Discharge from the low pressure side of the hydraulic turbine is directed to a knock-out drum for the purpose of separating the vapor phase (mostly hydrogen gas) from the liquid product. The overhead vapor from the knock-out drum is recycled back to the hydrogen feed compressor. The liquid product from the bottoms of the knock-out drum is cooled to 50°C in a heat exchanger, and sent to an intermediate storage tank prior to being processed through the crystallization section of the plant.

Section 300—Adipic Acid Crystallization

Hydrodeoxygenation reactor liquid product is pumped from intermediate storage to a crude adipic acid crystallization unit designed to crystallize and separate adipic acid from the acetic acid solution, while recycling the mother liquor solution back to the hydrodeoxygenation mixing tank. A process flow diagram for section 300 is presented in the figure below.

Figure 9.19
ADIPIC ACID CRYSTALLIZATION PROCESS FLOW DIAGRAM



Rennovia's patent applications indicate that adipic acid will crystallize out of the acetic acid/HBr solution at room temperature. The table below shows that adipic acid is moderately soluble in

acetic acid (0.364 molar, equivalent to 53 gm/liter), at standard temperature (0°C), compared to other common organic solvents. Since the acetic acid solution contains approximately 20% adipic acid (200 gm/liter), approximately $\frac{3}{4}$ of the adipic acid can be crystallized out of the acetic acid mother liquor.

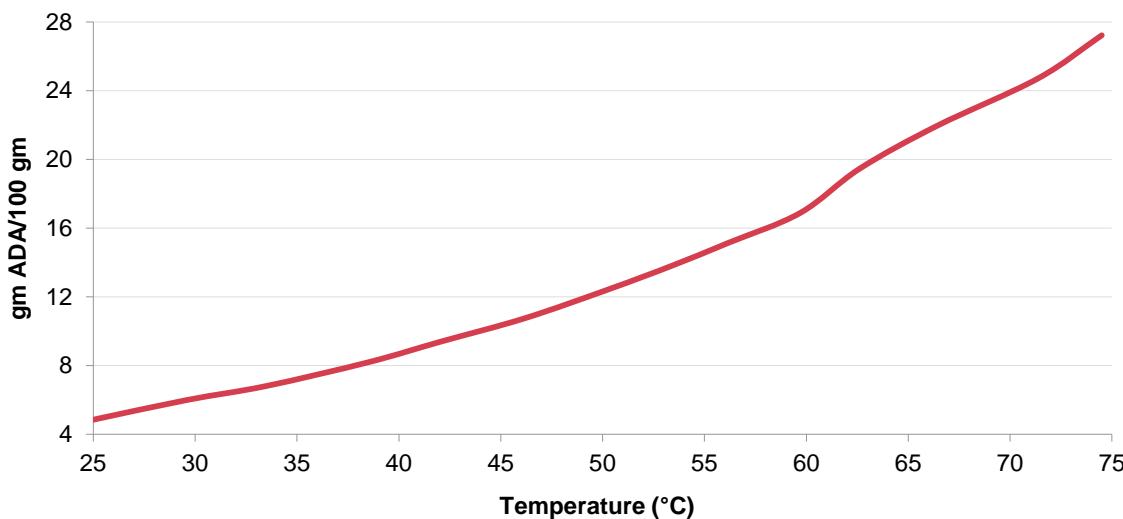
Table 9.16
ADIPIC ACID SOLUBILITY IN COMMON SOLVENTS

Solvent	Avg. (M)
1,4-Dioxane	0.465
1-Butanol	0.286
1-Propanol	0.371
2-Methyl-2-propanol	0.616
2-Propanol	0.458
DMF	0.303
DMSO	3.748
Acetic acid	0.364
Acetone	0.229
Acetophenone	0.038
Chloroform	0.027
Cyclohexanone	0.142
Dimethylacetamide	2.86
Ethanol	0.651
Methanol	1.079
Toluene	0

Source: Royal Society of Chemists (284063)

On the basis of Rennovia's patent applications, the warm (80°C) adipic acid solution is pumped to an Oslo crystallizer operating at 20°C and atmospheric pressure. The solubility of adipic acid in acetic is shown in the figure below. The warm solution of adipic acid in acetic acid will be solubility to nearly 30 parts per 100 parts at 80°C, while the solubility is less than 5 parts per 100 parts at 20°C. The concentration of adipic acid leaving the hydrogenation reactor is expected to be approximately 20 parts per 100 parts acetic acid solution. Consequently, about $\frac{3}{4}$ of the dissolved adipic acid will crystallize during each pass through the crystallizer/centrifuge combination. As a result, the centrifuge filtrate is 100% recycled back to the hydro reactor make-up tank to avoid significant losses of produced adipic acid. To maximize adipic acid recovery, the adipic acid filter cake from the crude centrifuge is sent to a drier to recover and recycle the acetic acid solvent as an overhead product.

Figure 9.20
ADIPIC ACID SOLUBILITY IN ACETIC ACID



Crystallized slurry is pumped through an external cooler designed to maintain the temperature at the desired 20°C, using chilled glycol solution refrigerant. Adipic acid crystallizes out of solution at 20°C, and forms a crystal slurry suspension at the bottom of the Oslo crystallizer. The crystal slurry is pumped through a pusher centrifuge to form a solid adipic acid filter cake (80% adipic acid, 20% acetic acid). The filter cake is conveyed to a rotary dryer to reduce the acetic acid/HBr content to less than 2% by evaporating the acetic acid solvent. The vaporized solvent leaves the top of the rotary dryer and passes through a heat exchanger to condense the acetic acid back to liquid, which is then recycled back to the mixing tank via pumping. The mother liquor from the pusher centrifuge is also recycled back to the mixing tank, with a small amount purged to prevent a build-up of contaminants and by-products.

The dried adipic acid-rich residue from the rotary dryer is conveyed to a mixing tank where it combines with hot water (80°C), and is redissolved in the water at a concentration of 10 weight percent. The aqueous adipic acid solution is pumped to the 1st-stage aqueous Oslo crystallizer for the purpose of crystallizing out a higher concentration of adipic acid crystals. The 1st-stage aqueous crystallizer operates at 50°C and 2 psia, and is maintained at the desired temperature using an external pump around loop through a heat exchanger than uses glycol solution refrigerant. Vacuum in the 1st-stage crystallizer is created by an overhead vacuum pump that draws off water vapor from the very top of the Oslo crystallizer. The water vapor is first passed through a knock-out drum to remove mist, and then passes through the vacuum pump (3-stage centrifugal compressor), and then a condenser. The condensate is collected in a receiving drum, and pumped to wastewater treatment.

The formed adipic acid crystal slurry in water at the bottom of the Oslo crystallizer is pumped through a 1st-stage pusher centrifuge, which forms a solid filter cake of adipic acid having a moisture content of less than 20%. The liquid product stream (absent adipic acid crystals) from the 1st-stage pusher centrifuge is pumped back to the aqueous redissolving tank. The solid filter cake from the 1st-stage pusher centrifuge is conveyed to mixing tank where it is redissolved in hot water (80°C) at a 10% weight concentration for the purpose of recovering final adipic acid crystals at high purity.

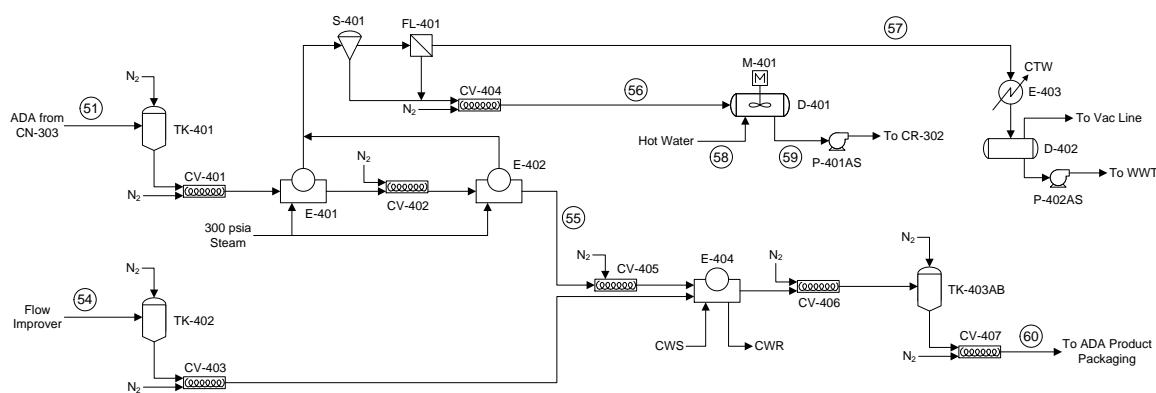
The aqueous adipic acid solution is pumped to a 2nd-stage Oslo crystallizer to crystallize out of solution high-purity adipic acid crystals. The 2nd-stage Oslo crystallizer operates at 35°C and one psia pressure, and is maintained at that temperature using an external pump around loop through a heat exchanger that uses glycol solution refrigerant. Vacuum is maintained in the crystallizer using an overhead 3-stage centrifugal compressor. Overhead vapor from the 2nd-stage crystallizer first passes through a knock-out drum to remove water mist. The overhead stream from the knock-out drum is directed to the inlet of the vacuum compressor, which compresses the water vapor from one psia to atmospheric pressure (15 psia). The pressurized water vapor then passes through a heat exchanger that uses cooling water to condense the vapor back to liquid. The liquid is pumped to wastewater treatment.

The crystal suspension at the bottom of the 2nd-stage Oslo crystallizer is pumped through a 2nd-stage pusher centrifuge to separate out adipic acid crystals as a solid filter cake. The liquid product from the 2nd-stage pusher centrifuge is pumped to wastewater treatment. The solid filter cake from the 2nd-stage pusher centrifuge is conveyed to a day silo prior to being processed through the drying and packaging section of the plant.

Section 400—Adipic Acid Drying and Packaging

Adipic acid filter cake is directed to a two-stage rotary dryer to remove moisture to below 0.2 weight percent. The two rotary dryers operate at atmospheric pressure in series sequence. Medium pressure steam (300 psia) is used to heat an internal metal surface within the dryers to drive off the moisture content of the filter cake as vapor. The overhead vapor streams from both dryers are interconnected, such that the overhead vapor is first directed to a cyclone separator, and then through a metal fabric filter for the purpose of removing residual adipic acid dust that has been entrained in the water vapor. The dust collected from both the cyclone separator and the fabric filter are conveyed to a mixing tank where hot water is used to redissolve the adipic acid dust into a 10% solution. The solution is recycled to the 1st-stage aqueous crystallizer. Overhead vapor from the dryers, with adipic acid dust removed, is condensed in a heat exchanger using cooling tower water. The condensate is pumped to wastewater treatment. A process flow diagram for section 400 is presented in the figure below.

Figure 9.21
ADIPIC ACID DRYING AND PACKAGING PROCESS FLOW DIAGRAM



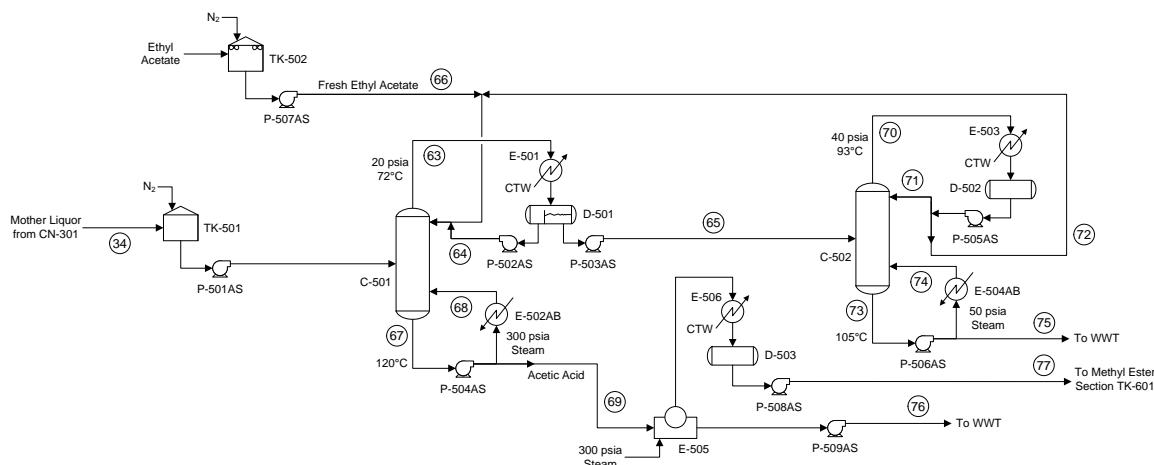
The hot and dry adipic acid crystals discharged from the 2nd-stage dryer are conveyed to a rotary cooler designed to cool the crystals down to ambient temperature. The rotary cooler uses a heat exchanger that is supplied with cooling tower water.

The now cooled and dry adipic acid crystals are conveyed to a product silo where they are conveyed to a modular, packaging system. The packaging systems produces packaged adipic acid in the form of 1-metric ton shrunk wrap and strapped pallets containing 25 kg bags, 500 kg and 1,000 kg ISO containers, and bulk 20 mt and 40 mt containers.

Section 500—Acetic Acid Recovery

The mixed stream of crude adipic acid centrifuge filtrate and dryer overhead condensate represent a mixture primarily of acetic acid and water. This mixture is hard to dehydrate due to the affinity between acid and the high hydrogen bonding of water, as well as the close proximity between boiling points (water at 100°C and acetic acid at 118°C). Although this mixture does not form an azeotrope, the separation by distillation requires a column with many stages and high reflux ratio. A process flow diagram for the proposed process configuration (section 500) is presented in the figure below.

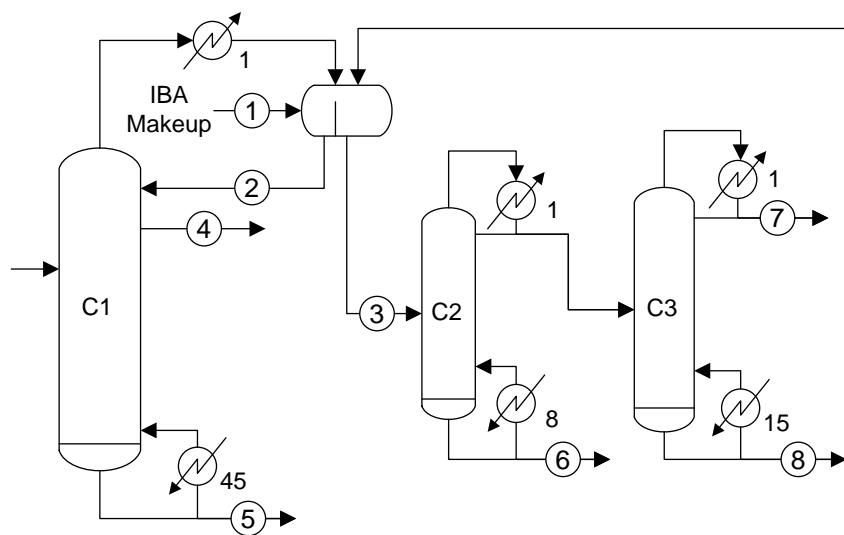
**Figure 9.22
ACETIC ACID RECOVERY PROCESS FLOW DIAGRAM**



An alternative process approach is to utilize heterogeneous extractive distillation. In this approach, a third chemical entrainer is added to the water and acetic acid mixture. We have chosen ethyl acetate as the entrainer. The entrainer has low solubility in the overhead product stream (water). As a result, in a distillation column, acetic acid is taken as a nearly pure bottoms product, and is recycled back to the process. A mixture of water and ethyl acetate are taken together as the overhead distillate product from the distillation column at the azeotropic composition and temperature for ethyl acetate: water (70°C, 8.5% water, 91.5% ethyl acetate).

Due to the limited solubility of ethyl acetate in water, the condenser receiver is designed to form two separate liquid phases in the drum, with the upper-phase ethyl acetate (96.7% ethyl acetate at equilibrium), and the lower-phase primarily water (8.7% ethyl acetate). The ethyl acetate upper phase is refluxed back to the distillation column, as shown in the figure below.

Figure 9.23
HETEROGENEOUS EXTRACTIVE DISTILLATION

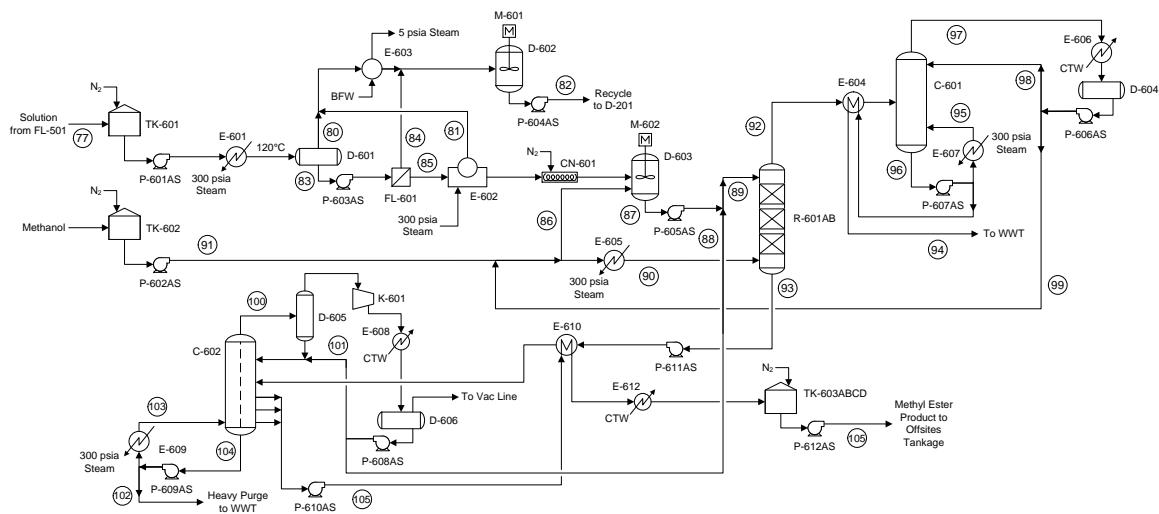


The lower water phase in the receiver is pumped to a second column for the purpose of recovering the ethyl acetate content, and discharging water to the wastewater treatment plant. The recovery column can recover nearly 100% water as the bottoms product, and recover an overhead product at the azeotropic condition (8.7% water content at 70°C). The upper phase is also recycled back to the first distillation column.

Section 600—Mixed Methyl Ester Production

The product stream from the acetic acid hydrodeoxygenation section of the plant contains a significant concentration of by-product mono- and dicarboxylic acids plus miscellaneous oxygenates that can be converted to salable product by esterifying them with methanol to produce mixed methyl esters. Smaller volume purge streams from the acetic acid mother liquor and hydrogenation reactor overhead vapor condenser also contain smaller concentrations of recoverable acid. These process streams are directed to a day tank prior to being processed through the mixed methyl esterification reaction and purification unit. A process flow diagram for this section appears in the figure below.

Figure 9.24
MIXED METHYL ESTER PRODUCTION PROCESS FLOW DIAGRAM



The first objective of this section is to separate the small quantity of adipic acid that is mixed with the other acids in the acetic acid mother liquor, with the intent to recycle both the acetic acid and adipic acid, while separating out the other oxygenates (including mono- and dicarboxylic acids). The mixed feed stream from tankage is first vaporized to drive off most of the acetic acid and small amount of water, leaving a liquid stream in which the adipic acid has precipitated, but dilute enough so that the other components remain dissolved. This stream is filtered for the purpose of recycling the adipic acid content in the acetic acid solution. The remaining acid components that are dissolved in acetic acid are further dried in a rotary dryer to a solid residue. The overhead vapor from the rotary dryer is acetic acid vapor which is also recycled to the hydrodeoxygenation feed mixing tank.

The dried acid residue is redissolved in methanol in a mixing tank equipped with a mechanical agitator, and pumped to the top of an esterification reactor designed to react the mixed acids with methanol to produce methyl esters plus water. Vaporized methanol enters the bottom of the reactor, and flows upward where it meets the downward flowing acid liquid (in methanol solution) and reacts. A 10:1 ratio of methanol to mixed acid assures complete conversion of the mixed acid to mixed ester. The upward flowing methanol also captures water vapor produced by the esterification reaction, and removes it from the multiple beds of fixed catalyst that enhance the reaction. The esterification reaction occurs at 120°C and 60 psia.

The overhead vapor exiting the reactor is principally excess methanol and water vapor, which is directed to a methanol purification column designed to separate the methanol from water, and recycle the methanol to the esterification reactor. The water discharged from the bottom of the distillation column is directed to the plant's wastewater treatment facility.

The bottoms liquid exiting the esterification reactor is principally mixed methyl ester product diluted in liquid methanol. This stream is directed to a mixed methyl ester purification column that recovers the methanol as an overhead distillate product for recycle to the esterification reactor, and purifies the mixed methyl ester to product specifications.

MATERIAL BALANCE

We have prepared a stream-by-stream material balance table representing our understanding of a Rennovia adipic acid plant designed to produce 160 kty of fiber-grade adipic acid product at a 90% capacity utilization rate. The table summarizes the feedstock hourly consumptions, and consumption per ton of final adipic acid product.

Table 9.17
RENNOVIA PROCESS MATERIAL BALANCE SUMMARY

Component	Stream #	mt/hr	mt/mt-ADA
Glucose	1	36.97	1.8221
Hydrogen	29	2.16	0.1065
Acetic acid	17	1.74	0.0858
Caustic soda	14	0.73	0.0360
Hydrogen bromide	18	0.05	0.0025
Ethyl acetate	66	0.01	0.0005
Flow improver	54	0.0002	0.0000
ADA final product	60	20.29	1.0000
Glucaric acid intermediate product	12	36.05	1.7767
Methanol	91	2.08	0.1025
Mixed methyl ester by-product	105	4.98	0.2454

The following table is the complete stream-by-stream material balance, consistent with the process flow diagrams presented above.

Table 9.18
RENNOVIA PROCESS MATERIAL BALANCE

Label	Stream Number							
	1 Glucose from BL	2 Fresh Distilled Water	4 Oxy Rx Liq Feed	5 Fresh Air Feed	6 R-101 O/H Gas	7 R-101 O/H Purge	8 R-101 O/H Recycle	9 Combined Air to Oxy Rx
From	BL	BL	Tk-101	Atm	R-101	D-102	D-102	K-101
To	Tk-101	Tk-101	R-101	K-101	D-102	V-101	K-101	R-101
Temperature (°C)	60	25	100	25	100	100	100	150
Pressure (psia)	50	50	400	15	400	400	375	450
Total Flow (mt/hr)	36.97	5.51	236.49	90.26	477.27	91.15	396.12	486.38
Components	MW	BP (°C)						
Hydrogen	2	-253						
Methane	16	-162						
Water	18	100	5.51	156.08				
Nitrogen	28	-210			70.40	376.35	70.40	305.95
Carbon Monoxide	28	-191			0.21	0.04	0.17	0.17
Oxygen	32	-218			19.86	93.87	19.43	84.44
Methanol	32	65						
Sodium Hydroxide	40	na						
Propane	44	-42						
Carbon Dioxide	44	-79			6.84	1.28	5.56	5.56
Acetic Acid	60	118						
Hydrogen Bromide	81	-67						
Ethyl Acetate	88	77						
C ₆ Keto Aldehydes	114	187		0.07				
Hydroxy Monocarboxylic Acids	196	decomp		21.14				
Monocarboxylic Acids	116	205						
Hydroxy Di-carboxylic Acids	150	decomp		10.57				
Di-carboxylic Acids	132	303						
Succinic Acid	118	235						
Glutaric Acid	132	303						
Adipic Acid	146	338						
Mixed Methyl Ester	166	85 (vac)						
Glucose/Dextrose	180	decomp	36.57	36.57				
Fructose	180	decomp	0.04	0.04				
Gluconic/Glucaronic Acid	196	decomp						
Glucaric Acid	210	766		11.66				
Dodecanedioic Acid	230	250 (vac)						
Maltose	342	decomp	0.24	0.24				
Maltotriose	504	decomp	0.08	0.08				
Higher Saccharides	668	decomp	0.04	0.04				

Table 9.18 (Continued)
RENNOVIA PROCESS MATERIAL BALANCE

Label	Stream Number							
	10 Oxy Rx Liq Prod	11 Dryer O/H Vapor	12 Dry Glucaric Acid	13 Scrubber B/S	14 Caustic Feed	15 Caustic Purge	16 Vent Gas	17 Fresh Acetic Acid
From	R-101	E-102	E-102	V-101	Tk-102	E-104	FL-104	BL
To	E-102	D-101	Tk-103	P-104	V-101	WWT	Atm	D-201
Temperature (°C)	100	120	120	75	25	25	25	25
Pressure (psia)	400	30	15	30	50	50	20	50
Total Flow (mt/hr)	243.69	24.03	41.97	91.15	1.82	1.82	91.15	1.74
Components	MW	BP (°C)						
Hydrogen	2	-253						
Methane	16	-162						
Water	18	100	161.59	24.03	54.69	1.09	1.09	
Nitrogen	28	-210						70.40
Carbon Monoxide	28	-191						0.04
Oxygen	32	-218						19.43
Methanol	32	65						
Sodium Hydroxide	40	na			36.46	0.73	0.73	
Propane	44	-42						
Carbon Dioxide	44	-79						1.28
Acetic Acid	60	118						1.74
Hydrogen Bromide	81	-67						
Ethyl Acetate	88	77						
C ₆ Keto Aldehydes	114	187	0.08		0.01			
Hydroxy Monocarboxylic Acids	196	decomp	21.14		3.70			
Monocarboxylic Acids	116	205						
Hydroxy Di-carboxylic Acids	150	decomp	12.43		1.85			
Di-carboxylic Acids	132	303						
Succinic Acid	118	235						
Glutaric Acid	132	303						
Adipic Acid	146	338						
Mixed Methyl Ester	166	85 (vac)						
Glucose/Dextrose	180	decomp						
Fructose	180	decomp						
Gluconic/Glucaronic Acid	196	decomp						
Glucaric Acid	210	766	48.08		36.05			
Dodecanedioic Acid	230	250 (vac)						
Maltose	342	decomp	0.24		0.24			
Maltotriose	504	decomp	0.08		0.08			
Higher Saccharides	668	decomp	0.04		0.04			

Table 9.18 (Continued)
RENNOVIA PROCESS MATERIAL BALANCE

Components	Label	Stream Number							
		18	19	20	21	22	23	24	25
		Fresh Hydrogen Bromide	Rx Feed	Hydro Rx O/H Gas	Hydro Rx B/S Liq Prod	Hydro Rx O/H Condensate	Hydro Rx Gas	Hydro Rx Gas Purge	Hydro Rx Gas Recycle
From	BL	D-201	R-201	R-201	D-202	D-202	D-202	D-202	D-202
To	D-201	R-201	D-202	P-203	D-201	K-201	Burner	K-201	
Temperature (°C)	25	160	160	160	160	160	160	160	160
Pressure (psia)	50	1050	1000	1000	1000	1000	1000	1000	1000
Total Flow (mt/hr)	0.05	194.89	16.56	199.46	3.56	13.00	0.52	12.48	
Hydrogen	2	-253		12.45	4.15	12.45	0.50	11.95	
Methane	16	-162		0.55	0.55	0.55	0.02	0.53	
Water	18	100			12.80				
Nitrogen	28	-210							
Carbon Monoxide	28	-191							
Oxygen	32	-218							
Methanol	32	65							
Sodium Hydroxide	40	na							
Propane	44	-42		3.56	2.33	3.56			
Carbon Dioxide	44	-79							
Acetic Acid	60	118		145.68	145.68				
Hydrogen Bromide	81	-67	0.0450	3.6400	4.21				
Ethyl Acetate	88	77							
C ₆ Keto Aldehydes	114	187		0.01					
Hydroxy Monocarboxylic Acids	196	decomp		3.70					
Monocarboxylic Acids	116	205			2.57				
Hydroxy Di-carboxylic Acids	150	decomp		1.85					
Di-carboxylic Acids	132	303			1.29				
Succinic Acid	118	235							
Glutaric Acid	132	303							
Adipic Acid	146	338		3.60	25.52				
Mixed Methyl Ester	166	85 (vac)							
Glucose/Dextrose	180	decomp							
Fructose	180	decomp							
Gluconic/Glucaronic Acid	196	decomp							
Glucaric Acid	210	766		36.05					
Dodecanedioic Acid	230	250 (vac)							
Maltose	342	decomp		0.24	0.24				
Maltotriose	504	decomp		0.08	0.08				
Higher Saccharides	668	decomp		0.04	0.04				

Table 9.18 (Continued)
RENNOVIA PROCESS MATERIAL BALANCE

Label	Stream Number							
	26	27	28	29	30	31	32	33
Rx Liq	Hydro	Hydro Rx	Hydro	Fresh	Hydro Rx	Crude	Crude	Crude
Gas	Degassed	Rx	H ₂	Combined	Crystallizer	Crystallizer	Centrifuge	
	Liq	Pump	Makeup	H ₂ Feed	Cooling	Slurry	Cake	
		Around						
From	D-203	D-203	P-202	BL	K-201	P-302	CR-301	CN-301
To	K-201	Tk-201	R-201	K-201	R-201	CR-301	CN-301	E-302
Temperature (°C)	160	160	160	25	215	20	20	20
Pressure (psia)	50	50	1000	250	1050	15	50	15
Total Flow (mt/hr)	6.82	192.43	265.04	2.60	21.90	472.09	192.43	27.55
Components	MW	BP (°C)						
Hydrogen	2	-253	4.15	4.98	2.60	18.70		
Methane	16	-162	0.34	0.66		0.87		
Water	18	100		12.80	45.36		32.00	12.80
Nitrogen	28	-210						0.41
Carbon Monoxide	28	-191						
Oxygen	32	-218						
Methanol	32	65						
Sodium Hydroxide	40	na						
Propane	44	-42	2.33	2.80	2.33			
Carbon Dioxide	44	-79						
Acetic Acid	60	118	145.68	174.82		364.20	145.68	5.38
Hydrogen Bromide	81	-67	4.21	5.05		10.53	4.21	0.11
Ethyl Acetate	88	77						
C ₆ Keto Aldehydes	114	187						
Hydroxy Monocarboxylic Acids	196	decomp						
Monocarboxylic Acids	116	205	2.57	3.08		6.43	2.57	0.09
Hydroxy Di-carboxylic Acids	150	decomp						
Di-carboxylic Acids	132	303	1.29	1.55		3.23	1.29	0.05
Succinic Acid	118	235						
Glutaric Acid	132	303						
Adipic Acid	146	338	25.52	26.30		54.80	25.52	21.50
Mixed Methyl Ester	166	85 (vac)						
Glucose/Dextrose	180	decomp						
Fructose	180	decomp						
Gluconic/Glucaronic Acid	196	decomp						
Glucaric Acid	210	766						
Dodecanedioic Acid	230	250 (vac)						
Maltose	342	decomp	0.24	0.29		0.60	0.24	0.01
Maltotriose	504	decomp	0.08	0.10		0.20	0.08	
Higher Saccharides	668	decomp	0.04	0.05		0.10	0.04	

Table 9.18 (Continued)
RENNOVIA PROCESS MATERIAL BALANCE

	Label	Stream Number							
		34 Mother Liquor	35 Crude Centrifuge Filtrate	36 Crude Dryer O/H Vapor	37 Crude Dryer Crystals	38 Hot Water Dissolving Feed	39 Dissolved Crude ADA	40 1st Stage Cooling Loop	41 1st Stage Crystallizer O/H Purge
From	CN-301	CN-301	E-302	E-302	BL	D-302	CR-302	K-301	
To	D-201	D-201	D-301	D-302	D-302	CR-302	E-304	D-304	
Temperature (°C)	20	20	150	150	80	80	50	50	
Pressure (psia)	50	50	50	15	50	50	50	15	
Total Flow (mt/hr)	170.78	164.88	5.90	21.65	9.21	62.58	145.85	13.95	
Components	MW	BP (°C)							
Hydrogen	2	-253							
Methane	16	-162							
Water	18	100	12.80	12.39	0.41		9.21	40.50	91.75
Nitrogen	28	-210							13.95
Carbon Monoxide	28	-191							
Oxygen	32	-218							
Methanol	32	65							
Sodium Hydroxide	40	na							
Propane	44	-42							
Carbon Dioxide	44	-79							
Acetic Acid	60	118	145.68	140.30	5.38				
Hydrogen Bromide	81	-67	4.21	4.10	0.11				
Ethyl Acetate	88	77							
C ₆ Keto Aldehydes	114	187							
Hydroxy Monocarboxylic Acids	196	decomp							
Monocarboxylic Acids	116	205	2.48	2.48		0.09		0.09	0.23
Hydroxy Di-carboxylic Acids	150	decomp							
Di-carboxylic Acids	132	303	1.24	1.24		0.05		0.05	0.13
Succinic Acid	118	235							
Glutaric Acid	132	303							
Adipic Acid	146	338	4.02	4.02		21.50		21.93	53.75
Mixed Methyl Ester	166	85 (vac)							
Glucose/Dextrose	180	decomp							
Fructose	180	decomp							
Gluconic/Glucaronic Acid	196	decomp							
Glucaric Acid	210	766							
Dodecanedioic Acid	230	250 (vac)							
Maltose	342	decomp	0.23	0.23		0.01		0.01	
Maltotriose	504	decomp	0.08	0.08					
Higher Saccharides	668	decomp	0.04	0.04					

Table 9.18 (Continued)
RENNOVIA PROCESS MATERIAL BALANCE

Components	MW	BP (°C)	Stream Number							
			42	43	44	45	46	47	48	49
Label			1st Stage Crystallizer Slurry	1st Stage Centrifuge Filtrate	1st Stage Centrifuge Cake	Dissolving Hot Water Feed	2nd Stage Crystallizer Cooling Loop	2nd Stage Crystallizer O/H Purge	2nd Stage Crystallizer Slurry	
From	CR-302	CN-302	CN-302		BL	D-305	P-314	CR-303	CR-303	
To	CN-302	D-302	D-305		CR-303	CR-302	K-302		CN-303	
Temperature (°C)	50	50	50	80	80	35	35			35
Pressure (psia)	30	50	50	50	50	50	1			50
Total Flow (mt/hr)	58.78	31.86	26.93	35.91	91.54	194.52	27.30			64.84
Hydrogen	2	-253								
Methane	16	-162								
Water	18	100	36.70	31.29	5	35.91	69.00	125.10	27.30	41.70
Nitrogen	28	-210								
Carbon Monoxide	28	-191								
Oxygen	32	-218								
Methanol	32	65								
Sodium Hydroxide	40	na								
Propane	44	-42								
Carbon Dioxide	44	-79								
Acetic Acid	60	118								
Hydrogen Bromide	81	-67								
Ethyl Acetate	88	77								
C ₆ Keto Aldehydes	114	187								
Hydroxy Monocarboxylic Acids	196	decomp					0.21		0.07	
Monocarboxylic Acids	116	205	0.09	0.08	0.01		0.01			
Hydroxy Di-carboxylic Acids	150	decomp								
Di-carboxylic Acids	132	303	0.05	0.05	0.01		0.01			
Succinic Acid	118	235					0.21		0.07	
Glutaric Acid	132	303								
Adipic Acid	146	338	21.93	0.43	21.50		22.52	69.00		23.00
Mixed Methyl Ester	166	85 (vac)								
Glucose/Dextrose	180	decomp								
Fructose	180	decomp								
Gluconic/Glucaronic Acid	196	decomp								
Glucaric Acid	210	766								
Dodecanedioic Acid	230	250 (vac)								
Maltose	342	decomp	0.01	0.01						
Maltotriose	504	decomp								
Higher Saccharides	668	decomp								

Table 9.18 (Continued)
RENNOVIA PROCESS MATERIAL BALANCE

	Label	Stream Number							
		50	51	52	53	54	55	56	57
	2nd Stage Centrifuge Filtrate	2nd Stage Centrifuge Cake	2nd Stage Centrifuge Filtrate	2nd Stage Centrifuge Recycle	2nd Stage Filtrate	Flow Improver	Hot ADA Crystals	ADA Dust	Dryer Purge Gas
From	CN-303	CN-303	CN-303	CN-303	Tk-402	E-402	CV-404	FL-401	
To	D-305	Tk-401	D-305	WWT	E-404	E-404	D-401	E-403	
Temperature (°C)	35	35	35	35	25	140	140	140	
Pressure (psia)	50	15	50	50	15	15	15	15	
Total Flow (mt/hr)	36.42	28.42	29.14	7.28	0.00	20.35	1.01	7.06	
Components	MW	BP (°C)							
Hydrogen	2	-253							
Methane	16	-162							
Water	18	100	34.60	7.10	27.68	6.92		0.04	7.06
Nitrogen	28	-210							
Carbon Monoxide	28	-191							
Oxygen	32	-218							
Methanol	32	65							
Sodium Hydroxide	40	na							
Propane	44	-42							
Carbon Dioxide	44	-79							
Acetic Acid	60	118							
Hydrogen Bromide	81	-67							
Ethyl Acetate	88	77							
C ₆ Keto Aldehydes	114	187							
Hydroxy Monocarboxylic Acids	196	decomp	0.06	0.01	0.05	0.01		0.01	
Monocarboxylic Acids	116	205							
Hydroxy Di-carboxylic Acids	150	decomp							
Di-carboxylic Acids	132	303							
Succinic Acid	118	235	0.06	0.01	0.05	0.01		0.01	
Glutaric Acid	132	303							
Adipic Acid	146	338	1.70	21.30	1.36	0.34		20.29	1.01
Mixed Methyl Ester	166	85 (vac)							
Glucose/Dextrose	180	decomp							
Fructose	180	decomp							
Gluconic/Glucaronic Acid	196	decomp							
Glucaric Acid	210	766							
Dodecanedioic Acid	230	250 (vac)				0.00			
Maltose	342	decomp							
Maltotriose	504	decomp							
Higher Saccharides	668	decomp							

Table 9.18 (Continued)
RENNOVIA PROCESS MATERIAL BALANCE

	Label	Stream Number							
		58	59	60	61	63	64	65	66
	ADA Dust Dissolving Water	ADA Dust Solution	ADA Product	Hydro Rx Condensate Purge	C-501 O/H Stream	C501 Reflux	D-501 Bottom Water	Ethyl Acetate Phase	
From	BL	D-401	Tk-403	D-202	C-501	D-501	D-501	Tk-502	
To	D-401	CR-302	Packagin	WWT	E-501	C-501	C-502	C-501	
Temperature (°C)	80	80	25	160	72	72	72	25	
Pressure (psia)	50	50	15	1000	20	50	50	50	
Total Flow (mt/hr)	10.15	11.16	20.35	3.56	155.62	141.69	13.93	0.01	
Components	MW	BP (°C)							
Hydrogen	2	-253							
Methane	16	-162							
Water	18	100	10.15	10.15	0.04		17.36	4.68	12.68
Nitrogen	28	-210							
Carbon Monoxide	28	-191							
Oxygen	32	-218							
Methanol	32	65							
Sodium Hydroxide	40	na							
Propane	44	-42			3.56				
Carbon Dioxide	44	-79							
Acetic Acid	60	118				0.13		0.13	
Hydrogen Bromide	81	-67							
Ethyl Acetate	88	77				138.13	137.01	1.12	0.01
C ₆ Keto Aldehydes	114	187							
Hydroxy Monocarboxylic Acids	196	decomp			0.01				
Monocarboxylic Acids	116	205							
Hydroxy Di-carboxylic Acids	150	decomp							
Di-carboxylic Acids	132	303							
Succinic Acid	118	235		0.01					
Glutaric Acid	132	303							
Adipic Acid	146	338	1.01	20.29					
Mixed Methyl Ester	166	85 (vac)							
Glucose/Dextrose	180	decomp							
Fructose	180	decomp							
Gluconic/Glucaronic Acid	196	decomp							
Glucaric Acid	210	766							
Dodecanedioic Acid	230	250 (vac)		0.00					
Maltose	342	decomp							
Maltotriose	504	decomp							
Higher Saccharides	668	decomp							

Table 9.18 (Continued)
RENNOVIA PROCESS MATERIAL BALANCE

Components	MW	BP (°C)	Stream Number							
			67	68	69	70	71	72	73	74
			Label	C-501 B/S	C-501 Reboil	C-501 Bottoms Discharge	C-502 O/H Stream	C-502 Reflux	C-502 Distillate Product	C-502 Bottoms
Hydrogen	2	-253								
Methane	16	-162								
Water	18	100	0.23	0.11	0.12	0.11	0.10	0.01	26.61	13.94
Nitrogen	28	-210								
Carbon Monoxide	28	-191								
Oxygen	32	-218								
Methanol	32	65								
Sodium Hydroxide	40	na								
Propane	44	-42								
Carbon Dioxide	44	-79								
Acetic Acid	60	118	276.55	131.00	145.55				0.27	0.14
Hydrogen Bromide	81	-67	8.00	3.79	4.21					
Ethyl Acetate	88	77				12.21	11.10	1.11	0.02	0.01
C ₆ Keto Aldehydes	114	187								
Hydroxy Monocarboxylic Acids	196	decomp								
Monocarboxylic Acids	116	205	4.71	2.23	2.48					
Hydroxy Di-carboxylic Acids	150	decomp								
Di-carboxylic Acids	132	303	2.36	1.12	1.24					
Succinic Acid	118	235								
Glutaric Acid	132	303								
Adipic Acid	146	338	7.64	3.62	4.02					
Mixed Methyl Ester	166	85 (vac)								
Glucose/Dextrose	180	decomp								
Fructose	180	decomp								
Gluconic/Glucaronic Acid	196	decomp								
Glucaric Acid	210	766								
Dodecanedioic Acid	230	250 (vac)								
Maltose	342	decomp	0.44	0.21	0.23					
Maltotriose	504	decomp	0.15	0.07	0.08					
Higher Saccharides	668	decomp	0.08	0.04	0.04					

Table 9.18 (Continued)
RENNOVIA PROCESS MATERIAL BALANCE

Components	MW	BP (°C)	Stream Number							
			75 Label C-502 B/S Discharge	76 WWT Purge	77 Acetic Acid Recycle	78 Oxidation Purge to WWT	79 Filtrate Water Recycle	80 Acetic Acid Vapor - D601 O/H	81 Rotary Dryer O/H Vapor	82 Acetic Acid Recycle
From	P-506	FL-501	FL-501	FL-102AB	FL-102AB	D-601	E-602	P-604		
To	WWT	WWT	D-201	Tk-601	D-101	E-603	E-603	D-201		
Temperature (°C)	105	50	50	100	100	120	120	120		
Pressure (psia)	50	50	50	400	400	20	20	75		
Total Flow (mt/hr)	12.81	0.36	157.62	4.59	176.83	142.00	4.64	148.23		
Hydrogen	2	-253								
Methane	16	-162								
Water	18	100	12.67	0.00	0.12	4.17	133.39	0.12	0.12	
Nitrogen	28	-210								
Carbon Monoxide	28	-191								
Oxygen	32	-218								
Methanol	32	65								
Sodium Hydroxide	40	na								
Propane	44	-42								
Carbon Dioxide	44	-79								
Acetic Acid	60	118	0.13	145.55			137.89	4.51	143.94	
Hydrogen Bromide	81	-67		4.21			3.99	0.13	4.17	
Ethyl Acetate	88	77	0.01							
C ₆ Keto Aldehydes	114	187				0.07				
Hydroxy Monocarboxylic Acids	196	decomp				0.04	21.14			
Monocarboxylic Acids	116	205			2.48					
Hydroxy Di-carboxylic Acids	150	decomp				0.02	10.57			
Di-carboxylic Acids	132	303			1.24					
Succinic Acid	118	235								
Glutaric Acid	132	303								
Adipic Acid	146	338			4.02					
Mixed Methyl Ester	166	85 (vac)								
Glucose/Dextrose	180	decomp								
Fructose	180	decomp								
Gluconic/Glucaronic Acid	196	decomp								
Glucaric Acid	210	766				0.36	11.66			
Dodecanedioic Acid	230	250 (vac)								
Maltose	342	decomp		0.24						
Maltotriose	504	decomp		0.08						
Higher Saccharides	668	decomp		0.04						

Table 9.18 (Continued)
RENNOVIA PROCESS MATERIAL BALANCE

Components	MW	BP (°C)	Stream Number							
			83	84	85	86	87	88	89	90
Hydrogen	2	-253								
Methane	16	-162								
Water	18	100								
Nitrogen	28	-210								
Carbon Monoxide	28	-191								
Oxygen	32	-218								
Methanol	32	65					9.24	9.24	8.40	17.64
Sodium Hydroxide	40	na								26.46
Propane	44	-42								
Carbon Dioxide	44	-79								
Acetic Acid	60	118	7.66	1.54	6.12					
Hydrogen Bromide	81	-67	0.22	0.05	0.18		0.61			0.61
Ethyl Acetate	88	77					0.05			0.05
C ₆ Keto Aldehydes	114	187								
Hydroxy Monocarboxylic Acids	196	decomp								
Monocarboxylic Acids	116	205	2.48	0.26	2.22					
Hydroxy Di-carboxylic Acids	150	decomp					2.22			2.22
Di-carboxylic Acids	132	303	1.24	0.13	1.11		1.11			1.11
Succinic Acid	118	235								
Glutaric Acid	132	303								
Adipic Acid	146	338	4.02	3.60	0.42		0.42			0.42
Mixed Methyl Ester	166	85 (vac)								
Glucose/Dextrose	180	decomp					0.42			0.42
Fructose	180	decomp								
Gluconic/Glucaronic Acid	196	decomp								
Glucaric Acid	210	766								
Dodecanedioic Acid	230	250 (vac)								
Maltose	342	decomp								
Maltotriose	504	decomp								
Higher Saccharides	668	decomp								

Table 9.18 (Continued)
RENNOVIA PROCESS MATERIAL BALANCE

Components	MW	BP (°C)	Stream Number							
			91	92	93	94	95	96	97	98
Label	Total	R-601AB	R-601AB	C-601	C-601	C-601	C-601	C-601	C-601	C-601
Methanol	Rx O/H	Rx B/S	B/S	Reboil	B/S	O/H				Reflux
Fresh	Product	Product	Product	Liquid	Vapor					
Feed										
From	Tk-602	R-601AB	R-601AB	C-601	E-607	C-601	C-601	P-606AS		
To	R-601AB	E-604	P-611AS	WWT	C-601	P-607AS	E-606	C-601		
Temperature (°C)	25	120	120	130	130	130	93	93		
Pressure (psia)	100	60	60	40	40	40	40	40		
Total Flow (mt/hr)	2.08	35.13	13.38	1.17	93.52	94.69	101.88	67.92		
Hydrogen	2	-253								
Methane	16	-162								
Water	18	100	0.84		0.50	40.32	40.82	1.02	0.68	
Nitrogen	28	-210								
Carbon Monoxide	28	-191								
Oxygen	32	-218								
Methanol	32	65	2.08	33.63	8.40	0.01	0.80	0.81	100.86	67.24
Sodium Hydroxide	40	na								
Propane	44	-42								
Carbon Dioxide	44	-79								
Acetic Acid	60	118								
Hydrogen Bromide	81	-67	0.61		0.61	48.80	49.41			
Ethyl Acetate	88	77	0.05		0.05	3.60	3.65			
C ₆ Keto Aldehydes	114	187								
Hydroxy Monocarboxylic Acids	196	decomp								
Monocarboxylic Acids	116	205								
Hydroxy Di-carboxylic Acids	150	decomp								
Di-carboxylic Acids	132	303								
Succinic Acid	118	235								
Glutaric Acid	132	303								
Adipic Acid	146	338								
Mixed Methyl Ester	166	85 (vac)		4.98						
Glucose/Dextrose	180	decomp								
Fructose	180	decomp								
Gluconic/Glucaronic Acid	196	decomp								
Glucaric Acid	210	766								
Dodecanedioic Acid	230	250 (vac)								
Maltose	342	decomp								
Maltotriose	504	decomp								
Higher Saccharides	668	decomp								

Table 9.18 (Concluded)
RENNOVIA PROCESS MATERIAL BALANCE

Components	MW	BP (°C)	Stream Number						
			99	100	101	102	103	104	105
Hydrogen	2	-253							
Methane	16	-162							
Water	18	100	0.34						
Nitrogen	28	-210							
Carbon Monoxide	28	-191							
Oxygen	32	-218							
Methanol	32	65	33.62	33.40	25.00	0.00	25.20	25.20	4.98
Sodium Hydroxide	40	na							
Propane	44	-42							
Carbon Dioxide	44	-79							
Acetic Acid	60	118							
Hydrogen Bromide	81	-67							
Ethyl Acetate	88	77							
C ₆ Keto Aldehydes	114	187							
Hydroxy Monocarboxylic Acids	196	decomp							
Monocarboxylic Acids	116	205							
Hydroxy Di-carboxylic Acids	150	decomp							
Di-carboxylic Acids	132	303							
Succinic Acid	118	235							
Glutaric Acid	132	303							
Adipic Acid	146	338							
Mixed Methyl Ester	166	85 (vac)				25.20	25.20	4.98	
Glucose/Dextrose	180	decomp							
Fructose	180	decomp							
Gluconic/Glucaronic Acid	196	decomp							
Glucaric Acid	210	766							
Dodecanedioic Acid	230	250 (vac)							
Maltose	342	decomp							
Maltotriose	504	decomp							
Higher Saccharides	668	decomp							

EQUIPMENT LIST

We have prepared the following equipment list for tagged process equipment using the material balance, and provide below duty specifications for the equipment.

Table 9.19
RENOVIA PROCESS EQUIPMENT LIST

Distillation Columns		# Installed	Materials of Construction	L x D (ft)	DesP (psia)	DesT (°C)	# of Trays	Internals Details
C-501		1	304SS	92 x 16	50	200	36	Sieve trays
C-502		1	304SS	124 x 4	70	140	52	Sieve trays
C-601		1	CS	128 x 3	50	300	54	316L SS sieve trays
C-602		1	CS	84 x 4	Full Vac	450	32	Divided wall—struc packing
Centrifuges		# Installed	Materials of Construction	L x D (ft)	DesP (psia)	DesT (°C)	Duty (BHP)	Screen Opening (mils) Type (Bowl or Screen)
CN-301		4	304SS	8 x 6	150	250	125	Pusher 0.1
CN-302		4	304SS	8 x 6	150	250	125	Pusher 0.1
CN-303		4	304SS	8 x 6	150	250	125	Pusher 0.1
Crystallizers		# Installed	Materials of Construction	L x D (ft)	DesP (psia)	DesT (°C)	Duty (MM-btu/hr)	Suspension or Draft Tube? Surf Area (ft2)
CR-301		1	304SS	32 x 8	Full Vac	250	0	Suspension 0
CR-302		1	304SS	32 x 8	Full Vac	250	0	Suspension 0
CR-303		1	304SS	32 x 8	Full Vac	250	0	Suspension 0
Solids Conveyors		# Installed	Materials of Construction	L x w (ft)	DesP (psia)	DesT (°C)	Mass Flow (lbs/hr)	Belt, Pneumatic, or Screw? Motor HP
CV-101		1	304SS	50 x 6	15	150	86,921	Closed Belt conveyor 73
CV-102		1	304SS	50 x 6	15	150	94,617	Closed Belt conveyor 80
CV-103		1	304SS	50 x 6	15	150	94,617	Closed Belt conveyor 80
CV-301		1	304SS	50 x 4	15	150	57,683	Closed Belt conveyor 49
CV-302		1	304SS	50 x 4	15	150	46,040	Closed Belt conveyor 39
CV-303		1	304SS	50 x 4	15	150	59,733	Closed Belt conveyor 51
CV-304		1	304SS	50 x 4	15	150	62,666	Closed Belt conveyor 53
CV-401		1	304SS	50 x 4	15	150	62,666	Closed Belt conveyor 53
CV-403		1	304SS	50 x 0.5	15	150	1	Closed Belt conveyor 0
CV-404		1	304SS	50 x 0.5	15	150	2,426	Closed Belt conveyor 2
CV-405		1	304SS	50 x 4	15	150	44,872	Closed Belt conveyor 38
CV-406		1	304SS	50 x 4	15	150	44,872	Closed Belt conveyor 38
CV-407		1	304SS	50 x 4	15	150	44,872	Closed Belt conveyor 38
CV-601		1	304SS	50 x 1	15	150	11,929	Closed Belt conveyor 10
Drums		# Installed	Materials of Construction	Vol (ft3)	L x D (ft)	DesP (psia)	DesT (°C)	Orientation
D-101		1	304SS	7,000	52 x 13	15	150	Vertical-API 510
D-102		1	304SS	200	16 x 4	450	150	Vertical-API 510
D-103		1	304SS	1,750	32 x 8	50	150	Horiz-API 510
D-201		1	304SS	7,000	52 x 13	15	200	Vertical-API 510
D-202		1	304SS	200	16 x 4	1,250	200	Horiz-API 510
D-203		1	304SS	678	24 x 6	1,250	200	Vertical-API 510
D-301		1	304SS	200	16 x 4	50	200	Horiz-API 510
D-302		1	304 SS	893	26.3 x 6.5	50	250	Horiz-API 510
D-303		1	304 SS	25	8 x 2	Full Vac	150	Vertical-API 510
D-304		1	304 SS	67.9	10 x 2.5	Full Vac	250	Horiz-API 510
D-305		1	304 SS	893	26.3 x 6.5	50	250	Horiz-API 510
D-306		1	304 SS	25	8 x 2	Full Vac	150	Vertical-API 510
D-307		1	304SS	200	16 x 4	50	200	Horiz-API 510
D-401		1	304 SS	893	26.3 x 6.5	50	250	Horiz-API 510
D-402		1	304SS	200	16 x 4	50	200	Horiz-API 510

Table 9.19 (Continued)
RENOVIA PROCESS EQUIPMENT LIST

Drums	# Installed	Materials of Construction	Vol (ft3)	L x D (ft)	DesP (psia)	DesT (°C)	Orientation
D-501	E-501 Receiver	1	304SS	200	16 x 4	50	200 Horiz-API 510
D-502	E-503 Receiver	1	304SS	200	16 x 4	50	200 Horiz-API 510
D-503	E-506 Receiver	1	304SS	200	16 x 4	50	200 Horiz-API 510
D-601	Vapor Separating Drum	1	304SS	1,379	32 x 8	100	200 Horiz-API 510
D-602	Slurry Dissolving Drum	1	304SS	200	16 x 4	100	200 Vert-API 510
D-603	Acid Mixing Tank	1	304SS	122	12 x 3.5	100	200 Vert-API 510
D-604	E-606 Receiver	1	304SS	891	26 x 6.5	100	150 Horiz-API 510
D-605	K-601 K/O Drum	1	304SS	200	16 x 4	50	200 Vert-API 510
D-606	E-608 Receiver	1	304SS	292	18 x 4.5	50	200 Horiz-API 510
Heat Exchangers	# Installed	Materials of Construction Shell Side/Tube Side	Duty (MM-btu/hr)	Surf Area (ft2)	DesP (psia) Tube/Shell	DesT (°C) Tube/Shell	HX Configuration
E-101	Glucose Feed Heater	1	CS/304SS	22.1	1,470	450/75	150/150 S&T—API660
E-102	Glucaric Acid Evaporator	1	304SS	355	35,500	75	150 Rotary evaporator
E-103	E-102 Condenser	1	304SS/CS	350	35,500	75/75	150/100 S&T—API660
E-104AB	Recycle Caustic Coolers	2	CS/304SS	2.55	252	450/75	150/75 S&T—API660
E-105	Rx Liquids Chiller	1	CS/304SS	24.2	3,224	450/100	150/75 S&T—API660
E-201	Feed/Product Exchanger	1	CS/304SS	39.8	1,990	1,250/350	200/300 S&T—API660
E-202	Hydro Trim Heater	1	304SS/304SS	7.5	375	1,250/250	200/200 S&T—API660
E-203	Hydro Product Cooler	1	304SS/304SS	21.4	1,070	1,250/75	200/75 S&T—API660
E-204	Hydro Condenser	1	CS/304SS	17.64	882	1,250/75	200/75 S&T—API660
E-205	Rx Liquid Cooler	1	CS/304SS	42.8	2,140	250/75	200/75 S&T—API660
E-301	CR-301 Glycol Cooler	1	CS/304SS	29.9	1,490	75/75	150/150 S&T—API660
E-302	Crude ADA Rotary Dryer	1	304SS	7.3	367	350	450 Rotary evaporator
E-303	E-302 Condenser	1	CS/304SS	7.4	375	50/350	150/450 S&T—API660
E-304	1st Stage Glycol Cooler	1	CS/304SS	4.8	240	75/75	150/150 S&T—API660
E-305	K-301 Condenser	1	CS/304SS	47.6	2,381	50/75	150/150 S&T—API660
E-306	2nd Stage Glycol Cooler	1	CS/304SS	7.6	381	75/75	150/150 S&T—API660
E-401	1st Stage Rotary Dryer	1	304SS	21.98	2,250	350	450 Rotary Dryer (Atm P)
E-402	2nd Stage Rotary Dryer	1	304SS	9.42	975	350	450 Rotary Dryer (Atm P)
E-403	Dryer O/H Condenser	1	304SS/304SS	15.65	1,520	15/75	250/150 S&T—API660
E-404	ADA Cooler	1	304SS	4.5	550	50	250 Rotary Dryer (Atm P)
E-501	C-501 Condenser	1	CS/304SS	525.7	35,048	75/75	125/75 S&T—API660
E-502AB	C-501 Reboiler	2	CS/304SS	291.8	14,590	50/350	150/250 S&T—API660
E-503	C-502 Condenser	1	CS/304SS	3.5	176	75/75	150/75 S&T—API660
E-504AB	C-502 Reboiler	2	CS/304SS	16.7	834	75/75	150/175 S&T—API660
E-505	Acetic Acid Rotary Dryer	1	304SS	196.8	9,842	350	275 Rotary Dryer (Atm P)
E-506	Acetic Acid Condenser	1	CS/304SS	196.8	9,842	75/50	150/75 S&T—API660
E-601	Solution Vaporizer	1	304SS/CS	225	11,232	350/50	200/200 S&T—API660
E-602	Acetic Acid Rotary Dryer	1	304SS	14.3	716	50	200 Rotary Dryer (Atm P)
E-603	LLP Steam Generator	1	304SS/CS	202	10,105	50/50	200/200 S&T—API660
E-604	Methanol Column Pre-Heater	1	CS/CS	0.4	39	75/75	150/100 S&T—API660
E-605	Methanol Vaporizer	1	CS/CS	30	1,500	350/100	250/200 S&T—API660
E-606	C-601 Condenser	1	CS/CS	287	14,350	100/100	150/75 S&T—API660
E-607AB	C-601 Reboilers	2	CS/304SS	124	12,400	350/75	250/150 S&T—API660
E-608	K-601 Condenser	1	CS/304SS	37.8	2,520	75/75	100/75 S&T—API660
E-609AB	C-602 Reboilers	2	CS/CS	13.9	1,390	350/100	250/250 S&T—API660
E-610	Ester Preheat Exchanger	1	304SS/304SS	1.1	110	100/100	150/250 S&T—API660
E-612	Ester Cooler	1	CS/304SS	0.55	55	75/75	150/75 S&T—API660

Table 9.19 (Continued)
RENOVIA PROCESS EQUIPMENT LIST

Filters		# Installed	Materials of Construction	Flow Rate (lbs/hr)	DesP (psia) Tubes	Dest (°C)	Opening Size (microns)	
FL-101 Compressed Air filter		1	CS	200,000	Full Vac	100	0.05	Pulsed air baghouse
FL-102AB R-101 Product Filters		2	304L SS	226,000	450	150	0.5	Dual basket, 3way valve
FL-103 Glucaric acid vapor filter		1	304L SS	355,500	50	150	0.05	Fibreglas cartridge filter
FL-104AB Scrubber Exhaust Filters		2	CS	201,000	100	100	0.05	Pulsed air baghouse
FL-401 Dryer Vapor Filter		1	304 SS	15,567	15	150	0.05	Pulsed air baghouse
FL-601AB Crystal Filter		2	304 SS	17,221	100	175	0.5	Continuous pressure liquid filter
Compressors		# Installed	Fluid/Type Machine	BHP	SCFM	Pin (psia)	Pout (psia)	Matl of Construction/Design Details
K-101 Feed Air Compressor		1	Air/Centrif	2,100.0	247,000	400	450	CS/1-stage centrifugal
K-201 Hydrogen Compressor		1	Hydrogen/Twin screw	5,000.0	143,000	950	1,050	304SS/Twin screw
K-301 1st Stage Compressor		1	H2O /Liq Ring	11,000	46,400	2	15	304SS/Liquid ring vac pump
K-302 2nd Stage Compressor		1	H2O /Liq Ring	8,000	16,800	1	15	304SS/Liquid ring vac pump
K-601 C-602 Vacuum Pump		1	Methanol/Liq Ring	9,200	19,350	1	15	304SS/Liquid ring vac pump
Mixers and Agitators		# Installed	Materials of Construction	BHP	DesT (°C)	Liquid	Viscosity (cs)	Mixer Type
M-101 D-101 Agitator		1	304SS	70	150	GLU Soln	1.5	Top entering
M-201 D-201 Agitator		1	304SS	70	200	GLC Acid Soln	1.5	Top entering
M-202 TK-201 Agitator		1	304SS	500	200	ADA Soln	1.5	Side entering
M-301 D-302 Agitator		1	304SS	9	125	ADA Soln	1.5	Top entering
M-302 D-305 Agitator		1	304SS	9	125	ADA Soln	1.5	Top entering
M-401 D-401 Agitator		1	304SS	9	125	ADA Soln	1.5	Top entering
M-601 D-602 Agitator		1	304SS	4	150	Acetic Acid	0.8	Top entering
M-602 D-603 Agitator		1	304SS	2	150	Methanol	0.5	Top entering
Pumps		# Installed	Materials of Construction	gpm x hd (ft)	Liquid	DesP (psia)	DesT (°C)	Type Pump
P-101AS Caustic Feed Pumps		2	304 SS	8 x 1,040	NaOH Soln	450	100	Centrifugal-API 610
P-102AS Glucose Feed Pumps		2	304 SS	862 x 1,040	GLU soln	450	100	Centrifugal-API 610
P-103AS D-103 Pumps		2	304 SS	713 x 230	H2O	450	100	Centrifugal-API 610
P-104AS Caustic Recycle Pumps		2	304 SS	402 x 150	NaOH Soln	450	125	Centrifugal-API 610
P-201AS Hydro Feed Pumps		2	304 SS	848 x 2,300	GLU soln	1,100	125	Centrifugal-API 610
P-202AS Hydro Recycle Pumps		2	304 SS	1,725 x 230	ADA Soln	1,100	200	Centrifugal-API 610
P-203 Hydro Turbo Generator		1	304 SS	856 x 2,150	ADA Soln	1,100	200	Moyno Turbine Generator
P-204AS Hydro Condensate Pumps		2	304 SS	40 x 150	H2O	100	200	Centrifugal-API 610
P-205AS Crude ADA Pumps		2	304 SS	800 x 150	ADA Soln	100	200	Centrifugal-API 610
P-301AS Crude ADA Pumps		2	304 SS	800 x 150	ADA Soln	100	100	Moyno slurry pumps
P-302AS CR-301 Circulating Pumps		2	304 SS	2,390 x 150	ADA Soln	100	100	Centrifugal-API 610
P-303AS CN-301 Filtrate Pumps		2	304 SS	682 x 150	Acetic Acid	100	100	Centrifugal-API 610
P-304AS D-301 Recycle Pumps		2	304 SS	24 x 150	Acetic Acid	100	150	Centrifugal-API 610
P-305AS D-302 Pumps		2	304 SS	340 x 150	ADA Soln	100	100	Centrifugal-API 610
P-306AS D-304 Pumps		2	304 SS	95 x 150	H2O	100	100	Centrifugal-API 610
P-307AS 1st Stage Slurry Pumps		2	304 SS	295 x 150	ADA Soln	100	100	Moyno slurry pumps
P-308AS CN-302 Filtrate Pumps		2	304 SS	175 x 150	H2O	100	100	Centrifugal-API 610
P-309AS D-305 Pumps		2	304 SS	406 x 150	ADA Soln	100	100	Centrifugal-API 610
P-310AS CR-303 Circulating Pumps		2	304 SS	858 x 150	ADA Soln	100	100	Centrifugal-API 610
P-311AS D-307 Pumps		2	304 SS	120 x 150	H2O	100	100	Centrifugal-API 610
P-312AS 2nd Stage Slurry Pumps		2	304 SS	286 x 150	ADA Soln	100	100	Moyno slurry pumps
P-313AS CN-303 Filtrate Pumps		2	304 SS	161 x 150	ADA Soln	100	100	Centrifugal-API 610
P-314AS CR-302 Cooling Pumps		2	304 SS	882 x 150	ADA Soln	100	100	Centrifugal-API 610

Table 9.19 (Continued)
RENOVIA PROCESS EQUIPMENT LIST

Pumps		# Installed	Materials of Construction	gpm x hd (ft)	Liquid	DesP (psia)	DesT (°C)	Type Pump	Pump HP		
P-401AS	Dust Solution Pumps	2	304 SS	49 x 150	ADA Soln	100	100	Centrifugal-API 610	1.9		
P-402AS	Condensate Pumps	2	304 SS	31 x 150	H2O	100	150	Centrifugal-API 610	1.2		
P-501AS	Acetic Acid Feed Pumps	2	304 SS	705 x 100	Acetic Acid Soln	100	100	Centrifugal-API 610	17.8		
P-502AS	C-501 Reflux Pumps	2	304 SS	852 x 150	Ethyl Acetate	50	100	Centrifugal-API 610	32.3		
P-503AS	Water Pumps	2	304 SS	50 x 150	H2O	100	150	Centrifugal-API 610	1.9		
P-504AS	C-501 B/S Pumps	2	304 SS	1,650 x 150	Acetic Acid	50	150	Centrifugal-API 610	62.5		
P-505AS	C-502 Reflux Pumps	2	304 SS	55 x 150	Ethyl Acetate	75	125	Centrifugal-API 610	2.1		
P-506AS	C-502 B/S Pumps	2	304 SS	101 x 150	H2O	75	125	Centrifugal-API 610	3.8		
P-507AS	Ethyl Acetate Pumps	2	304 SS	0.04 x 150	Ethyl Acetate	75	75	Metering pump	0.002		
P-508AS	Acetic Acid Recycle Pumps	2	304 SS	605 x 150	Acetic Acid	75	150	Centrifugal-API 610	22.9		
P-509AS	E-505 WWT Pumps	2	304 SS	54 x 150	Heavies	75	150	Centrifugal-API 610	2.1		
P-601AS	Acid Solution Feed Pumps	2	304 SS	695 x 250	Acetic Acid	100	175	Centrifugal-API 610	43.9		
P-602AS	Methanol Feed Pumps	2	304 SS	9 x 150	Methanol	100	100	Centrifugal-API 610	0.3		
P-603AS	Crystal Slurry Pumps	2	304 SS	69 x 250	Acetic Acid	100	175	Myno slurry pumps	4.4		
P-604AS	Slurry Recycle Pumps	2	304 SS	654 x 150	Acetic Acid	100	175	Centrifugal-API 610	24.8		
P-605AS	Mixed Methanol Feed Pumps	2	304 SS	62 x 150	Methanol	100	175	Centrifugal-API 610	2.3		
P-606AS	C-601 Reflux Pumps	2	304 SS	450 x 150	Ethyl acetate	100	175	Centrifugal-API 610	17.1		
P-607AS	C-601 B/S Pumps	2	304 SS	418 x 150	Methanol	100	175	Centrifugal-API 610	15.8		
P-608AS	C-602 Reflux Pumps	2	304 SS	150 x 150	Methanol	100	200	Centrifugal-API 610	5.7		
P-609AS	C-602 B/S Pumps	2	CS	111 x 150	Ester	100	250	Centrifugal-API 610	4.2		
P-610AS	Ester Pumps	2	CS	22 x 150	Ester	100	250	Centrifugal-API 610	0.8		
P-611AS	R-601 B/S Pumps	2	304SS	59 x 150	Methanol	100	175	Centrifugal-API 610	2.2		
P-612AS	TK-603 Pumps	2	CS	22 x 150	Ester	100	250	Centrifugal-API 610	0.8		
Reactors		# Installed	Materials of Construction	Vol (ft3)	L x D (ft)	DesP (psia)	DesT (°C)	Internals			
R-101AB	Glucose Oxidation Reactors	2	304 SS	855	24 x 6	450	125	4 catalyst support beds with inter-cooling manifolds, bottom vapor distributor & top liquid distributor			
R-201AB	Hydro Reactors	2	304 SS	3,365	40 x 10	1,100	200	Single trickle catalyst bed with top liq distributor & bottom vapor distributor			
R-601AB	Mixed Ester Reactors	2	304SS	150	48 x 3	50	400	8 RX zones, w 6 trays above and below beds			
Specially Packaged Equipment		# Installed	Duty								
S-101	R-101 Vapor Cyclone	1	4.5L x 3D								
S-301	E-302 Overhead Cyclone	1	4.5L x 3D								
S-401	Cyclone Dust Separator	1	4.5L x 3D								
S-102	Process Flare System	2	100 MM Btu/hr each	250 ft x 24 inch				John Zink or equiv	auto strm inject		
S-103	Process Computer Control System	1	800 loops Honeywell Experion				Honeywell Experion or equiv				
S-104	Vacuum Line Compression System	1	5 psia x 50 MM scf/hr								
S-105	N2 PSA System	1	10 MM-scfh at 99% N2								
S-106	Packaged Glycol Refrigeration System	1	20 MM Btu/hr at 0 oC								

Table 9.19 (Concluded)
RENNOVIA PROCESS EQUIPMENT LIST

Steam Turbine Drivers	# Installed	Mechanical or Electrical?	BHP	KW	Inlet Steam (Pres/ Temp)	Outlet Steam (Pres/ Temp)	Steam Turbine Details
					DesP (psia)	DesT (°C)	
ST-301	K301Driver	1	Mech	22,000	16,500	1,200/800	50/375 Horiz Split-Centrif
ST-302	K-302 Driver	1	Mech	8,000	6,000	1,200/800	50/375 Horiz Split-Centrif
ST-601	K-601 Driver	1	Mech	9,200	6,570	1,200/800	50/375 Horiz Split-Centrif
Storage Tanks	# Installed	Materials of Construction	Vol (ft3)	H x D (ft)	DesP (psia)	DesT (°C)	Type Tank w Details (API?)
					Atm	150	API650 w N2 blanket
TK-101	Glucose Feed Tank	1	304SS	54,800	26 x 52	Atm	150 API650 w N2 blanket
TK-102	Caustic soda feed tank	1	304SS	1,530	8 x 16	Atm	75 API650 w N2 blanket
TK-103	Glucaric acid silo	1	304SS	12,015	96 x 12	Atm	150 Vertical silo w N2 blanket
TK-201	Crude ADA Tank	1	304SS	50,680	25 x 50	Atm	150 API650 w N2 blanket
TK-401	Drying Feed Silo	1	304SS	2,873	40 x 10	15	250 Vertical silo w N2 blanket
TK-402	Flow Improver Silo	1	304SS	3	4 x 1	25	150 Vertical silo w N2 blanket
TK-403AB	ADA Product Silos	2	304SS	2,873	40 x 10	15	250 Vertical silo w N2 blanket
TK-501	Acetic Acid Feed Tank	1	304SS	44,744	24 x 48	15	250 API650 w N2 blanket
TK-502	Ethyl Acetate Tank	1	304SS	25	2 x 4	15	75 API650 w N2 blanket
TK-601	Acid Solution Tank	1	304SS	132,384	35 x 70	15	250 API650 w N2 blanket
TK-602	Methanol Feed Tank	1	CS	588	10 x 10	15	150 Floating Roof-API650
TK-603ABCD	Ester Tanks	4	CS	1,560	12 x 12	15	400 API 650
Pressure Vessels (API 510-ASME BPVC)	# Installed	Materials of Construction	Vol (ft3)	L x D (ft)	Orientation	DesP (psia)	DesT (°C)
						50	150
V-101AB	Caustic Scrubbers	2	304SS	8,000	52 x 14	Vertical	50 150
V-102AB	Activated Carbon Filters	2	304SS	4,070	36 x 12	Vertical	75 150
V-301AB	Activated Carbon Filters	2	304SS	1,600	32 x 8	Vertical	75 150

ITEMIZED CAPITAL COST ESTIMATE

Combining the equipment list duty specifications with FOB and installation costs estimates using the PEPCOST computer program, we provide below the itemized capital cost at a PEPCOST factor of 789, and location factor of 1.00.

Table 9.20
RENNOVIA ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Distillation Columns					
C-501	Water Extraction Column	941.2	941.2	555.5	555.5
C-502	Ethyl Acetate Recovery Column	311.9	311.9	402.1	402.1
C-601	Methanol Purification Column	217.3	217.3	362.3	362.3
C-602	Ester Purification Column	122.0	122.0	330.7	330.7
Centrifuges					
CN-301	Crude ADA Centrifuge	505.6	2,022.4	95.5	382.0
CN-302	1st Stage Centrifuge	505.6	2,022.4	95.5	382.0
CN-303	2nd Stage Centrifuge	505.6	2,022.4	95.5	382.0
Crystallizers					
CR-301	Crude ADA Crystallizer	3,128.0	3,128.0	414.0	414.0
CR-302	1st Stage Crystallizer	3,128.0	3,128.0	414.0	414.0
CR-303	2nd Stage Crystallizer	3,128.0	3,128.0	414.0	414.0
Solids Conveyors					
CV-101	Glucose Feed Conveyor	156.0	156.0	230.0	230.0
CV-102	Glucaric acid conveyor	156.0	156.0	230.0	230.0
CV-103	TK-103 Conveyor	156.0	156.0	230.0	230.0
CV-301	Crude ADA Conveyor	125.0	125.0	185.0	185.0
CV-302	E-302 Conveyor	125.0	125.0	185.0	185.0
CV-303	1st Stage Conveyor	125.0	125.0	185.0	185.0
CV-304	CN-303 Filter Cake Conveyor	125.0	125.0	185.0	185.0
CV-401	Drying Feed Conveyor	125.0	125.0	185.0	185.0
CV-403	Flow Improver Conveyor	48.5	48.5	62.7	62.7
CV-404	Dust Conveyor	48.5	48.5	62.7	62.7
CV-405	Hot ADA Conveyor	125.0	125.0	185.0	185.0
CV-406	E-404 Conveyor	125.0	125.0	185.0	185.0
CV-407	TK-403 Conveyor	125.0	125.0	185.0	185.0
CV-601	Dry Acid Conveyor	75.0	75.0	86.0	86.0

Table 9.20 (Continued)
RENNOVIA ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Drums					
D-101	Glucose Mixing Tank	202.7	202.7	79.7	79.7
D-102	R-101 K/O Drum	58.5	58.5	39.5	39.5
D-103	E-103 Receiver	77.1	77.1	48.1	48.1
D-201	Hydro Mixing Drum	197.6	197.6	78.2	78.2
D-202	E-204 Receiver	98.0	98.0	43.2	43.2
D-203	Hydro DePressuring Drum	299.4	299.4	56.4	56.4
D-301	E-303 Receiver	27.7	27.7	38.9	38.9
D-302	Crude ADA Dissolving Drum	44.2	44.2	42.5	42.5
D-303	K-301 K/O Drum	14.0	14.0	35.1	35.1
D-304	E-305 Receiver	19.6	19.6	36.7	36.7
D-305	1st Stage Dissolving Drum	50.6	50.6	43.9	43.9
D-306	K-302 K/O Drum	17.4	17.4	33.7	33.7
D-307	E-307 Receiver	27.7	27.7	38.9	38.9
D-401	Dust Dissolving Drum	50.6	50.6	43.9	43.9
D-402	E-403 Receiver	27.7	27.7	38.9	38.9
D-501	E-501 Receiver	27.7	27.7	38.9	38.9
D-502	E-503 Receiver	27.7	27.7	38.9	38.9
D-503	E-506 Receiver	27.7	27.7	38.9	38.9
D-601	Vapor Separating Drum	76.3	76.3	46.8	46.8
D-602	Slurry Dissolving Drum	33.9	33.9	38.1	38.1
D-603	Acid Mixing Tank	28.0	28.0	36.5	36.5
D-604	E-606 Receiver	57.7	57.7	44.5	44.5
D-605	K-601 K/O Drum	33.9	33.9	38.1	38.1
D-606	E-608 Receiver	32.7	32.7	40.2	40.2
Heat Exchangers					
E-101	Glucose Feed Heater	111.7	111.7	45.7	45.7
E-102	Glucaric Acid Evaporator	2,977.8	2,977.8	372.6	372.6
E-103	E-102 Condenser	1,490.0	1,490.0	185.4	185.4
E-104AB	Recycle Caustic Coolers	27.6	55.2	40.4	80.8
E-105	Rx Liquids Chiller	206.7	206.7	50.8	50.8

Table 9.20 (Continued)
RENNOVIA ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Heat Exchangers					
E-201	Feed/Product Exchanger	146.4	146.4	48.4	48.4
E-202	Hydro Trim Heater	39.8	39.8	41.8	41.8
E-203	Hydro Product Cooler	91.6	91.6	45.0	45.0
E-204	Hydro Condenser	78.6	78.6	44.2	44.2
E-205	Rx Liquid Cooler	147.1	147.1	47.2	47.2
E-301	CR-301 Glycol Cooler	107.4	107.4	44.5	44.5
E-302	Crude ADA Rotary Dryer	75.6	75.6	82.1	82.1
E-303	E-302 Condenser	37.7	37.7	41.1	41.1
E-304	1st Stage Glycol Cooler	25.3	25.3	39.6	39.6
E-305	K-301 Condenser	154.4	154.4	46.8	46.8
E-306	2nd Stage Glycol Cooler	36.7	36.7	40.4	40.4
E-401	1st Stage Rotary Dryer	315.2	315.2	95.7	95.7
E-402	2nd Stage Rotary Dryer	164.4	164.4	87.4	87.4
E-403	Dryer O/H Condenser	110.3	110.3	44.5	44.5
E-404	ADA Cooler	99.4	99.4	82.4	82.4
E-501	C-501 Condenser	1,388.7	1,388.7	176.7	176.7
E-502AB	C-501 Reboiler	695.4	1,390.8	88.1	176.2
E-503	C-502 Condenser	20.5	20.5	39.7	39.7
E-504AB	C-502 Reboiler	68.2	136.4	42.3	84.6
E-505	Acetic Acid Rotary Dryer	931.6	931.6	117.1	117.1
E-506	Acetic Acid Condenser	465.8	465.8	58.5	58.5
E-601	Solution Vaporizer	536.4	536.4	61.9	61.9
E-602	Acetic Acid Rotary Dryer	180.8	180.8	125.7	125.7
E-603	LLP Steam Generator	461.0	461.0	58.4	58.4
E-604	Methanol Column Pre-Heater	11.1	11.1	31.5	31.5
E-605	Methanol Vaporizer	67.6	67.6	39.7	39.7
E-606	C-601 Condenser	641.8	641.8	160.2	160.2
E-607AB	C-601 Reboilers	609.5	1,219.0	77.3	154.6
E-608	K-601 Condenser	162.6	162.6	47.4	47.4
E-609AB	C-602 Reboilers	64.5	129.0	39.4	78.8
E-610	Ester Preheat Exchanger	14.9	14.9	38.7	38.7
E-612	Ester Cooler	12.8	12.8	37.9	37.9

Table 9.20 (Continued)
RENNOVIA ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Filters					
FL-101	Compressed Air filter	3,850.0	3,850.0	762.0	762.0
FL-102AB	R-101 Product Filters	325.6	651.2	158.2	316.4
FL-103	Glucaric Acid Vapor Filter	478.4	478.4	245.5	245.5
FL-104AB	Scrubber Exhaust Filters	4,015.0	8,030.0	810.0	1,620.0
FL-401	Dryer Vapor Filter	458.0	458.0	106.0	106.0
FL-601AB	Crystal Filter	34.8	69.6	16.5	33.0
Compressors					
K-101	Feed Air Compressor	1,150.0	1,150.0	1,875.0	1,875.0
K-201	Hydrogen Compressor	4,560.0	4,560.0	7,490.0	7,490.0
K-301	1st Stage Compressor	11,360.0	11,360.0	27,360.0	27,360.0
K-302	2nd Stage Compressor	4,794.0	4,794.0	10,910.0	10,910.0
K-601	C-602 Vacuum Pump	6,877.0	6,877.0	13,030.0	13,030.0
Mixers and Agitators					
M-101	D-101 Agitator	75.6	75.6	18.1	18.1
M-201	D-201 Agitator	75.6	75.6	18.1	18.1
M-202	TK-201 Agitator	540.0	540.0	129.6	129.6
M-301	D-302 Agitator	9.7	9.7	2.3	2.3
M-302	D-305 Agitator	9.7	9.7	2.3	2.3
M-401	D-401 Agitator	9.7	9.7	2.3	2.3
M-601	D-602 Agitator	4.3	4.3	1.0	1.0
M-602	D-603 Agitator	2.2	2.2	0.5	0.5
Pumps					
P-101AS	Caustic Feed Pumps	10.3	20.6	19.2	38.4
P-102AS	Glucose Feed Pumps	62.6	125.2	115.7	231.4
P-103AS	D-103 Pumps	42.9	85.8	139.2	278.4
P-104AS	Caustic Recycle Pumps	20.8	41.6	68.2	136.4
P-201AS	Hydro Feed Pumps	231.5	463.0	168.2	336.4
P-202AS	Hydro Recycle Pumps	81.2	162.4	290.1	580.2
P-203	Hydro Turbo Generator	194.0	194.0	169.2	169.2
P-204AS	Hydro Condensate Pumps	9.0	18.0	26.3	52.6
P-205AS	Crude ADA Pumps	30.0	60.0	111.7	223.4

Table 9.20 (Continued)
RENNOVIA ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Pumps					
P-301AS	Crude ADA Pumps	60.0	120.0	223.4	446.8
P-302AS	CR-301 Circulating Pumps	61.4	122.8	223.8	447.6
P-303AS	CN-301 Filtrate Pumps	27.4	54.8	92.2	184.4
P-304AS	D-301 Recycle Pumps	8.0	16.0	25.2	50.4
P-305AS	D-302 Pumps	19.2	38.4	64.2	128.4
P-306AS	D-304 Pumps	11.6	23.2	36.1	72.2
P-307AS	1st Stage Slurry Pumps	36.0	72.0	61.3	122.6
P-308AS	CN-302 Filtrate Pumps	14.4	28.8	44.5	89.0
P-309AS	D-305 Pumps	20.9	41.8	68.5	137.0
P-310AS	CR-303 Circulating Pumps	31.3	62.6	115.4	230.8
P-311AS	D-307 Pumps	12.5	25.0	37.8	75.6
P-312AS	2nd Stage Slurry Pumps	35.4	70.8	60.8	121.6
P-313AS	CN-303 Filtrate Pumps	14.0	28.0	43.6	87.2
P-314AS	CR-302 Cooling Pumps	31.8	63.6	116.9	233.8
P-401AS	Dust Solution Pumps	9.5	19.0	30.0	60.0
P-402AS	Condensate Pumps	8.5	17.0	25.7	51.4
P-501AS	Acetic Acid Feed Pumps	27.9	55.8	93.6	187.2
P-502AS	C-501 Reflux Pumps	31.1	62.2	115.0	230.0
P-503AS	Water Pumps	9.6	19.2	30.1	60.2
P-504AS	C-501 B/S Pumps	47.3	94.6	177.4	354.8
P-505AS	C-502 Reflux Pumps	9.8	19.6	30.4	60.8
P-506AS	C-502 B/S Pumps	11.8	23.6	36.4	72.8
P-507AS	Ethyl Acetate Pumps	2.5	5.0	3.6	7.2
P-508AS	Acetic Acid Recycle Pumps	25.7	51.4	87.3	174.6
P-509AS	E-505 WWT Pumps	9.8	19.6	30.3	60.6
P-601AS	Acid Solution Feed Pumps	55.3	110.6	120.4	240.8
P-602AS	Methanol Feed Pumps	7.0	14.0	15.7	31.4
P-603AS	Crystal Slurry Pumps	24.5	49.0	34.2	68.4
P-604AS	Slurry Recycle Pumps	29.9	59.8	99.2	198.4
P-605AS	Mixed Methanol Feed Pumps	10.8	21.6	31.8	63.6
P-606AS	C-601 Reflux Pumps	24.3	48.6	77.4	154.8

Table 9.20 (Continued)
RENNOVIA ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Pumps					
P-607AS	C-601 B/S Pumps	23.4	46.8	75.0	150.0
P-608AS	C-602 Reflux Pumps	14.7	29.4	45.0	90.0
P-609AS	C-602 B/S Pumps	9.0	18.0	28.7	57.4
P-610AS	Ester Pumps	5.7	11.4	15.3	30.6
P-611AS	R-601 B/S Pumps	10.6	21.2	31.6	63.2
P-612AS	TK-603 Pumps	5.7	11.4	15.3	30.6
Reactors					
R-101AB	Glucose Oxidation Reactors	153.7	307.4	185.6	371.2
R-201AB	Hydro Reactors	1,042.0	2,084.0	311.3	622.6
R-601AB	Mixed Ester Reactors	50.1	100.2	138.7	277.4
Specially Packaged Equipment					
S-101	R-101 Vapor Cyclone	20.4	20.4	10.8	10.8
S-301	E-302 Overhead Cyclone	20.4	20.4	10.8	10.8
S-401	Cyclone Dust Separator	20.4	20.4	10.8	10.8
S-102	Process Flare System	5,600.0	11,200.0	3,800.0	7,600.0
S-103	Process Computer Control System	11,340.0	11,340.0	5,880.0	5,880.0
S-104	Vacuum Line Compression System	8,500.0	8,500.0	9,620.0	9,620.0
S-105	N ₂ PSA System	2,400.0	2,400.0	1,600.0	1,600.0
S-106	Packaged Glycol Refrigeration System	1,600.0	1,600.0	1,850.0	850.0
Steam Turbine Drivers					
ST-301	K-301 Driver	2,550.0	2,550.0	2,784.0	2,784.0
ST-302	K-302 Driver	1,024.0	1,024.0	1,264.0	1,264.0
ST-601	K-601 Driver	1,178.0	1,178.0	1,454.0	1,454.0

Table 9.20 (Concluded)
RENNOVIA ITEMIZED CAPITAL COST ESTIMATE
(US\$ THOUSANDS)

Equipment		FOB (1 Unit)	FOB (All Units)	Install (1 Unit)	Install (All Units)
Storage Tanks					
TK-101	Glucose Feed Tank	877.6	877.6	233.1	233.1
TK-102	Caustic Soda Feed Tank	164.4	164.4	24.1	24.1
TK-103	Glucaric Acid Silo	327.0	327.0	86.9	86.9
TK-201	Crude ADA Tank	834.0	834.0	221.5	221.5
TK-401	Drying Feed Silo	241.5	241.5	86.9	86.9
TK-402	Flow Improver Silo	11.9	11.9	32.2	32.2
TK-403AB	ADA Product Silos	122.4	244.8	61.8	123.6
TK-501	Acetic Acid Feed Tank	769.3	769.3	204.3	204.3
TK-502	Ethyl Acetate Tank	27.1	27.1	4.0	4.0
TK-601	Acid Solution Tank	1,568.0	1,568.0	416.5	416.5
TK-602	Methanol Feed Tank	37.0	37.0	17.4	17.4
TK-603ABCD	Ester Tanks	52.0	208.0	24.4	97.6
Pressure Vessels (API 510-ASME BPVC)					
V-101AB	Caustic Scrubbers	225.2	450.4	399.8	799.6
V-102AB	Activated Carbon Filters	153.9	307.8	301.2	602.4
V-301AB	Activated Carbon Filters	83.0	166.0	213.2	426.4

The sum of the itemized capital costs for tagged process equipment, when segmented between the FOB purchase price, and the installation cost, is presented in the table below.

Table 9.21
RENNOVIA SEGMENTED ITEMIZED CAPITAL COST ESTIMATE

	US\$-MM
FOB Purchased Cost	128,835.9
Installation Cost	117,159.5
Installed Cost	245,995.5

When segmented by type of process equipment, the Rennovia itemized capital cost shows that the largest cost categories are for compressors and for special packaged equipment. The special packaged equipment includes major costs for the process flare and header system, computerized process control system, vacuum line compressor system, and refrigerated glycol system. This information is presented in the table below.

Table 9.22
RENNOVIA ITEMIZED CAPEX SEGMENTED BY EQUIPMENT TYPE

	FOB	Installation	Installed
Distillation Columns	1,592.4	1,650.6	3,243.0
Centrifuges	6,067.2	1,146.0	7,213.2
Crystallizers	9,384.0	1,242.0	10,626.0
Solids Conveyors	1,640.0	2,381.4	4,021.4
Process Drums	1,558.4	1,058.5	2,616.9
Heat Exchangers	14,242.1	3,054.0	17,296.1
Filters	13,537.2	3,082.9	16,620.1
Compressors	28,741.0	60,665.0	89,406.0
Mixers and Agitators	726.8	174.4	901.3
Pumps	2,767.2	6,972.6	9,739.8
Reactors	2,491.6	1,271.2	3,762.8
Specially Packaged Equipment	35,101.2	25,582.4	60,683.6
Steam Turbine Drivers	4,752.0	5,502.0	10,254.0
Storage Tanks	5,310.6	1,548.1	6,858.7
Pressure Vessels	924.2	1,828.4	2,752.6
Total	128,835.9	117,159.5	245,995.5

When segmented by type of section of plant as shown in the table below, the sections of the plant with the highest itemized capital costs are for adipic acid crystallization, and hydrodeoxygenation of glucaric acid to crude adipic acid.

Table 9.23
RENNOVIA ITEMIZED CAPEX SEGMENTED BY PLANT SECTION

Section		US\$-MM
100	Glucose oxidation with air	31,822.2
200	Glucaric acid hydrodeoxygenation to adipic acid	20,337.5
300	Adipic acid crystallization	86,139.4
400	Adipic acid drying and packaging	4,087.2
500	Acetic acid recovery	9,961.0
600	Methyl ester production	32,964.5
Special Equipment		60,683.6
Total		245,995.5

TOTAL FIXED CAPITAL COST ESTIMATE

Using the itemized capital cost estimate, we have prepared a total fixed capital cost estimate that includes the offsites requirements plus the build-up of construction cost items, plus our standard 25% contingency cost factor. This information is presented in the table below.

Table 9.24
RENNOVIA TOTAL FIXED CAPITAL COST ESTIMATE

CAPACITY: 160,000 MT/YR AT 0.90 STREAM FACTOR

PEP COST INDEX: 795

	COST (\$US-MM)	CAPACITY EXPONENT	
	-----	UP	DOWN
BATTERY LIMITS EQUIPMENT, FOB			
DISTILLATION COLUMNS	1,592	0.55	0.53
CENTRIFUGES	6,067	0.70	0.60
CRYSTALLIZERS	9,384	0.61	0.58
SOLIDS CONVEYORS	1,640	0.67	0.62
PROCESS DRUMS	1,558	0.67	0.62
HEAT EXCHANGERS	14,242	0.65	0.63
FILTERS	13,537	0.62	0.60
COMPRESSORS	28,741	0.69	0.60
MIXERS & AGITATORS	727	0.67	0.62
PUMPS	2,767	0.85	0.85
REACTORS	2,492	0.65	0.65
SPECIALY PACKAGED EQUIPMENT	35,101	0.70	0.70
STEAM TURBINE DRIVERS	4,752	0.85	0.85
STORAGE TANKS	5,311	0.55	0.53
PRESSURE VESSELS	924	0.65	0.65

TOTAL BLE	128,836		
DIRECT INSTALLATION COSTS	117,160	0.66	0.62
INDIRECT COSTS	87,870	0.63	0.59
UNSCHEDULED EQUIPMENT, 20%	23,432	0.65	0.62

BATTERY LIMITS, INSTALLED	357,298	0.65	0.62
BLI CONTINGENCY, 25%	89,325	0.65	0.62

BATTERY LIMITS INVESTMENT	446,623	0.65	0.62
OFF-SITES, INSTALLED			
COOLING WATER	18,260	0.65	0.62
PROCESS WATER	3,875	0.65	0.62
BOILER FEEDWATER	3,980	0.65	0.62
PROCESS STEAM	36,500	0.55	0.53
FUEL GAS SYSTEM	1,400	0.55	0.53
INERT GAS & INSTRUMENT AIR	850	0.55	0.53
OFFSITES TANKAGE	12,400	0.55	0.53

UTILITIES & STORAGE	77,265	0.65	0.62
GENERAL SERVICE FACILITIES	6,600	0.65	0.62
WASTEWATER TREATMENT	38,500	0.65	0.62

TOTAL OFFSITES	122,365	0.65	0.62
OFFSITES CONTINGENCY 25%	30,591	0.65	0.62
OFFSITES CAPITAL INVESTMENT	152,956	0.65	0.62
TOTAL FIXED CAPITAL	599,579	0.65	0.62

We have prepared a factored total fixed capital cost estimate for half the base case capacity, and double the base case capacity. They are presented in the table below.

Table 9.25
FACTORED TOTAL FIXED CAPITAL COST ESTIMATES

Capacity	MT/Y	80,000	160,000	320,000
Production	MT/Y	<u>80,000</u>	<u>160,000</u>	<u>320,000</u>
Investment (US\$ millions)				
Battery Limits		284.6	(0.65)	446.6
Off-Sites		<u>108.9</u>	<u>(0.49)</u>	<u>152.9</u>
Total Fixed Capital		393.5		599.5
				945.3

PRODUCTION COST ESTIMATE

We have prepared an estimate cost for producing adipic acid using our understanding of Rennovia technology. The method combines the variable costs developed from the heat and material balance, with unit market pricing consistent with mid-2012 timeframe.

Variable Production Cost Estimate

Our variable cost estimate for producing adipic acid using Rennovia technology is \$1,019.2 per metric ton, segmented as \$887.1 per metric ton for raw materials, plus \$132.1 per metric ton for utilities and energy. One major uncertainty is the unit cost of catalyst. Since the Rennovia process depends upon unique precious metal catalysts, there is no published data on expected productivity of the catalyst. However, since most precious metal catalysts can be recovered and reprocessed, we expect a unit cost for both the oxidation catalyst and the hydrodeoxygenation catalyst to be comparable to unit costs for other precious metal catalysts used in oxidation and hydrogenation service. Variable production costs are segmented in the table below.

Table 9.26
RENNOVIA PROCESS VARIABLE PRODUCTION COST ESTIMATE

	Unit Cost	Consumption	\$/mt
Raw Materials			
Glucose	300 \$/mt	1.8221 mt/mt	546.6
Hydrogen	565 \$/mt	0.1065 mt/mt	60.2
Acetic Acid	675 \$/mt	0.0858 mt/mt	57.9
Caustic Soda	300 \$/mt	0.0025 mt/mt	0.8
Hydrogen Bromide	2,000 \$/mt	0.0025 mt/mt	5.0
Ethyl Acetate	1,400 \$/mt	0.0005 mt/mt	0.7
Methanol	360 \$/mt	0.1025 mt/mt	36.9
Mixed Methyl Ester By-Product	500 \$/mt	-0.2454 mt/mt	-122.7
Oxidation Catalyst			15.5
Hydrogenation Catalyst			10.5
Net Raw Material Cost			611.4
Utilities			
Process Water	0.2803 \$/m3	0.35 m3/mt	0.1
Cooling Water	0.0187 \$/m3	40.5 m3/mt	0.8
Electricity	60 \$/mwh	0.4 mwh/mt	24.0
Process Steam	8.28 \$/mt	12.5 mt/mt	103.5
Fuel Gas	3.05 \$/MM-Btu	0.325 MM-Btu/mt	1.0
Glycol Refrigeration	0.18 \$/ton	15.5 ton/mt	2.8
Net Utility Cost			132.1
Variable Cost			743.5

Total Production Cost Estimate

We believe that the total production cost for producing adipic acid from glucose using Rennovia process technology is approximately \$1,581 for a 160 kty capacity industrial scale plant. The total production costs are segmented in the table below for three different production capacity plants (80 kty, 160 kty, 320 kty), and by production cost component.

Table 9.27
RENNOVIA PROCESS TOTAL PRODUCTION COST ESTIMATE

Capacity	MT/Y	80,000	160,000	320,000
Production	MT/Y	<u>80,000</u>	<u>160,000</u>	<u>320,000</u>
Investment (US\$ millions)				
Battery Limits		284.6	(0.65)	446.6
Off-Sites		<u>108.9</u>	<u>(0.49)</u>	<u>152.9</u>
Total Fixed Capital		393.5		599.5
Production Cost (\$/MT)				
Net Raw Materials		611.4		611.4
Net Utilities		<u>132.1</u>	<u>132.1</u>	<u>132.1</u>
Variable Costs		743.5		743.5
Direct Costs				
Maintenance Materials		53.4		41.9
Operating Supplies		2.7		1.3
Operating Labor		26.9		13.5
Maintenance Labor		53.4		41.9
Control Laboratory		<u>5.4</u>	<u>2.7</u>	<u>1.3</u>
Total Direct Costs		885.2		844.7
Plant Overhead		51.4		34.8
Taxes & Insurance		98.4		74.9
Depreciation		<u>491.9</u>	<u>374.7</u>	<u>295.4</u>
Plant Gate Cost		1,526.9		1,329.2
G&A, Sales, R&D		48.0		48.0
Total Production Cost				
At 100% Capacity		1,574.9		1,377.2
At 75% Capacity		1,852.0		1,588.4
At 50% Capacity		2,406.3		2,010.9
Product Value (Cost + 25%/Yr ROI Before Taxes)				
At 100% Capacity		2,841.8		2,336.1
At 75% Capacity		3,081.7		2,525.2
At 50% Capacity		3,636.0		2,947.7
Cash Cost		1,083.03		1,002.50
Cash Cost Profitability		516.97		597.50
Total Cost Profitability		25.10		222.80
				953.21
				646.79
				351.37

Appendix A

PATENT SUMMARY TABLES

Table A.1
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
USPA 20110229959	Verdezyne	30-Sep-2011
	Genetically modified microorganisms that have enhanced fermentation activity, and methods for making and using such microorganisms.	
8227236	Verdezyne	24-Jul-2012
	Genetically modified microorganisms that have enhanced fermentation activity, and methods for making and using such microorganisms	
USPA 201201884465	Verdezyne	19-Jul-2012
	Described herein are compositions and methods for combinatorial metabolic pathway optimization	
USPA 20120184020	Verdezyne	19-Jul-2012
	Genetically modified microorganisms that have enhanced fermentation activity, and methods for making and using such microorganisms	
USPA 20120077252	Verdezyne	21-Jun-2012
	The technology relates in part to biological methods for producing adipic acid and engineered microorganisms capable of such production	
USPA 20120095263	Inventors	19-Apr-2012
	A method for producing crystals of adipic acid is described. In particular, a method for recovering adipic acid in the form of crystals with low impurity content, obtained by crystallization steps in particular using reaction media for synthesizing adipic acid is described. A purification method including a step of crushing the crystals for easier removal or the migration of the impurities in the crystals is also described.	
EP 2440515	Rennovia	18-Apr-2012
	The present invention generally relates to processes for the chemocatalytic conversion of a carbohydrate source to an adipic acid product. The present invention includes processes for the conversion of a carbohydrate source to an adipic acid product via a furanic substrate, such as 2,5-furandicarboxylic acid or derivatives thereof. The present invention also includes processes for producing an adipic acid product comprising the catalytic hydrogenation of a furanic substrate to produce a tetrahydrofuranic substrate and the catalytic hydrodeoxygenation of at least a portion of the tetrahydrofuranic substrate to an adipic acid product. The present invention also includes products produced from adipic acid product and processes for the production thereof from such adipic acid product.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
EP 2440514	Rennovia	18-Apr-2012
	The present invention generally relates to processes for the chemocatalytic conversion of a glucose source to an adipic acid product. The present invention includes processes for the conversion of glucose to an adipic acid product via glucaric acid or derivatives thereof. The present invention also includes processes comprising catalytic oxidation of glucose to glucaric acid or derivative thereof and processes comprising the catalytic hydrodeoxygenation of glucaric acid or derivatives thereof to an adipic acid product. The present invention also includes products produced from adipic acid product and processes for the production thereof from such adipic acid product.	
EP 2440513	Rennovia	18-Apr-2012
	The present invention generally relates to processes for the chemocatalytic conversion of a pentose source to a glutaric acid product. The present invention includes processes for the conversion of pentose to a glutaric acid product via pentaric acid or derivatives thereof. The present invention also includes processes comprising the catalytic oxidation of pentose to pentaric acid and catalytic hydrodeoxygenation of pentaric acid or derivatives thereof to a glutaric acid product.	
20120077252 A1	Verdezyne	29-Mar-2012
	The technology relates in part to biological methods for producing adipic acid and engineered microorganisms capable of such production.	
20120077237 A1	Verdezyne	29-Mar-2012
	The technology relates in part to biological methods for producing adipic acid and engineered microorganisms capable of such production.	
USPA 20120156761	Verdezyne	29-Mar-2012
	The technology relates in part to biological methods for producing adipic acid and engineered microorganisms capable of such production	
USPA 20120064252	Invista	15-Mar-2012
	Disclosed are ester compositions, solvents, cleaning formulations, curing agents, reactive diluent solvents, controlled acid function release agents, polyol monomers, drilling mud and methods of making and using the same. Disclosed compositions include: a) about 10 to 60 weight percent methyl hydroxycaproate; b) about 20 to 80 weight percent dimethyl adipate; c) about 1 to 15 wt% of dimethyl glutarate; d) about 0.1 to 5 wt% of dimethyl succinate; e) about 0.1 to 7 wt% of at least one cyclohexanediol; and f) less than about 20 wt% oligomeric esters.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
8133704	Celexion	13-Mar-2012
	Aspects of the invention relate to methods for the production of difunctional alkanes in host cells. In particular, aspects of the invention describe components of genes associated with the difunctional alkane production from carbohydrate feedstocks in host cells. More specifically, aspects of the invention describe metabolic pathways for the production of adipic acid, aminocaproic acid, caprolactam, and hexamethylenediamine via 2-ketopimelic acid.	
8,114,974	Verdezyne	14-Feb-2012
	Provided herein are genetically modified microorganisms that have enhanced fermentation activity, and methods for making and using such microorganisms.	
20120021473 A1	BioAmber	26-Jan-2012
	Processes for making SA from either a clarified DAS-containing fermentation broth or a clarified MAS-containing fermentation broth that include distilling the broth under super atmospheric pressure at a temperature of >100°C to about 300°C to form an overhead that comprises water and ammonia, and a liquid bottoms that includes SA, and at least about 20 wt% water; cooling the bottoms to a temperature sufficient to cause the bottoms to separate into a liquid portion and a solid portion that is substantially pure SA; and separating the solid portion from the liquid portion. A method also reduces the broth distillation temperature and pressure by adding an ammonia separating and/or water azeotroping solvent to the broth.	
USPA 20120021474	Verdezyne	26-Jan-2012
	The technology relates in part to biological methods for producing adipic acid and engineered microorganisms capable of such production	
8093037	Verdezyne	10-Jan-2012
	Provided herein are genetically modified microorganisms that have enhanced fermentation activity, and methods for making and using such microorganisms.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
8088607	Genomatica	3-Jan-2012
	The invention provides a non-naturally occurring microbial organism having an adipate, 6-aminocaproic acid or caprolactam pathway. The microbial organism contains at least one exogenous nucleic acid encoding an enzyme in the respective adipate, 6-aminocaproic acid or caprolactam pathway. The invention additionally provides a method for producing adipate, 6-aminocaproic acid or caprolactam. The method can include culturing an adipate, 6-aminocaproic acid or caprolactam producing microbial organism, where the microbial organism expresses at least one exogenous nucleic acid encoding an adipate, 6-aminocaproic acid or caprolactam pathway enzyme in a sufficient amount to produce the respective product, under conditions and for a sufficient period of time to produce adipate, 6-aminocaproic acid or caprolactam.	
8084626	BioAmber	27-Dec-2011
	A process for making a hydrogenated product includes providing a clarified DAS-containing fermentation broth; distilling the broth under super atmospheric pressure at a temperature of >100°C to about 300°C to form an overhead that includes water and ammonia, and a liquid bottoms that includes SA, and at least about 20 wt% water; cooling the bottoms to a temperature sufficient to cause the bottoms to separate into a liquid portion in contact with a solid portion that is substantially pure SA; separating the solid portion from the liquid portion; recovering the solid portion; hydrogenating the solid portion in the presence of at least one hydrogenation catalyst to produce the hydrogenated product including at least one of THF, GBL or BDO; and recovering the hydrogenated product.	
20110306790	Rennovia	15-Dec-2011
	Disclosed are catalysts comprised of platinum and gold. The catalysts are generally useful for the selective oxidation of compositions comprised of a primary alcohol group and at least one secondary alcohol group wherein at least the primary alcohol group is converted to a carboxyl group. More particularly, the catalysts are supported catalysts including particles comprising gold and particles comprising platinum, wherein the molar ratio of platinum to gold is in the range of about 100:1 to about 1:4, the platinum is essentially present as Pt(0) and the platinum-containing particles are of a size in the range of about 2 to about 50 nm. Also disclosed are methods for the oxidative chemocatalytic conversion of carbohydrates to carboxylic acids or derivatives thereof. Additionally, methods are disclosed for the selective oxidation of glucose to glucaric acid or derivatives thereof using catalysts comprising platinum and gold. Further, methods are disclosed for the production of such catalysts.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
WO 2011/155964	Rennovia	15-Dec-2011
	Disclosed are catalysts comprised of platinum and gold. The catalysts are generally useful for the selective oxidation of compositions comprised of a primary alcohol group and at least one secondary alcohol group wherein at least the primary alcohol group is converted to a carboxyl group. More particularly, the catalysts are supported catalysts including particles comprising gold and particles comprising platinum, wherein the molar ratio of platinum to gold is in the range of about 100:1 to about 1:4, the platinum is essentially present as Pt(0) and the platinum containing particles are of a size in the range of about 2 to about 50 nm. Also disclosed are methods for the oxidative chemocatalytic conversion of carbohydrates to carboxylic acids or derivatives thereof. Additionally, methods are disclosed for the selective oxidation of glucose to glucaric acid or derivatives thereof using catalysts comprising platinum and gold. Further, methods are disclosed for the production of such catalysts.	
USPA 20110274591	Rhodia	10-Nov-2011
	A plant for the crystallization of adipic acid is described. A plant for the crystallization of adipic acid, some parts of which are made of a corrosion-resistant material, is also described. The corrosion-resistant material used can be a reference austenitic stainless steel of AISI 310L type, according to the AISI (USA) nomenclature, or X1 CrNi 25-21 (1.4335) type, according to the European nomenclature.	
20110269993 A1	BioAmber	3-Nov-2011
	Processes for making AA from either a clarified DAA-containing fermentation broth or a clarified MAA-containing fermentation broth that include distilling the broth under super atmospheric pressure at a temperature of >100°C to about 300°C to form an overhead that comprises water and ammonia, and a liquid bottoms that includes AA, and at least about 20 wt% water; cooling the bottoms to a temperature sufficient to cause the bottoms to separate into a liquid portion and a solid portion that is substantially pure AA; and separating the solid portion from the liquid portion. A method also reduces the broth distillation temperature and pressure by adding an ammonia separating and/or water azeotroping solvent to the broth.	
USPA 20110266133	BioAmber	3-Nov-2011
	A process for making MAA from a clarified DAA-containing fermentation broth includes (a) distilling the broth to form an overhead that includes water and ammonia, and a liquid bottoms that includes MAA, at least some DAA, and at least about 20 wt% water; (b) cooling the bottoms to a temperature sufficient to cause the bottoms to separate into a DAA-containing liquid portion in contact with a MAA-containing solid portion that is substantially free of DAA; (c) separating the solid portion from the liquid portion; and (d) recovering the solid portion.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
USPA 20110269993	BioAmber	3-Nov-2011
	Processes for making AA from either a clarified DAA-containing fermentation broth or a clarified MAA-containing fermentation broth that include distilling the broth under super atmospheric pressure at a temperature of >100°C to about 300°C to form an overhead that comprises water and ammonia, and a liquid bottoms that includes AA, and at least about 20 wt% water; cooling the bottoms to a temperature sufficient to cause the bottoms to separate into a liquid portion and a solid portion that is substantially pure AA; and separating the solid portion from the liquid portion. A method also reduces the broth distillation temperature and pressure by adding an ammonia separating and/or water azeotroping solvent to the broth.	
20110251420	BASF	13-Oct-2011
	The invention relates to a method for producing carboxylic esters by converting a carboxylic acid or a carboxylic acid anhydride or a mixture thereof with an alcohol in a reaction system comprising one or more reactors, wherein reaction water is distilled as alcohol-water-azeotrope with the vapors, the vapors are at least partially condensed, the condensate is separated into an aqueous phase and an organic phase and said organic phase is supplied at least partially back into said reaction system. Components boiling lower than the alcohol are at least partially removed from said returned organic phase such as wherein components boiling lower than alcohol are evaporated and/or distilled off. An enrichment in the reaction system of by-products boiling lower than alcohol is avoided. Alcohol losses can be minimized by discharge currents.	
8026398	Inventors	27-Sep-2011
	Catalyst comprising a combination of oxidized metals and processes for cleaving phenylalkyl hydroperoxides in the presence of the catalyst.	
USPA 20110224416	Verdezyne	15-Sep-2011
	Provided herein are genetically modified microorganisms that have enhanced fermentation activity, and methods for making and using such microorganisms	
WO 2011/109051	Rennovia	9-Sep-2011
	Disclosed are compositions of matter comprising an adipic acid product of formula (1) wherein R is independently a salt-forming ion, hydrogen, hydrocarbyl, or substituted hydrocarbyl, and at least one constituent selected from the group consisting of formula (2) wherein R is as defined above and each of R1 is, independently, H, OH, acyloxy or substituted acyloxy provided, however, that at least one of R1 is OH, and formula (3) wherein R is as above defined and R1 is OH, acyloxy or substituted acyloxy. Also disclosed are compositions of matter comprising at least about 99 wt% adipic acid and least two constituents selected from the group consisting of formula (2) and formula (3), above.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
20110218318	Rennovia	8-Sep-2011
	Disclosed are compositions of matter comprising an adipic acid product of formula (1) ##STR00001## wherein R is independently a salt-forming ion, hydrogen, hydrocarbyl, or substituted hydrocarbyl, and at least one constituent selected from the group consisting of formula (2) ##STR00002## wherein R is as defined above and each of R1 is, independently, H, OH, acyloxy or substituted acyloxy provided, however, that at least one of R1 is OH, and formula (3) ##STR00003## wherein R is as above defined and R1 is OH, acyloxy or substituted acyloxy. Also disclosed are compositions of matter comprising at least about 99 wt% adipic acid and least two constituents selected from the group consisting of formula (2) and formula (3), above.	
USPA 20110165661	Verdezyne	7-Jul-2011
	Provided herein are genetically modified microorganisms that have enhanced fermentation activity, and methods for making and using such microorganisms	
USPA 20110165660	Verdezyne	7-Jul-2011
	Provided herein are genetically modified microorganisms that have enhanced fermentation activity, and methods for making and using such microorganisms	
WO 2011/003034 A2	Verdezyne	6-Jan-2011
	The technology relates in part to biological methods for producing adipic acid and engineered microorganisms capable of such production.	
7951742	BASF	31-May-2011
	A gas stream containing nitrous oxide and ammonia is contacted with a catalyst composition containing a zeolite. N ₂ O is reduced to N ₂ and H ₂ O at low temperatures in a highly efficient manner. Ammonia-mediated reduction of nitrous oxide can be effectuated from gas streams having N ₂ O concentrations as low as 1%. The gas stream may also contact a catalytic composition selective for the reduction of NOx. In this way, N ₂ O and NOx treatment may be effectuated in a single process stream.	
20110124065 A1	MIT	26-May-2011
	The invention relates to the production of glucuronic and glucaric acid in cells through recombinant expression of myo-inositol 1-phosphate synthase, myo-inositol oxygenase and uronate dehydrogenase. Cloning and characterization of the gene encoding uronate dehydrogenase is also disclosed.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
7938981	BioAmber	10-May-2011
	A composition for deicing or for the preparation of a heat transfer fluid is provided. The composition comprises a mixture of at least two carboxylic acid salts having a t/c ratio of 2 or lower, including a dicarboxylic salt and a monocarboxylic salt, said dicarboxylic salt being present in the mixture in an amount of at least 50 wt% of the weight of the mixture, on a dry basis. More particularly, said mixture is including a succinate and a formate, wherein the succinate is in an amount of at least 50 wt%, on a dry basis. Also provided is a method for deicing a surface or preventing the accumulation of ice, snow or a mixture thereof on a surface, comprising a step of applying on a surface covered by ice, snow or a mixture thereof, or susceptible of being covered by ice, snow or a mixture thereof, the above composition. The composition is also useful for the preparation of a heat transfer fluid coolant to be used in a heat transfer system comprising a heat transfer fluid provided with a cooling system.	
20100317825	Rennovia	16-Dec-2010
	The present invention generally relates to processes for the chemocatalytic conversion of a pentose source to a glutaric acid product. The present invention includes processes for the conversion of pentose to a glutaric acid product via pentaric acid or derivatives thereof. The present invention also includes processes comprising the catalytic oxidation of pentose to pentaric acid and catalytic hydrodeoxygenation of pentaric acid or derivatives thereof to a glutaric acid product.	
20100317822	Rennovia	16-Dec-2010
	The present invention generally relates to processes for the chemocatalytic conversion of a carbohydrate source to an adipic acid product. The present invention includes processes for the conversion of a carbohydrate source to an adipic acid product via a furanic substrate, such as 2,5-furandicarboxylic acid or derivatives thereof. The present invention also includes processes for producing an adipic acid product comprising the catalytic hydrogenation of a furanic substrate to produce a tetrahydrofuranic substrate and the catalytic hydrodeoxygenation of at least a portion of the tetrahydrofuranic substrate to an adipic acid product. The present invention also includes products produced from adipic acid product and processes for the production thereof from such adipic acid product.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
WO 2010/144862	Rennovia	16-Dec-2010
	The present invention generally relates to processes for the chemocatalytic conversion of a glucose source to an adipic acid product. The present invention includes processes for the conversion of glucose to an adipic acid product via glucaric acid or derivatives thereof. The present invention also includes processes comprising catalytic oxidation of glucose to glucaric acid or derivative thereof and processes comprising the catalytic hydrodeoxygenation of glucaric acid or derivatives thereof to an adipic acid product. The present invention also includes products produced from adipic acid product and processes for the production thereof from such adipic acid product.	
WO 2010/144871	Rennovia	16-Dec-2010
	The present invention generally relates to processes for the chemocatalytic conversion of a pentose source to a glutaric acid product. The present invention includes processes for the conversion of pentose to a glutaric acid product via pentanic acid or derivatives thereof. The present invention also includes processes comprising the catalytic oxidation of pentose to pentanic acid and catalytic hydrodeoxygenation of pentanic acid or derivatives thereof to a glutaric acid product	
WO 2010/144873	Rennovia	12-Dec-2010
	The present invention generally relates to processes for the chemocatalytic conversion of a carbohydrate source to an adipic acid product. The present invention includes processes for the conversion of a carbohydrate source to an adipic acid product via a furanic substrate, such as 2,5-furandicarboxylic acid or derivatives thereof. The present invention also includes processes for producing an adipic acid product comprising the catalytic hydrogenation of a furanic substrate to produce a tetrahydrofuranic substrate and the catalytic hydrodeoxygenation of at least a portion of the tetrahydrofuranic substrate to an adipic acid product. The present invention also includes products produced from adipic acid product and processes for the production thereof from such adipic acid product.	
7803968	Rhodia	28-Sep-2010
	The present invention relates to a process for producing carboxylic acids. It relates more particularly to a process for producing carboxylic acids by oxidation of a hydrocarbon with oxygen or a gas containing oxygen, and even more particularly to the oxidation of cyclohexane to adipic acid. The invention relates to a process for producing carboxylic acids by oxidation with oxygen or a gas containing oxygen of a cycloaliphatic hydrocarbon in the presence of an oxidation catalyst and of a monocarboxylic oxidation solvent that is lipophilic in nature, comprising a step of extraction of the dicarboxylic acids formed in the oxidation step, consisting in carrying out, in liquid phase, an extraction of the diacids using water.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
7799545	Genomatica	21-Sep-2010
	The invention provides a non-naturally occurring microbial organism having an adipate, 6-aminocaproic acid or caprolactam pathway. The microbial organism contains at least one exogenous nucleic acid encoding an enzyme in the respective adipate, 6-aminocaproic acid or caprolactam pathway. The invention additionally provides a method for producing adipate, 6-aminocaproic acid or caprolactam. The method can include culturing an adipate, 6-aminocaproic acid or caprolactam producing microbial organism, where the microbial organism expresses at least one exogenous nucleic acid encoding an adipate, 6-aminocaproic acid or caprolactam pathway enzyme in a sufficient amount to produce the respective product, under conditions and for a sufficient period of time to produce adipate, 6-aminocaproic acid or caprolactam.	
WO 2010/068944 A2	Celexion	17-Jun-2010
	Aspects of the invention relate to methods for the production of difunctional alkanes in host cells. In particular, aspects of the invention describe components of genes associated with the difunctional alkane production from carbohydrate feedstocks in host cells. More specifically, aspects of the invention describe metabolic pathways for the production of adipic acid, aminocaproic acid, caprolactam, and hexamethylenediamine via 2-ketopimelic acid.	
7728149	Daicel Industries	1-Jun-2010
	A process produces a corresponding dicarboxylic acid by subjecting a cycloalkane to an oxidative cleavage reaction with oxygen in the presence of a catalyst in a liquid phase using a continuous reactor, in which a residence time τ (hr) satisfies the following condition: $0.1 \leq \tau \leq 50/c$, wherein c is the proportion (% by weight) of the cycloalkane to the total weight of a charged liquid. The catalyst includes, for example, cobalt compounds, manganese compounds, and mixtures of these compounds, as well as imide compounds having at least one cyclic imide skeleton.	
USPA 20100025635	Invista	4-Feb-2010
	A method of improving flowability of adipic acid includes adding to the adipic acid at a relatively low temperature a flowability improving agent, such as an acyclic saturated monobasic acid containing 10 to 22 carbon atoms or an acyclic saturated dibasic acid containing 10 to 14 carbon atoms.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
WO 2010/003728	DSM	14-Jan-2010
	The present invention relates to a process for the production of a dicarboxylic acid. The process comprises fermenting a yeast in the presence of a carbohydrate-containing substrate and low amounts of oxygen at a pH value at which at least 50% of the dicarboxylic acid is in the acid form. The process of the present invention allows for high yields of the dicarboxylic acid product and is more cost-effective than existing processes in which the salt is produced which during recovery has to be converted to the acid. It also leads to a simpler and more convenient downstream processing.	
7399883	Invista	15-Jul-2008
	Disclosed in a process for making (1) a compound of the formula NC--CH ₂ --CH ₂ --CH ₂ --CH ₂ --CO ₂ R', wherein R' is H or C ₁ to C ₁₂ alkyl, or (2) adipic acid or (3) dimethyl adipate, using as the substrate, 3-pentenenitrile, (2) 3-pentenoic acid or methyl 3-pentenoate, respectively, by contacting the substrate with carbon monoxide and a nucleophile in the presence of a Group VIII metal, a selected ligand, and an acid promoter. The nucleophile, which (a) an alcohol or water, or (b) water or (c) methanol, respectively, in the presence of a Group VIII metal, preferably palladium, a selected phosphine ligand, and an acid promoter.	
7396961	Rhodia	8-Jul-2008
	The present invention relates to a process for decomposing organic hydroperoxides in the presence of a catalyst. It provides a process for decomposing organic hydroperoxides in the presence of a catalyst into a mixture of alcohols and ketones, in which the catalyst comprises at least one ruthenium-based catalytically active metallic element incorporated into a solid support chosen from the group comprising metal oxides and carbon blacks, such as the carbon blacks obtained by the pyrolysis of organic compounds. The process of the invention is especially useful in the decomposition of important chemical intermediates such as cyclohexyl hydroperoxide.	
7312357	Tokuyama Corp	25-Dec-2007
	The present invention discloses a process for producing an aliphatic dicarboxylic acid compound, which comprises oxidizing, with a nitrite or a nitrate in the presence of trifluoroacetic acid, an alicyclic secondary alcohol compound or an alicyclic ketone compound, in each of which at least one methylene group is bonded to the carbon atom having hydroxyl group bonded thereto or the carbon atom as a member of carbonyl group, wherein the reaction is conducted in the presence of water of 5 mass % or less relative to 100 mass % of the total of the trifluoroacetic acid and the water.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
7186856	Cargill	6-Mar-2007
	Processes for preparing carboxylic acids and derivatives thereof in which an ammonium salt of the carboxylic acid is heated in the presence of an organic reagent to split the salt and form the acid or, where the organic reagent is an esterifying agent, the corresponding ester. Both the acid and the ester may be dehydrated to form unsaturated counterparts	
7081552	Solutia	25-Jul-2006
	A cyclic ketone/alcohol mixture is prepared by catalytic oxidation of the corresponding cycloalkane or catalytic decomposition of the corresponding cycloalkyl hydroperoxide. Gold supported on a porous crystalline silicate containing less than about 2 wt% aluminum or a crystalline phosphate is used as a catalyst. The support material optionally contains one or more heteroatoms.	
7078555	Invista	18-Jul-2006
	Disclosed in a process for making (1) a compound of the formula NC--CH ₂ --CH ₂ --CH ₂ --CH ₂ --CO ₂ R', wherein R' is H or C ₁ to C ₁₂ alkyl, or (2) adipic acid or (3) dimethyl adipate, using as the substrate, 3-pentenenitrile, (2) 3-pentenoic acid or methyl 3-pentenoate, respectively, by contacting the substrate with carbon monoxide and a nucleophile in the presence of a Group VIII metal, a selected ligand, and an acid promoter. The nucleophile, which (a) an alcohol or water, or (b) water or (c) methanol, respectively, in the presence of a Group VIII metal, preferably palladium, a selected phosphine ligand, and an acid promoter.	
6946572	Invista	20-Sep-2005
	Process for drying moist, solid adipic acid using at least two drying stages in which moist solid adipic acid is progressively dried by contacting it in at least two successive stages with a nonreactive gas, the temperature of the first stage being lower than the temperature in any of the subsequent stages.	
6927311	Sumitomo	9-Aug-2005
	A method for producing an oxygenated compound from a cycloalkane compound which method is characterized in that a cycloalkane compound is contacted with oxygen in the presence of a cobalt compound and a ruthenium compound.	
5849765	Asahi Kasei	1-Feb-2005
	A method for producing cyclohexanone oxime, comprising the steps of: (1) subjecting cyclohexene or cyclohexanol to amination to obtain cyclohexylamine, and (2) subjecting the obtained cyclohexylamine to partial oxidation to obtain cyclohexanone oxime.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
6806390	Invista	19-Oct-2004
	An improved catalytic process for decomposing alkyl or aromatic hydroperoxides is disclosed which utilizes a catalytic amount of a heterogeneous Au catalyst that has been treated with an organosilicon reagent.	
6710010	DuPont	23-Mar-2004
	This invention relates to methods of producing catalysts comprising zirconia and their use in nitrous oxide abatement. The catalysts have relatively high crush strength and relatively low density when compared to those catalysts made by previously known methods	
6706932	Asahi Kasei	16-Mar-2004
	Disclosed is a method for producing a diol mixture comprising 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol, which comprises: (A) providing a dicarboxylic acid mixture comprising succinic acid, glutaric acid and adipic acid and having a nitric acid content of 3% by weight or less, based on the total weight of the succinic, glutaric and adipic acids, wherein the dicarboxylic acid mixture is prepared by denitrating an aqueous by-product solution obtained in an adipic acid production process, and (B) subjecting the dicarboxylic acid mixture to hydrogenation in the presence of water, hydrogen gas and a hydrogenation catalyst containing an active metal species comprising ruthenium and tin, to thereby obtain a hydrogenation reaction mixture comprising a diol mixture comprising 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol.	
6703529	DuPont	9-Mar-2004
	Disclosed herein is a process for the production of a mixture of cyclohexanone and cyclohexanol by oxidation of cyclohexane and decomposition of cyclohexyl hydroperoxide.	
6552235	Asahi Kasei	22-Apr-2003
	A method for producing cyclohexanol by subjecting cyclohexene to a hydration reaction in the presence of water using a solid acid as a catalyst in which as a reaction solvent, there is used an organic solvent having a solubility in water at 25°C of not higher than 5% by weight, a boiling point which is at least 20°C higher than that of the cyclohexanol produced, a conversion rate of not more than 3% under the hydration reaction conditions, and a solvent effect index of not less than 1.5 which indicates the effect of making the distribution of cyclohexene into the aqueous phase predominate.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
6534680	BASF	18-Mar-2003
	Dicarboxylic acid crystals are prepared from a solution containing at least one organic dicarboxylic acid in a process in which at least one anionic polyelectrolyte having a molecular weight of at least 2,000 is added to the solution before or during the crystallization.	
6498269	U of Connecticut	24-Dec-2002
	A method for the oxidation of substrates comprising treating an aqueous, basic solution of a substrate having an oxidizable functionality using an elemental halogen as terminal oxidant in the presence of an oxoammonium catalyst/halide co-catalyst system. Use of elemental halogen, preferably chlorine gas or elemental bromine, unexpectedly allows oxidation without significant degradation of the substrate. The substrate is preferably a monosaccharide, oligosaccharide, or polysaccharide, and the oxidizable functionality is preferably an aldehyde, hemiacetal, or a primary alcohol. An effective source of the oxoammonium catalyst is 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and a particularly economical and effective catalyst is 4-acetylamo-2,2,6,6-tetramethylpiperidinyl-1-oxy.	
6433221	RPC Inc.	13-Aug-2002
	This invention relates to methods of controlling the oxidation of cyclohexane to adipic acid in the presence of a monobasic acid solvent, by separating the catalyst from the reaction mixture, outside the reaction zone. Substantially all the unreacted cyclohexane, the majority of adipic acid, and substantially all the monobasic acid solvent are preferably removed. A protic solvent, may be added intermittently or continuously in the reaction mixture during the removal of the monobasic acid solvent, preferably by distillation, for preventing solids precipitation. A dipolar aprotic solvent is then added in the presence of an adequate amount of the protic solvent to maintain a single liquid phase, followed by a step of formation of two liquid phases, a solids-free protic liquid phase containing substantially all the catalyst, and a solids-free aprotic liquid phase containing at least the majority of ingredients of the reaction mixture. The formation of the two phases is performed by a process selected from a group consisting of lowering the first temperature to a second temperature, adding additional protic solvent, adding an apolar aprotic solvent, and a combination thereof.	
6429168	DuPont	6-Aug-2002
	This invention relates to a process for the conversion of nitrous oxide to nitrogen and oxygen using a supported catalyst comprising iron and, optionally, certain other metals and to a novel catalyst composition.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
WO 2002/090312	Cargill	7-May-2002
	Processes for preparing carboxylic acids and derivatives thereof in which an ammonium salt of the carboxylic acid is heated in the presence of an organic reagent to split the salt and form the acid or, where the organic reagent is an esterifying agent, the corresponding ester. Both the acid and the ester may be dehydrated to form unsaturated counterparts.	
6379640	DuPont	30-Apr-2002
	This invention relates to a process for the conversion of nitrous oxide (N_2O) to nitrogen and oxygen using a supported catalyst comprising iron and, optionally, certain other metals and to a novel catalyst composition.	
6359173	DuPont	19-Mar-2002
	Methods and devices for controlling the reaction of a hydrocarbon to an acid by making phase-related adjustments are disclosed. In order to improve reaction rate and reactivity of the oxidation, a single phase at the operating temperature is attained and maintained by adjusting one or more of gaseous oxidant flow rate, pressure in the reaction zone, temperature in the reaction zone, feed rate of hydrocarbon, feed rate of solvent, feed rate of water if water is being fed, feed rate of the catalyst and other parameters. Methods and devices are also disclosed, wherein a hydrocarbon is reacted at a steady state with a gaseous oxidant to form an acid in a liquid mixture. The amount of water is maintained between a maximum level of water, over which maximum level the substantially single liquid phase is transformed to two liquid phases, and a minimum level under which catalyst precipitates. Further, methods are disclosed, wherein the temperature of the mixture is lowered to a point at which solid dibasic acid is precipitated, while maintaining a single liquid phase, and optionally all the catalyst in solution. At least part of the formed acid is then removed. The preferred hydrocarbon is cyclohexane, the preferred acid is adipic acid, the preferred solvent is acetic acid, and the preferred catalyst is cobalt(II) acetate tetrahydrate.	
6284927	DuPont	4-Sep-2001
	An improved process for decomposing alkyl or aromatic hydroperoxides to form a decomposition reaction mixture containing the corresponding alcohol and ketone. The improvement relates to decomposing the hydroperoxide by contacting the hydroperoxide with a catalytic amount of a heterogeneous catalyst of Au, Ag, Cu or a sol-gel compound containing particular combinations of Fe, Ni, Cr, Co, Zr, Ta, Si, Mg, Nb, Al and Ti wherein certain of those metals have been combined with an oxide, such as an inorganic matrix of hydroxides or oxides, or combinations thereof. The catalysts may also optionally be supported on a suitable support member and used in the presence of an additional metal.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
6222069	Rhodia	24-Aug-2001
	The invention discloses a method for purifying adipic acid in water. More precisely it discloses an improvement in adipic acid crystallization or recrystallization in water, characterised in that the said crystallization or recrystallization is effected in presence of a strong proton acid and/or in the presence of carbon monoxide. This crystallization or recrystallization particularly enables the content of metal catalyst traces in the adipic acid to be reduced.	
6235932	Chemintel (India)	22-May-2001
	The present invention relates to one-step oxidation process for preparation of cyclohexane to adipic acid, using molecular oxygen, in liquid phase, in the presence of catalyst, containing either cobalt or cobalt and iron. The catalyst is activated outside the reactor and molecular oxygen is used as an oxidant. The use of molecular oxygen as oxidant along with preactivated catalyst in the reactor and also by restricting the conversion of cyclohexane between 20–30% with catalyst in the reactor results in enhanced selectivity to adipic acid. The reaction mixture of cyclohexane and preactivated catalyst is subjected to oxidation by bubbling pure molecular oxygen while stirring the homogenous mixture while bubbling the oxygen at a predetermined temperature, pressure and space velocity conditions. The product selectivity to form adipic acid is found to be at least 5% better than the maximum attainable using the conventional processes.	
6160183	DuPont	12-Dec-2000
	A catalytic process is disclosed for oxidizing cycloalkanes directly to form, in a single step, a mixture containing the corresponding alcohol and ketone. In particular, the invention relates to oxidizing a cycloalkane by contacting it with a source of oxygen and a catalytic amount of a heterogeneous catalyst. The catalysts of the invention include gold (including gold sol-gel compounds) and sol-gel compounds containing particular combinations of Cr, Co, Zr, Ta, Si, Mg, Nb, Al and Ti, wherein certain of those metals have been combined with an oxide, such as an inorganic matrix of hydroxides or oxides, or combinations thereof. The catalysts may also optionally be supported on a suitable support member.	
6080226	UOP	27-Jun-2000
	A feedstream comprising nitrous oxide is purified by a pressure swing adsorption process employing a copurge with an oxygen-lean stream to produce a high purity nitrous oxide stream. The high purity nitrous oxide stream can be incorporated in a complex for the production of adipic acid to recover nitrous oxide from a dilute waste stream and pass the recovered nitrous oxide to a process for the production of phenol from an aromatic hydrocarbon. Unreacted nitrous oxide from the phenol production step acid can be recovered in a second, or vent PSA step, and combined with the recovery of by-product nitrous oxide waste streams from the production of adipic for the overall recovery of nitrous oxide, thereby significantly reducing nitrous oxide emissions from the production of adipic acid.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
6049004	Kiely & Ponder	11-Apr-2000
	A method for synthesizing and isolating an oxidation product is disclosed wherein nitric acid is reacted with an oxidizable reactant and the desired oxidized product is extracted using an organic solvent such as a dialkyl ether. The method permits the direct crystallization of aldaric acids such as glucaric acid and mannaric acid and eliminates the necessity of employing complicated, time consuming and wasteful neutralization/acidification steps.	
6015924	RP Fiber (France)	18-Jan-2000
	The present invention relates to a process for the preparation of diacids or mixtures of diacids from aqueous solutions derived from the washing of cyclohexane oxidation products. More specifically, the present invention provides a process for the preparation of aliphatic diacids from washing waters derived from a process for the oxidation of cyclohexane and containing peroxides, the process of the invention comprising successively: (a) at least partially deperoxidizing said washing waters by subjecting them to catalytic hydrogenation at a temperature of between about 0°C and about 100°C, in the presence of at least one platinum group metal; (b) oxidizing with nitric acid the products contained in the washing waters after deperoxidation.	
5900513	Asahi Kasei	4-May-1999
	The present invention provide a method for producing 2-cyclohexene-1-ol which comprises using a catalyst containing an intermetallic compound of palladium and lead and/or bismuth when cyclohexenyl hydroperoxide is subjected to hydrogenolysis to produce 2-cyclohexene-1-ol. If the catalyst of the present invention is employed, it is possible to obtain the desired 2-cyclohexene-1-ol at a high selectivity with a much simpler reaction system than the prior art and, in addition, to inhibit the hydrogenation of coexisting cyclohexene sufficiently.	
5905173	DSM	18-Mar-1999
	The invention relates to a process for decomposing a mixture containing cycloalkyl hydroperoxide with an aqueous phase containing alkali metal hydroxide where, besides the alkali metal hydroxide, there is also at least 10 wt% of the aqueous phase of one or more alkali metal salts. The alkali metal salts are preferably alkali metal carbonates, or alkali metal salts of mono- and poly-carboxylic acids, with the carboxylic acid moiety containing 1–24 carbon atoms	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
5859301	DSM	12-Jan-1999
	An improved process for preparing alkanones and alkanols by oxidizing an alkane and/or alkene having from 3 to 30 carbon atoms to form an oxidation mixture containing alkylhydroperoxide. A basic, aqueous solution is added to the oxidation mixture so that a separate basic water phase with a pH higher than 8.5 is formed. The alkylhydroperoxide is then decomposed in the presence of a heterogeneous catalyst which contains a metal compound immobilized on a carrier material. The metal of the catalyst is selected from the group consisting of Mn, Fe, Co, Ni, and Cu. The carrier material is stable in the presence of the separate basic water phase.	
5772013	Sudzucker	30-Jun-1998
	A method is disclosed for producing di- and more highly oxidized carboxylic acids from a compound selected from a first group consisting of carbohydrates, carbohydrate derivatives and carbohydrate derivatives having more than one primary alcohol group, comprising oxidizing, in an aqueous solution in a concentration between 0.1% and 60%, the compound selected from said first group and a compound selected from a second group consisting of monooxidized carbohydrates, monooxidized carbohydrate derivatives and monooxidized carbohydrate derivatives having more than one primary alcohol group, with one of oxygen and an oxygen-containing gas, on one of a noble metal catalyst and a mixed metal catalyst; electrodialyzing the oxidized compounds in at least one electrodialysis stage; and removing said di- and more highly oxidized carboxylic acids in said at least one electrodialysis stage.	
5746837	Rhone-Poulenc	26-May-1998
	A process for recycling a catalyst containing cobalt including treating a reaction mixture obtained during the direct oxidation of cyclohexane to adipic acid by extracting at least some of the glutaric acid and succinic acid which are formed in the reaction.	
5723098	Inventors	3-Mar-1998
	The invention relates to a process for the selective recovery of catalysts used in the production of adipic acid by (a) separating adipic acid from the reaction solution, (b) exposing the resultant reaction solution to a sulfonated ion exchanger, thereby binding iron, copper, and vanadium ions to said sulfonated ion exchanger, (c) separating the ion-exchanger from the reaction solution, (d) washing the separated ion exchanger with nitric acid to obtain an acid eluate, and (e) exposing the acid eluate to an ion exchanger modified with aminophosphonic acid groups, thereby removing the iron ions from the acid eluate.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
5710325	DuPont	20-Jan-1998
	This invention provides a process for the preparation of adipic acid from pentenoic acids or esters of pentenoic acids by hydrocarboxylation of a reaction mixture in which gamma-valerolactone constitutes 30 to 70% by weight of the reaction mixture.	
5616496	Purdue U (Karen Draths)	1-Apr-1997
	A heterologous cell transformant is provided that biocatalytically converts a carbon source to catechol and cis, cis muconic acid. The cell transformant expresses heterologous genes encoding the enzymes 3-dehydroshikimate dehydratase, protocatechuate decarboxylase, and catechol 1,2-dioxygenase.	
5599977	Kiely, Carter & Shrout	4-Feb-1997
	Rapid temperature rises which characterize carbohydrate-nitric acid oxidation reactions used to form carbohydrate-derived acids may be moderated and temperature control readily maintained by blowing a gas such as air, oxygen, nitrogen or the like into the reaction mixture as needed to control the temperature of the reaction. The more moderate reaction conditions afford higher yield of the desired product with a concomitant reduction of by-products which may be difficult to remove and usually are unwanted as well. Upon completion the oxidation mixture is made basic (e.g., with an alkali metal base hydroxide or carbonate, ammonia or an amine) to a pH at which the carboxyl group or groups of the product carbohydrate-derived acid are entirely in the salt form. The aqueous solution is then passed through an ion retardation resin column to recover the carbohydrate-derived salt, using water as the eluent. If desired, the carbohydrate-derived acid salt may then be recovered easily by removal of solvent water or by precipitation by addition of a water-miscible organic compound such as methanol, ethanol, acetone, isopropanol, etc.).	
5587511	Bayer	24-Dec-1996
	The present invention relates to a process for obtaining adipic acid from the aqueous nitric acid mother liquors that arise during industrial adipic acid production by (i) removing nitric acid from the aqueous mother liquor by evaporation to a concentrate having a residual content of at most about 2.5 wt% of HNO ₃ , (ii) mixing the concentrate obtained according to step (i) with water or dilute aqueous nitric acid in a quantity corresponding to a weight ratio of solid to liquid of about 1:2.1 to about 1:1.2, (iii) allowing the water added in step (ii) or the nitric acid added in step (ii) to act upon the concentrate for at least about 10 minutes at about 20° to about 80°C, and (iv) separating adipic acid as crystals that are formed (1) during step (iii) at temperatures of no more than about 35°C or (2) after step (iii) by cooling the mixture from step (iii) to about 10° to about 35°C	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
5573931	Michigan Biotechnology Institute	12-Nov-1996
	A method for producing succinic acid in high concentration by fermentation employs a variant of strain 130Z which is resistant to concentrations of about 1 g/l to about 8 g/l of sodium monofluoroacetate. The variant produces succinic acid in concentrations of about 80 g/l to about 110 g/l and the fermentation product contains less formic and acetic acids than the product obtained using the parent strain under identical conditions. The novel variants and a method of obtaining such variants also are described.	
5772013	Sudzucker	14-Sep-1996
	A method is disclosed for producing di- and more highly oxidized carboxylic acids from a compound selected from a first group consisting of carbohydrates, carbohydrate derivatives and carbohydrate derivatives having more than one primary alcohol group, comprising oxidizing, in an aqueous solution in a concentration between 0.1% and 60%, the compound selected from said first group and a compound selected from a second group consisting of monooxidized carbohydrates, monooxidized carbohydrate derivatives and monooxidized carbohydrate derivatives having more than one primary alcohol group, with one of oxygen and an oxygen-containing gas, on one of a noble metal catalyst and a mixed metal catalyst; electrodialyzing the oxidized compounds in at least one electrodialysis stage; and removing said di- and more highly oxidized carboxylic acids in said at least one electrodialysis stage.	
5487987	Purdue U (Karen Draths)	30-Jan-1996
	A method is provided for producing adipic acid. The method comprises the steps of culturing a cell transformant capable of converting a carbon source to catechol for a period of time sufficient to convert said carbon source to catechol, biocatalytically converting the catechol to cis, cis-muconic acid using catechol 1,2-dioxygenase, and hydrogenating the cis, cis-muconic acid to produce adipic acid. Also provided is a heterologous transformant of the host cell having an endogenous common pathway of aromatic amino acid biosynthesis. The heterologous transformant is characterized by the constitutive expression of structural genes encoding 3-dehydroshikimate dehydratase, protocatechuate decarboxylase, and catechol 1,2-dioxygenase.	
5471001	DuPont	28-Nov-1995
	Crystallization of adipic acid using low intensity ultrasonic agitation during crystallization results in purer product that is more readily handled. Apparatus for carrying out the process is also disclosed	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
5455375	Asahi Kasei	3-Oct-1995
	A process for preparing adipic acid from cyclohexene oxide comprising the following steps (a) and (b): (a) hydrating cyclohexene oxide to obtain 1,2-dihydroxycyclohexane and an oligomers represented by formula (I): ##STR1## wherein n represents a number of from 1 to 5 in number average, and (b) oxidizing the 1,2-dihydroxycyclohexane and the oligomers represented by formula (I) in a nitric acid aqueous solution.	
5300472	Degussa	5-Apr-1994
	A catalyst for the selective reduction of nitrous oxide with ammonia contains, in addition to titanium oxide as component (A), at least one oxide of W, Si, B, Al, P, Zr, Ba, Y, La, Ce and at least one oxide of Y, Nb, Mo, Fe, Cu as component (B), whereby the atomic ratio between the elements of components (A) and (B) amounts to 1:0.001 up to 1. The catalyst can be obtained by kneading reactive titanium oxide with a high specific surface of predominantly anatase with the substances of component (B) or their preliminary stages, adding processing agents, winding up with a homogeneous kneaded mass, extruding the latter, drying the extrudate and calcining in air at 300°–800°C.	
5296639	DuPont	22-Mar-1994
	A process for purification of adipic acid during crystallization by modifying the crystal morphology to decrease incorporation of impurities through the introduction of an effective amount of an additive to the crystallizing solution.	
5264624	Bayer	23-Nov-1993
	This invention relates to a process for the recovery of adipic acid from mother liquors collected during commercial production of adipic acid, wherein said mother liquors contain from 52 to 60% by weight of nitric acid calculated as HNO ₃ , not taking into account the organic constituents, from 2 to 6% by weight of succinic acid, from 4 to 9% by weight of glutaric acid, and from 5 to 10% by weight of adipic acid, by selective crystallization of the adipic acid dissolved in said mother liquors by (a) adding an aqueous adipic acid solution having an adipic acid content of from 0.5 to 6% by weight to said mother liquor in the temperature range of from 30° to 60°C in such a quantity that the concentration of nitric acid in the mixture is reduced to 35 to 50% by weight; (b) cooling the mixture by at least 5 degrees Celsius within a period of from 0.5 to 5 hours to induce crystallization of the adipic acid; (c) isolating the crystallized adipic acid by filtration; and (d) transferring the filtrate obtained in step (c) to a distillation apparatus for distillative workup of the glutaric acid contained therein.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
5235117	IFP	10-Aug-1993
	For preparing at least one boric oxide in an anhydrous or hydrated form and of general formula B_2O_3, xH_2O , in which x is a number from 0 to 3, a methyl borate hydrolyzate comprising boric oxide and methanol is introduced into a distillation column is introduced the product from, at least one compound (preferably a hydrocarbon such as, e.g., 2,3-dimethyl butane or 2-methyl pentane) forming a heteroazeotrope with methanol, said heteroazeotrope having a boiling point below that of the azeotrope formed by methyl borate with methanol and at least one compound having a boiling point higher than that of methyl borate, said compound not forming an azeotrope with a boiling point below that of said heteroazeotrope and then at the head of the column said heteroazeotrope is recovered and at the bottom of the column a suspension containing at least one boric oxide. A description is also given of a process for the oxidation of at least one saturated hydrocarbon into a product incorporating the corresponding alcohol wherein oxidation is carried out with oxygen in the presence of a boric oxide with. The oxidation product is hydrolyzed into orthoboric acid and alcohol, which is recovered by separation from the organic phase. The aqueous phase containing the boric acid is fed into a methyl borate formation zone and the methyl borate is recovered in the form of its azeotrope with methanol. The recovery of the boric oxide from said azeotrope is performed in accordance with the aforementioned process, the recovered boric oxide being recycled to the oxidation stage.	
5221800	Amoco	22-Jun-1993
	A process for the manufacture of adipic acid is disclosed. In this process, cyclohexane is oxidized in an aliphatic monobasic acid solvent in the presence of a soluble cobalt salt wherein water is continuously or intermittently added to the reaction system after the initiation of oxidation of cyclohexane as indicated by a suitable means of detection, and wherein the reaction is conducted at a temperature of about 50°C to about 150°C at an oxygen partial pressure of about 50 to about 420 pounds per square inch absolute.	
5210297	BASF	11-May-1993
	A process for working up mother liquors resulting from the preparation of adipic acid by oxidation of cyclohexanol or cyclohexanone or mixtures thereof with nitric acid entails removal of nitric acid by azeotropic distillation with water, heating the resulting melt at from 130° to 180°C and then dissolving it in water, treating the aqueous solution with cation exchangers, subsequently again evaporating off the water and heating the resulting dicarboxylic acid melt at from 200° to 240°C and then obtaining a mixture of dicarboxylic acids by distillation.	
5025087	DuPont	13-Feb-1990
	66 nylon filaments of improved dyeability, because of small content of dodecanedioic acid component.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
4442303	EI Paso Products	10-Apr-1987
	In one of its embodiments this invention provides a process for recovering C ₄ –C ₆ dicarboxylic acid components contained in a waste by-product stream derived from a reaction system in which adipic acid is produced by nitric acid oxidation of cyclohexanone/cyclohexanol. An important aspect of the process is the esterification and extraction of the C ₄ –C ₆ dicarboxylic acids in the aqueous by-product stream with a mixture of C ₁ –C ₃ alkanol and C ₆ –C ₂₀ alkanol, and the subsequent recovery of di(C ₆ –C ₂₀ alkyl) esters of succinic acid, glutaric acid and adipic acid. In a broader aspect this invention provides a process for recovery of water miscible organic acid components contained in an aqueous solution as C ₆ –C ₂₀ alkyl esters of the organic acids.	
4543427	BASF	24-Sep-1985
	Cyclohexanol and cyclohexanone are prepared by treating cyclohexyl hydroperoxide with a supported catalyst containing from 2 to 30% by weight, calculated as cobalt, of cobalt in oxidic form, at from 30° to 160°C, by a process wherein a zeolite is used as the carrier.	
4525574	Centre de Recherche Industrielle de Quebec	25-Jun-1985
	Preparation of new polyols from mixtures of dicarboxylic acids comprising glutaric acid, succinic acid and adipic acid and polyhydric alcohols, such as mixtures of acids which are derived from treated residues resulting from the industrial production of adipic acid. Preparation of new polyurethanes from these polyols by reacting the latter with polyisocyanates. Obtaining products possessing advantageous properties and interesting market for treated residues resulting from the industrial production of adipic acid.	
4400468	HRI	23-Aug-1983
	A process is provided for producing adipic acid from a renewable resource, i.e., biomass. The process comprises: hydrolyzing the renewable resource to provide 5-hydroxymethylfurfural, hydrogenating the 5-hydroxymethylfurfural in the presence of a catalyst to provide 2, 5-tetrahydrofuran diol, treating the 2, 5-tetrahydrofuran diol with hydrogen in the presence of a catalyst to provide 1, 6 hexanediol, and oxidizing the 1, 6 hexanediol in the presence of a microorganism to provide adipic acid. The formation of the adipic acid is provided with the microorganism of <i>Gluconobacter oxydans</i> subsp. <i>oxydans</i> . The renewable resources are wastes selected from the group consisting of paper, wood, corn stalks, and logging residues.	
4543427	BASF	6-Jun-1983
	Cyclohexanol and cyclohexanone are prepared by treating cyclohexyl hydroperoxide with a supported catalyst containing from 2 to 30% by weight, calculated as cobalt, of cobalt in oxidic form, at from 30° to 160°C, by a process wherein a zeolite is used as the carrier.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
4375552	CP Hall	1-Mar-1983
	Waste streams from adipic acid manufacture containing nitric, succinic, glutaric and adipic acids and valuable catalytic metal as salts are treated with alcohols, thereby separating, as esters, succinic and glutaric acids which would contaminate pure adipic acid on recycling, and allowing the reuse of the resulting stream containing nitric acid and metal catalytic salts.	
4322558	ICI	30-Mar-1982
	The oxidation product of cyclohexane with an oxygen-containing gas in presence of a boron compound is, after hydrolysis and separation of boric acid, deperoxidized with a heavy metal catalyst, especially a chromium salt	
4254283	Monsanto	3-Mar-1981
	In the manufacture of adipic acid by nitric acid oxidation of cyclohexanol and cyclohexanone glutaric and succinic acids are recovered from the reaction by-product and waste stream by crystallizing adipic acid and succinic acid out of the stream leaving glutaric acid in the residue; forming succinic anhydride from the succinic acids so obtained; separating the succinic anhydride from the adipic acid by distillation thereby to recover succinic acid in anhydride form; and crystallizing, thereby to recover, the glutaric acid from the residue.	
4233408	Witco Chemical	13-Sep-1977
	A waste stream of nonvolatiles is recovered (NVR) as a by-product from the oxidation of cyclohexane to cyclohexanone and cyclohexanol in the process for making adipic acid. The NVR is partially dehydrated, and then reacted with an esterifying polyol to form a polyester polyol product which is useful in producing polyurethane foams. A particularly useful end-product is a rigid polyurethane foam having good cell structure and a density of at least 2.0 lb./cu. ft.	
4227021	BASF	7-Oct-1980
	An improved process for producing adipic acid from the acidic wash waters which arise in the process for oxidizing cyclohexane with air, by treatment with nitric acid at from 10° to 50°C, with removal of the heat of reaction by external cooling, wherein the reaction mixture is led, at a flow velocity of at least 2.0 m/sec, as a thin layer spirally in counter-current to the coolant, under conditions which do not perturb the flow of the reaction mixture.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
4183904	Monsanto	15-Jan-1980
	A method for the recovery of boron compounds from waste streams containing boric acid and combustible organic materials in water by incineration of the combustible organic materials and dehydration of the boric acid to boric oxide. Quenching of the boric oxide, depending upon temperature and water content, yields orthoboric and/or metaboric acids in vapor phase and polyboric acid in liquid phase which is cooled along with the products of the combustion of the organic materials and, in the presence of water, converted to a mixture of boric acids in solid and liquid phase leaving the products of combustion in vapor phase. The mixture of boric acids is then separated from the products of combustion.	
4166056	Witco Chemical	28-Aug-1979
	A waste stream of non-volatiles is recovered (NVR) as a by-product from the oxidation of cyclohexane to cyclohexanone and cyclohexanol in the process for making adipic acid. The NVR is dehydrated, and then reacted with an esterifying polyol to form a polyester polyol which was found to be useful in the dispersion of vinyl resins. Those polyester polyols with low acid numbers of less than 10, and, preferably less than 2, were found to be most effective as vinyl dispersion plasticizers. A particularly useful end-product is a tough vinyl resin film having a Shore A hardness of approximately 55. End-products may also be used in wire coatings and coverings.	
4146730	Asahi Kasei	27-Mar-1979
	A method for obtaining glutaric acid, succinic acid, and adipic acid from an acid mixture obtained as a by-product in the industry and comprising glutaric acid, succinic acid and adipic acid, which comprises the steps of: (1) contacting the acid mixture with urea of 1 to 2 moles per mole of the acid mixture, in solution, to deposit a urea-glutaric acid adduct so that the weight ratio of glutaric acid remaining in the solution to succinic acid is 1.2 or less when the adipic acid content is in the range of 0% by weight to 7% by weight and 1.4 or less when the adipic acid content is larger than 7% by weight and 30% by weight or less; separating the deposited urea-glutaric acid adduct out of the solution; (2) adding further urea to the solution and/or concentrating the solution obtained in the step (1) to deposit a urea-succinic acid adduct; separating the deposited urea-succinic acid adduct out of the solution; and (3) decomposing the separated urea-dicarboxylic acid adducts each into respective dicarboxylic acids and urea. With this method, the mixture comprising glutaric acid, succinic acid and adipic acid can, for the first time, be successfully and effectively separated into the respective components.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
4058565	Bayer	15-Nov-1977
	Hydrocarbons containing 4 to 20 carbon atoms are oxidized by a process which includes the following steps: A. Reacting the hydrocarbons with a gas containing molecular oxygen in the presence of a boron compound; B. hydrolyzing the resulting reaction mixture which contains at least one boric acid ester with an aqueous medium containing boric acid; C. separating the hydrolyzate into a substantially organic component from which the oxidation product is recovered and a substantially aqueous component containing boric acid and water-soluble organic secondary products; D. recovering boric acid from the aqueous component; E. oxidizing the residual boric acid mother liquor from (d), or a part thereof in the liquid phase with a gas containing molecular oxygen; and F. returning the resulting solution from (e) to hydrolysis step (b).	
4058555	EI Paso Products	15-Nov-1977
	Complex mixtures of polycarboxylic organic acids and their precursors, such as the by-products from the air oxidation of cyclohexane and its derivatives, are treated with nitric acid under hydrolytic conditions, esterified with an alcohol, extracted with an immiscible solvent such as benzene, the extraction preferably being carried out simultaneously with esterification, and separated into component diesters.	
4042630	Stamicarbon	16-Aug-1977
	An improved process for preparing cycloalkanones and cycloalkanols from cycloalkylhydroperoxides. Cycloalkylhydroperoxides are converted under the influence of a solid heterogeneous chromium oxide catalyst and the reaction mixture is stripped with a stripping gas which reduces the content of water which is formed in the reaction mixture during conversion. As a result, the catalyst activity and selectivity is maintained.	
4014903	Allied Chemical	29-Mar-1977
	A process for treating an adipic acid bleed stream obtained in the manufacture of adipic acid, said adipic acid bleed stream consisting mainly of nitric, adipic, glutaric, and succinic acids and a catalyst; the process comprising maintaining said adipic acid bleed stream in aqueous solution, and stripping nitric acid from said aqueous solution with steam at a temperature of about 100°–110°C while maintaining in said aqueous solution a water to nitric acid weight ratio of at least 6, to remove substantially all of the nitric acid therefrom, thereby forming an aqueous nitric acid free mixture of said dibasic acids and said catalyst which can be safely dehydrated and distilled to produce useful chemicals.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
3997601	ICI	14-Dec-1976
	In the continuous manufacture of adipic acid by nitric acid oxidation of an organic feedstock oxidisable thereto in which cooling is effected by recycling the reaction mixture through a cooling circuit external to the reactor, improved temperature control is achieved by feeding the feedstock to the cooling circuit upstream of at least one cooler.	
3987100	DuPont	19-Oct-1976
	The process of oxidizing cyclohexane to produce cyclohexanone and cyclohexanol in the weight ratio of 0.5 to 1.5 of cyclohexanone to cyclohexanol, said process comprising contacting a stream of liquid cyclohexane with oxygen in each of at least three successive oxidation stages by introducing into each stage a mixture of gases comprising molecular oxygen and inert gas, said oxygen being introduced in amounts that may range from an amount that will substantially all react with the cyclohexane under the particular conditions involved to an amount in excess of the amount required to react with the cyclohexane, said excess being such that the overall oxygen consumed in the oxidation zone is not more than 95 mole percent of the amount fed under the particular conditions involved, in the presence of a binary catalyst system comprising 0.02 to 0.9 ppm chromium and 0.1 to 5 ppm cobalt at a temperature of from 130° to 200°C and a pressure of from 60 to 350 psig, reacting any cyclohexylhydroperoxide that may be formed in the presence of said binary catalyst system and recovering a product of cyclohexanone and cyclohexanol in the above ratio.	
3983220	US Government	28-Sep-1976
	The recovery of boric acid from an anion exchange resin is improved by eluting the boric acid with an aqueous solution of ammonium bicarbonate. The boric acid can be readily purified and concentrated by distilling off the water and ammonium bicarbonate. This process is especially useful for the recovery of boric acid containing a high percentage of ¹⁰ B which may be found in some nuclear reactor coolant solutions.	
3965164	Celanese	22-Jun-1976
	In a process for the production of adipic acid by nitric acid oxidation of cyclohexanol and/or cyclohexanone wherein copper and vanadium values are recovered by ion exchange means, the improvement which comprises utilizing the off-gas from the nitric acid oxidation to treat the solution being passed to the ion exchange zone.	
3932513	Halcon	13-Jan-1976
	The present invention relates to the oxidation of cyclohexane with molecular oxygen in a series of reaction zones, with vaporization of cyclohexane from the last reactor effluent and parallel distribution of this cyclohexane vapor among the series of reaction zones.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
3927105	Rhone-Poulenc	16-Dec-1975
	Mixtures of cycloalkanones and cycloalkanols rich in the former are made by heating solutions of cycloalkyl hydroperoxides in cycloalkanes in the presence of a chromium catalyst in a series of separate reaction zones each essentially uniform.	
3895067	Monsanto	15-Jul-1975
	In a process wherein a saturated C ₄ to C ₂₀ hydrocarbon is oxidized in the presence of a boron compound and at least a portion of the resulting mixture is hydrolyzed and then separated into an organic phase and an aqueous phase containing ortho boric acid and carbonaceous impurities, the boric acid can be efficiently recovered for reuse in the process by crystallizing 35–75 percent of the boric acid from said aqueous phase for reuse in the oxidation reaction, recycling 85–99 percent of the aqueous residual liquid for reuse as the hydrolysis medium, removing water from the remaining residual liquid until the concentration of said impurities therein is substantially increased to more than 25 percent by weight and then crystallizing and removing additional boric acid from said remaining residual liquid.	
3818081	DuPont	18-Jun-1974
	A process for separating adipic acid from a mixture of adipic, glutaric and succinic acids which comprises treating the mixture of acids under substantially anhydrous conditions with less than the stoichiometric amount of ammonia for complete ammoniation, separating the glutaric and succinic acids in the form of their corresponding imides and recovering adipic acid.	
3987101	Stamicarbon	19-Oct-1973
	A process for preparing cycloalkanones and cycloalkanols by conversion of cycloalkylhydroperoxides under the influence of a solid heterogeneous catalyst wherein cycloalkylhydroperoxides having 5–12 carbon atoms in the ring are converted under the influence of an oxidic, chromium catalyst which does not contain any copper oxide	
3761517	Huls	25-Sep-1973
	Process for the production of adipic acid and other aliphatic dicarboxylic acids by the continuous catalytic nitric acid oxidation of cyclohexanol or cyclohexanone and other cycloalkanols and cycloalkanones in which the weight ratio of nitric acid to organic compound is 5:1 to 20:1, the oxidation temperature is 20° to 50°C., the residence time is 20 to 70 minutes and the nitrogen oxides produced in the oxidation are recycled.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
3679751	Halcon	25-Jul-1972
	This invention relates to an improved process for the recovery of boron compounds used to form borate esters in hydrocarbon oxidation processes, which comprises removing dissolved and entrained organic material from the aqueous phase of the hydrocarbon oxidation process by extraction with a hydrocarbon or alcohol solvent.	
3673245	EI Paso Products	27-Jun-1972
	Off-gases, obtained from the nitric acid oxidation of an organic feed comprising cyclohexanol and cyclohexanone and mixtures thereof by contact in a reactor with nitric acid at an elevated temperature whereby adipic acid is produced, the mixture of off-gases comprising nitric oxide, nitrogen dioxide, other oxides of nitrogen, carbon dioxide, nitrogen and carbon monoxide, are mixed with an oxygen-containing gas and the resultant mixture is passed through the organic feed being passed to the nitric acid reactor. This results in utilizing all reactive oxidizing agents in the off-gases and transferring a portion of the highly exothermic reaction from the main reactor to the off-gas scrubber	
3665028	Halcon	23-May-1972
	This invention relates to the oxidation of hydrocarbons in the presence of boron compounds. More specifically, the invention teaches a method of improving the selectivity of the reaction and the distribution of the oxidation products.	
3818081	DuPont	7-Oct-1971
	A process for separating adipic acid from a mixture of adipic, glutaric and succinic acids which comprises treating the mixture of acids under substantially anhydrous conditions with less than the stoichiometric amount of ammonia for complete ammoniation, separating the glutaric and succinic acids in the form of their corresponding imides and recovering adipic acid.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
3476805	Vickers-Zimmer	4-Nov-1969
	Method of recovery of adipic acid from a product stream of a reaction mixture wherein a mixture of cyclohexanol and cyclohexanone is oxidized with a concentrated nitric acid solution, the product stream containing 12–28 weight percent adipic acid and from 70–90 percent of the concentrated nitric acid oxidant, the steps including diluting the product stream to a nitric acid concentration of about 38% by weight, crystallizing in a first crystallizer to obtain coarse crystals of adipic acid under a vacuum at a temperature of about 35°C, centrifuging the coarse crystals to provide a crystal cake and a nitric acid mother liquor, separating the crystal cake and mother liquor, concentrating the mother liquor by evaporation of volatiles, passing the concentrated mother liquor to a crystallizer, cooling and then filtering to produce additional adipic acid crystals, redissolving the additional adipic acid crystals in water, recycling the redissolved adipic acid to the product stream and distilling the filtrate from the crystallizer to produce a nitric acid aqueous mixture.	
3459798	DuPont	5-Aug-1969
	Adipic acid is rendered free flowing by the addition of 25–200 ppm of an anticaking agent which is an acyclic saturated monobasic acid containing 10–22 carbon atoms or an acyclic saturated dibasic acid containing 10–14 carbon atoms or mixture of the aforesaid acids.	
3365490	DuPont	23-Jan-1968
	This invention relates to an improvement in the process for preparing adipic acid by first subjecting cyclohexane to oxidation with air and subsequently separating the cyclohexanone and cyclohexanol formed from the by-products and oxidizing this mixture of cyclohexanol and cyclohexanone with aqueous HNO ₃ to produce adipic acid. The improvement is achieved by concentrating the effluent from the air-oxidizer to 60–80% cyclohexane, extracting a useful portion of the non-volatile by-products from the organic phase with water, concentrating the aqueous extract and employing the resultant steam to steam distill the cyclohexanol and cyclohexanone away from the non-useful portion of the non-volatile residue remaining in the organic phase and oxidizing the residue from the aqueous extract to adipic acid with aqueous HNO ₃ at a low temperature (35–50°C) in the presence of added NO ₂ ⁻	
3359308	DuPont	19-Dec-1967
	The invention relates to a process for the preparation of alkane dicarboxylic acids. More specifically, it relates to a liquid phase nitric acid oxidation process for the production of alkane dicarboxylic acids from cycloalkanols and/or cyclokanones.	

Table A.1 (Continued)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
3359283	Monsanto	19-Dec-1967
	A method for the reclamation of organic dibasic acids from certain process streams. More particularly, the present invention relates to a method of producing succinic anhydride and glutaric anhydride and separating these anhydrides from a mixture of dibasic acids including succinic acid, glutaric acid and adipic acid, such as a mixture of these acids contained in liquors originated from the mother liquors obtained in the manufacture of adipic acid.	
3232704	Esso	1-Feb-1966
	The present invention is directed to the oxidation of naphthenes to the corresponding cyclic alcohols and ketones in the presence of a boric acid compound. More particularly the invention deals with the recovery of boric acid from the reaction products formed in the oxidation of naphthenes in the presence of a boric acid compound. In its more specific aspects, the invention is concerned with recovering substantially pure boric acid from the reaction products formed in the oxidation of naphthenes in the presence of a boric acid compound by water washing the oxidation reaction products and extracting the water wash aqueous phase with the corresponding cyclic alcohol of the naphthenes oxidized.	
3186952	Monsanto	1-Jun-1965
	This invention relates to the recovery of certain catalyst values from process streams by means of ion exchange. More particularly, the invention relates to a process for selectively removing vanadium ions and copper ions from liquors containing these ions and ferric ions and obtained in the manufacture of adipic acid by oxidation of cyclohexanol and/or cyclohexanone with nitric acid or the like	
3096369	Stamicarbon	2-Jul-1963
	The present invention relates to a method of crystallizing adipic acid by cooling an adipic acid solution until a crystal suspension is obtained.	
3564051	BASF	16-Feb-1961
	Production of adipic acid by oxidation of cyclohexanol, cyclohexanone, w-hydroxycaproic acid or mixtures containing such compounds with nitric acid in the presence of vanadium and optionally copper catalysis wherein the excess nitric acid is distilled off, the residue is fractionated under subatmospheric pressure without previous separation of the catalyst and the catalyst-containing bottoms product is fed into the next charge	
2557281	DuPont	19-Jun-1951
	This invention relates to the oxidation of liquid hydrocarbons with gaseous oxygen and more particularly to oxidation of cyclohexane-containing petroleum fractions	

Table A.1 (Concluded)
PATENT SUMMARY

Reference Number	Assignee	Earliest Date Shown
2557282	DuPont	19-Jun-1951
	This invention relates to the production of adipic acid and related aliphatic dibasic acids and more particularly to the production of adipic acid by the oxidation of cyclohexane. This application is a continuation in part of US application SN 789924 filed December 7, 1947, now abandoned, which is a division of application SN 632081, files November 30, 1945, now US patent 2439513.	
2497349	Union Oil	14-Feb-1950
	This invention relates to the production of synthetic organic chemicals and is particularly directed to the preparation of organic derivatives of petroleum hydrocarbon hydroperoxides. The invention is more particularly directed to the preparation of alicyclic alcohols from such hydroperoxides.	
2439513	DuPont	13-Apr-1948
	This invention relates to the production of adipic acid and related aliphatic dibasic acids and more particularly to the production of adipic acid by the oxidation of cyclohexane	
2410642	Union Oil	5-Nov-1946
	This invention relates to partial oxidation products and methods of producing such products from hydrocarbons or hydrocarbon oils, such as petroleum and petroleum fractions. The invention also relates to alcohols and/or ketones and to methods of producing such alcohols and/or ketones from non-aromatic cyclic hydrocarbons. The invention also relates to polyvalent metal salts of phosphate esters of the partial oxidation of hydrocarbons or hydrocarbon fractions and to lubricating oil compositions containing these metal salts.	
2223493	DuPont	3-Dec-1940
	This invention relates to the production of aliphatic dibasic acids and more particularly to the production of aliphatic dibasic acids by oxidation of cyclic saturated hydrocarbons with an oxygen containing gas.	
2223494	DuPont	3-Dec-1940
	This invention relates to the production of aliphatic dibasic acids and more particularly to the production of aliphatic dibasic acids by oxidation of cyclic saturated hydrocarbons with an oxygen containing gas.	

Appendix B

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Appendix C

PROCESS FLOW DIAGRAMS

Figure 7.48 (1 of 8)
ADIPIC ACID FROM CYCLOHEXANE VIA CONVENTIONAL
TWO-STAGE OXIDATION PROCESS
PROCESS FLOW DIAGRAM

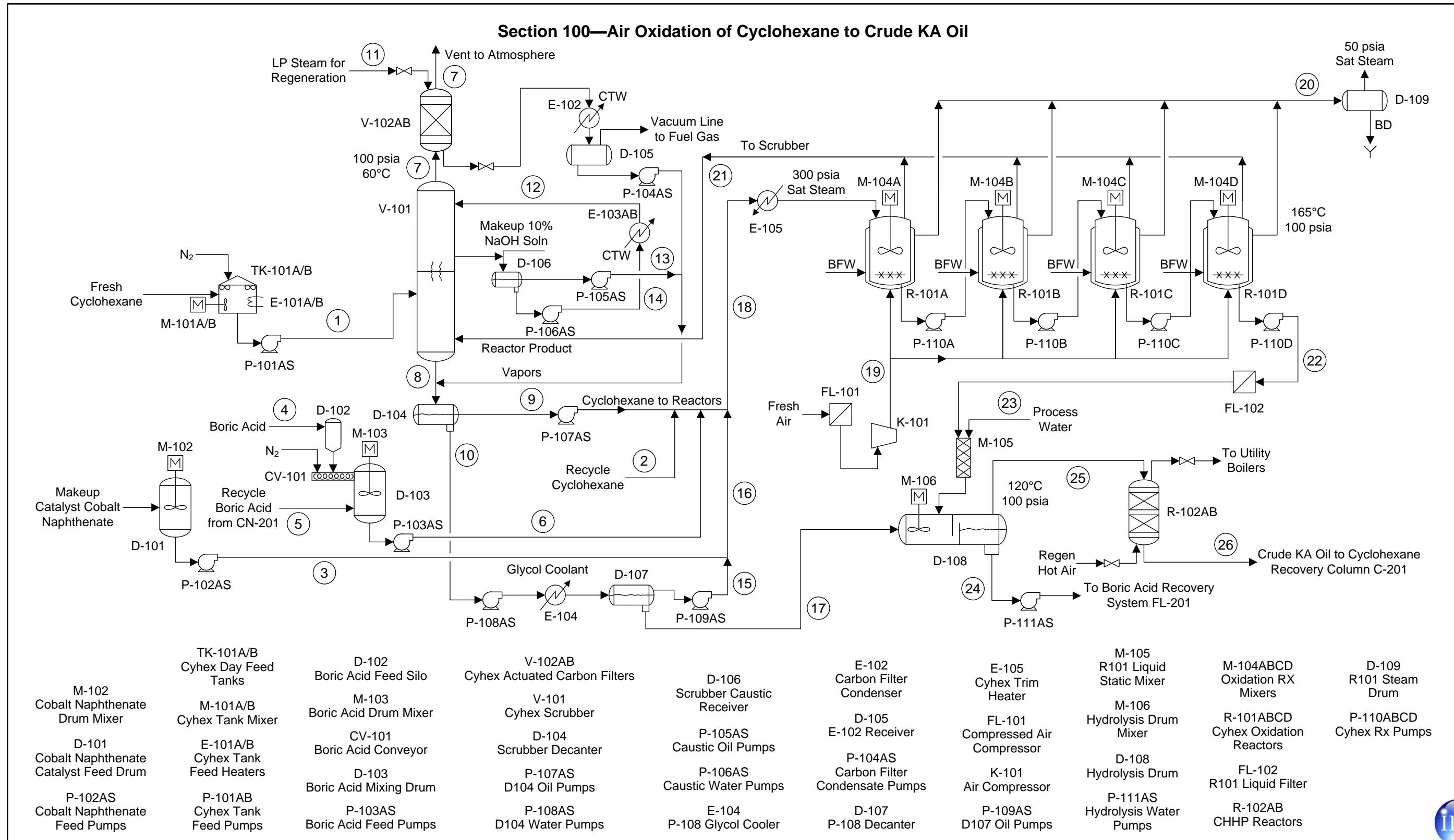


Figure 7.48 (2 of 8)
ADIPIC ACID FROM CYCLOHEXANE VIA CONVENTIONAL
TWO-STAGE OXIDATION PROCESS
PROCESS FLOW DIAGRAM

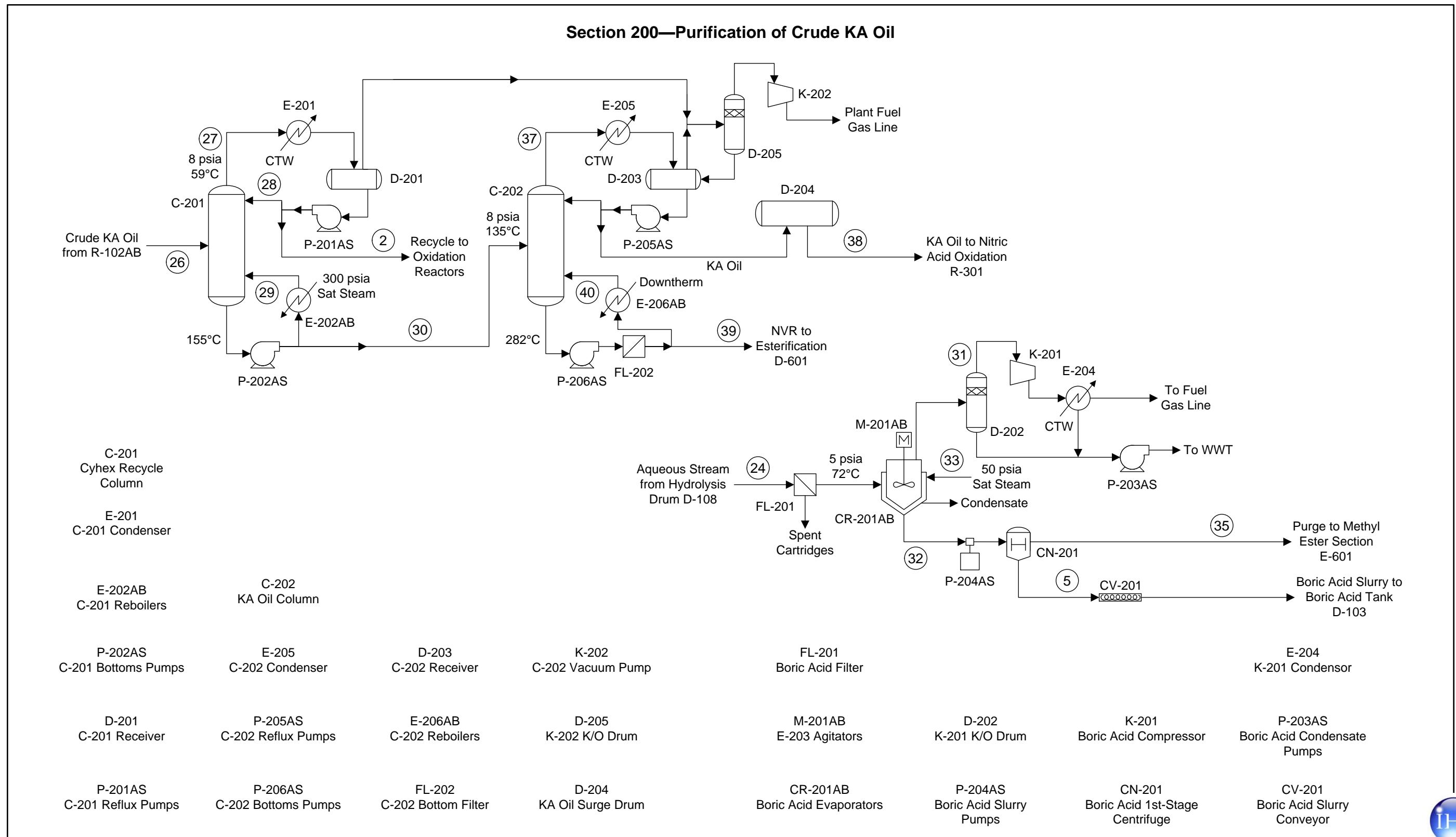


Figure 7.48 (3 of 8)
ADIPIC ACID FROM CYCLOHEXANE VIA CONVENTIONAL
TWO-STAGE OXIDATION PROCESS
PROCESS FLOW DIAGRAM

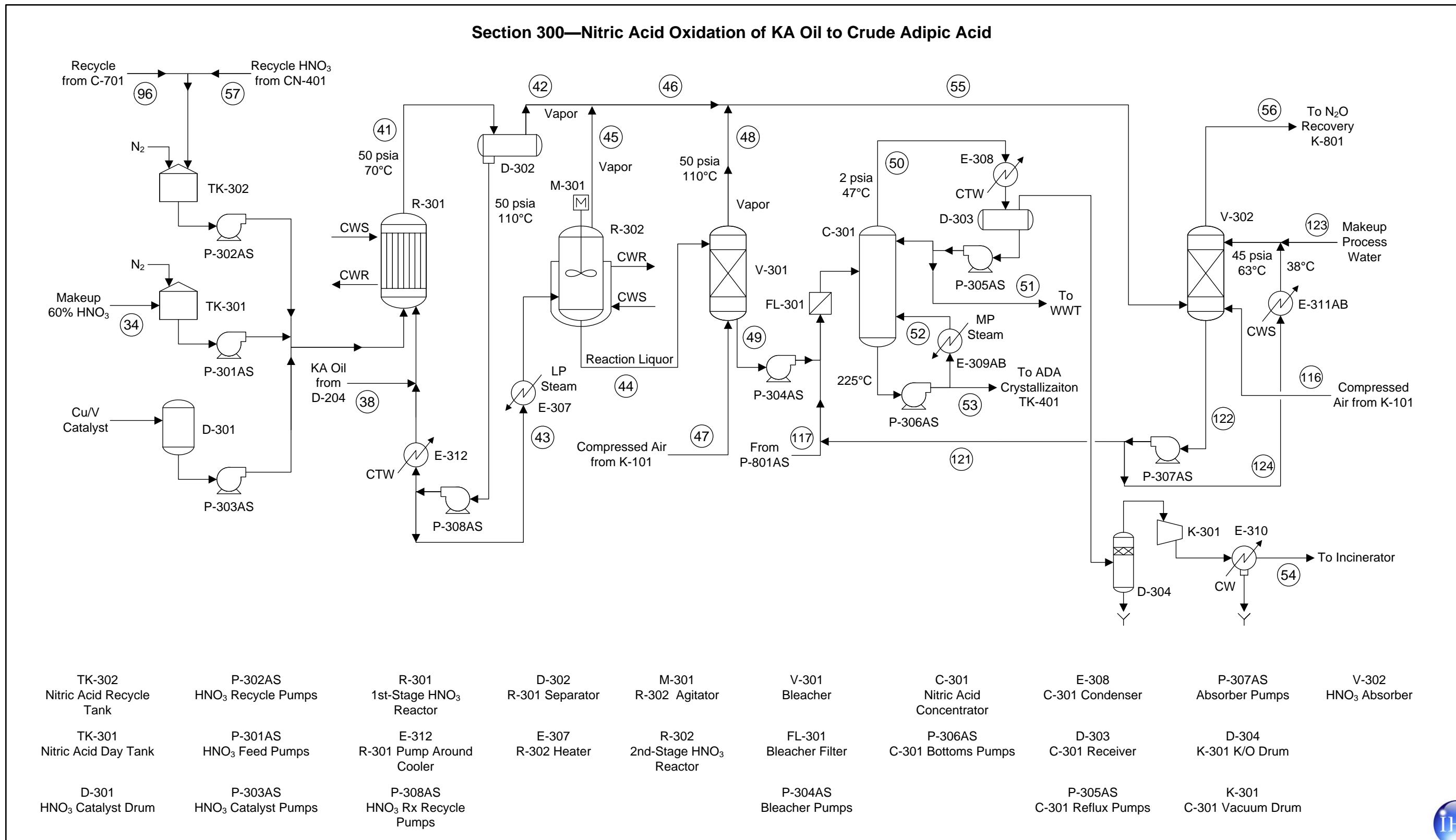


Figure 7.48 (4 of 8)
ADIPIC ACID FROM CYCLOHEXANE VIA CONVENTIONAL
TWO-STAGE OXIDATION PROCESS
PROCESS FLOW DIAGRAM

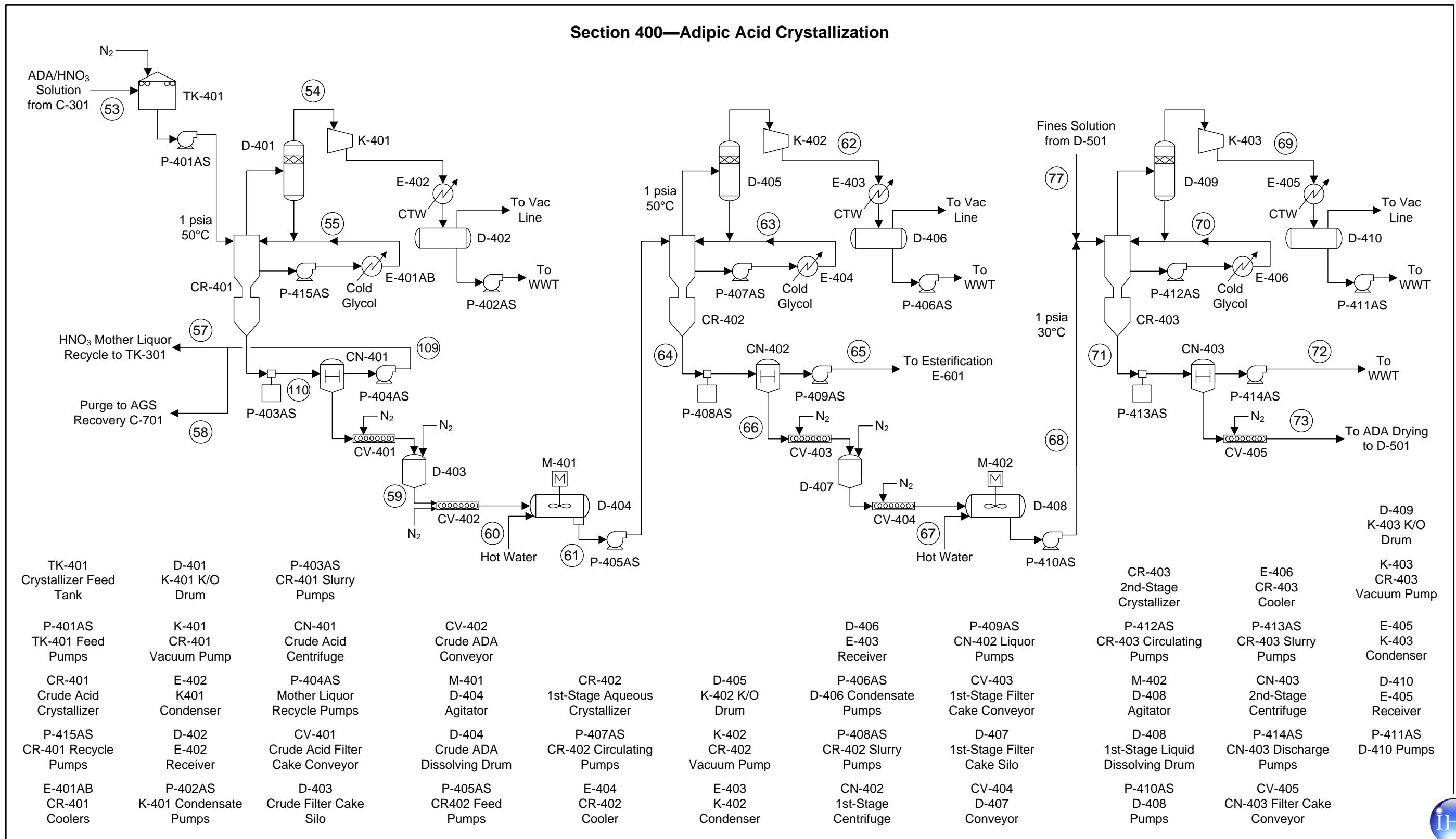


Figure 7.48 (5 of 8)
ADIPIC ACID FROM CYCLOHEXANE VIA CONVENTIONAL
TWO-STAGE OXIDATION PROCESS
PROCESS FLOW DIAGRAM

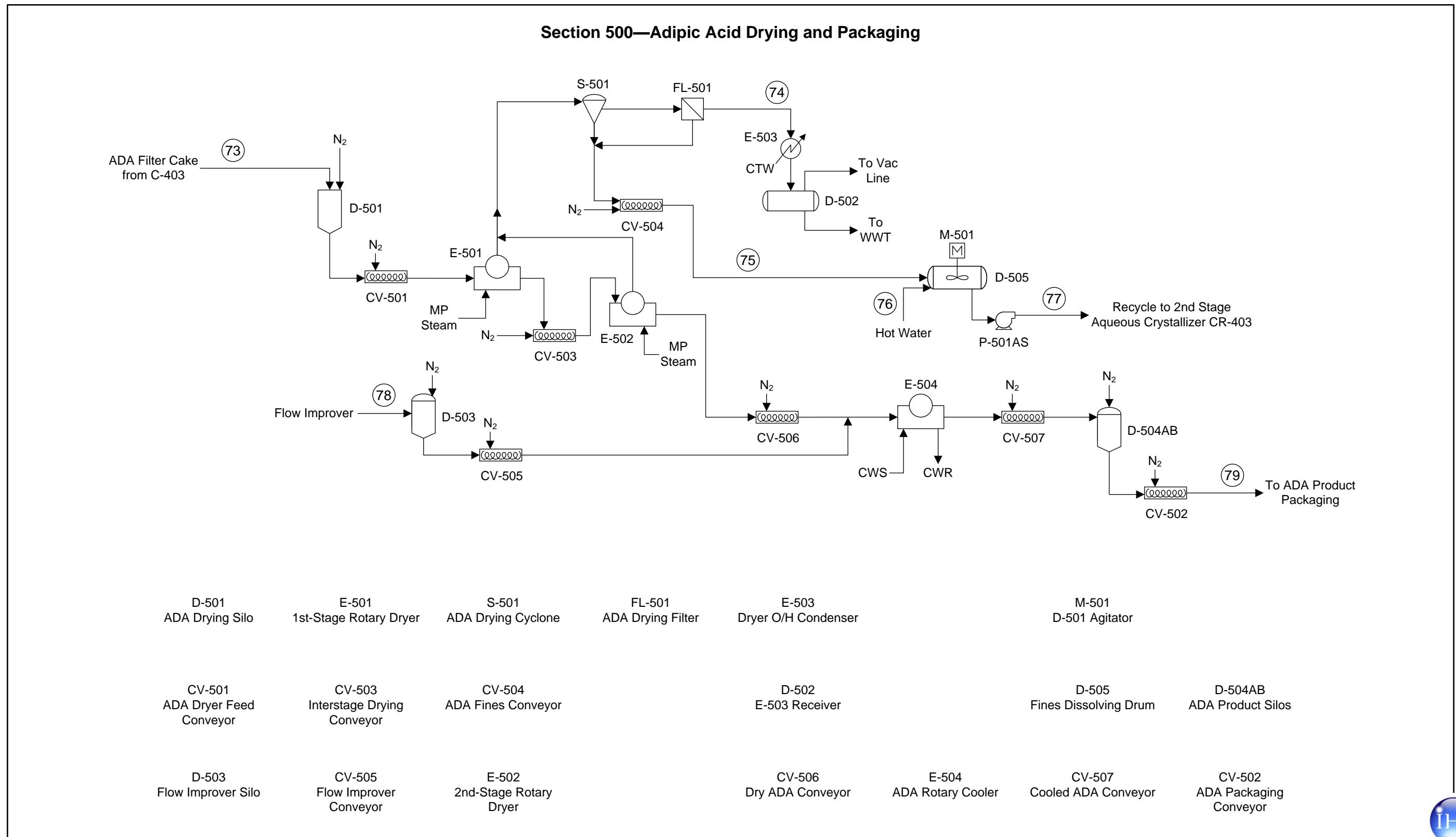


Figure 7.48 (6 of 8)
ADIPIC ACID FROM CYCLOHEXANE VIA CONVENTIONAL
TWO-STAGE OXIDATION PROCESS
PROCESS FLOW DIAGRAM

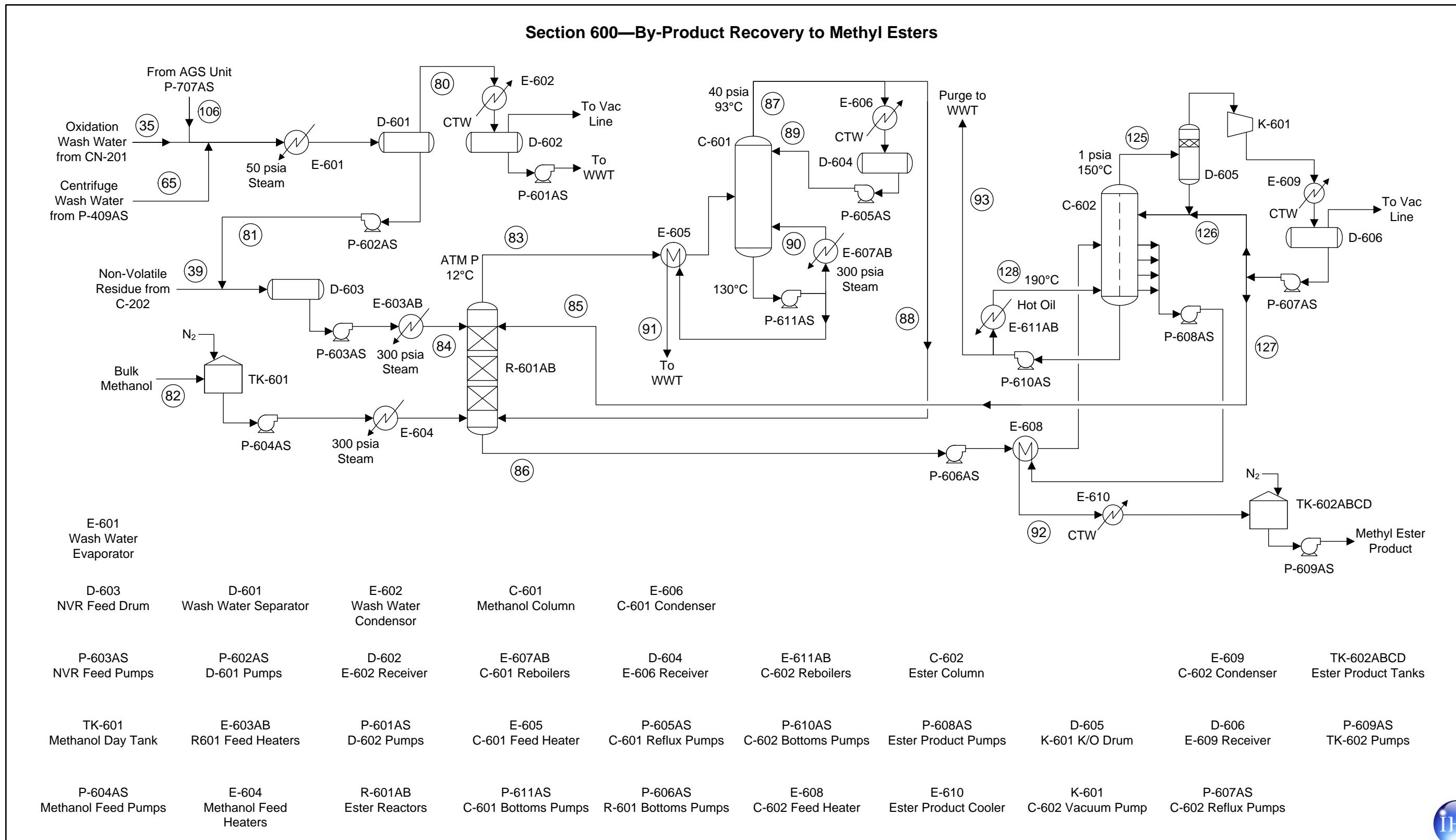


Figure 7.48 (7 of 8)
ADIPIC ACID FROM CYCLOHEXANE VIA CONVENTIONAL
TWO-STAGE OXIDATION PROCESS
PROCESS FLOW DIAGRAM

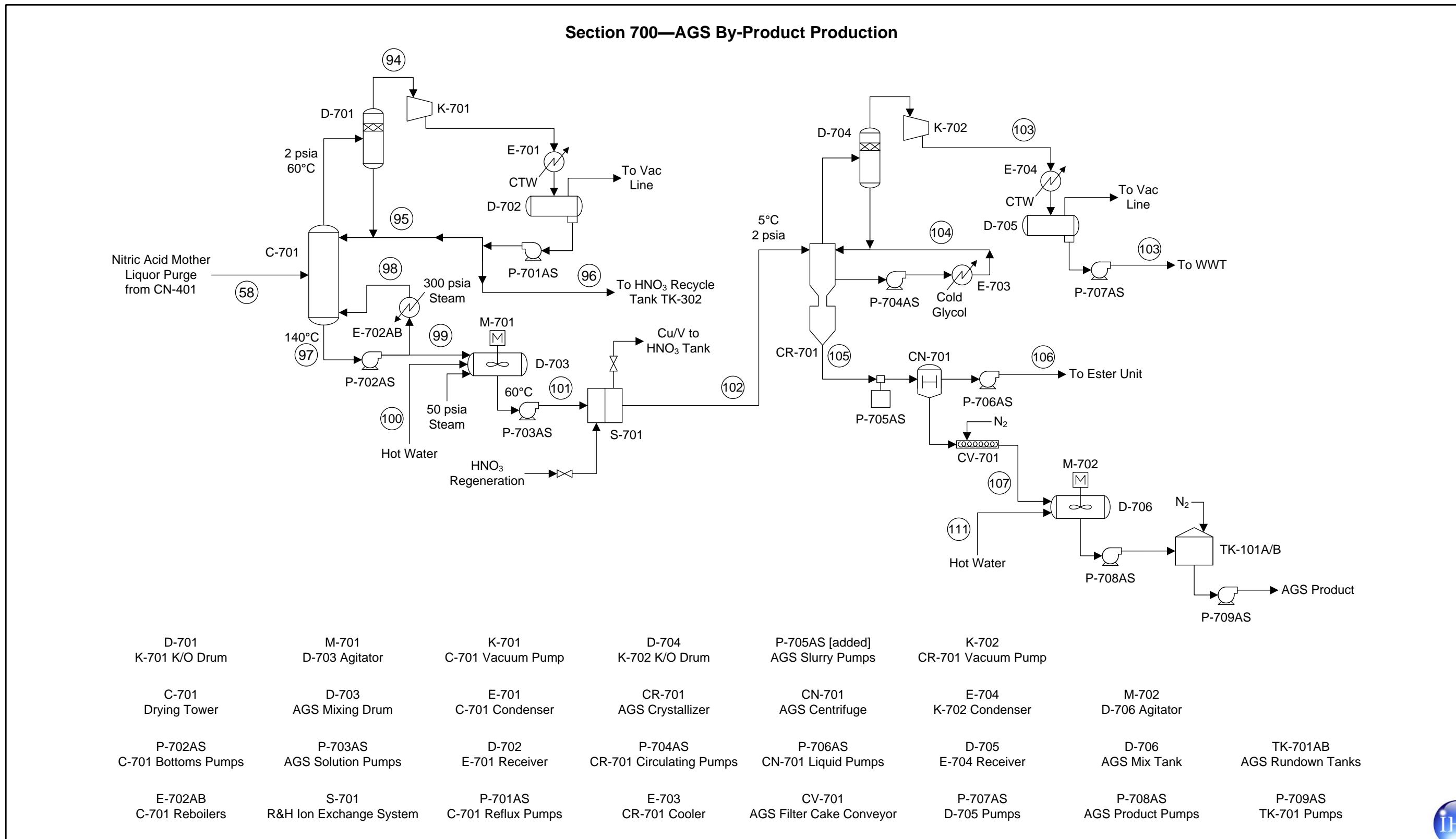


Figure 7.48 (8 of 8)
ADIPIC ACID FROM CYCLOHEXANE VIA CONVENTIONAL
TWO-STAGE OXIDATION PROCESS
PROCESS FLOW DIAGRAM

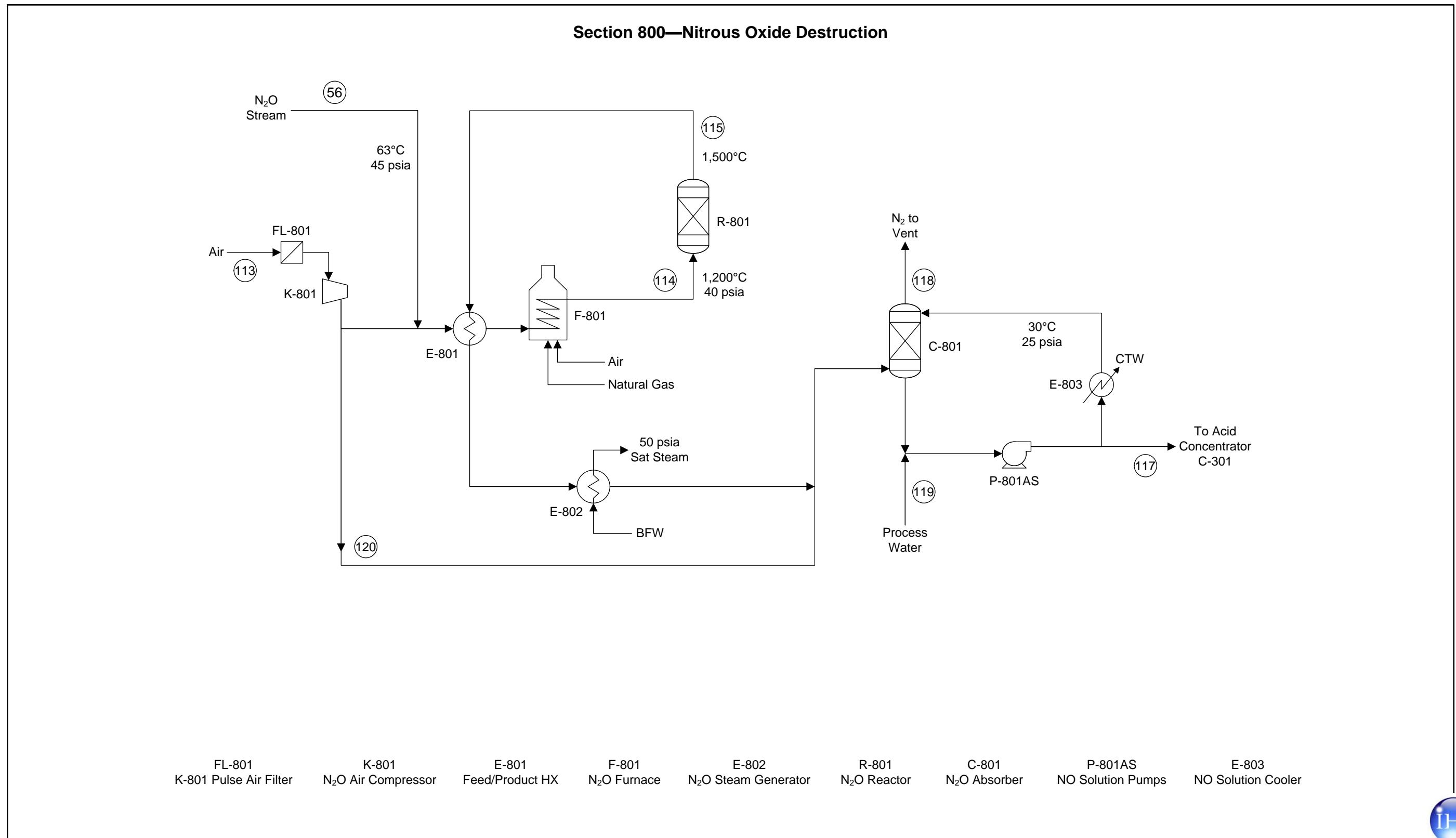


Figure 8.21 (1 of 6)
VERDEZYNE FERMENTATION PROCESS FOR MAKING ADIPIC ACID FROM GLUCOSE
PROCESS FLOW DIAGRAM

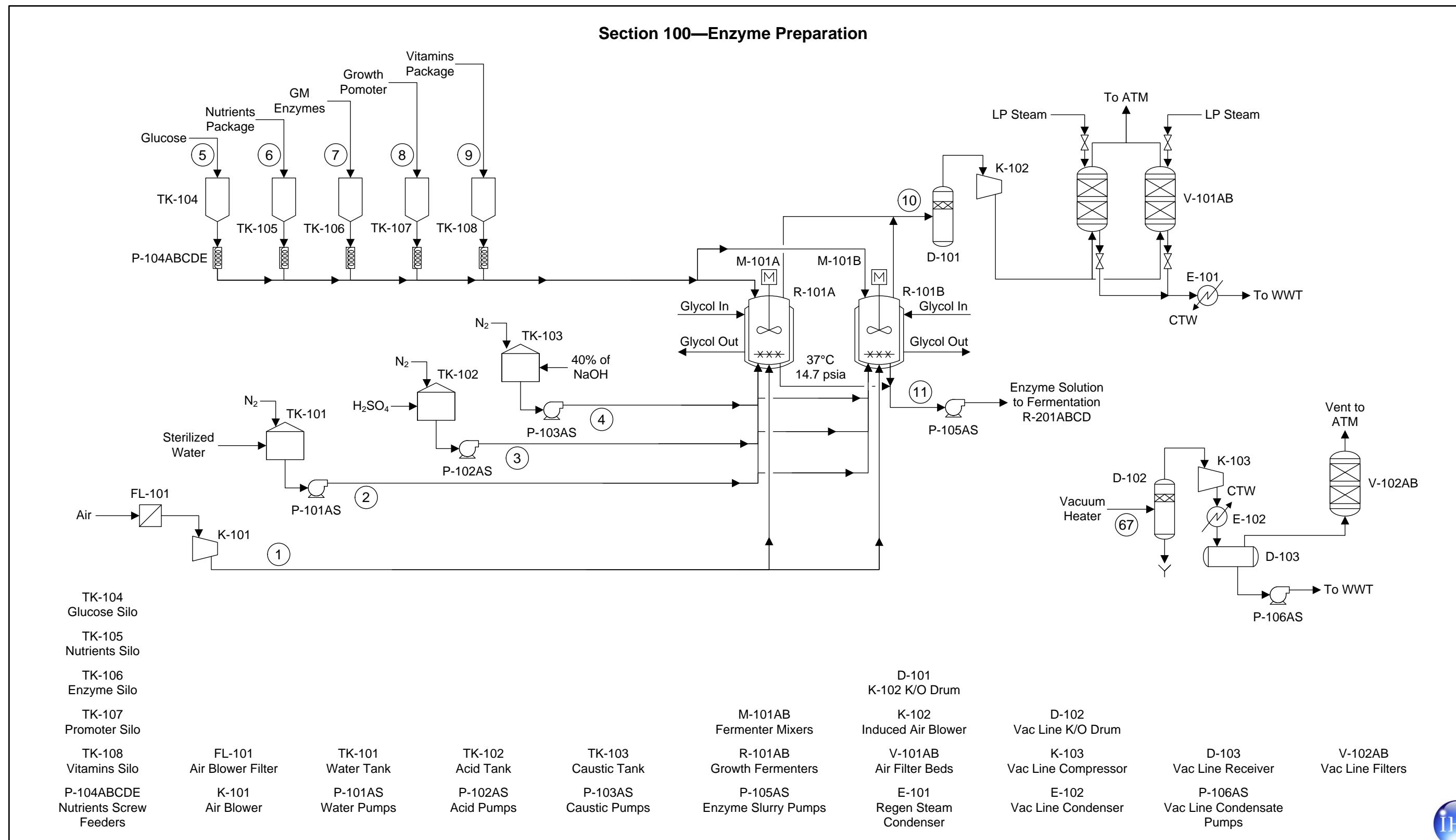


Figure 8.21 (2 of 6)
VERDEZYNE FERMENTATION PROCESS FOR MAKING ADIPIC
ACID FROM GLUCOSE
PROCESS FLOW DIAGRAM

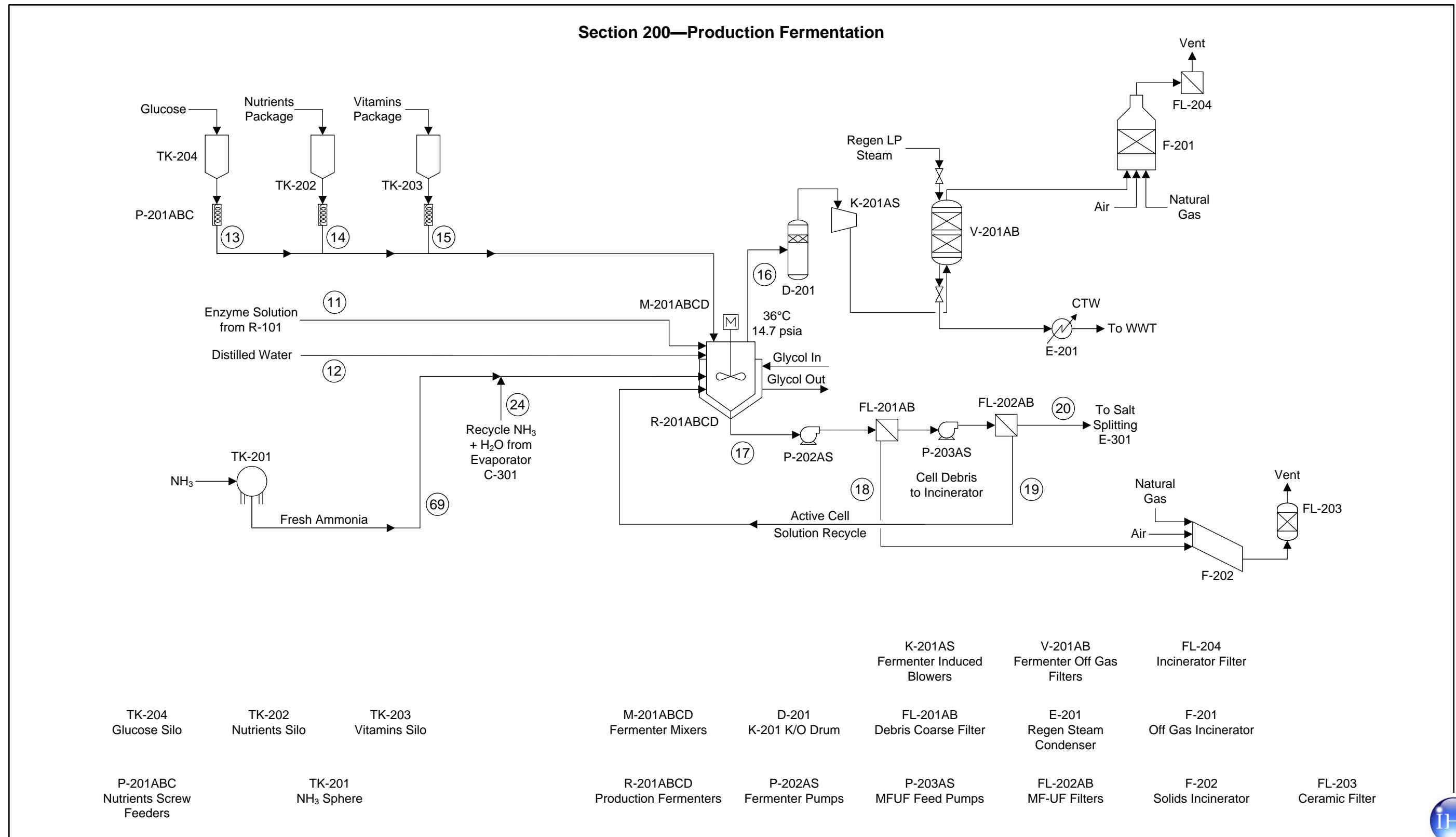


Figure 8.21 (3 of 6)
VERDEZYNE FERMENTATION PROCESS FOR MAKING ADIPIC
ACID FROM GLUCOSE
PROCESS FLOW DIAGRAM

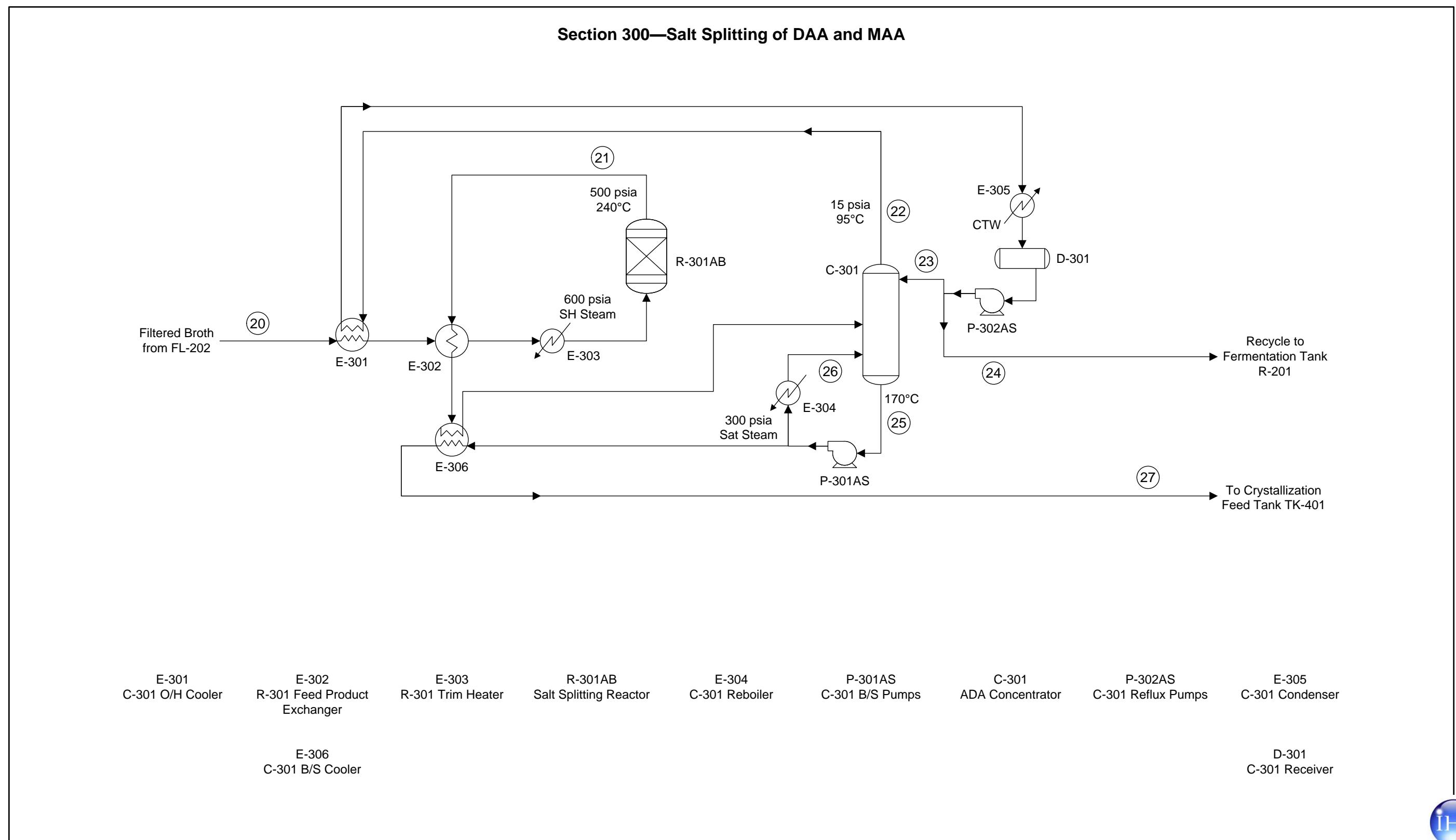


Figure 8.21 (4 of 6)
VERDEZYNE FERMENTATION PROCESS FOR MAKING ADIPIC ACID FROM GLUCOSE
PROCESS FLOW DIAGRAM

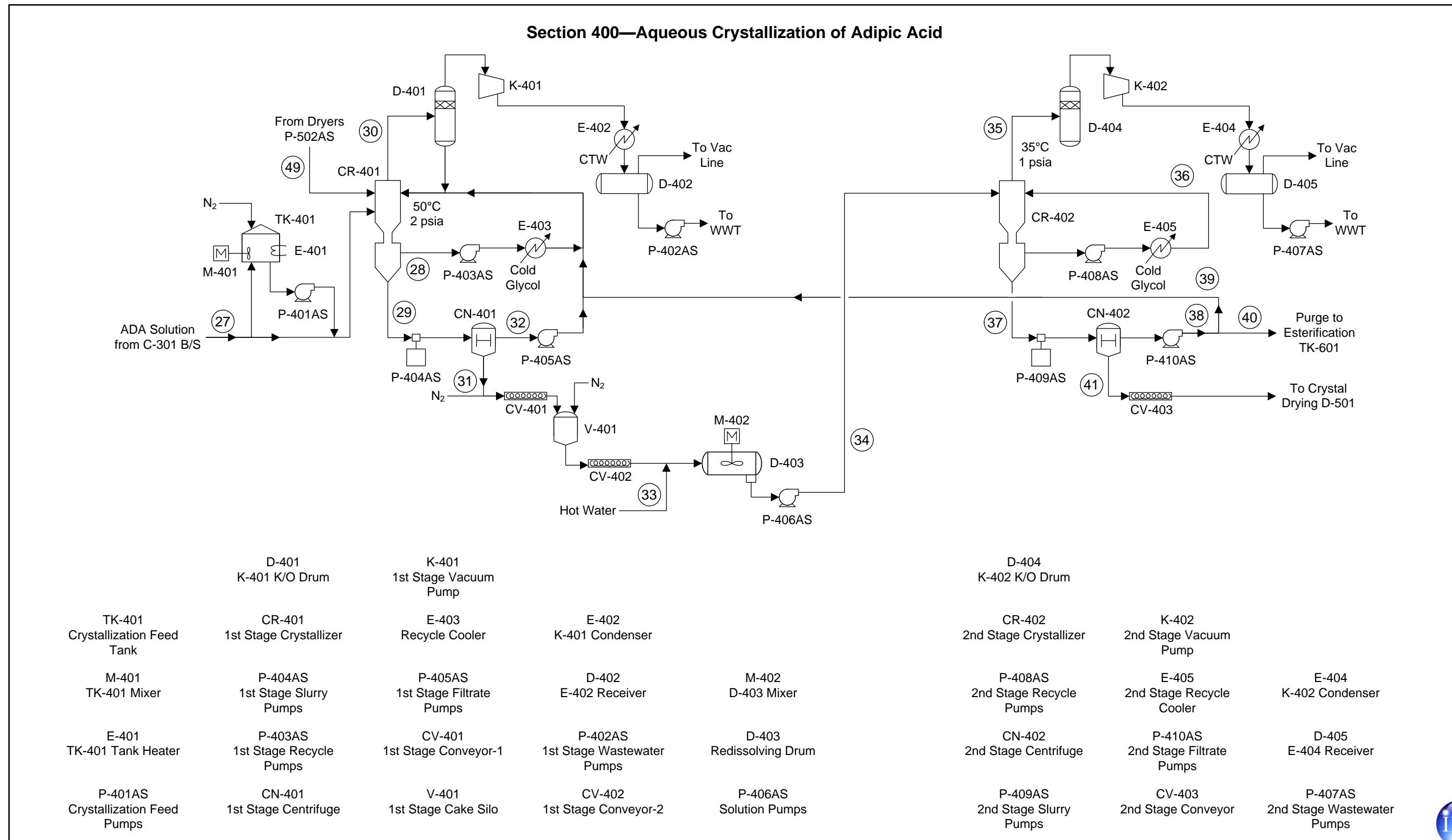


Figure 8.21 (5 of 6)
VERDEZYNE FERMENTATION PROCESS FOR MAKING ADIPIC ACID FROM GLUCOSE
PROCESS FLOW DIAGRAM

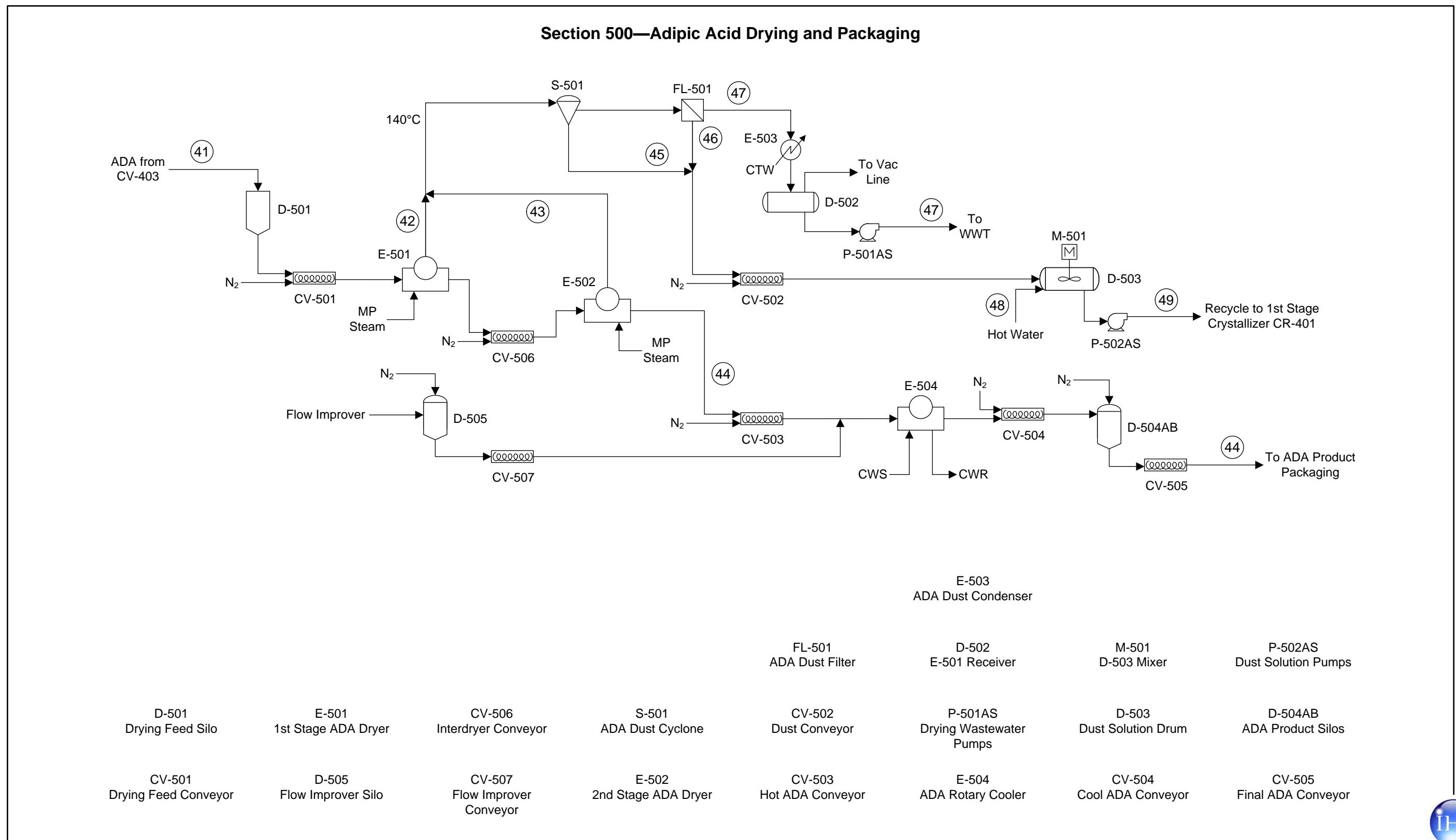


Figure 8.21 (6 of 6)
VERDEZYNE FERMENTATION PROCESS FOR MAKING ADIPIC ACID FROM GLUCOSE
PROCESS FLOW DIAGRAM

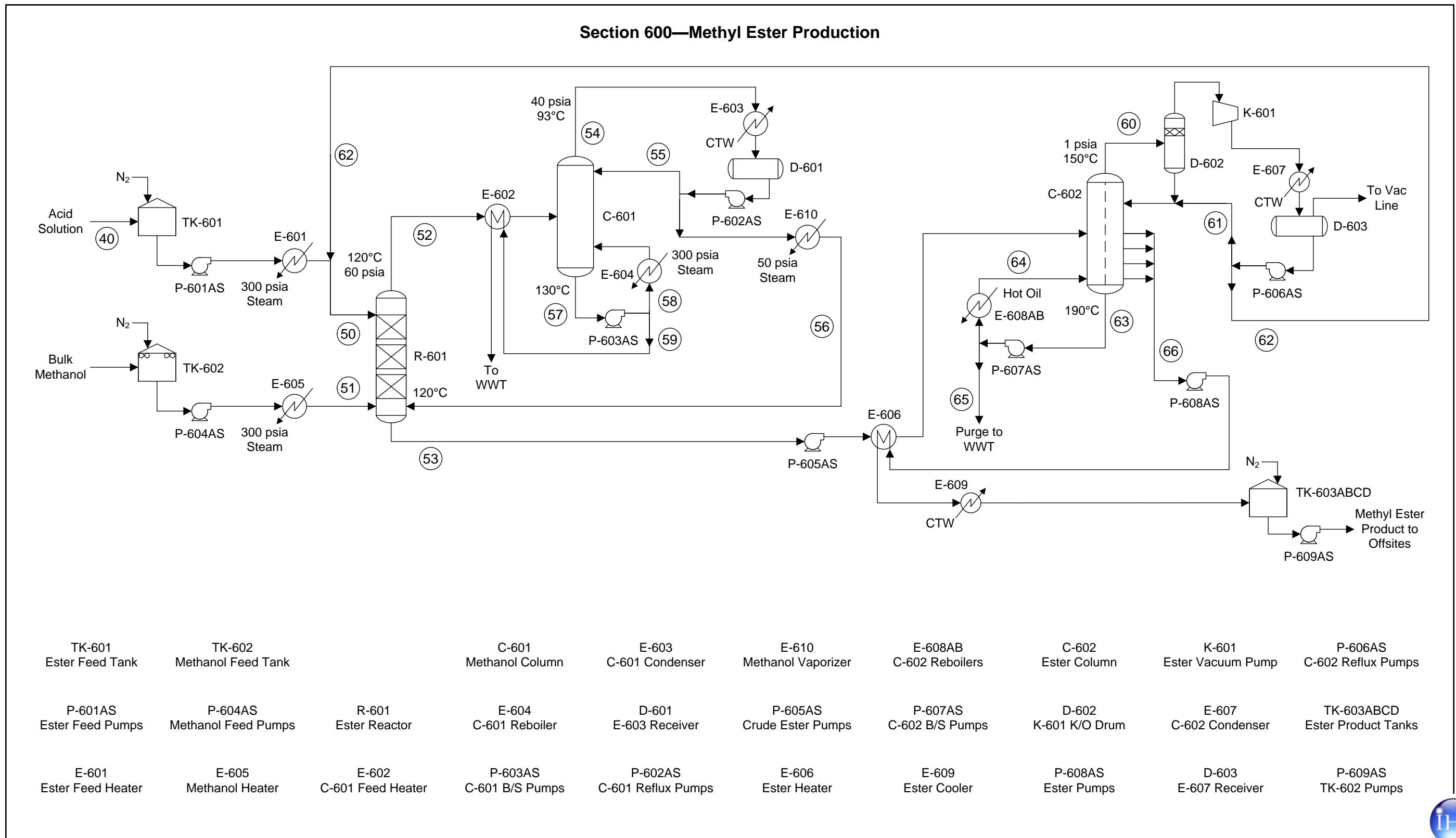


Figure 9.25 (1 of 6)
RENOVIA PROCESS FOR MAKING ADIPIC ACID
PROCESS FLOW DIAGRAM

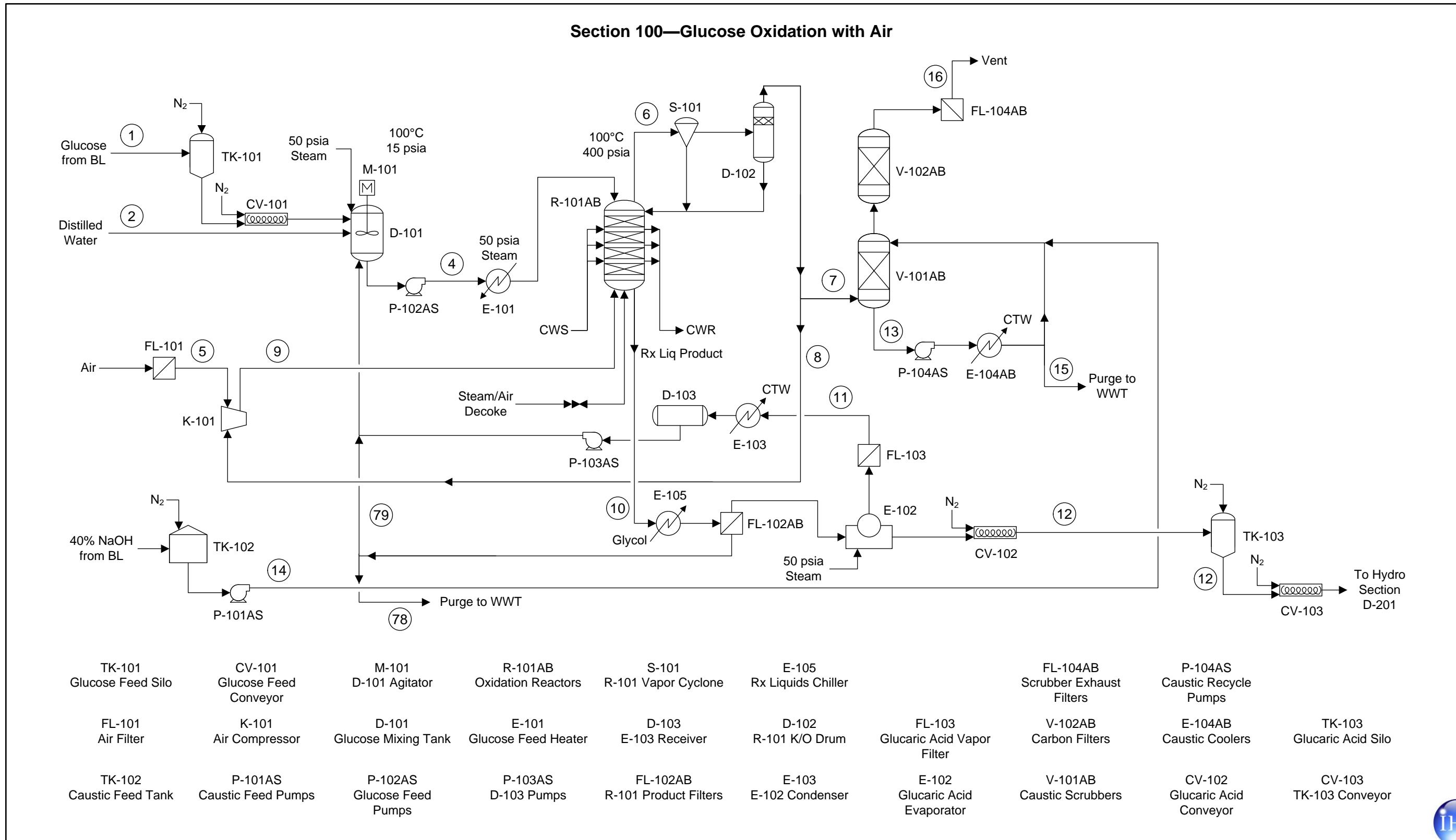


Figure 9.25 (2 of 6)
RENNOVIA PROCESS FOR MAKING ADIPIC ACID
PROCESS FLOW DIAGRAM

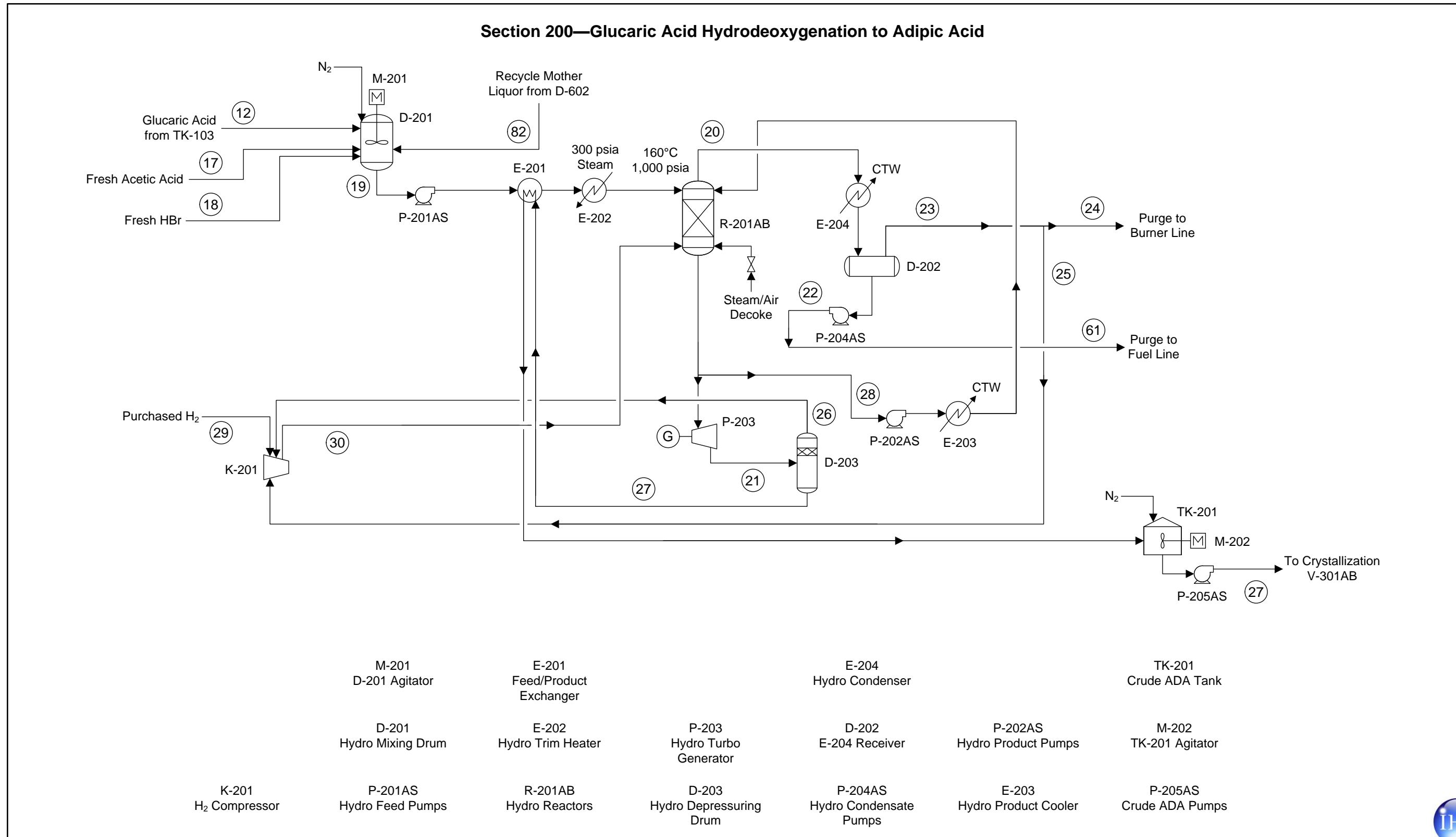


Figure 9.25 (3 of 6)
RENNOVIA PROCESS FOR MAKING ADIPIC ACID
PROCESS FLOW DIAGRAM

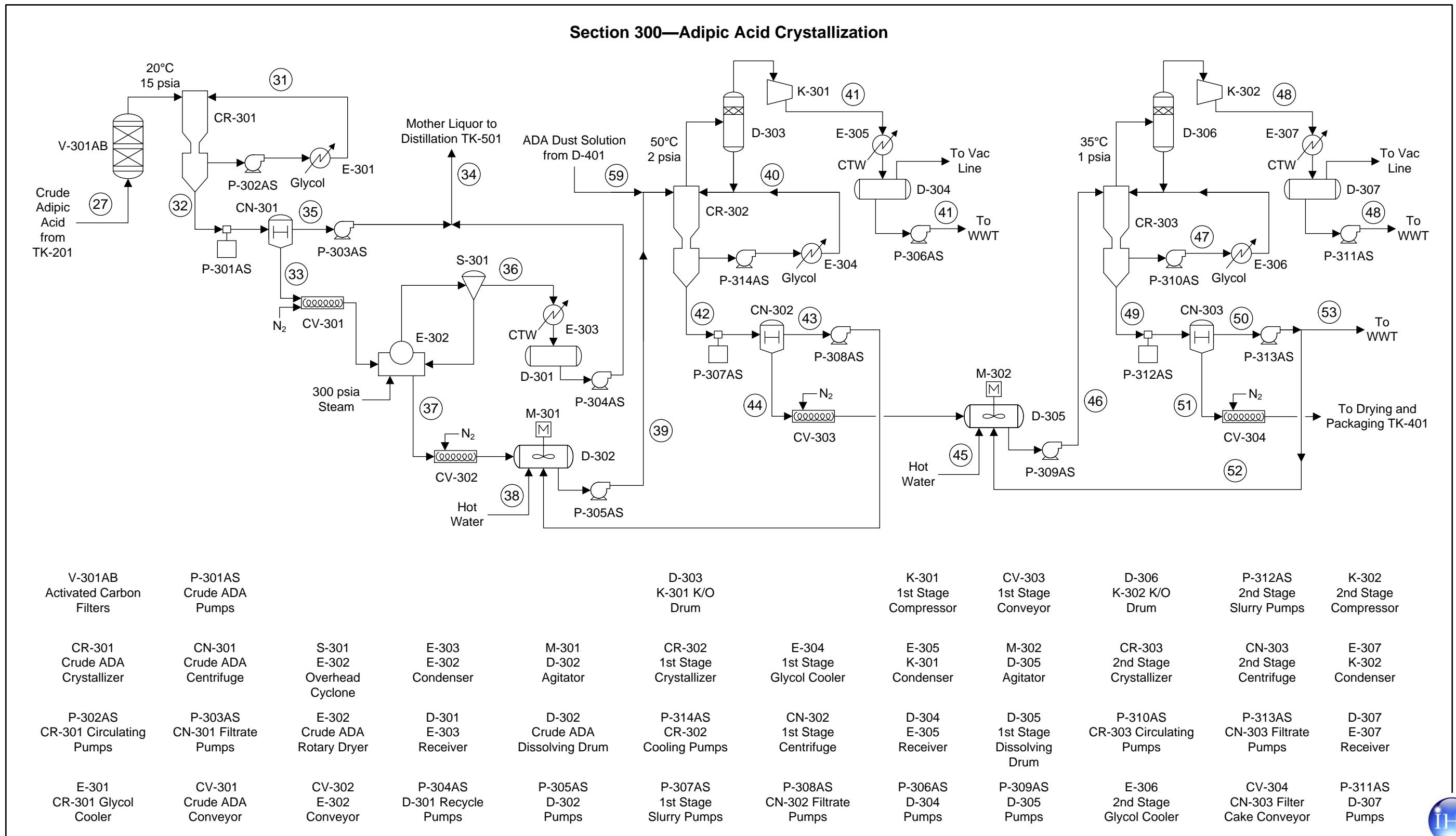
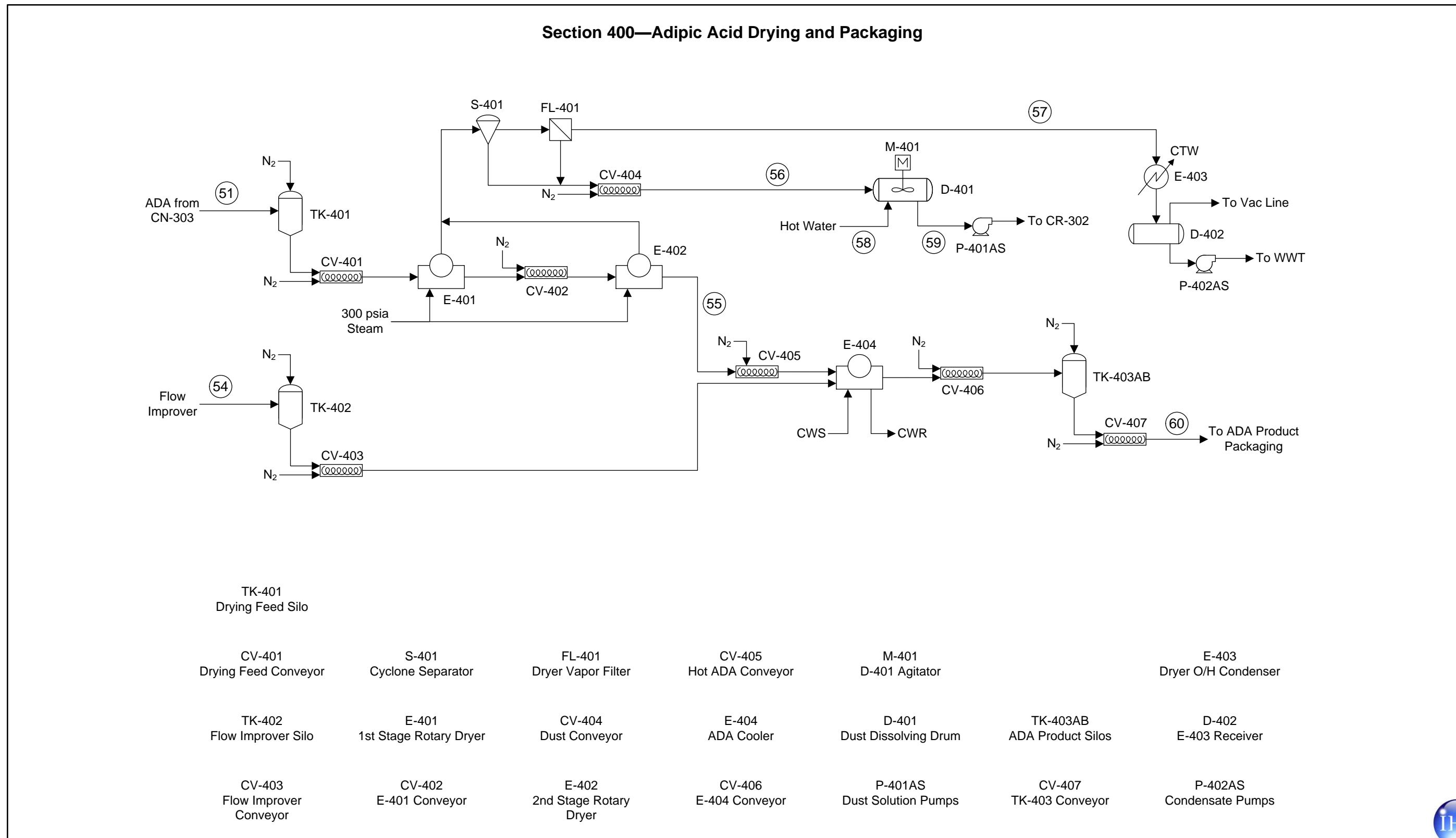


Figure 9.25 (4 of 6)
RENNOVIA PROCESS FOR MAKING ADIPIC ACID
PROCESS FLOW DIAGRAM



**Figure 9.25 (5 of 6)
RENNOVIA PROCESS FOR MAKING ADIPIC ACID
PROCESS FLOW DIAGRAM**

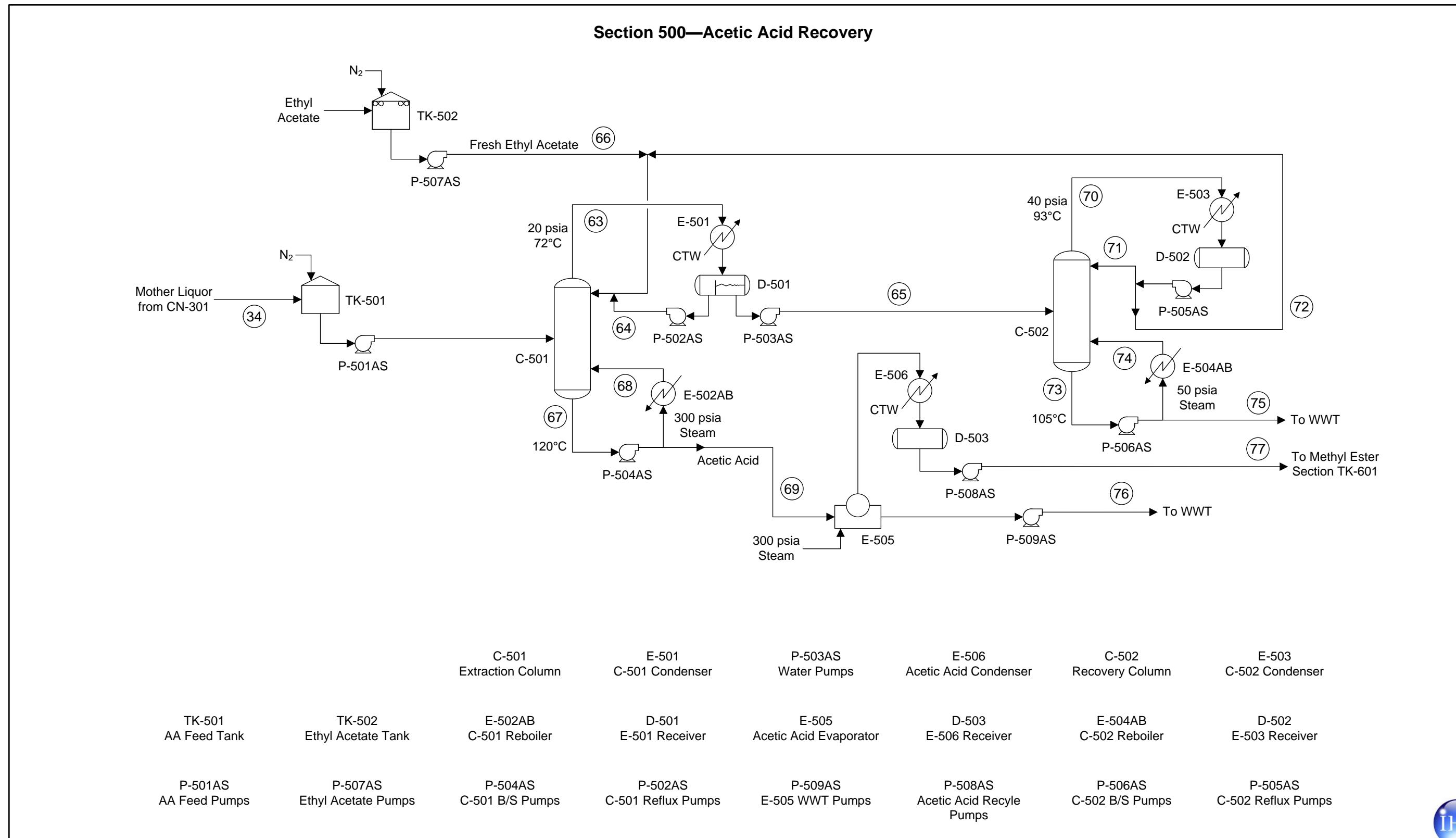


Figure 9.25 (6 of 6)
RENOVIA PROCESS FOR MAKING ADIPIC ACID
PROCESS FLOW DIAGRAM

